SYNTHESIS OF HIGHLY SILICEOUS ZSM-5 USING DIAMINOALKANES AND THEIR APPLICATION FOR THE CONVERSION OF METHANOL TO LIGHT OLEFINS

By

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ABSTRACT

The use of organic bases in the synthesis of zeolites can lead to the crystallisation of several completely original structures. Zeolite ZSM-5 is produced using tetrapropylammonium cations. This cationic material can be replaced by amines or diamines, although in this case it becomes more difficult to synthesise the zeolite. ZSM-5 has a three dimensional channel system, having apertures which are slightly larger than 0,5 nm. This means that during reactions, there is a control over the size of the molecules that can enter or exit from the pores of the zeolite: this process is called "shape selective" catalysis.

The conversion of methanol over ZSM-5 proceeds via dehydration to give firstly dimethyl ether and then light olefins. The olefins may subsequently undergo dehydrocyclisation to produce a mixture of light paraffins and aromatics, which are restricted to monocyclics and do not contain more than ten carbon atoms. As a result of these properties, ZSM-5 is an ideal catalyst for several industrial processes. Methanol can be converted directly to synthetic gasoline, or by restricting the conversion, olefins can be obtained. Naturally olefins themselves, as well as alkanes, can be converted to aromatics. An entirely different reaction has been found by using a high pressure and relative low temperature, where olefins can be oligomerised to produce diesel.

The zeolite ZSM-5 which is suitable for the conversion of methanol to light olefins, should have a low concentration of active sites, which, if expressed in terms of its silica to alumina mole ratio, means that this value should be approximately 400 : 1. This is readily achieved if the ZSM-5 is synthesised with tetrapropyl-ammonium compounds. An investigation using α,ω-diaminoalkanes for an alternative structure directing agent that could produce siliceous ZSM-5, found that 1,6-diaminohexane was the most

successful, but that the highest silica to alumina mole ratio attainable is about 200 : 1. This value can be subsequently increased to the desired level through partial de-alumination by calcination at 500 °C in the presence of steam.

In the synthesis using diaminoalkanes it is ideal if the amine groups are located at intersections and the hydrocarbon chain in the channels of the ZSM-5 crystals, and because of its size the 1,6-diaminohexane fits neatly into such an arrangement. There is some interaction between the carbon atoms and the zeolite, and requires a temperature in the region of 450 °C for it to be removed. This firm bond means that 1,6 diaminohexane must to some significant degree act as a template during crystallisation of ZSM-5.

1,6-diaminohexane, together with a small amount (about 4 %) of tetrapropylammonium cations, which seed the crystallisation, can be used to synthesise ZSM-5 on an industrial scale. It is possible to recycle the filtrate which contains excess chemicals not consumed in forming the crystallites. This reduces both the need for subsequent effluent control and the amount of raw materials required. Under these conditions the raw materials required, including the alumina binder needed to make extrudates, form only about 6 % of the total cost of the finished catalyst.

Although the main emphasis was in preparing a siliceous ZSM-5 for an MTO catalyst, some experimental work on its reactivity during the conversion of methanol to prove its practical acceptability, was also carried out. These reactivity studies were therefore done wherein it was aimed to have virtually complete conversion of the methanol. With this stipulation, it was found that the optimum selectivity to light olefins requires a reaction temperature of around 450 °C and a methanol partial pressure of about 0,2 bar. The latter requirement is readily attained by using an aqueous feed containing 30 % methanol. Under these conditions, light olefin selectivities in excess of 70 % are obtained.

The initial product formed from methanol or dimethyl ether, is ethene. Further olefins are formed mainly through methylation of

ethene, with the rate of methylation increasing as the reaction temperature is raised. Opposing this reaction is the cracking of these products back to ethene, where again the rate increases with temperature. At a temperature of 450 °C, the major portion of the product spectrum is propene, followed by butene. The process yields only around 15 % ethene.

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LIST OF PUBLICATIONS

During the course of this study, the following papers have been published:

Journals:

M.G.Howden and J.J.C.Botha. *Synthesis of highly siliceous ZSM-5 using diaminoalkanes as templates*, Appl. Catal., 73 (1991) 27.

M.G.Howden. *Thermogravimetry of α,ω-diaminoalkanes used in synthesising ZSM-5*, Zeolites, 13 (1993) 315.

Conference Proceedings:

M.G.Howden, J.J.C.Botha and M.S.Scurrell. *Factors influencing the light olefin selectivity during the conversion of methanol over ZSM-5*, "Novel Production Methods for Ethylene, Light Hydrocarbons, and Aromatics" (Ed. L.F.Albright, B.L.Crynes and S.Nowak) Marcel Dekker, New York, 1992, p. 391. This paper was initially presented at the 199th ACS National Meeting, Boston, USA, April 1990.

In terms of paragraph GP 8 of "General Rules for the degree of Ph.D.", I, Prof. C.T.O'Connor, as supervisor of the candidate, M.G.Howden, certify that I approve of the incorporation in this thesis of material that has been published.

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CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1. HISTORICAL BACKGROUND

Around 1950 the Union Carbide Corporation in the USA started a research programme with the aim of making synthetic zeolites. Their first success was in the preparation of the mineral which they designated zeolite A [1,2]. This zeolite was crystallised from a gel made from a mixture of sodium silicate and sodium aluminate. Naturally, such a mixture would contain a significant amount of sodium hydroxide.

About ten years later two separate sets of researchers began work wherein some of the sodium hydroxide was replaced by the organic compound tetramethylammonium hydroxide, which is itself also a strong base. The people concerned were Barrer and Denny from the UK, who made zeolite N-Q [3], and Kerr and Kokotailo from the Mobil Corporation in the USA, who synthesised zeolite ZK-4 [4,5]. Subsequently Mobil also patented a method to make zeolite α [6]. The X-ray diffractograms of these three zeolites are almost the same as zeolite A mentioned above, which clearly indicated that they all have a similar structure. However, they do differ in their compositions. Zeolite A having equal amounts of silicon and aluminium atoms, gives it a silica to alumina (SiO_2 : Al_2O_3) mole ratio of 2 : 1. Zeolites N-Q, ZK-4 and α all had slightly higher silica to alumina mole ratios; their values were 4,4 : 1, 3,2 : 1 and 6,1 : 1 respectively.

The following organic base to be examined in zeolite synthesis was tetraethylammonium hydroxide and the crystalline product that was formed was called zeolite β [7]. Its X-ray diffractogram differed from that of zeolite A, and its structure has only recently

been fully resolved [8]. A further difference was that its silica to alumina mole ratio could be in excess of 70 : 1. This was unusual because no known zeolites at the time contained such a high proportion of silica. This was an important development as it was already well established that the stability of zeolites was enhanced by increasing their silica to alumina ratio.

As to be expected one of the next organic bases to be examined was tetrapropylammonium hydroxide. Two relatively junior workers, Bob Argauer and George Landolt, at Mobil eventually successfully synthesised ZSM-5 [9]. The acronym ZSM is derived from the three words Zeolite and Secony Mobil, the organisation at which it was synthesised. The ZSM-5 produced a distinctive X-ray diffractogram which indicated that it had an unique structure unlike any other zeolite. Further, it had a silica to alumina mole ratio of around 30 : 1 and was also thermally very stable. Patents on its preparation were granted around 1970 [10]. The use of tetrabutylammonium hydroxide gave the zeolite ZSM-11 [11], which had a similar X-ray diffractogram to that of ZSM-5.

From a review on the preparation of zeolites in 1973, Flanigen [12] observed that the role of organic bases, such as the tetrapropylammonium cations in ZSM-5, seemed to be not only as an alkali needed for synthesis, but that they were also molecules around which crystallisation took place. As will be shown later in this chapter, the tetrapropylammonium compound fits neatly into the channels of ZSM-5. Hence she introduced the term "template" for such organic materials used in the preparation of zeolites.

Although having patented a new zeolite, which was very active and thermally stable, little attention was paid to ZSM-5 as it appeared that there was no practical application for it. This situation remained so for a few years until an unexpected result was obtained by Chang and Silvestri at Mobil [13]. While trying to use methanol as a methylating agent and ZSM-5 as the catalyst, it was found that only a limited amount of methylation took place, but that the methanol itself was completely converted. When pure methanol

was the feed, the product consisted of hydrocarbons containing between five and ten molecules, and which contained a significant amount of aromatic compounds. Their results were to be published a few years later [14].

Researchers at Mobil naturally observed that the composition of the product from methanol is very similar to that of gasoline. Around this period there was also a world-wide shortage of crude oil caused by the Arab oil embargo of 1973. As the synthesis of methanol was established, the discovery at Mobil meant that a new technique had been found to make synthetic motor fuel. This discovery naturally created a wide interest in determining the structure of ZSM-5, elucidating its method of synthesis, studying the conversion of methanol including identifying the reaction mechanism, and optimising conditions to obtain the ideal product spectrum.

The initial success of crystallising these zeolites, led to various other organic compounds being examined in this field, and as a result, numerous other novel zeolites were discovered. Those discovered by researchers at Mobil were identified by the acronynic letters ZSM and a sequential number. One of them was zeolite ZSM-48, which will be encountered in this work.

Following recommendations on "*Chemical Nomenclature and Formulation of Compositions of Synthetic and Natural Zeolites*" by IUPAC in 1978 a mnemonic code consisting of three capital letters was adopted for each type of zeolite structure. Thus, ZSM-5 and ZSM-11 became MFI and MEL respectively; FI and EL coming from the first two letters of five and eleven. However, due to inadequacies in this system caused by discovery of so many new zeolites, it has not been fully accepted and the terminology ZSM is still more generally used.

1.2. ZEOLITE STRUCTURES

1.2.1. STRUCTURE AND COMPOSITION OF ZSM-5

The crystalline structure of zeolite ZSM-5 was determined by Kokotailo and co-workers in the late 1970s [15,16]. The structure consists of the linking of tetrahedra and forming a series of five-membered rings, the size or shape of which gives rise to this zeolite and related types called pentasils. From the information that was presented, a wire model of the ZSM-5 was reproduced and a photograph is shown in Figure 1.1. The series of five-membered rings are vertical in the photograph.

As a result of its structure, ZSM-5 contains two types of intersecting channels. Both are slightly elliptical ten-membered rings; the one being straight and the other sinusoidal or "zig-zag". The straight channels are clearly seen in Figure 1.1, but the sinusoidal ones, together with their system of interconnection, are better illustrated in Figure 1.2. The opening of the straight channels is 0,53 x 0,56 nm, while that of the sinusoidal ones is slightly narrower being 0,51 x 0,54 nm [17,18].

ZSM-5 crystallises in the orthorhombic system, with the model in Figure 1.1 showing the *010* face. The lattice constants are a = 2,01, b = 1,99 and c = 1,34 nm. The material can be reversibly converted by thermal or other means to the monoclinic system [16]. The structure of ZSM-11 has also been resolved [19] and is similar to that of ZSM-5. However, it has a tetragonal crystal system with lattice constants of a = b = 2,01 and c = 1,34 nm.

The tetrahedral positions of the ZSM-5 structure are mostly occupied by silicon atoms, but are substituted regularly by aluminium ones. In the unit cell there are 96 silicon plus aluminium atoms, which are naturally connected by 192 oxygen atoms. The zeolite also contains a number of exchangeable cations, which after synthesis are usually sodium cations. This means that the composition of the unit cell is Na_n Si/Al_{96} O_{192}. The lowest Si : Al mole ratio is about 10 : 1, and this value can be increased to several thousand [20]. A material that is virtually free of

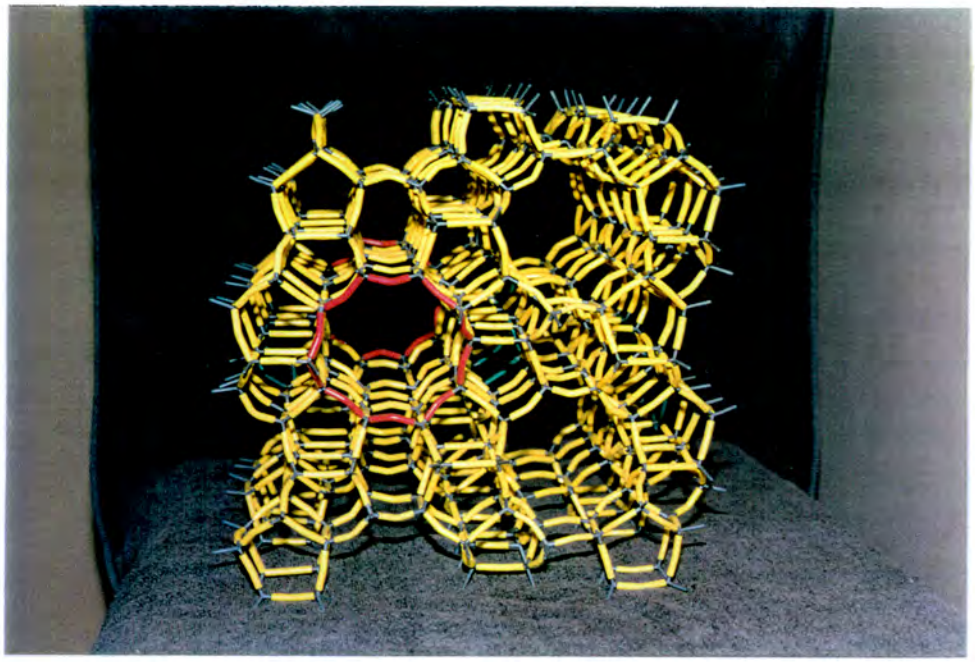

Figure 1.1. Model of the structure of zeolite ZSM-5.

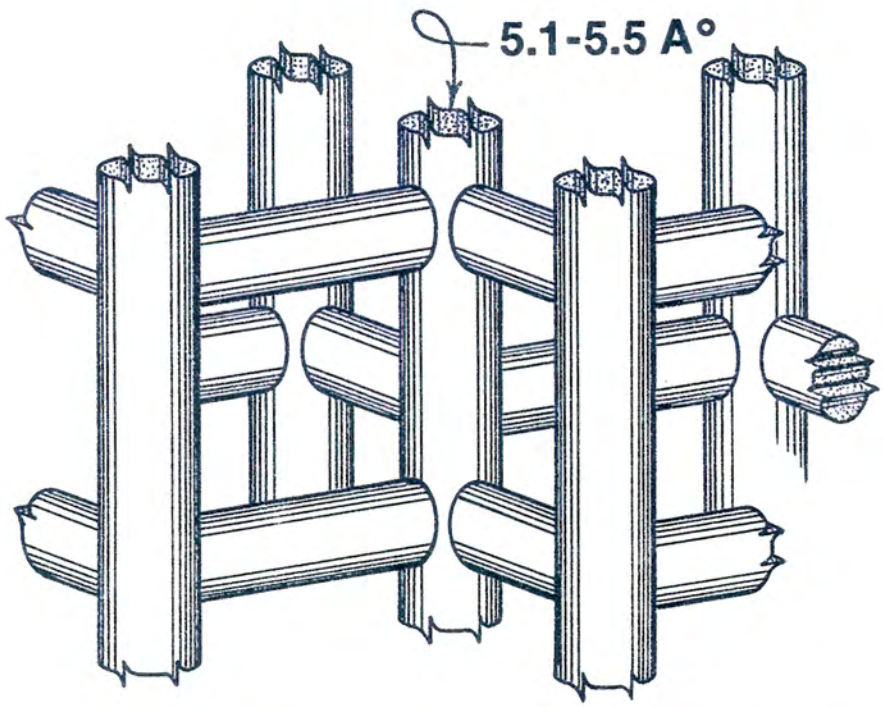

Figure 1.2. Channel system in ZSM-5. Reproduced from ref. 15.

aluminium was prepared and is called silicalite [17]. The variations that exist in the silica to alumina composition, do however lead to important changes in the catalytic performance of the ZSM-5 zeolite.

1.2.2. STRUCTURE OF ZSM-48

The structure of ZSM-48 was established by Schlenker *et al* [21] in 1985. From the information which they provided, a wire model was made and a photograph thereof is shown in Figure 1.3. Just like ZSM-5, the structure consists of the linking of tetrahedra forming the pentasil series of five-membered rings. ZSM-48 also crystallises in the orthorhombic system, with lattice constants of a = 1,42, b = 2,01 and c = 0,84 nm. The model in Figure 1.3 shows the *001* face, and is very similar to the *010* face of ZSM-5 shown in Figure 1.1.

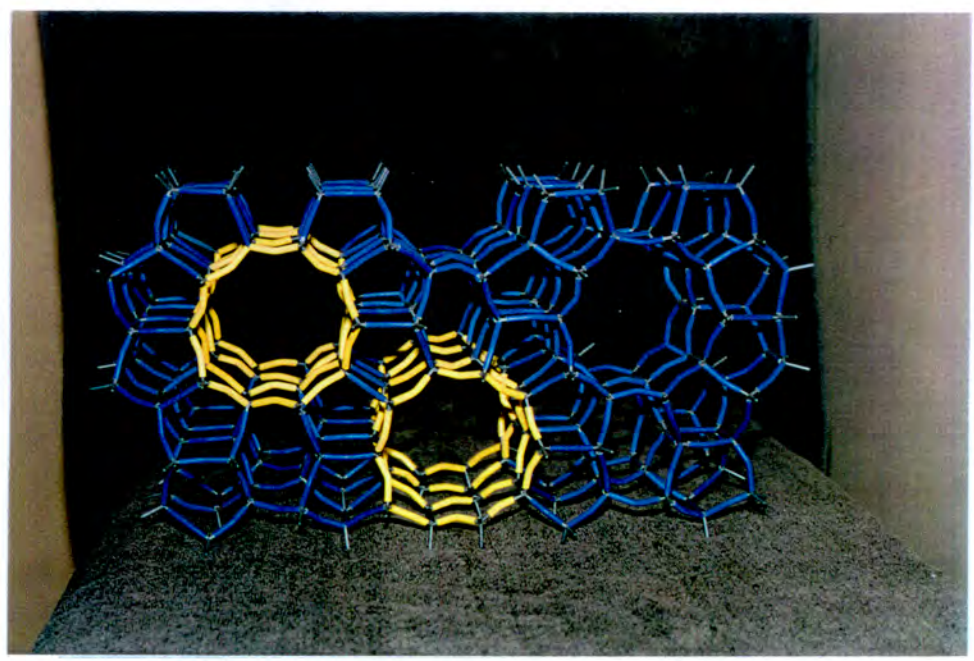

Figure 1.3. Model of the structure of zeolite ZSM-48.

As shown by the model in Figure 1.3, ZSM-48, like ZSM-5, has straight channels formed by ten-membered ring apertures producing an opening of 0,53 x 0,56 nm [21]. However, unlike ZSM-5, there are no other significant channels connecting these linear ones. Electron microscopy have confirmed the existence of these isolated linear channels in ZSM-48 [22]. With this structure it is not surprising that the crystallites of ZSM-48 are elongated or "needle" shaped [21,22]. Other zeolites, namely EU-2, EU-11 and ZBM-30, which have been reported in the literature, are in fact indistinguishable from ZSM-48 [21].

1.3. SYNTHESIS OF ZEOLITES

The hydrothermal reaction of a gel consisting of an alkali-aluminosilicate leads to the crystallisation of zeolites. The composition of the mixture and conditions used in the synthesis determine which zeolite is actually formed [23-26]. In order to form the gel, it is necessary that the aluminium and silica be dissolved in the alkaline solution. Although this is easy for aluminium compounds, the silica requires that the pH of the solution be at least 11 [23,27,28]. Further, the rate at which the silica is dissolved depends on its fineness and the temperatures of the alkaline solution. The inclusion of certain organic compounds to the reaction mixture leads to the crystallisation of a host of different zeolites [26,29], and which naturally includes zeolite ZSM-5.

1.3.1. SYNTHESIS OF ZSM-5 IN THE PRESENCE OF TETRAPROPYLAMMONIUM COMPOUNDS

The original mixture for preparing zeolite ZSM-5 was made from an aqueous gel consisting of various sources of alumina and silica, as well as containing sodium and tetrapropylammonium cations. A

general formula for describing the reaction mixture is:

$$x\ Na_2O \quad z\ Pr_4NBr \quad y\ Al_2O_3 \quad 20\ SiO_2 \quad 1000\ H_2O$$

where the values of x, y and z vary between certain limits.

Due to the siliceous nature of the product, the value of y will always be less than about one. Jacobs and Martens [30] have reviewed the effect of different aluminium concentrations in the reaction mixture. They found that all investigations tended to show that after a certain period and at a particular temperature, the degree of crystallisation (as measured by X-ray diffraction intensity) of ZSM-5 increases as the aluminium content of the gel is decreased. The summary of their main observation is reproduced in Figure 1.4.

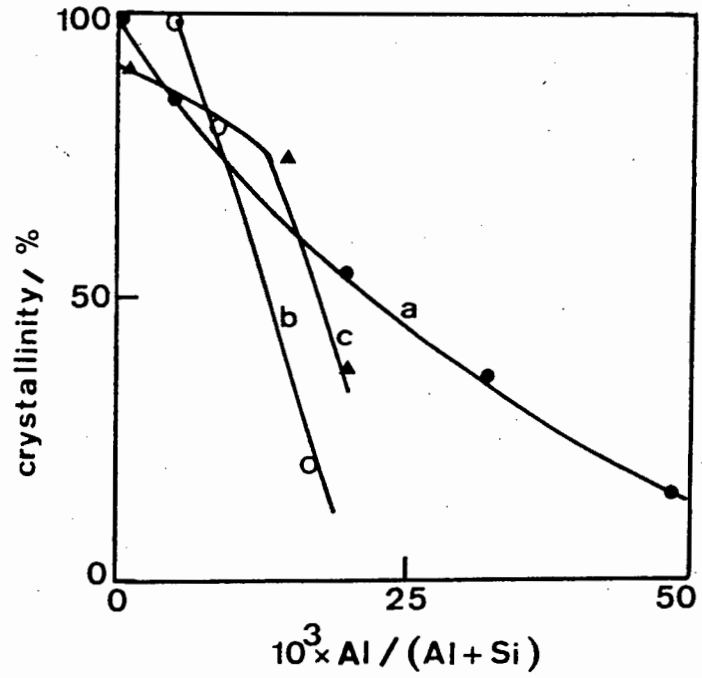

Figure 1.4. Influence of the Al / (Al + Si) composition of the synthesis gel on the crystallinity of ZSM-5. Reproduced from ref. 30, where graphs a, b and c are data taken from earlier researchers.

In the original patent [10] a fairly wide range in the composition of sodium oxide was used to synthesise ZSM-5. The actual limits on this range were established by Erdem and Sand [31]; their principal result is reproduced in Figure 1.5. It is clearly shown that if a high concentration of Na_2O is used, the reaction will give a co-crystallisation of other zeolites, which mainly would be mordenite and possibly also analcime. Thus, in the above formula, the value for x should not exceed about 3. Using a similar formula to that above, Fegan and Lowe [32,33] also studied variations in the Na_2O concentration: they found that as the value of x increased, the yield of ZSM-5 decreased and extrapolates to zero at x = 6,7. On the other side, they found that the minimum value of x to permit the crystallisation of ZSM-5 was 0,5.

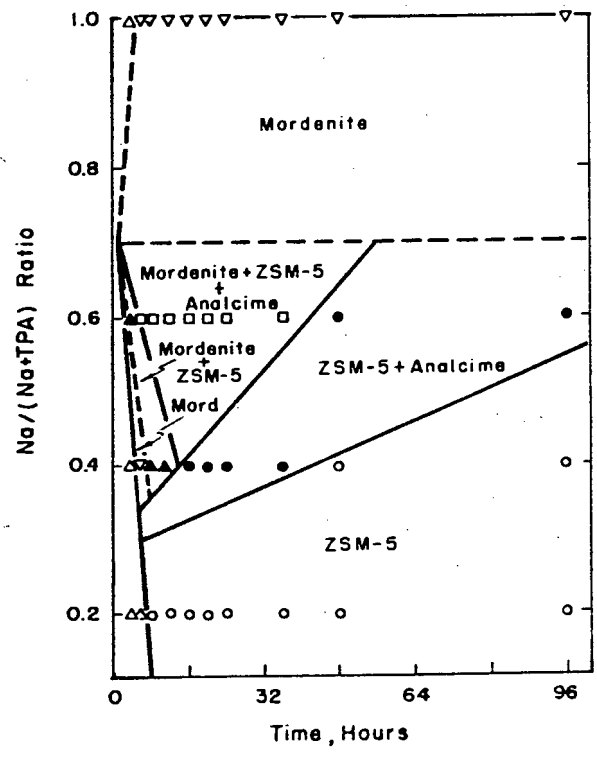

Figure 1.5. Isothermal metastable phase transformation diagram for the reaction system $10(TPA,Na)_2O$-Al_2O_3-$28SiO_2$-$750H_2O$ at 175 °C showing the different zeolites formed. Reproduced from ref. 31.

According to Rollmann [34], the addition of a quaternary ammonium cation to a reaction mixture can effect changes of three types: (a) a different zeolite structure is obtained; (b) a zeolite crystallises where the reaction mixture would otherwise remain amorphous indefinitely; (c) the same zeolite is obtained as without quaternary, but it possess an altered chemical composition.

It now known that the presence of the tetrapropylammonium cations does lead to the crystallisation of ZSM-5, and it is therefore necessary to asses the dependence of the rate of crystallisation on the tetrapropylammonium concentration. This was done by Romannikov *et al* [35], and this parameter is illustrated in Figure 1.6. It is obvious that the more tetrapropylammonium cations used in the reaction mixture, the faster crystallisation takes place. Their results indicate that to ensure the formation of ZSM-5, the value of z in the foregoing formula should be in the region of 3 to 5. Crea *et al* [36] studied the synthesis where much lower concentrations of tetrapropylammonium cations were used: they found with an equivalent concentration of z being between 3 and 1, the degree of crystallisation was reduced to 80 %, and with a value of less than one only about 20 % of the expected crystallisation had taken place.

Not all the tetrapropylammonium cations are incorporated into the ZSM-5 structure. It has been determined [37-39] that after synthesis there are almost four TPA cations per unit cell of the ZSM-5 crystals. There are 96 silicon or aluminium atoms per unit cell, whereas the synthesis formula has 20 silicon and a very small amount of aluminium atoms. This means that pro rata the crystalline material contains about 0,8 of the Pr_4N cations that were used, and therefore with $z = 3$, a moderate excess of about four times of tetrapropylammonium cations needed, is required for the synthesis.

Intersections are where the channels in a zeolite meet. In ZSM-5 each unit cell has four intersections. It appears logically that a TPA cations must be located at each of these intersections, with a propyl chain extending into each of the four channels leading

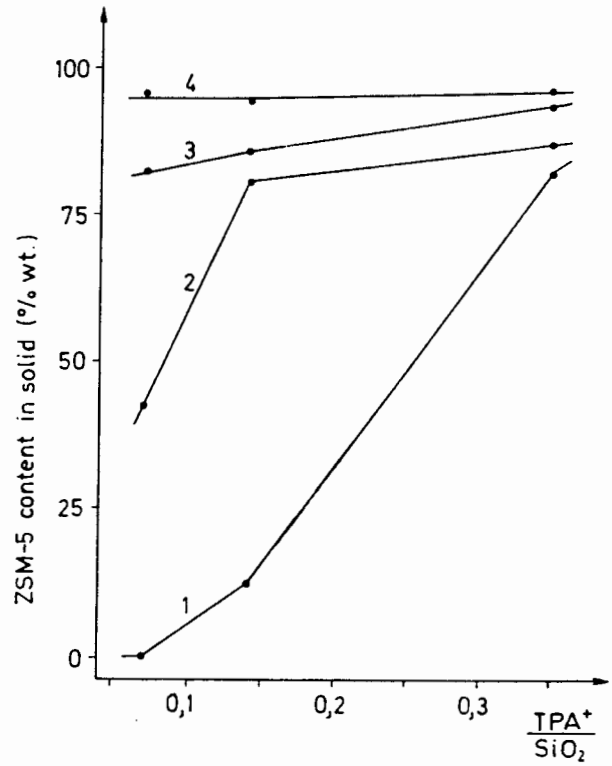

Figure 1.6. Dependence of the yield of the ZSM-5 zeolite upon the initial molar ratio of (TPA / SiO_2). Crystallisation temperature 175 °C; crystallisation time: (1) 24 h; (2) 48 h; (3) 72 h; (4) (108-144) h. Adapted from ref. 35.

from the intersections. This neat fitting arrangement of the organic compound within the ZSM-5 structure probably led to the concept that it acted as a template during synthesis.

In the synthesis, nuclei of silicate and aluminate ions are formed around the tetrapropylammonium cations, and then proceed to grow into larger crystals. Derouane and co-workers [37,40] identified two ways in which crystallisation proceeds. If the rate of nuclei formation is much faster than that of crystal growth, the reaction mixture becomes saturated with nuclei and eventually they agglomerate into crystallites consisting of smaller ZSM-5 crystals. If, however, crystal growth is faster than the formation of nuclei,

the appearance of the final crystallite is much more uniform. Irrespective of method of formation, the size of the crystallites in both cases are about the same, being a few micron in diameter.

Derouane and co-workers [37,40] found that these two procedures lead to a difference in the distribution of aluminium in the crystallites. With the slow nuclei formation, there is a preference for silicon atoms to form the nuclei, and only as a result of the concomitant increase in aluminium concentration still in solution, are these atoms ultimately to be found in the crystallites. This leads to an uneven distribution of the aluminium atoms. This phenomenon was clearly illustrated by work of von Ballmoos and Meier [41] who used a slow process to make relatively large crystals of ZSM-5. An electron microprobe of these crystals showed a distribution of aluminium across the crystals: there was a low concentration in the centre, but as the probe moved towards the outside there was a gradual increase in the concentration of aluminium.

1.3.2. SYNTHESIS OF ZSM-5 IN THE PRESENCE OF AMINES

After the original preparation using tetrapropylammonium compounds, numerous other organic compound [29,42] were subsequently tested for their suitability in synthesising ZSM-5. The best achievements were made using various types of amines.

Rubin *et al* of Mobil [43] obtained a patent which showed that primary monoalkylamines, containing between 2 to 9 carbon atoms, can be used successfully to synthesise ZSM-5. These same workers, however, found that dialkylamines were less effective. Further investigations by other researchers [38,40,44] found that trialkylamines could be successful used in making ZSM-5, but that the products tend to have high intergrowths of ZSM-11. It has shown in another patent [45] that additions of monoethanolamine or monopropanolamine to the synthesis mixture were also capable of leading to the synthesis of ZSM-5.

Probably the most successful alternate templates are α,ω-diaminoalkanes; these are compounds consisting of normal alkanes with an amine at each end of the chain. The propane and butane derivatives lead to the synthesis of ZSM-5 [46], but they can also produce ferrierite [47]. The use of 1,5-diaminopentane and 1,6-diaminohexane have proved successful for preparing ZSM-5 [42,46-48], with the pentane compound, which due to its smaller size fitting more neatly into the ZSM-5 structure, apparently the better of the two [42]. However, as this chemical is not readily available, 1,6-diaminohexane is more generally preferred [49-51]. A problem with 1,6-diaminohexane is that if little or no aluminium is used in the preparation mixture, ZSM-48 can under certain conditions often co-crystallise, or even be the only zeolite that is formed [52-54]. When the diaminoalkane contains seven or more carbon atoms ZSM-11 is produced [42,47,55], with 1,8-diaminooctane being the most suited size for this zeolite structure [42]. Although there appears to be a preferential size of the alkane portion of the diamine for the formation of either ZSM-5 or ZSM-11, Gabelica *et al* [46] generally found intergrowths of both these zeolites when using all these diamine compounds.

In all the examples reported above when α,ω-diaminoalkanes was used as the synthesising template [46-51,55], the silica to alumina mole ratio of the reaction mixture was generally in the region of 50 : 1, and never exceeded 90 : 1. Some restrictions on the composition were indicated from the work of van der Gaag *et al* [50] who showed that with 1,6-diaminohexane, ZSM-5 did not crystallise when the silica to alumina mole ratios of the reaction mixture was in excess of 200 : 1. This clearly means that these templates are not ideally suited to synthesise ZSM-5 with low aluminium contents.

Valyocsik and Rollmann [47] found that when ZSM-5 was synthesised in the presence of diaminopentane and diaminohexane, there were respectively 9,6 and 7,7 of these organic molecules per unit cell. Lowe and co-workers [51,53] found a similar value for the hexane derivative. As the ZSM-5 unit cell has four channel intersections, it was logically concluded that eight of these linear

molecules, with a terminal amine portion in an intersection, would neatly fill the entire zeolite. Gabelica *et al* [46] however, found that with diaminopentane and diaminohexane there were only 5,6 and 5,4 molecules respectively, included in the unit cell of ZSM-5. Similarly, Jacobs and Martens [42] found that the pore filling was about 60 % of the values determined by Valyocsik and Rollmann mentioned above.

Another question is the nature of the organic compound within the synthesised ZSM-5. Nuclear magnetic resonance spectra for carbon, have indicated that the chemical composition of the diaminoalkanes remains unaltered when they are occluded in the ZSM-5 framework [46,56]. However, direct analysis of the organic compound showed that the number of nitrogen atoms in the incorporated zeolite was always less than the two per molecule of the organic compound that was initially used [42,47]. This means that there would not necessarily be an amine group at each end of the linear hydrocarbon portion of the molecule.

When using α,ω-diaminoalkanes as the organic directing agent, it has been found that after synthesis the zeolite contains low amounts of sodium [42,47-49,51,55]. This is attributed to the fact that these compounds nearly completely fill the channels of ZSM-5 and thereby reduce the chances of also including sodium cations. A low initial sodium content is a distinct advantage when trying to remove the remaining amount to the low limits required for an active catalyst.

Jacobs and Martens [42] expressed the view that in the absence of tetrapropylammonium cations, the synthesis of ZSM-5 require the presence of small amounts of seeds for crystallisation. The most convenient method for satisfying this requirement would be to include a small amount of tetrapropylammonium cations in the reaction mixture. It has been shown [57] that the minimum amount should be sufficient to fill 10 % of the intersections of the ZSM-5 crystals. The effectiveness of seeds has been demonstrated, where without the addition of any organic compounds as structure directing

agents, the addition of small amounts of ZSM-5 crystals have propagated the growth of the zeolite [58,59].

1.3.3. SYNTHESIS OF ZSM-48

Zeolite ZSM-48 was initially identified when it occurred as an impurity during the synthesis of ZSM-39 [21,60], where either tetramethylammonium or tetraethylammonium cations were used as the structure directing agent. One of the early successes in preparing pure ZSM-48 was achieved around 1980 by Chu [61], who used a mixture of tetramethylammonium chloride and n-propylamine for the synthesis.

The use of α,ω-diaminoalkanes to synthesise ZSM-48 was demonstrated by Rollmann and Valyocsik [52]. There was very little aluminium present in their preparations, with the silica to alumina ratio more than 500 : 1, and the crystallisation was done at 160 °C. In the work of Araya and Lowe [62], small amounts of aluminium were added to the reaction mixture containing 1,6-diaminohexane, but the synthesis was carried out at the higher temperature of 180 °C. Franklin and Lowe [53], who also used 1,6-diaminohexane but without any aluminium, found that when using lower reaction temperatures of either 90 °C or 120 °C, that ZSM-5 crystallised from the system, but that at a higher temperature of either 150 °C or 180 °C, ZSM-48 was formed.

Franklin and Lowe [54] found that there were numerous templates that could be used to prepare ZSM-48. In all their experiments, no aluminium was added to the reaction mixtures. When aluminium is to be included in the zeolite ZSM-48 framework, it appears that the organic compound, hexamethonium bromide, ought be used [63,64]. Even here the amount of aluminium incorporated into the zeolite is rather low, and unless the silica to aluminium mole ratio is higher than about 120 : 1, other zeolites are preferentially formed [64]. The hexamethonium compound is cationic, and this must be the reason why it would support the inclusion of aluminium in the zeolite framework. Giardano *et al* [64,65] found in their study on the

incorporation of the hexamethonium cations in ZSM-48, that this material remained unaltered during crystallisation.

1.4. CONCEPT OF SHAPE SELECTIVITY

The dimensions of the pores of a zeolite vary between about 0,3 and 1,4 nm, and when used as a catalyst causes restrictions on the type of reactant that can participate in, and products that are formed during the reaction. This was first observed by Weisz and Frilette in 1960 and they called this effect *shape selective catalysis* [66].

After synthesis both an organic compound and sodium cations are in the pores or channels of zeolite ZSM-5, and it is necessary to remove these materials before it can function as a shape selective catalyst. It has been shown that the organic tetrapropylammonium compound can be removed by calcination in air by using a temperature of at least 530 °C [67,68]. The sodium cations are removed by repeated exchanges with an ammonium salt solution, followed by air calcination at 538 °C in order to de-ammoniate the cations and convert them into protons [20]. An alternate method to remove the sodium cations and acidify the ZSM-5, is treatment with mineral acids [69], but this method unfortunately also results in the removal of some of the aluminium atoms from the zeolite framework.

In studies with methanol over ZSM-5 [14], the the product consisted of a large amount of aromatics which did not contain more than ten carbon atoms. Additional work showed that this product distribution was also obtained when reactants other than methanol were used [70]. It has been shown [71] that monomethyl substituted paraffins and monocyclic hydrocarbons can diffuse easily through the pores, whereas dimethyl substituted paraffin diffuse slowly. Furthermore, ZSM-5 excludes molecules with dimensions much larger than 1,3,5-trimethylbenzene. In another paper [72] it was reported that the methylation of toluene gave almost 100 % para-xylene. These restrictions on the size and preferential type of products

formed, are due to the aperture of the channels being about 0,55 nm, thus making ZSM-5 highly effective as a shape selective catalyst.

The overall shape-selectivity of ZSM-5 was summarised in 1980 by Derouane [73]. Subsequently, a number of extensive reviews on shape-selectivity, in which ZSM-5 was compared to other zeolites were published; good examples are by Weisz [74], Csicsery [75] and Chen and Garwood [76]. In these articles it was clearly demonstrated what effect the size of the ZSM-5 channels had on reactant and product selectivity, and restriction on any transition state. Possible applications of these properties were given [75,76], and the advantages thereof will be become clearer later in this chapter.

1.5. COKE DEACTIVATION

There are two ways in which the deposition of extraneous material can cause zeolite catalysts to deactivate [77-80]. Firstly, polymerised products condense within the pores and restrict access to the active sites. Polymerisation takes place at lower temperatures, and this tendency will decrease as the temperature is raised [77,79,80]. A second product that causes deactivation is coke, which is formed at higher temperatures [79-81]. This coke can form either inside the pores or on the outside of the catalyst, which then blocks or restricts the entrance to the pores [77,80,82].

Due to shape selectivity, coke-precursors are not easily formed within the pores of ZSM-5. Consequentially the formation of coke and the subsequent deactivation of ZSM-5 is relatively slow, and therefore the ZSM-5 catalyst can remain active for lengthy periods [81,83-86]. Although its formation of coke within the channels of ZSM-5 is inhibited, it still occurs and its deposition takes place on the outside surface of the crystals [79,80,82,87]. In the case of the conversion of methanol over ZSM-5 this coke starts forming around 380 °C, and the rate of formation increases with temperature [80,88].

1.6. REACTION PATH AND MECHANISM DURING CONVERSION OF METHANOL OVER ZSM-5

In the proton form zeolite ZSM-5 is a highly acidic catalyst. Microcalorimetric determination of ammonia adsorption at 143 °C has been measured at about 160 kJ mol^{-1} [89,90]; this is a relatively high value indicating strong acidity. Temperature programmed desorption of ammonia has been found to take place at about 450 °C [91-93], which again indicates a strong acidity.

By being strongly acidic, ZSM-5 should naturally also be a very active catalyst. The high activity of ZSM-5 has also been demonstrated by its ability to crack n-hexane [94,95]; it far more active than most other materials including zeolite Y [94]. The α-value (a measure of cracking activity) of ZSM-5 is between 10^2 and 10^3 [94,95]. Further, it was also clearly shown that the activity of ZSM-5 is directly dependant on the amount of aluminium it contains [94,95], and the activity of this catalyst is therefore increased or reduced by variations in its aluminium content.

In the original paper on the conversion of methanol, Chang and Silvestri [14] identified that the reaction proceeds via a number of steps. As shown in Figure 1.7, methanol is first dehydrated to dimethyl ether. Further dehydration of dimethyl ether yields light olefins, which then proceed to produce a mixture of paraffins and aromatics. Chang [96] in 1983, Derouane [97] in 1984 and Hutchings and Hunter [98] in 1990 reviewed the position, and a summary of their observations on the subject is given below. This will also include specific information given in the most important publications.

Probably the most contentious point was which olefin was the first to be formed from dimethyl ether, and by what mechanism did this take place. In 1978 Derouane *et al* [99] deduced that via an intermolecular mechanism, ethene is the primary product formed from the dehydration of dimethyl ether. However, they were unable to observe the presence of ethene in their ^{13}C NMR studies. They concluded that its absence was due to the fact that it reacted very

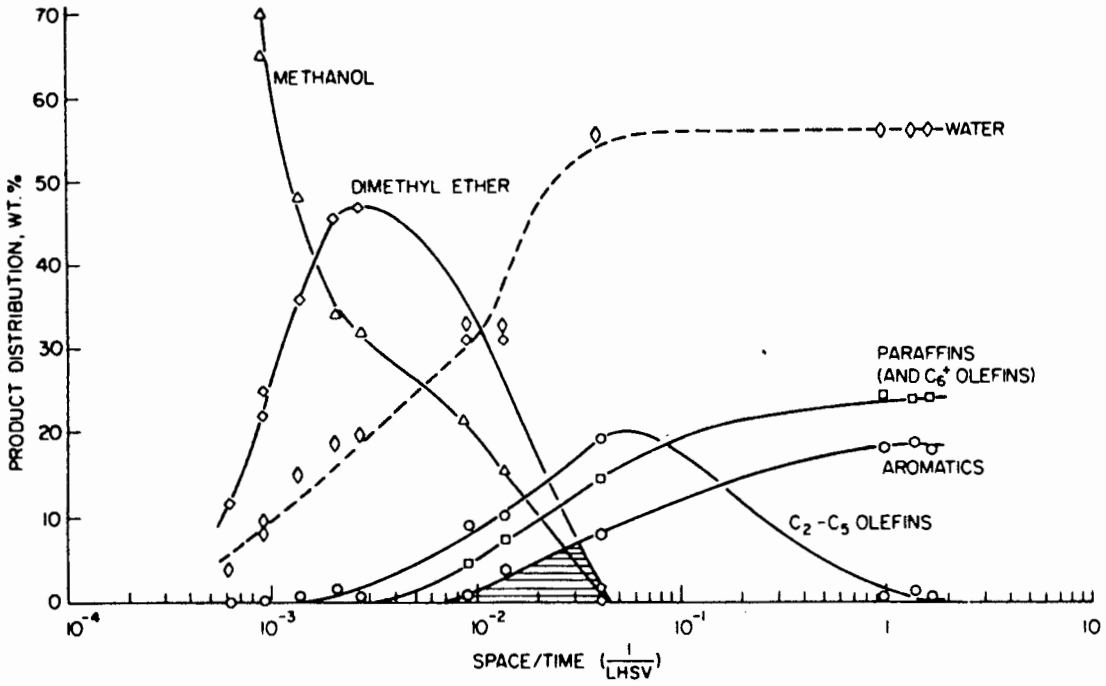

Figure 1.7. Reaction path for the conversion of methanol to hydrocarbons at 371 °C. Reproduced from ref. 14.

rapidly with methanol to form propene. This reaction took place rather than dimerisation to butene. Based on the fact that ethene as such is unreactive, Anderson *et al* [91] in 1979 disputed these findings. Because they observed no ethene, but some propene in the product, they concluded that propene was the primary olefin formed.

In 1980, van den Berg *et al* [100] found when using a reaction temperature below 290 °C, the product to be mainly ethene and propene. They re-established that ethene is the primary olefin formed, and in the presence of dimethyl ether the ethene is easily methylated to form propene. Haag *et al* [101] studied the reaction at very low conversion levels at 371 °C, and under these conditions the product consisted of both ethene and propene, but through extrapolation to zero conversion, ethene was deduced to be the primary product. A co-author of Anderson [91], Mole identified the

mechanism of the formation of ethene and produced significant quantities thereof at 320 °C [102,103]. This lower temperature is the main difference between this work and that done earlier by Anderson *et al* [91], where their experiments were carried out at 400 °C. Chu and Chang [104] suggested that most of the confusion stems from neglect of thermodynamic and kinetic contributions, and when they took these into account they concluded that ethene is the initial olefin formed.

The mechanism by which the ethene is formed was initially postulated by van den Berg *et al* [100]; first dimethyl ether is adsorbed onto the catalyst surface to give a dimethyloxonium ion. In the next step, it is attacked by a second DME molecule to produce a trimethyloxonium ion. Via a Stevens rearrangement, a ethylmethyloxonium ion is formed, which in turn finally gives ethene and methanol. By using isotopes Mole *et al* [102,103] proceeded to verify the above mechanism, and also identified an additional step wherein the trimethyloxonium ion deprotonates to give an oxonium ylide. Additional evidence for the validity to the proposed mechanism has been produced by ^{13}C NMR spectra which supported the existence of the trimethyloxonium cation [105]. These reaction steps are shown in Figure 1.8. Olah *et al* [106] agreed with the existence of the ylide, but disputed that the Stevens rearrangement took place. In their work, evidence was presented that another methyl ion became attached to the ylide to give an ethyl chain. From this last compound, ethene and dimethyl ether are produced. This mechanism is also shown in Figure 1.8.

Additional confusion to the picture was caused by Dessau *et al* [107-109] by finding that ethene is also formed through re-equilibrium of higher olefins. In their work cracking was identified as a prevalent reaction, which could be expected to take place since reaction temperatures as high as 450 °C were used. However, it must be stressed that these results do not disprove that ethene is the primary product.

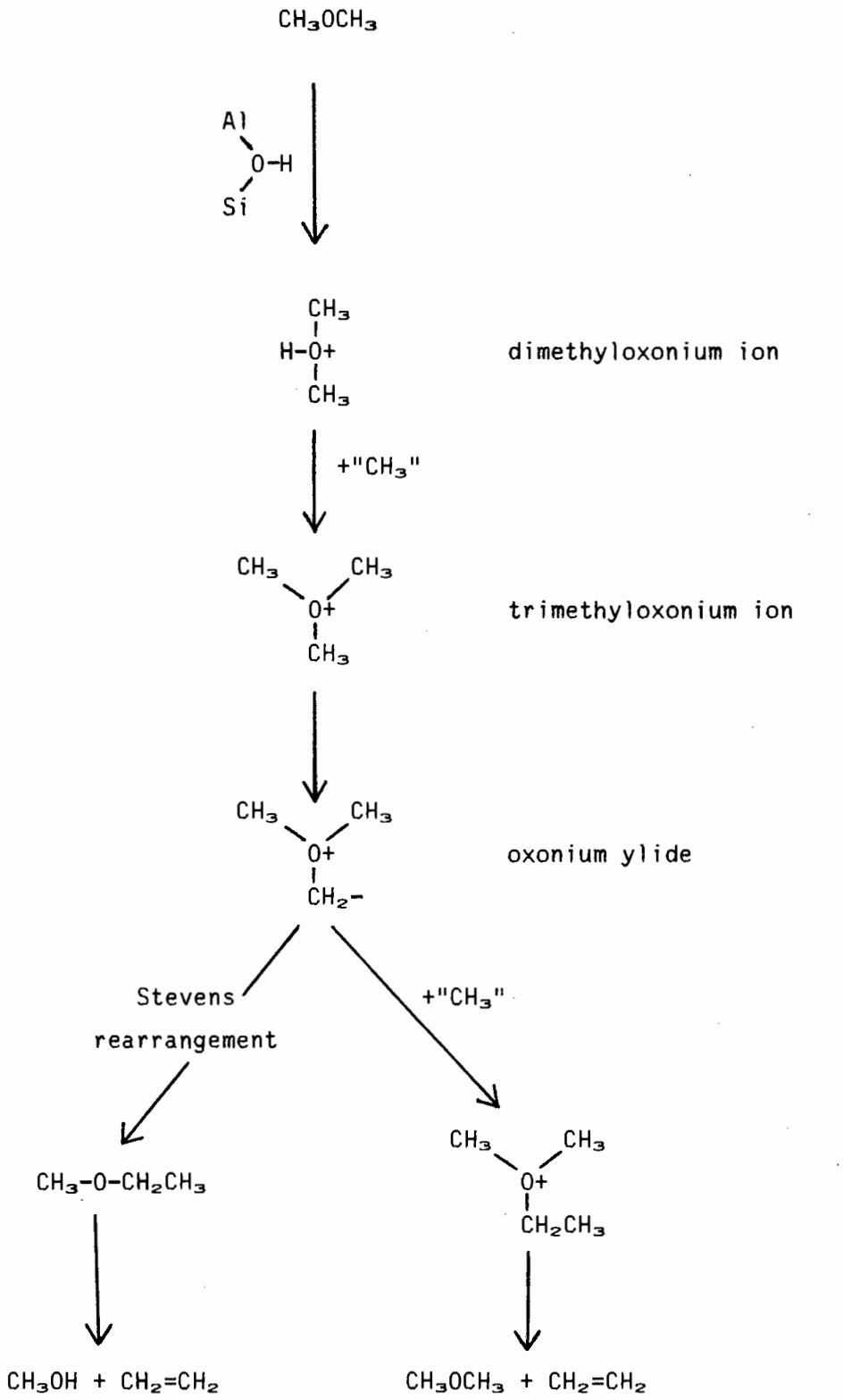

Figure 1.8. Mechanism by which ethene is formed from dimethyl ether.

Propene formation takes place via subsequent methylation of a carbenium ion, $CH_2-CH_3^+$, [99] by dimethyl ether [100]. The strong methylating nature of dimethyl ether was demonstrated by Espinoza and Mandersloot [110], who by using DME as the feed obtained large quantities of propene and not much ethene. Dejaifve *et al* [111] have shown that dimerisation of ethene leads to butene. However, since less butene is formed than propene, this indicates that methylation is the more prevalent reaction. Further electrophyllic methylation leads to a chain growth of larger olefins [104,112].

The conversion of methanol produces methane at temperatures in excess of 400 °C [113]. The formation of methane is concomitantly formed with coke [113], as shown in the following reaction:

$$2\ CH_3OH \quad \text{------>} \quad C_{coke} + CH_4 + 2\ H_2O$$

Finally, Dejaifve *et al* [111] has shown that the co-addition of a carbenium ion and an olefin leads to a mixture of monocyclic aromatics and aliphatics. By gathering data from numerous results, Weisz [86] has shown that the molar ratio between the quantities of paraffins and of aromatics produced, is on average 3 : 1.

1.7. CONVERSION OF METHANOL TO LIQUID FUELS AND CHEMICALS

The conversion of methanol over ZSM-5 can be divided into three major categories. Firstly, the conversion of methanol can proceed through all the stages discussed to yield gasoline: this is the methanol-to-gasoline (MTG) process. Secondly, the reaction is curtailed so that not all the olefins are converted: these are the methanol-to-chemicals (MTC) process, the chemicals being a mixture of gasoline and olefins, and the conversion which aims to produce mainly light olefins called the methanol-to-olefins (MTO) process.

Olefins themselves can be used as the feed. Thus, thirdly, there are those processes by which olefins are converted into aromatics, a mixture of diesel and gasoline or a product rich in

gasoline: they are called respectively M2 forming, the Mobil olefins-to-gasoline-and-distillate (MOGD) process and the Mobil olefins-to-gasoline (MOG) process.

1.7.1. METHANOL TO GASOLINE PROCESS (MTG)

Based on the initial work of Chang and Silvestri [13,14], Mobil embarked on an extensive programme on the development of this process [114]. A number of pilot-plant studies were carried out by Mobil and their findings were reported in three papers [115-117], and subsequently reviewed by Chang [96] and Gebelica [118]. A summary of the main observations is given below.

The conversion is effected in two stages: first, methanol is dehydrated at about 300 °C over a catalyst such as γ-alumina to give an equilibrium mixture of dimethyl ether, methanol and water. The second stage is the ZSM-5 reactor, either a fixed or a fluidised bed. The pressure in the fixed bed reactor is approximately 20 bar and that in the fluidised system is slightly above atmospheric pressure. The liquid hourly space velocity is between 1,5 and 5.

The reaction over ZSM-5 is normally carried out at about 370 °C. However, as the reaction is highly exothermic, and temperature increase can be as much as 150 °C over fixed beds. The reaction requires that excess heat be removed and for this reason the use of a fluidised system has advantages over a fixed bed system. In addition, to minimise rises in temperature, it is advisable to use a high ratio of recycle to fresh feed.

With the fixed bed system, the catalyst deactivates after about 20 days on stream due to the build-up of coke, which can be removed by calcination in air. Therefore, the system consists of a train of several reactors, with one being in the regeneration mode. It has been found that after nine regenerations the catalyst still retains a considerable amount of its original activity. However, some activity is irreversibly lost due to steaming and other factors, and the ultimate life of the catalyst is about one year. Tests with

the fluidised system, in which the catalyst was regenerated both batch-wise and with continual recycle, showed that the ZSM-5 still retained a significant amount of its activity after being in use for 54 days.

The findings were summarised by Meisel [119] as follows. The conversion of methanol produces about 80 % C_{5+} hydrocarbons. With alkylation of the lower olefins, the selectivity for gasoline can be increased to 85 %. The gasoline is free of sulphur, nitrogenous compounds and oxygenates. The research octane rating of the unleaded product is around 93.

In 1980 it was decided that in a joint venture between Mobil and the New Zealand government, to build a commercial plant to convert methane to 12 500 barrels per day gasoline [119,120]. The methane is first reformed to syngas from which methanol is produced. The methanol is then converted to gasoline using Mobil's fixed bed technology. The plant came on stream in 1986 [121,122].

1.7.2 METHANOL TO CHEMICALS (MTC) AND METHANOL TO OLEFINS (MTO) PROCESSES

During the conversion of methanol over ZSM-5 to aromatics, the reaction must pass through an intermediate stage where olefins are made. By decoupling the subsequent aromatisation step, the reaction will naturally be a source of olefins, which are important raw chemicals. Chang [123] has reviewed the various ways in which this can be done. Based on his work and a few other publication, the principle of this aspect will be discussed below.

It has already been mentioned in the discussion on the reaction mechanism in section 1.6, that if the reaction temperature is reduced to 300 °C, or that if the degree of conversion is low, the reaction produces a significant amount of olefins. Further, Chang *et al* [124] have shown that if the partial pressure of the methanol feed is sub-atmospheric, the proportion of olefins produced is

increased. The application of these conditions yields the MTC process, where in practice the methanol feed is diluted with water to obtain a low partial pressure. Under these conditions selectivities of more than 50 % light olefin, of which about 30 % is ethene, are attained [123,125].

Another technique to reduce the reactivity of the ZSM-5 catalyst is by poisoning some of the active sites with phosphorus [126,127], or by exchanging the zeolite with cations such as either manganese or magnesium [123]. Not exchanging all the sodium cations from the synthesised ZSM-5 naturally also reduces the number of active sites [128]. However, the most effective way to reduce the activity is to have a catalyst that has relatively few active sites and this is achieved by using ZSM-5 with high silica to alumina ratios. This was demonstrated by Chang *et al* [128] where they studied the selectivity of light olefins on a series of samples with different aluminium contents. Their main result is reproduced in Figure 1.9, and shows that the best results are achieved with a silica to alumina mole ratio in the region of 400 : 1. In the extreme silicalite, which has hardly any active sites, has an excellent selectivity, but unfortunately its conversion is very low [129].

Another requirement in the technique developed by Chang *et al* [128] is that a reaction temperature of about 500 °C has to be used in combination with the high silica to alumina ratio of the ZSM-5 catalyst. However, temperatures above 500 °C cause severe cracking, and so to reduce the risk of exceeding this temperature it is preferable to use a fluidised bed reactor for the process [130,131].

The ZSM-5 catalysts used by Chang *et al* [128] were directly prepared with high silica to alumina ratios. Besides direct synthesis, it is well-known that calcination in the presence of steam removes aluminium from a zeolite structure, and is thus a technique to increase the silica to alumina ratio in

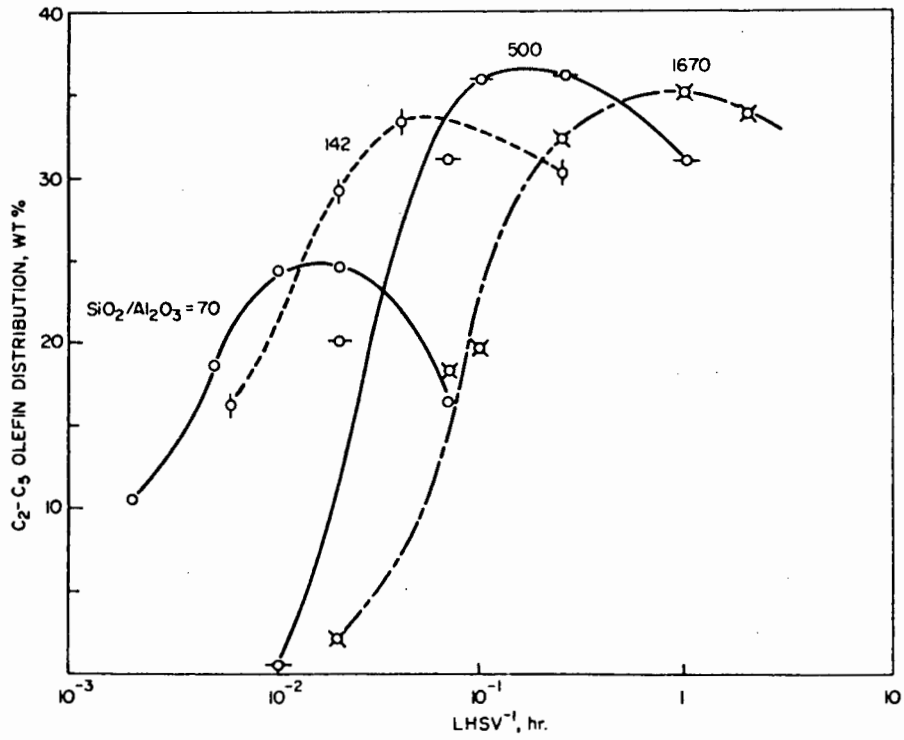

Figure 1.9. Effect of the silica to alumina ratio of ZSM-5 on the olefin selectivity obtained during the conversion of methanol. Reaction was carried out at 500 °C and one atmosphere pressure. Reproduced from ref. 128.

ZSM-5 [132,133]. Sano *et al* [133] found that the rate of de-alumination of ZSM-5 depends on the calcination temperature, duration of treatment as well as the aluminium concentration.

Besides de-alumination there is simultaneously but much slower re-insertion of aluminium into the framework from sources such as removed material or the binder used in the catalyst support [134,135]. If the insertion of aluminium into the zeolite framework is actually desired, this is more easily achieved by exposing the material to a vapour of aluminium halides at high temperatures [136].

A strange anomaly has been found when steaming ZSM-5. Lago *et al* [137] showed that although mild steaming de-aluminates ZSM-5 it actually increases its activity. Continued steaming eventually causes the expected deactivation. These results were substantiated by Brunner *et al* [138], who reported that interaction between bridging hydroxyl groups and the non-framework aluminium species is responsible for the enhanced activity.

1.7.3. AROMATISATION OF LIGHT HYDROCARBONS (M2 Forming)

In the early 1970's patents [139,140] were issued showing that by using ZSM-5 and a reaction temperatures around 500 °C, olefins and paraffins can be converted selectively into monocyclic aromatics. As a result of the shape selectivity of the ZSM-5 these products are restricted to products with not more than ten carbon atoms, and are mostly benzene, toluene and xylene (BTX). The reactions are carried out at pressures up to 20 bar and yields of 40 to 50 % BTX were obtained [139-141], with the remainder of the products being mostly light alkanes. The process is called M2 forming [141].

There is a relationship between the aluminium concentration in the ZSM-5 and the number of active sites needed for the reaction, and it has been shown that the more aluminium present the higher is the yield of BTX [142,143]. However, a more definitive method of increasing the aromatic yield is to add certain promoters to the catalyst. Zinc, either by cation exchanging or as a physical admixture, was one of the first promoters to be tested [139,140]. Mole *et al* [144] concentrated their work using ZSM-5 where the zinc was introduced through cation exchange. Irrespective of the method of addition, the BTX selectivity was increased to more than 60 %, and the amount promoter needed in the catalyst was in the region of 1 to 2 % Zn [139,140,145,146].

Moderate results were obtained by Inui and Okazumi [147] when using platinum as the promoter. Extensive work has been done,

particularly by Ono and co-workers [143,148,149], to show that gallium, whether introduced by cation exchange, impregnation or a mechanical mixture of Ga_2O_3 to give about 2 % Ga, successfully produces BTX from light alkanes or alkenes. Although no promoter is mentioned for the catalyst in the *Cylar* process [150], where light alkanes are converted into aromatics, Guisnet *et al* [151] have stated that it was gallium.

Although various comparisons have been made between the use of different promoters, Sneddon [152] in a review on the conversion of olefins to aromatics when using zinc, gallium and platinum promoters on ZSM-5, concluded that because of experimental differences, it is difficult to judge relative catalyst performances except in broad descriptive terms. He did however, feel that zinc is probably more effective than gallium, and that platinum alone was inferior to both these metals.

In these bi-functional catalyst the ZSM-5 and the promoters appear to act independently [143,144,146,148,149,153]. Olefins are the reactive feed, and in the case of the alkanes, they are first dehydrogenated by the promoters to olefins. Cracking, oligomerisation and selective aromatisation would no doubt be catalysed by ZSM-5. Aromatisation naturally requires further dehydrogenation, which is again facilitated by the promoter. When the promoter is added as a physical mixture of the metal oxide, it is naturally not located in the close proximity of the active sites of the ZSM-5, and the process by which the dehydrogenation takes place is called long distance hydrogen back-spillover [154,155].

As a result of this dehydrogenation, the secondary products are hydrogen and / or paraffins. The latter are formed through the hydrogenation of olefins. By operating the reaction to the limit, the final products contain the very light alkanes, methane and ethane, and relatively little propane [156]. By forming methane and ethane, the mole ratio of alkanes to aromatics is reduced to 0,9 [156] from a value of about 3 when no promoter is present [86,156]. A second reason for the formation of light alkanes is that due to

their thermodynamics they themselves will not readily form aromatics at a temperature of about 500 °C [144,152,157,158].

1.7.4. MOBIL'S OLEFINS TO GASOLINE AND DIESEL (MOGD) AND MOBIL'S OLEFINS TO GASOLINE (MOG) PROCESSES

Garwood [159] studied the high pressure reaction of light olefins over zeolite ZSM-5 at the relatively low reaction temperatures of 200 °C to 260 °C. His main result is reproduced in Figure 1.10. The shape selectivity caused by the long narrow channels of ZSM-5 restricts oligomerisation of the product to give only fairly linear material [160]. Any secondary reactions such as isomerisation, aromatisation and cracking, is reduced by using the low temperature.

By increasing the temperature of the reaction, thermodynamic and kinetic factors begin to have an important role on the products formed [160,161]. Increasing the reaction temperature will increase the rate of oligomerisation. However, raising the temperature further will cause the secondary reactions, such as cracking, to increase and hence give lighter products. The presence of lighter hydrocarbons reduces the boiling point of the product spectrum. This effect is illustrated in Figure 1.11, where the heaviest material is obtained with a reaction temperature of about 300 °C (573 °K), and as the reaction temperature is increased the mid boiling point (where half the material is distilled off) of the product decreases.

The MOGD process operates at a relatively high pressure, and it is therefore necessary to use a fixed bed system [160,162]. Mobil do not specify the actual pressure used, but judging from the result of Garwood [159] it is probably about 50 bar. As can be seen in Figure 1.11, to get the optimum amount of diesel the reaction temperature should be around 300 °C. Using a higher temperature increases the yield of gasoline. In the MOG process a fluidised bed

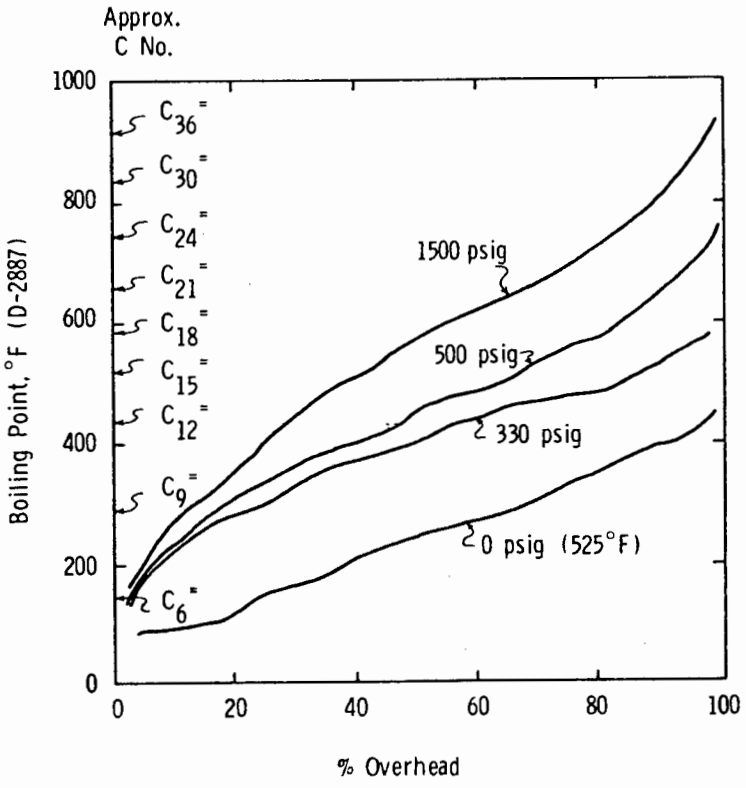

Figure 1.10. Effect of pressure on propene oligomerisation at 205 °C and MHSV of 0,4. Reproduced from ref. 159.

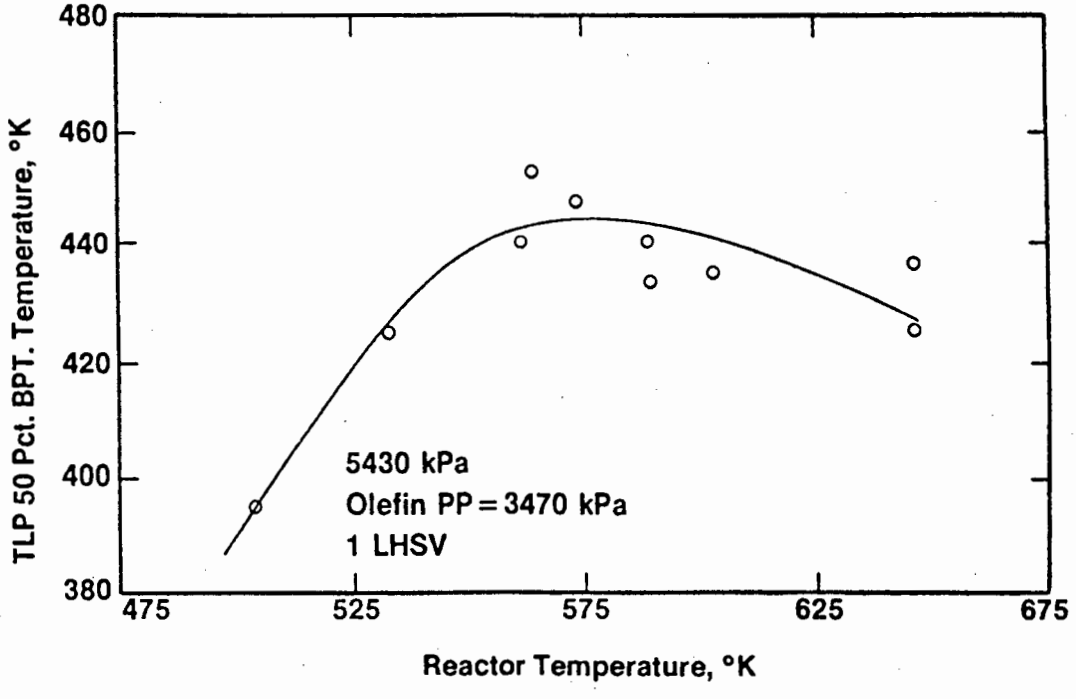

Figure 1.11. Effect of reaction temperature on the 50 % boiling point of the product. Reproduced from ref. 160.

system is used and the reaction conditions are more severe [163]. Presumably more severe means a higher reaction temperature. The gasoline product contains a large amount of aromatics and has an octane number of 95 [163].

Tabak *et al* [160,162] have reported that the reaction is very exothermic and recycling of the product should be used to counteract this problem. Further, the process is highly flexible and can be designed to produce diesel / gasoline ratios of 0 / 100 to 90 / 10. The cetane number of the diesel product after hydrogenation is around 52 [160,162]. The branching of the diesel is not extensive, with most branches being methyl groups and at about one branch per five carbon atoms [160]. The pour point is low, being below -60 °C. The gasoline product from the MOGD process is very olefinic and has an octane number of around 92.

Nowhere do Mobil report on the composition of the ZSM-5 catalyst. However, Schwarz *et al* [164] found that the optimum balance between selectivity and activity for the MOGD process is achieved when the ZSM-5 had a silica to aluminia mole ratio of 96 : 1.

1.8. CATALYTIC ACTIVITY OF ZEOLITE ZSM-48

To-date, very little has been published on the catalytic performance of ZSM-48. Using the original samples, Chu [61] examined the cracking of hydrocarbons and found an α-value of only 6,4: this is much lower than the value of several hundred found for ZSM-5 [94,95]. Froment *et al* [165] also found the cracking activity of ZSM-48 to be lower than that of ZSM-5. Further, they found that as a consequence of the cracking reaction, ZSM-48 deactivated more rapidly due to coke formation which blocks the pores. This is a typical result with a one-dimensional zeolite. Derouane *et al* [166] has reported that when ZSM-48 rather ZSM-5 or ZSM-11 is used as the catalyst, ethene is less reactive and results in smaller oligomers and lower amounts of aromatics being formed.

Kumar *et al* [167,168] have studied the isomerisation of m-xylene, and found that ZSM-48 is very selective towards p-xylene formation: they found an ortho to para ratio of 0,36 : 1 compared to a value of 0,74 : 1 with ZSM-5. This increased selectivity is attributed to the longer linear channels of ZSM-48.

1.9. EXTRUSION WITH PSEUDO-BOEHMITE

The synthesised ZSM-5 product is a powder and it is necessary that it be mixed with a binder and be formed into catalyst agglomerates. It is generally accepted that extrusion with the aid of pseudo-boehmite is the best method of binding ZSM-5. For a fixed bed reactor, the extrudates should be a few millimetres in both diameter and length, and also be strong enough to withstand the load of the catalyst bed above.

Boehmite is the natural occurring mineral aluminium oxy-hydroxide, AlO(OH). It loses 15 % of its mass through dehydroxylation at around 550 °C and is transformed into γ-Al_2O_3 [169]. Pseudo-boehmite is a hydrated form of boehmite, and has a surface area in the region of 300 m^2 / g [170]. On firing it naturally has a far higher loss in mass, about 26 %. This total consists of two components: dehydration which takes place at around 100 °C, and dehyroxylation at approximately 450 °C [169]. By calcining at around 550 °C, pseudo-boehmite is also transformed into γ-Al_2O_3 [171].

The techniques which manufacturers apply to make pseudo-boehmite, are closely guarded secrets. However, there does seem to be certain general methods by which it can be made: they are aqueous ageing of $Al(OH)_3$ from either the Bayer process or from precipitated material, or the hydration of aluminium tri-alcoholates [170].

In the extrusion process, one part pseudo-boehmite is usually mixed with two parts ZSM-5, sufficient water and a small amount of a peptising agent [172]. Peptisation is the creation of an inorganic

gel through the addition of a small amount of a chemical to an unstable dispersion [172]. The application of this technique is used to make a paste of pseudo-boehmite more workable and thus capable of being extruded. With pseudo-boehmite the peptising agent is about 1 % of an acid, such as nitric or acetic acid [173]. Finally, by calcining the extrudates at 550 °C, they are given their permanent shape and strength.

1.10 OBJECTIVES OF RESEARCH

The first aim of the work is to identify the properties of the catalyst needed and reaction conditions required, to give an acceptable light olefin selectivity from the conversion of methanol. For this, the catalyst will be made via the well-known method using tetrapropylammonium in the synthesis system. Based on this information, the main objectives of the research was to establish a system for both the catalyst synthesis and MTO operating conditions, which could be employed on an industrial scale. For this, key questions to be answered are:

a. Is it possible to synthesise highly siliceous ZSM-5 using industrial chemicals, such as α,ω-diaminoalkanes?

b. What are the problems and limitations when using these chemicals to synthesise ZSM-5?

c. How do these diaminoalkanes function in the synthesis of ZSM-5? Some information has been published, but the evidence is still incomplete.

d. Can such a technique be scaled-up for use in an industrial process?

e. Under what reaction conditions should the catalytic process be operated to give the optimum results?

f. ZSM-5 can be used in other reactions such as the aromatisation and oligomerisation of light olefins. In order to ensure maximum olefin selectivity in the MTO mode, identify the differences in the catalyst, reaction conditions and mechanism between these various processes?

g. What are the light olefin selectivities and product distribution, that can be obtained when using the most favourable conditions?

h. Can additional evidence be presented in elucidating which olefin is initially formed in the MTO reaction, and how it reacts further?

CHAPTER 2

EXPERIMENTAL PROCEDURES

2.1. PREPARATION OF SAMPLES OF ZSM-5

2.1.1. SYNTHESIS OF ZSM-5 USING TETRAPROPYLAMMONIUM CATIONS

2.1.1.1. SYNTHESIS FORMULA

In the original patent [10] various reactants were used to synthesise ZSM-5. In the last examples of the patent, numbers 23 to 27, the source of silica was an aqueous dispersion of small particles called *Ludox* which is manufactured by Du Pont. The template was a pure grade of tetrapropylammonium bromide. These are convenient chemicals to use, and as the syntheses were obviously also successful, it was decided to employ these reactants in the initial preparations.

When scanning through the examples, it was found that a wide range of compositions were mentioned. The averages of the values were taken, and this led to the following formula for the reaction mixture:

$$2{,}10\ Na_2O \quad 9\ Pr_4NBr \quad 0{,}53\ Al_2O_3 \quad 20\ SiO_2 \quad 1000\ H_2O$$

The concentration of tetrapropylammonium (TPA) compound in the formula is rather high. In section 1.3.1, work from Romannikov *et al* [35] was reviewed and it was shown that to ensure the formation of ZSM-5, the number of moles of TPA cations need not be more than about 3 or 5. Further, when using the above mixture, but with only 0,22 moles of Al_2O_3, it was confirmed that 3 moles of TPA cations were enough to ensure crystallisation of ZSM-5 [174], and this value was used for the preparation of the samples in this section.

2.1.1.2. EQUIPMENT AND METHOD OF SYNTHESIS

An example is given in Table 2.1 of the amounts of various reactants that were needed to arrive at the required reaction mixture. In the preparation the aluminium hydroxide was dissolved by boiling in the sodium hydroxide and a small portion of the de-ionised water. After dissolution more water was added. The tetrapropylammonium bromide was dissolved in the remainder of the water and added to the sodium aluminate solution. Finally the *Ludox* was added while stirring vigorously.

Table 2.1. Quantities of materials used to prepare sample 3-A.

Material component	Amount g	Moles				
		Na_2O	Pr_4NBr	Al_2O_3	SiO_2	H_2O
Aluminium hydroxide	0,407			0,00261		
Sodium hydroxide	11,27	0,141				0,1
De-ionised water	1200					66,6
TPA bromide	59,2		0,222			
Ludox HS-40	222	0,014		0,00087	1,478	7,3
Total		0,156	0,222	0,00348	1,478	74,0
Relative moles		2,10	3,0	0,047	20	1001

The reaction mixture was put into either *Teflon* or stainless steel 2 litre beakers, which were then placed on a shelf in an autoclave, where sufficient water had been added to cover the lower portion of the beaker. The autoclave used was made by Deutsch & Neumann, Germany, and had a total capacity of 20 litres. The autoclave was then heated to 150 °C and maintained at this temperature for 96 hours. It should be noted that there was no stirring of the reaction mixture.

After the required period, the autoclave was switched off and allowed to cool. The beakers were removed and crystallised products

separated by filtration, washed with de-ionised water until free of all soluble materials and finally dried at 110 °C. The yield from the preparation in Table 2.1 was about 95 g.

After synthesis the crystals obviously contained organic material, which was removed by calcination in air. The samples were heated at 70 °C / h until 630 °C was reached and then maintained at this temperature for 3,5 hours. These products also contained sodium cations, which was removed through cation exchanging, involving four exchanges at ambient temperature with a 1 N ammonium salt solution in the ratio of 10 g material per 100 g solution. Finally, the product was de-ammoniated by calcination at 550 °C (heating rate again 70 °C / h) for 3 hours, which converts the ammonium cations into protons.

2.1.1.3. PREPARATION OF HIGHLY SILICEOUS ZSM-5 WHEN USING DIFFERENT SODIUM CONCENTRATIONS (A- & B-series)

The principal aim of this work was to prepare a ZSM-5 catalyst that was suitable for the MTO process. As discussed in section 1.7.2, the best method to achieve this would be to use ZSM-5 that has a silica to alumina mole ratio in excess of about 400 : 1 [128]. Therefore, in this section of the work, samples with this composition were to be synthesised.

The central preparation was to be a sample with a silica to alumina mole ratio of 425 : 1, and then to include others wherein the concentration of the alumina was varied around this amount. In the formula for the reaction mixture

$$x\ Na_2O \quad 3\ Pr_4NBr \quad y\ Al_2O_3 \quad 20\ SiO_2 \quad 1000\ H_2O$$

the value of y for the central sample should be 0,047, with larger and smaller amounts for the remaining preparations. The different values for y are listed in Table 2.2.

In this section of the work it was decided to simultaneously do some preliminary investigation on the role of different concentrations of sodium oxide in the reaction mixture. In the first set of samples, the A-series, the sodium oxide concentration was the same as used in the patent [10], namely that x has a value of 2,10. In the second set, the B-series, the sodium oxide concentration was reduced to minimum level which was discussed in section 1.3.1, and which gave x a value of around 0,48 [32,33]. However, slightly more NaOH had to be used in preparations 4-B and 5-B to dissolve all the $Al(OH)_3$. To compensate for this, small amounts of HCl were finally added to reduce the pH so that it was the roughly the same for all the samples in the B-series.

Table 2.2. Concentrations of sodium and aluminium oxide used in the preparation mixtures of the A- and B-series of samples.

A-series				B-series			
Prep	x	y	pH	Prep	x	y	pH
1-A	2,10	0,012	12,3	1-B	0,48	0,012	11,3
2-A	2,10	0,024	12,4	2-B	0,48	0,024	11,6
3-A	2,10	0,047	12,4	3-B	0,48	0,047	11,7
4-A	2,10	0,094	12,5	4-B	0,58	0,094	11,7
5-A	2,10	0,188	12,6	5-B	0,95	0,188	11,7
6-A	2,10	0,376	12,7				

The preparations from the A-series had crystallised after being in the autoclave at 150 °C for 96 hours. However, the samples from the B-series had not crystallised after this treatment, and they were reacted for an additional 30 hours at 170 °C.

2.1.1.4. PREPARATIONS WHEREIN STIRRING WAS USED (D-series)

Stirring during synthesis of a zeolite has a large influence the type of product obtained [24,25]. Therefore, due to problems with the sodium content in the products from the A- and B-series, which will be handled in section 3.1.1.2, it was decided in the next stage of the work, to investigate the advantages of stirring the reaction mixture while crystallisation takes place. A series of reaction preparations were therefore made wherein the alumina concentration was kept constant, but the sodium concentration was varied in the mixture

$$x\ Na_2O \quad 3\ Pr_4NBr \quad 0{,}047\ Al_2O_3 \quad 20\ SiO_2 \quad 1000\ H_2O$$

The lowest concentration of the sodium oxide used was the same as that in the B-series, and the highest was just below the limit of about 3 [31] mentioned in section 1.3.1. The different preparations and their values for x are listed in Table 2.3.

Table 2.3. Concentrations of sodium oxide used in the preparation mixtures of the D-series of samples.

D-series		
Prep	x	pH
1-D	0,48	11,7
2-D	0,68	11,9
3-D	1,00	12,1
4-D	1,51	12,3
5-D	2,10	12,5
6-D	2,90	12,7

With the introduction of the stirring a larger container was used. This meant that in these preparations slightly more than twice as much reactants were used as is shown by the example of the mixture in Table 2.1. This increased the yield to approximately 210 g for each sample prepared. Included in Table 2.3 are the pHs of the reaction mixtures. Differences in the pHs were due to the increases in the amount of sodium hydroxide used, but in this series no compensations were made to keep the pHs similar. The crystallisation was carried out 170 °C for 36 hours while a stirrer in the mixtures was rotated at 25 rpm.

2.1.2. SYNTHESIS OF ZSM-5 USING α,ω-DIAMINOALKANES

2.1.2.1. REASON FOR USING AN ALTERNATE TEMPLATE

Synthesis of highly siliceous ZSM-5 is possible if tetrapropylammonium cations were present as the organic directing agent. However, as the latter material is both expensive and scarce, other chemicals should preferably be considered for use in practice. Reasonable success has been made with α,ω-diaminolkanes in preparing ZSM-5. However, as was outlined in section 1.3.2, all previous work reported with these templates showed that the silica to alumina mole ratio of the reaction mixture was generally in the region of 50 : 1, and never exceeding 90 : 1. When the silica to alumina mole ratio of the reaction mixture was in excess of 200 : 1, ZSM-5 was not synthesised [50]. Therefore, the aim the work in this section is to investigate whether it is possible by using a more strictly controlled technique, to synthesise siliceous ZSM-5 in the presence of these templates.

In this section, preparations were made to study four parameters; namely the use of different α,ω-diaminoalkanes, preliminary identification on the limit of the silica to alumina ratio, the influence of the concentration of sodium oxide, and the effects of a small addition of a tetrapropylammonium compound.

2.1.2.2. SYNTHESIS FORMULA

The same basic formula was again used to prepare the samples of this section except that different α,ω-diaminoalkanes instead of tetrapropylammonium cations were used as the main organic structure directing agent. The formula was:

$$x\ Na_2O \quad 5\ DAA \quad z\ Pr_4NBr \quad y\ Al_2O_3 \quad 20\ SiO_2 \quad 1000\ H_2O$$

where DAA is α,ω-diaminoalkane.

The value of 5 for the number of DAA molecules is equivalent to about 24 of these molecules per unit cell. The ZSM-5 unit cell is capable of holding eight DAA molecules, which means that the concentration in the formula is a moderate excess (about three times) of the amount that can possibly be incorporated into the zeolite. With *z* equal to 0,084, the amount of TPA in the formula is that recommended to facilitate the crystallisation of ZSM-5 [57], and is sufficient to fill 10 % of the intersections.

2.1.2.3. PREPARATION OF REACTION MIXTURES (E-series)

Although the main intention in this section was to identify a less expensive organic structure directing agents, a commercial source of silica should also be used when aiming to formulate a practical method of synthesising ZSM-5. A fine silica powder obtained from the precipitation of sodium silicate through acidification should be satisfactory, and the *Neosyl ET* variety, manufactured by Crosfield Chemicals, UK, was chosen for this purpose.

The other chemicals in the formula were sodium hydroxide, aluminium sulphate and the appropriate organic compounds, all of which were of analytical grade. An example of how the amounts of the various reactants needed to arrive at the required reaction mixture are given in Table 2.4. The aluminium sulphate was dissolved in de-ionised water, to which was added the sodium

hydroxide. Similarly, the tetrapropylammonium bromide and the diaminohexane were dissolved in de-ionised water, and this solution was added to the first one. The silica was suspended in de-ionised water and was finally added to the rest of the mixture while it was stirred vigorously. The reaction mixture was put into a stainless steel container, which was then placed on a shelf in the autoclave, where sufficient water had been added to cover the lower portion of the container.

Table 2.4. Quantities of materials used to prepare sample 5-E.

Material component	Amount g	Moles					
		Na_2O	Pr_4NBr	DAA	Al_2O_3	SiO_2	H_2O
$Al_2(SO_4)_3.16H_2O$	3,37				0,0053		0,09
NaOH	10,18	0,127					0,13
H_2O	451						25,03
Pr_4NBr	1,49		0,0056				
1,6-diaminohexane	38,78			0,3337			
H_2O	266						14,77
Neosyl ET *	91,1	0,013				1,355	0,56
H_2O	471						26,14
Total		0,140	0,0056	0,3337	0,0053	1,335	66,72
Relative moles		2,10	0,084	5,0	0,080	20	1000

* This batch of Neosyl ET contained 11 % moisture.

The actual concentrations used for the different samples are given in Table 2.5. The pH of the mixtures was about 12,4, and the crystallisations were carried out while the contents of the container were continuously stirred at 25 rpm. The reaction temperature was 170 °C and the duration of the crystallisations was 36 hours. The preparations were filtered, washed, dried, calcined

Table 2.5. Concentrations of chemicals used in the different preparations of the E-series. Details of certain preparations, marked with asterisks are repeated below purely for convenience in showing the variation being investigated.

Prep	*x*	Parent alkane of DAA	*z*	*y*	SiO_2 : Al_2O_3 mole ratio
1-E	2,10	ethane	0,084	0,080	250 : 1
2-E	2,10	propane	0,084	0,080	250 : 1
3-E	2,10	butane	0,084	0,080	250 : 1
4-E	2,10	pentane	0,084	0,080	250 : 1
5-E	2,10	hexane	0,084	0,080	250 : 1
6-E	2,10	octane	0,084	0,080	250 : 1
7-E	2,10	butane	0,084	0,133	150 : 1
3-E*	2,10	butane	0,084	0,080	250 : 1
8-E	2,10	butane	0,084	0,047	425 : 1
9-E	2,10	hexane	0,084	0,133	150 : 1
5-E*	2,10	hexane	0,084	0,080	250 : 1
10-E	2,10	hexane	0,084	0,047	425 : 1
11-E	1,00	hexane	0,084	0,080	250 : 1
12-E	1,50	hexane	0,084	0,080	250 : 1
5-E*	2,10	hexane	0,084	0,080	250 : 1
13-E	2,90	hexane	0,084	0,080	250 : 1
14-E	2,10	hexane	0	0,080	250 : 1
15-E	2,10	hexane	0,042	0,080	250 : 1
5-E*	2,10	hexane	0,084	0,080	250 : 1
16-E		hexane	0,420	0,080	250 : 1

to remove the organic templates, and converted to the acidic form as described earlier in section 2.1.1.2.

The yield from the preparation as shown in Table 2.4 was about 78 g. Both 1,5-diaminopentane and 1,8-diaminooctane are relatively expensive chemicals, and for the preparations where these chemicals were necessary, only a quarter of the amounts given in the example were used and naturally less product was obtained.

2.1.3. SYNTHESIS PROCEDURE SUITABLE FOR SCALING-UP

2.1.3.1. INTRODUCTION

The next stage of the research programme was done with the intention of establishing whether a practical and commercial method could be derived for manufacturing a suitable ZSM-5 product. From the work where different α,ω-diaminoalkanes were examined in the synthesis of relatively highly siliceous ZSM-5 (section 3.2), it was established that the 1,6-diaminohexane should be used (section 5.3), provided that the silica to alumina mole ratio of the zeolite was not higher than about 150 to 250 : 1. The chemical 1,6-diaminohexane is commercially available, and it was decided to use the product manufactured by BASF, Germany, in the preparation of these samples instead of the analytical grade that had been employed in the preceding section.

When making a highly siliceous product with the aid of 1,6-diaminohexane, it was to be found (see section 3.2.2) that the preparation could contain contain a significant amount of ZSM-48, which is formed at the expense of ZSM-5. The amount of ZSM-48 is dependent on the sodium and TPA contents of the reaction mixture, and enough samples were prepared in the E-series to assess these effects. However before arriving at a final conclusion, it was necessary to prepare several more samples to obtain certain additional experimental information. This entailed:

i). a more detailed study than was done with preparations 5-E, 9-E and 10-E, on the permissible silica to alumina ratio of the ZSM-5.

ii). the advantages of using lower temperatures for synthesis as has previously been found [53], and

iii). the effects of the reuse of the excess chemicals in the filtrate.

2.1.3.2 REUSE OF CHEMICALS FROM FILTRATE

Of the five chemicals (water excluded) mentioned in the preparation formula given in Table 2.4, it was assumed that the tetrapropylammonium cations and the alumina are completely incorporated into the ZSM-5 structure. Only a portion of the three other chemicals become part of the zeolite, and the remainder of them stay in the aqueous phase and are separated by filtration. If the filtrate containing these excess chemicals, is reused in subsequent syntheses there will be a saving on the raw materials needed. The next reaction mixture would consist of the filtrate plus the balance of the chemicals consumed in the previous crystallisation. This technique would obviously also eliminate the need to dispose of the filtrate.

The solubility of silica is dependent on the pH of the solution [27]. With a pH of 11 the solubility is only about 0,5 %, but increases rapidly as the pH increases [27]. The pH of the preparation mixture mentioned above is around 12,4, and it was found that the amount of silica that remained in the solution varied quite a lot, but on average was about 10 %.

As will be shown in section 3.2.5.2, the Na_2O content of the ZSM-5 product is around 0,5 %. This means that only about 5 % of the NaOH added to the reaction mixture eventually becomes part of the ZSM-5 product. About another 15 % of the Na_2O neutralises the bromide from the TPA compound and the sulphate from the aluminium salt.

From thermogravimetric results, which will be discussed in section 3.2.6.2, it will be shown that the unit cell of the zeolite contains 5,3 molecules of the diaminohexane. The concentration in the reaction mixture was calculated to be equivalent to 24 molecules per unit cell. Making some allowance for the fact that only 90 % of the mixture is crystallised into ZSM-5, it means that about 20 % of the 1,6-diaminohexane is to be found within the zeolite and the rest must be in the filtrate. This result was essentially confirmed from a determination of the solids in the filtrate.

2.1.3.3. PREPARATION OF MIXTURES (F-series)

For the preparation of the samples of this series it was decided that larger quantities should be made. Therefore, a stainless steel container having a diameter of 190 mm and height of 225 mm (effective capacity of approximately 5 litres) which could be attached to the inside of the autoclave, was constructed. To facilitate mixing during stirring, vertical baffles were welded to the inside of the container. A photograph of the container, as well as the stirrer, is given in Figure 2.1.

The preparation formula in this series is the same as that of the E-series, except that it was decided to use less water. The formula, with DAHX standing for 1,6-diaminohexane, was:

$$2{,}10\ Na_2O\ \ 0{,}084\ Pr_4NBr\ \ 5\ DAHX\ \ y\ Al_2O_3\ \ 20\ SiO_2\ \ 800\ H_2O$$

The central preparation in the F-series is F-13, which except for the water concentration, is similar to 9-E mentioned in section 2.1.2.3. For both these preparations y has a value of 0,133 in the formula, and therefore has a theoretical silica to alumina mole ratio of 150 : 1. Other preparations with higher and lower silica to alumina ratios, as well as two made at lower reaction temperatures, were made. Details of the various samples prepared are listed in Table 2.6.

Figure 2.1. Photograph of container and stirrer used for synthesising samples of the F-series.

Table 2.6. Details of the concentration of aluminium, temperature and duration of the crystallisation of the samples of the F-series.

Prep	*y*	SiO_2:Al_2O_3 mole ratio	Reaction temp.	Crystal. time
F-35	0,333	60 : 1	170 °C	36 hr
F-34	0,222	90 : 1	170 °C	36 hr
F-13	0,133	150 : 1	170 °C	36 hr
F-15	0,080	250 : 1	170 °C	36 hr
F-10	0,047	425 : 1	170 °C	36 hr
F-150	0,133	150 : 1	150 °C	3 days
F-130	0,133	150 : 1	130 °C	8 days

With the 5 litre container, the quantities of chemicals that were used to make sample F-13 are given in Table 2.7. Except for the water, these amounts are 4,58 times larger than those used for the preparation of 9-E. Apart from the obvious changes in the amount of aluminium sulphate, the same quantities were used for all the other mixtures in the F-series. The preparation wherein only small amounts of aluminium sulphate were used had a pH around 12,4. Where lower pHs were obtained, such as mixture F-35, more sodium hydroxide was added to increase the pH to 12,4.

Table 2.7. Quantities of materials to prepare the first and subsequent samples of F-13.

Material component	Amounts for first cryst. g	Amounts added to filtrate for subseq. cryst. g
$Al_2(SO_4)_3.16H_2O$	25,7	25,7
NaOH	46,6	± 20
H_2O	1463	
Pr_4NBr	6,83	6,83
1,6-diaminohexane	177,8	35,6
H_2O	926	
Neosyl ET	417,3	375,6
H_2O	1991	
TOTAL	5054	

The mixtures were reacted while stirring at 25 rpm and at the temperatures specified in Table 2.6. With a temperature of 170 °C, the samples were allowed to crystallise for 36 hours. As the activation energy for the formation of ZSM-5 is around 35 kJ mol^{-1} [175], the time required for crystallisation should be nearly doubled if the reaction temperature is reduced by 20 °C. Thus with reaction temperatures of 150 °C and 130 °C, 72 hours (3 days) and 8 days respectively were allowed for crystallisation.

After the completion of crystallisation, the mixtures were filtered. Before washing the solid material, the filtrate was removed for subsequent synthesis of the next batch of ZSM-5. The solid product was then washed separately, giving yields of around 360 g dry material.

For the subsequent reaction mixtures, the amounts of chemicals consumed in the previous synthesis were added to the filtrate. Some extra water also had to be added to compensate for loss due to evaporation. The pH of these reaction mixtures were adjusted to be the same as the first mixture, namely 12,4. Although it was estimated that about 14 g of NaOH would be needed, it was found that slightly more than this amount had to be added to give the correct pH. The same conditions regarding temperature, duration and stirring as mentioned for the initial preparations were again used for the crystallisation. Two or three additional crystallisations were made from the original mixtures used for preparations F-35, F-34, F-13, F-15 and F-150. The yields per synthesis was again about 360 g. Only the first single reaction was carried out with the other two mixtures, namely F-10 and F-130.

2.1.4. PREPARATION OF EXTRUDATES

In this work it was decided to use acetic acid as a peptiser, and the first step was to determine the required amount of this peptiser to produce an extrudable paste. To achieve this, samples were made by mixing the following components:

8 g ZSM-5
4 g Pseudo-boehmite
7 ml Water &
small addition of acetic acid.

The mixtures were then extruded by manual ramming action through a die plate having holes of 2 mm in diameter. This formed a "spaghetti-like" products, which after drying was broken into lengths of around 5 to 10 mm. The extrudates were normally heated

at 70 °C / h up to 550 °C, and then maintained at this temperature for 3 hours, to give them their permanent shape and strength. Having determined the required amount of peptiser to produce suitable pastes (section 3.4.2), all the extrudates were prepared according to this recipe.

2.2. CHARACTERISATION TECHNIQUES

2.2.1. X-RAY DIFFRACTOMETRY (XRD).

The X-ray diffractometry was done on the samples as synthesised. The XRDs were recorded on a Philips PW 1350 / 1390 diffractometer using CuK_{α} radiation, generated from an X-ray tube at 40 kV and 20 mA. The samples were scanned between 14° and 3° θ at a speed of 0,5° θ / min. The presence of the crystalline zeolites formed were determined by unscrambling the X-ray diffractogram. Identification of the presence of a particular mineral or zeolite was done by comparison with published XRD patterns.

The XRD intensity of a particular zeolite was determined from the height of the major diffraction peak, or the sum of the heights of several peaks. This value is within reasonable accuracy, proportional to the concentration of the zeolite present [176].

2.2.2. SCANNING ELECTRON MICROSCOPY (SEM)

The scanning electron microscopy was done on the samples as synthesised. The SEMs were observed with a Hitachi S 520 instrument.

2.2.3. MAGIC ANGLE SPINNING NUCLEAR MAGNETIC RESONANCE SPECTROMETRY (MAS NMR)

The nuclear magnetic resonance spectra were recorded on a

Bruker AM 300 instrument, having magic angle spinning for solid materials. The magic angle spinning ^{27}Al nuclear magnetic resonance spectrometry (MAS ^{27}Al NMR) was done on the samples after removal of the template by means of calcination. The spectra were recorded with the instrument operating at a frequency of 78,2 MHz, and spinning was carried out at 4 kHz. The Al shifts were measured with respect to $AlCl_3.6H_2O$, which was used as an external standard. The magic angle spinning ^{13}C nuclear magnetic resonance spectrometry (MAS ^{13}C NMR) was done on the samples after synthesis, and obviously before any calcination had taken place. The spectra were recorded on the instrument operating at a frequency of 75,5 MHz, and spinning was carried out at 4 kHz. The C shifts were measured with respect to adamantane, which was used as an external standard.

2.2.4. CHEMICAL ANALYSIS

The determination by chemical analysis of aluminium and sodium in the synthesised zeolites was done after removal of the organic material through calcination. The amount of sample used was 250 mg, which was first treated with hydrofluoric and mineral acid, and then evaporated to remove all the silica. The remainder of the elements were then again dissolved in mineral acid and finally diluted to 250 ml to give a nominal concentration of 1000 mg / l. The concentration of each element was measured on a Pye Unicam SP 9 atomic adsorption spectrophotometer.

Aluminium standard solutions were made from $Al_2(SO_4)_3.16H_2O$. The sensitivity of the aluminium detection is 0,39 mg / l [177], and this means that the accuracy of the Al_2O_3 determination is ±0,074 %. For the sodium determinations the original solutions were diluted to give a concentration of 100 mg / l. The standard solutions were made from NaCl. The sensitivity of the sodium detection is 0,0046 mg / l [177], and means that the accuracy of the Na_2O determination is ±0,0062 %.

2.2.5. CATION EXCHANGE CAPACITY (CEC)

To obtain the ammonium form, the calcined ZSM-5 was cation exchanged, involving four exchanges at ambient temperature with a 1 N ammonium salt solution in the ratio of 10 g material per 100 g solution. The ammonium contents were determined by measuring the amounts evolved on heating via the technique developed by Kerr and Chester [178]. This was done with a Du Pont 990 / 951 thermal analyser to which was coupled a Radiometer ABU 12 auto-titrator. The samples were heated at 10 °C / min and the ammonia was carried to the titrator in a stream of gas. In these experiments, hydrogen was used as the carrier gas to reduce possible oxidation of the ammonia which was being released. The ammonia released was continuously neutralised with sulphamic acid, and the amount was simultaneous recorded on the 990 analyser.

2.2.6. THERMOGRAVIMETRIC ANALYSIS (TGA)

The thermogravimetric analysis was carried out to determine information about the organic compound that was included inside the zeolite during synthesis; i.e. before its removal by calcination. The same technique as that described in section 2.2.5 above, was used. However, the titration recorded the thermally released compound, or fraction thereof, containing the nitrogen atom [174]. Hydrogen was again used as the carrier gas to reduce the possibility of oxidisation which would neutralise the organic compound being released.

2.2.7. ELEMENTAL ANALYSIS FOR CARBON AND NITROGEN

The carbon and nitrogen contents of the template in the zeolite were determined by a Carlo-Erba micro-analyser.

2.2.8. MICRO-SIEVE ANALYSIS

Micro-sieves from Buckbee Mears Corp. were used for the determining the fineness of the pseudo-boehmite. Five sieves, with apertures of 75, 40, 20, 10 and 5 µm, were used in the analysis. The material was suspended in acetone, and the sieves were vibrated ultrasonically. The results of the sieve analysis were plotted on a log-probability graph. From the straight line, the median size was read from the 50 % mark on the mass scale [179].

2.2.9. MEASUREMENT OF CRUSHING STRENGTH

The crushing resistance of a sample was determined by placing a single extrudate between the anvils of a Chatillon UTSE-2 tester, and then increasing an applied compressive force until the sample broke. This force is automatically recorded by the tester. Before being crushed the length of the sample was measured. The crushing strength of a catalyst is determined from its crushing resistance divided by its length.

2.3. MEASUREMENT OF CATALYTIC ACTIVITY

2.3.1. PREPARATION OF ACTIVE CATALYST

2.3.1.1. REMOVAL OF TEMPLATE AND SODIUM

For a sample of ZSM-5 to be an active catalyst, it is necessary that the channels be cleared of any organic compounds used during its synthesis. It has already been stated in section 2.1.1.2, that this was done through calcination in air at 630 °C for 3,5 hours. Secondly, it is necessary that virtually all that sodium in the synthesised product be removed and be replaced by protons. Ammonium cations readily exchange the sodium cations of ZSM-5 [180]. It was also said that this was done via four exchanges at ambient temperature with a 1 N ammonium salt solution in the ratio of 10 g

material per 100 g solution. Conversion of the ammonium cations to protons was achieved by calcination in air at 550 °C for 3 hours.

2.3.1.2. GRANULATION AND EXTRUSION

The ZSM-5 samples were powder and were thus too fine to be placed in a reactor bed. Granulation of the pure zeolite was done by placing the powder in a die having a diameter of 40 mm, and then compressing it in a hydraulic press to a pressure of 3 tonnes. This held the material lightly together, and then subsequently gentle crushing of the material followed by sieving to give particles which were between 355 and 500 µm.

The technique for the preparing of extrusions of the powder with pseudo-boehmite was discussed in section 2.1.4 above.

2.3.1.3. THERMAL TREATMENT

The equipment for thermal steam treatment consisted of a fused silica test-tube of 31 mm diameter and 470 mm long, which was placed in a vertical tube-furnace. The furnace was capable of drawing 1200 watts, and maintained isothermally by a Eurotherm temperature controller. Steam from a separate generator was carried to the bottom of the test-tube by a 3 mm stainless steel tubing. Samples of extrudates were placed in the test-tube and there was sufficient steam to ensure saturation during the treatment. To investigate the thermal treatment in air that was free of any steam, extrudates were also placed in open dishes in a large furnace and calcined at temperatures above the normal 550 °C.

2.3.1.4. ADDITION OF PROMOTERS

Zinc oxide was added as a promoter during certain catalytic experiments. This was done by first mixing powders of ZSM-5 and smaller amounts of ZnO, where the concentration of the ZnO added is

expressed as a percentage relative to ZSM-5 content. This mixture was then extruded with pseudo-boehmite and calcined as discussed in section 2.1.4.

2.3.2. LOW PRESSURE REACTOR SYSTEM

2.3.2.1. EQUIPMENT USED FOR TESTING

The low pressure reactor testing equipment consisted of an integrated system comprising of the following units:

a) feed of reactants
b) pre-heating of reactants
c) reactor containing the catalyst
d) sampling of product stream
e) analysis and quantitative measurement of products

a) The reactants were fed at a steady rate of around 1 ml / hr, by either a model 341A Sage Instruments syringe pump, or a model 7618-32 Isamatec cartridge peristaltic pump. Capillary tubing was used in the peristaltic pump. A second feed consisted of inert nitrogen, and its flow rate was monitored by a rotameter.

b) The pre-heater consisted of a 500 ml (diameter of 51 mm and 260 mm long) stainless steel tank. This unit was heated in a tube-furnace capable of drawing 650 watt, where the temperature was regulated by a variac and a RKC PN-4A1C-M temperature controller, and was usually around 200 °C. In order to ensure that the liquid feed did not evaporate in the line before reaching the pre-heater and thereby cause an uneven flow, this section of the line was a capillary stainless steel tubing having an internal diameter of 0,18 mm.

c) The reactor was made of *Pyrex* glass, and a drawing thereof is shown in Figure 2.2. The catalyst sample was placed in the reactor before replacing the socket containing the thermo-well. A chrome-alumel thermocouple was placed in the thermo-well, and recorded the temperature directly above the sample. The feed inlet is on the left-hand side, and therefore underwent a second pre-heating along the glass coil. The ends of the stainless steel lines to and from the reactor were fitted with custom made stainless steel cup joints that matched the standard 18 / 7 glass ball joints of the reactor.

The reactor shown in Figure 2.2 was capable of holding a catalyst sample of approximately one gram. A second reactor with a similar design but where the diameter of tube holding the sample was increased to 20 mm was also made. This reactor was capable of holding four grams of sample.

The reactor was placed in a tube-furnace also drawing 650 watt, and was capable of heating the system up to 550 °C. The temperature was regulated by a variac and a RKC PN-4A1C-M temperature controller.

d) A sample of the product stream was collected by a high temperature 6-port *Valco* valve and directed to gas chromatographs for analysis. The size of the sample loop was 0,5 ml. This valve system was housed in a small furnace kept at a temperature of between 150 °C and 200 °C.

The tubing connecting all the above unit were made of 3 mm stainless steel. Initially this tubing was wrapped with heating tapes, but it was subsequently found that the temperature was rather low, and condensation of certain compounds took place inside the lines. Thus, it was decided to incorporate all three furnaces into a single unit, and thereby enclosing the tubing within the insulation of the furnace. They were not exposed and their temperature was around 200 °C.

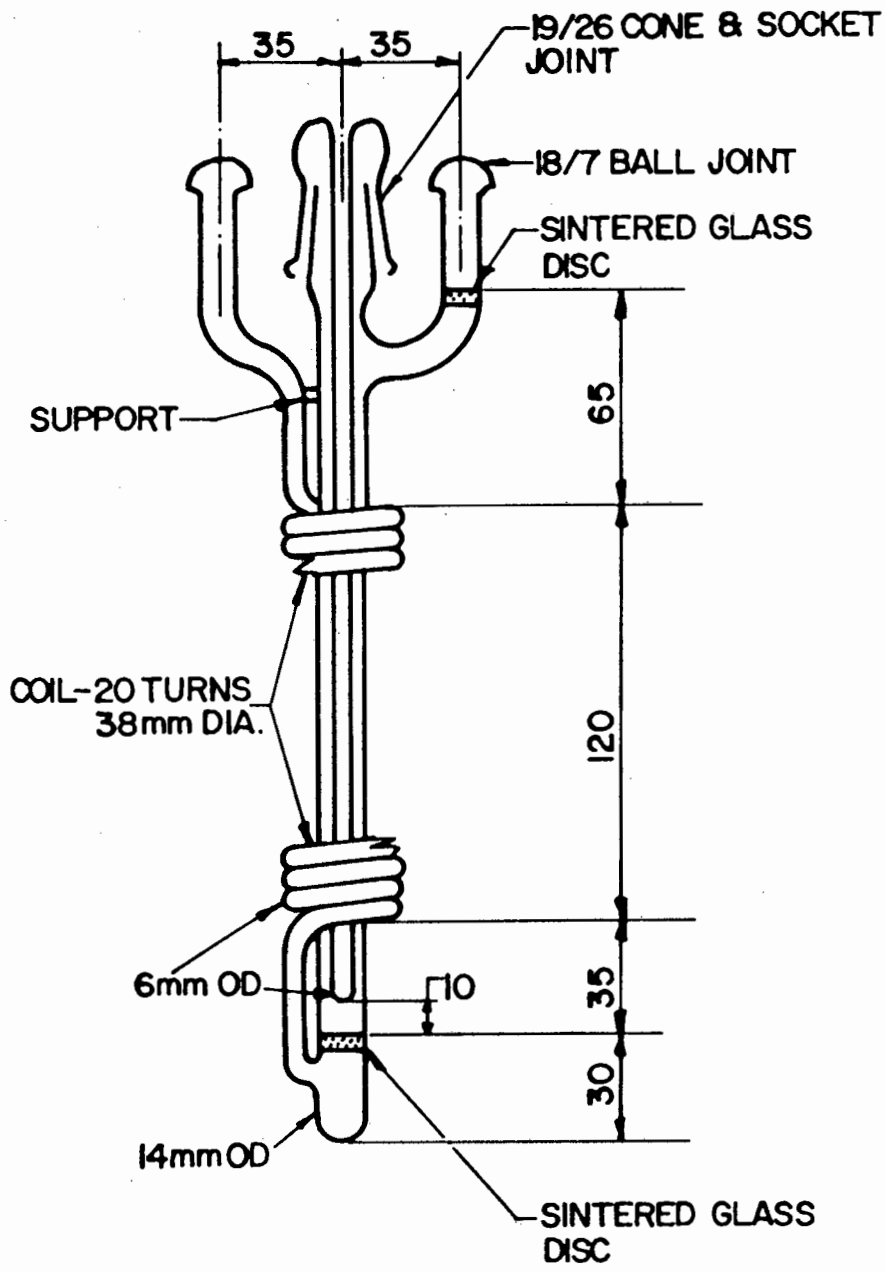

Figure 2.2. Sketch of the Pyrex glass reactor that was used.

e) The product in the sample loop was directed to one of two on-line gas chromatographs (GC). The GCs were manufactured by Carlo-Erba, one being a model 2150 *Fractovap*, and the other a model 4200. Each GC unit had a 2 m packed glass column, which was heated via a determined temperature programme. In each column nitrogen was used as the carrier gas.

Recording of the separated hydrocarbon components was done by a flame ionised detector (FID). The signal from each FID was amplified by an electrometer and sent to a Shimadzu C-R3A Chromatopac integrator, which automatically quantified and normalised this signal.

For the analysis of hydrogen, the model 4200 GC was fitted with a second packed column, into which a sample was injected. With nitrogen as the carrier gas, the hydrogen was measured by a thermal conductivity detector (TCD), whose signal was amplified and sent to a third Shimadzu C-R3A Chromatopac integrator.

2.3.2.2. EVALUATION OF TEST RESULTS FOR MTO PROCESS

The reactant in all these experiments was methanol. The partial pressure of the methanol was reduced by co-feeding nitrogen into the pre-heater or by using a methanol / water mixture as the feed. In the latter case the pressure of the methanol is reduced by steam. In all the experiments the rate at which methanol was fed was calculated as the mass hourly space velocity (MHSV) relative to the amount of ZSM-5, excluding the alumina binder, in each catalyst sample.

In the first gas chromatograph column, containing *Porapak Q*, the overall composition of the product was determined. The separation of the olefins from the paraffins, particularly butene from butane, was never clear and a second analysis was carried out with a F-1 active alumina column. Further separation after C_4 was not possible, but as the the quantities of these products were low, any errors were consequentially small.

All the products were hydrocarbons and they have similar response factors [181]. Therefore, the normalised area of each GC peak measured by the integrators was directly the concentration of the mass of the particular component. The GC spectrum from the active alumina column was not complete, and the amount of butane / butene present was taken as being the same as that from the other column: the remaining products were calculated proportionally from the integration data. An example (results from preparation 15-E) is shown in Appendix A.

2.3.2.3. EVALUATION OF TEST RESULTS FOR THE M2 PROCESS

In studying the M2 process, the feed was analytical grade 1-octene, which was diluted with nitrogen so that the feed vapour contained 80 % by volume of the reactant. In the experiments the rate at which the octene was fed was calculated as the mass hourly space velocity (MHSV) relative to the amount of ZSM-5, excluding the alumina binder, in each catalyst sample.

The overall composition of the products formed were determined from the spectrum of the first gas chromatograph column, containing 3 % silicone OV-101. This column did not separate the products below C_5, and the first peak is the total of these products. After this peak, the column separated all the remaining heavier components. By passing the product stream through an ice-trap it was cooled to about 0 °C to condense the material heavier than C_5, and two samples from the remaining light products were injected into *Porapak Q* columns for further analysis. One was coupled to the TCD to measure the amount of hydrogen that was formed, and other had a temperature programme and was coupled to a FID for the separation of the light hydrocarbons.

The concentration of hydrogen was determined from direct calibration of the TCD. Allowance also had to made for the amount of product that was condensed and the amount of nitrogen present. All the other products were hydrocarbons and they have similar

response factors [181]. Therefore, the normalised area of each GC peak measured by the integrators was directly the concentration of the mass of the particular component. The size of the first peak recorded from the silicone OV-101 column gave the total concentration of the light products. An example (results from preparation F-34 with 3 % ZnO) is shown in Appendix A.

2.3.3. HIGH PRESSURE REACTOR SYSTEM

2.3.3.1. EQUIPMENT USED FOR TESTING

The high pressure reactor testing equipment consisted of an integrated system comprising of the following units:

a) supply of propene
b) control of the feed-rate and pressurisation of the system
c) reactor
d) collection of liquid products

a) Propene was supplied from a gas bottle, which was placed on a Mettler KC 120 balance with an ID2 electronic read-out, in order to measure the amount delivered to the system. The propene, which was fed from the bottom of the gas bottle via a dip-tube, was kept as a liquid by applying an external source of nitrogen at a pressure of 17 bar.

b) A Lewa FCM-1 metering pump controlled the rate at which the propene was fed and simultaneously increased its pressure. The pressure in the system was controlled at 50 bar by a Tescom Corp. back-pressure regulator placed after the exit from the reactor.

c) The reactor was made from 2,77 mm thick 316 stainless steel tubing. It was 820 mm long with a outside diameter of 21,3 mm.

The top and bottom portions of the reactor were filled with glass beads, while the central section contained 50 g of catalyst.

In order to ensure that there was uniform temperature along the entire length of the reactor, an aluminium sleeve with an outside diameter of 80 mm, was fixed around the reactor. The reactor was heated by six band elements, each capable of drawing 350 watts, which were placed around the aluminium sleeve. The elements were connected in three pairs (two at the top, two in the centre and two at the bottom) and were kept isothermally around 295 °C by three RKC REX-C72 or REX-C9 temperature controllers.

d) After passing through the reactor and back-pressure regulator, the products were cooled by a series of water-fed condensers to reduce the temperature to about 25 °C. The liquid product was collected in a container for further analysis. The amount of gases produced were measured by passing them through a Ritter wet gas flow meter before being vented.

2.3.3.2. EVALUATION OF TEST RESULTS FOR MOGD PROCESS

The conversion level during the MOGD process was defined as the amount of propene gas that was changed to a liquid product: this excluded the gases formed. The liquid fraction was then divided by distillation to separate all the product with a boiling point below 180 °C. The fraction remaining after distillation (boiling point above 180 °C), was deemed to be the yield of raw diesel.

The bromine number, which is the number of grams bromine consumed by 100 g of a sample, was determined by the standard IP method 129 / 64 [182]. In the method bromine is liberated from a potassium bromide-bromate solution, which reacts immediately with the unsaturated organic material in acetic acid. In the test excess bromine is actually added, because on the addition of potassium

iodate, this excess is converted to the equivalent amount of iodine, which is then easily measured by back-titration with sodium thiosulphate, using starch as an indicator. The bromine number is determined from the amount of bromine added, less the excess.

In order to reduce the bromine number to below 10, the raw diesel was hydrogenated in an autoclave at a temperature of 150 °C and a pressure of 12 bar, using a Pd-charcoal catalyst. The cetane number of the finished diesel was determined according to standard techniques [183] of the SABS.

CHAPTER 3

RESULTS ON SYNTHESIS OF ZSM-5

3.1. ANALYSIS OF PRODUCTS FORMED WHEN USING TPA

3.1.1. SAMPLES FROM THE A- & B-SERIES

3.1.1.1. CRYSTALLINE MATERIALS FORMED

The X-ray diffractogram of sample 3-A is given in Figure 3.1. The d values of all the peaks were determined from the θ angles, and the relatively intensities of each of the peaks were measured. These values are listed in Table 3.1, and are similar to those of a standard X-ray diffractogram of ZSM-5 [184], which is also included in the table. Further, as no other diffraction peaks from any impurities were evident, the XRD clearly shows that this sample consisted essentially of zeolite ZSM-5. All the other preparation from the A- and B-series gave similar results (this can be seen from additional diffractograms of several other preparations included in Appendix B).

3.1.1.2. CHEMICAL ANALYSIS

In reaction mixture used for preparation 6-A, the value of y was 0,376. If all the aluminium is incorporated into the zeolite structure, this preparation would contain about 3,0 % Al_2O_3. The next sample, 5-A, should contain half this amount. Moving along this sequence, each successive sample should have half the amount as the preceding one. These theoretical values are included in Table 3.2. Naturally, the corresponding preparations from the B-series should have the same concentration of aluminium oxide.

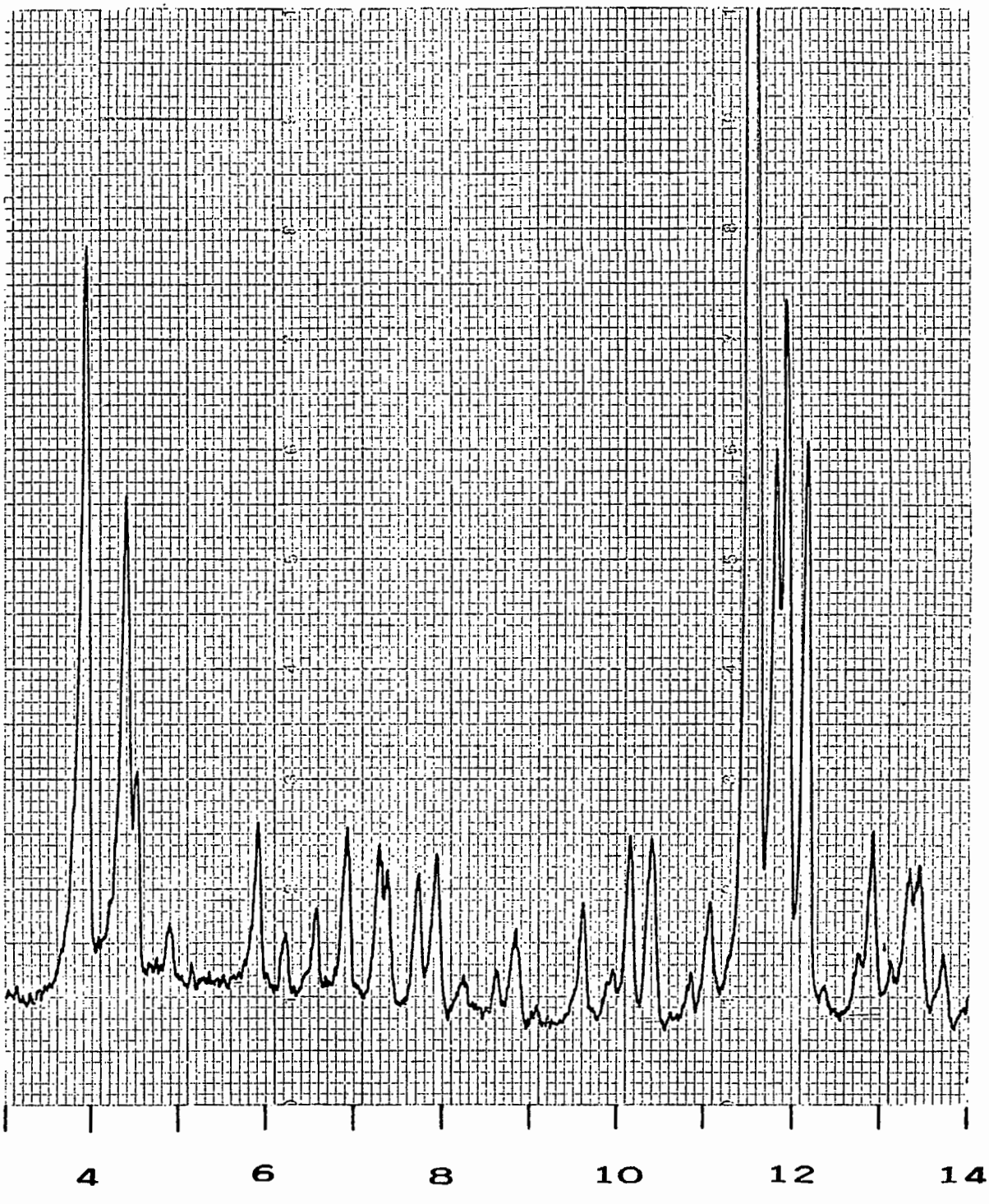

Figure 3.1 X-ray diffractogram of preparation 3-A. Radiation source from CuK_α, operating at 40 kV and 20 mA.

Table 3.1. The d values, relative intensities and Miller indices of ZSM-5 taken from ref. 184, and from the X-ray diffractogram of sample 3-A shown in Figure 3.1.

Ref. 184			Preparation 3-A		
d value nm	I/I_o	*hkl*	θ degrees	d value nm	I/I_o
1,1165	52,3	101	3,94	1,121	43
1,1140	47,5	011			
1,0048	29,4	200	4,40	1,004	27
0,9974	35,0	020			
0,9743	23,9	111	4,53	0,975	12
0,8974	4,8	210	4,90	0,902	3
0,7461	2,8	211	5,92	0,747	10
0,7438	9,3	121			
0,7079	5,5	220	6,22	0,711	4
0,6714	6,2	002	6,58	0,672	5
0,6368	16,6	102	6,93	0,638	10
0,6066	6,6	112	7,30	0,606	9
0,5994	11,0	301	7,39	0,599	8
0,5959	5,0	031			
0,5741	1,4	311	7,73	0,573	7
0,5713	10,8	131			
0,5582	6,2	202	7,93	0,558	9
0,5570	5,3	022			
0,5376	1,7	212	8,25	0,537	2
0,5367	2,6	122			
0,5138	2,7	321	8,61	0,515	2
0,5024	2,8	400	8,83	0,502	5
0,4987	5,5	040			
0,4614	7,0	312	9,61	0,461	7
0,4599	2,9	132			
0,4452	1,8	331	9,96	0,445	1
0,4367	13,2	013/103	10,15	0,437	10
0,4256	8,3	421	10,41	0,426	10
0,4089	3,1	203	10,86	0,409	2
0,4009	7,2	430	11,08	0,401	6
0,3850	100	501	11,56	0,384	100
0,3825	78,4	051			
0,3757	36,7	151	11,81	0,376	27
0,3722	53,7	303	11,93	0,373	38
0,3713	5,3	033			
0,3651	40,3	133	12,18	0,365	27
0,3487	3,4	323	12,78	0,348	1
0,3442	13,1	432	12,92	0,344	10
0,3398	1,2	512	13,13	0,339	1
0,3381	1,3	152			
0,3342	4,2	403	13,33	0,334	8
0,3311	9,4	104	13,46	0,331	8
0,3250	1,4	601			
0,3248	1,3	333	13,72	0,325	4
0,3246	1,6	252			

The actual amounts of Al_2O_3 found in the different preparations are given in Table 3.2. Comparing these results with those that were expected, it can be seen that except for preparation 6-A, the ZSM-5 samples in the A-series contained virtually all the aluminium that was added to the synthesis mixture. Most of the aluminium added was incorporated into the ZSM-5 structure in sample 6-A, but it should be remembered that its composition is approaching the limit for the amount that can be included. More significantly however, is that the samples from the B-series contained only about 70 % of the amount of aluminium that was used in the reaction mixture. The only difference between these two sets of samples is that in the B-series significantly less sodium hydroxide was used in the reaction mixture, and this must be the reason for not being able to incorporate all the aluminium into the zeolite structure.

Table 3.2. Chemical analysis for Al_2O_3 of the preparations from the A- and B-series. Figures reported are given as mass percentages.

Expected value	A-series		B-series	
Al_2O_3 %	Prep	Al_2O_3 %	Prep	Al_2O_3 %
0,09	1-A	0,06	1-B	0,03
0,19	2-A	0,17	2-B	0,15
0,38	3-A	0,41	3-B	0,26
0,75	4-A	0,77	4-B	0,53
1,5	5-A	1,47	5-B	0,91
3,0	6-A	2,61		

It is generally accepted that in a zeolite there is a connection between the number of tetrahedral co-ordination aluminium

atoms and the number of cations present [185]. However, although there were variations in aluminium concentration, there were no corresponding changes in the amounts of sodium in the samples. The Na_2O content after synthesis of all the sample in the A-series were more or less the same; namely around 1,07 %. Similarly, preparations 1-B to 4-B also contained the same Na_2O concentrations. This anomaly in the synthesis of ZSM-5 will be discussed in more detail in section 3.1.3.

Table 3.3. Chemical analysis for Na_2O of the preparations from the A- and B-series. Figures reported are given as mass percentages. Na_2O results are the amounts of this compound in the ZSM-5 after synthesis, while resid Na_2O are the residual concentrations of this chemical after its removal by cation exchange.

A-series			B-series		
Prep	Na_2O %	resid Na_2O %	Prep	Na_2O %	resid Na_2O %
1-A	1,19	0,30	1-B	0,13	0,09
2-A	0,93	0,16	2-B	0,11	0,04
3-A	1,21	0,04	3-B	0,12	0,02
4-A	0,94	0,02	4-B	0,14	0,02
5-A	1,07	0,04	5-B	0,44	0,02
6-A	1,06	0,08			

After synthesis and thermal removal of the template, the samples were subjected to several exchanges with an ammonium salt, and this should remove nearly all the zeolitic sodium cations [180]. If the synthesised material consists of pure ZSM-5, the sodium remaining after this treatment (residual sodium) should be low, with

the less sodium left in the ZSM-5, the purer the product. As can be seen in Table 3.3, several of the preparations of the A-series still contained some residual sodium, and were thus not very pure and must have contained some amorphous material. The samples from the B-series had less residual Na_2O than those from the A-series. This reduction must be due to using less in the preparation and thereby decreasing the possibility of occluding sodium in other parts of the preparation which were not zeolitic.

3.1.2. SAMPLES FROM THE D-SERIES

3.1.2.1. CRYSTALLINE MATERIALS FORMED

All the samples of the D-series were found to consist mainly of zeolite ZSM-5. The intensities of the X-ray diffraction peaks from the samples were similar in spite of there being a large difference in their alkalinities. Secondly, compared to the A- or B-sets of preparations, the XRD intensities of all the samples from the D-series were about 10 to 20 % larger (examples are included in Appendix B, and can be compared with those from the A- and B-series). This probably indicates an increase in the crystallinity, and must be attributed to the introduction of stirring while ZSM-5 was being formed [24,25].

The X-ray diffractogram of sample 6-D showed a small peak at θ = 4,70°, giving a d-value of 0,940 nm. This peak is attributed to the presence of zeolite D, a synthetic mordenite [186]. Positive identification was not possible as the other peaks of mordenite were masked by the much larger ones of ZSM-5. A smaller amount of zeolite D was also present in preparation 5-D, but none of this material was evident with any of the remaining samples of the series (1-D to 4-D). This shows that as the concentration of sodium in the preparation mixtures of the D-series decreased so did the amount of zeolite D.

3.1.2.2. SCANNING ELECTRON MICROSCOPY

Scanning electron micrographs of four of the preparations from the D-series are illustrated in Figure 3.2. The data confirms the observation of Fegan and Lowe [33] that the size of the crystallites become much larger when a low concentration of sodium is used in the preparation mixture; the crystallites of sample 1-D were approximately 30 µm, while those of the other preparations were all between 1 and 2 µm.

3.1.2.3. CHEMICAL ANALYSIS

The same amount of aluminium was added to each of these preparation mixtures, and as was calculated in section 3.1.1.2, that if all the aluminium was incorporated into the zeolite, the products would contain 0,38 % (by mass) Al_2O_3. As is evident from Table 3.4, the five samples, 2-D to 6-D, all had the expected concentration of Al_2O_3. The remaining sample, 1-D, contained significantly less Al_2O_3, and, as has been shown with the B-series above, if a relatively low sodium oxide concentration is used during the synthesis, there is a resultant decrease in the amount of aluminium that is incorporated into the ZSM-5 structure.

The products from the A- and B-series had variations in their Al_2O_3 contents, while the amount of Na_2O present remained constant. However, just the reverse was found with the preparations of the D-series; the amount of Al_2O_3 in the samples was constant, but the Na_2O contents changed, which also seems to dispute the claim that there is a connection between the aluminium content of a zeolite and the concentration of sodium cations [185]. As mentioned earlier, this point will be analysed next in section 3.1.3.

The residual sodium contents of all the preparations from the D-series were low. It is easier to remove sodium from zeolite ZSM-5 than from amorphous material. Thus, these preparations contained less amorphous material and consequentially more zeolite ZSM-5. The increase in the concentration of crystalline fraction, and thus

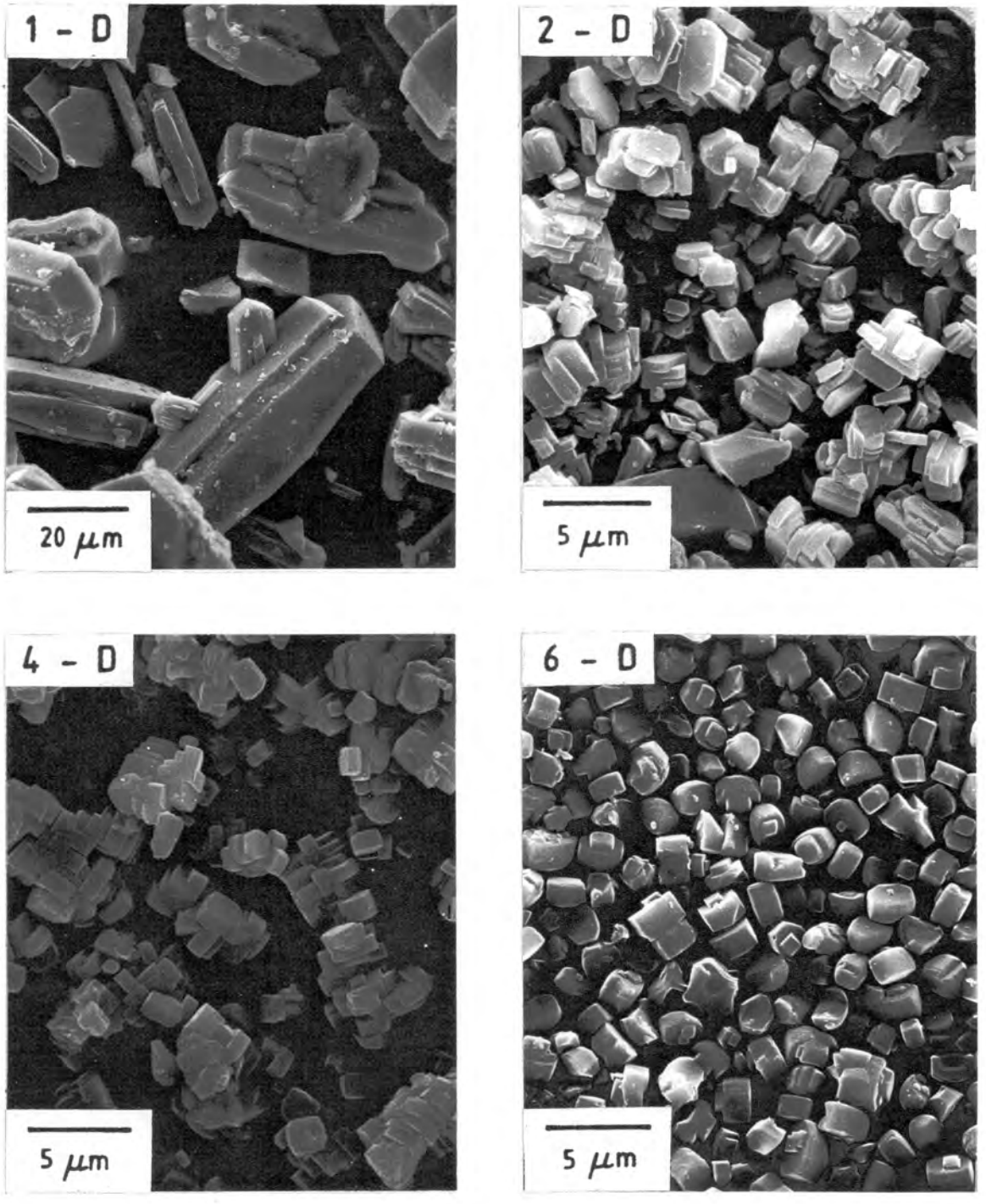

Figure 3.2. Scanning electron micrographs of four preparations from the D-series.

making a purer material is attributed to the introduction of stirring during the synthesis. This result clearly showed that stirring is beneficial during the synthesis of ZSM-5.

Table 3.4 Chemical analysis of the preparations from the D-series. Figures reported are given as mass percentages. Na_2O results are the amounts of this compound in the ZSM-5 after synthesis, while resid Na_2O are the residual concentrations of this chemical after its removal by cation exchange.

Prep	Al_2O_3 %	Na_2O %	resid Na_2O %
1-D	0,31	0,10	0,01
2-D	0,40	0,26	0,01
3-D	0,38	0,38	0,01
4-D	0,39	0,58	0,02
5-D	0,40	0,89	0,01
6-D	0,41	1,25	0,01

3.1.3. CATION CONCENTRATION OF ZSM-5 SYNTHESISED WITH TPA

3.1.3.1 AMOUNT OF SODIUM IN SYNTHESISED ZSM-5

In preparing a number of samples of silicalite, Fegan and Lowe [32] used a similar formula for the reaction mixture; namely

$$x\ Na_2O \quad z\ Pr_4NBr \quad 20\ SiO_2 \quad 1000\ H_2O$$

As they were preparing silicalite, there was naturally no aluminium in the mixture and their value of z was only 2. From their products, they found a linear relationship between the concentration

of sodium in the reaction mixture, expressed as $2x$ / $2x + z$, and the number of sodium atoms that were located in the unit cell. Through extrapolation, it was shown that ZSM-5 contains no sodium if the fraction is equal to 0,24. This value of 0,24 together with z equal to 3, which is the amount used in this work, makes x equal to 0,473. As the concentration of Na_2O in the preparation mixture is increased, the amount of sodium in ZSM-5 increases proportionally until there is a maximum of about 4,1 atoms per unit cell, which is equivalent to approximately 2,2 mass % Na_2O.

After converting the values obtained by Fegan and Lowe [32] from atoms per unit cell to mass concentration Na_2O, their result is the straight line shown in Figure 3.3. The Na_2O contents of all the preparations in this section, namely the A-, B- and D-series, were also plotted in Figure 3.3. The results of this investigation are in good agreement with the relationship of Fegan and Lowe [32], and show that in highly siliceous ZSM-5, like silicalite, the sodium content is directly proportional to the amount of sodium used in the reaction mixture.

3.1.3.2. CATION EXCHANGE CAPACITY

From the preceding section, it is obvious that the sodium content bears no relationship to the number of active sites stemming from the tetrahedral aluminium atoms in the ZSM-5 that was made. Secondly, there is generally more sodium than the equivalent amount of aluminium atoms. The excess sodium cations have being reported to be associated with silanol groups [187-189], and it has been shown than about 10 % of the silicon atoms of ZSM-5 can form these silanol groups [188,190,191].

Tetrahedrally co-ordinated aluminium atoms in a zeolite form a negative charge, and must be balanced by a cation [185]. Therefore, the cation exchange capacity, which in this case is not its sodium content, gives directly the number of aluminium atoms that result in active sites [178,187]. The ammonia contents of the samples of the

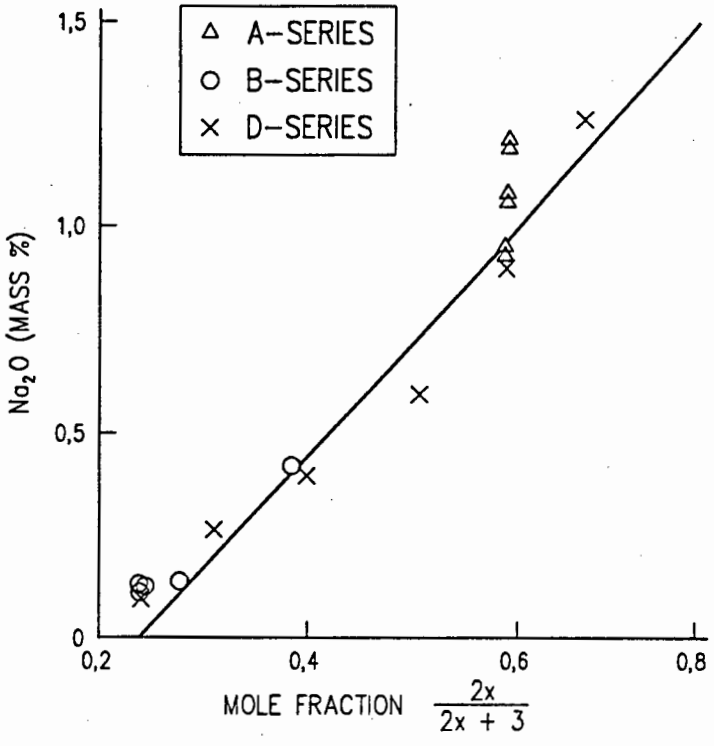

Figure 3.3. Na_2O content as a function of the ratio of the Na_2O : Pr_4N cations in the reaction mixture. Straight line is extracted from the work of Fegan and Lowe [32] and the points are data from this work.

D-series which had been ammonium cation exchanged, are given in Table 3.5. Also included in the table are the aluminium contents from Table 3.4. The results show that with samples 2-D to 6-D the ammonia mole concentration was on average 84 % of the aluminium mole concentration. This means that 84 % of the aluminium atoms are located in the ZSM-5 structure and the rest in an amorphous phase. With sample 1-D however, it appears that a far smaller fraction of the aluminium is housed in the ZSM-5 structure.

Table 3.5. Ammonia contents (as mass percentage) of the ammonia exchanged samples of the D-series and the cation exchanged capacities determined from these results. Included also is the total aluminium concentrations taken from Table 3.4.

Prep	NH_3 %	NH_3 mmoles/g	Al_2O_3 %	Al mmoles/g
1-D	0,046	2,70	0,31	6,08
2-D	0,107	6,28	0,40	7,85
3-D	0,098	5,75	0,38	7,45
4-D	0,111	6,52	0,39	7,65
5-D	0,126	7,40	0,40	7,85
6-D	0,115	6,75	0,41	8,04

3.2. ANALYSIS OF PRODUCTS FORMED WHEN USING α,ω-DIAMINOALKANES (SAMPLES FROM THE E-SERIES)

3.2.1. CRYSTALLINITY AND ZEOLITES FORMED

With minor exceptions which will be discussed in the text, it was found from that all the preparations produced X-ray diffractograms similar to that shown in Figure 3.1, and naturally means that these samples consisted mainly of zeolite ZSM-5. A section of the diffractograms, scanned between 14° and 10° θ, of preparations 1-E to 10-E are reproduced in Figure 3.4. The complete diffractograms are included in Appendix B.

The diffractogram of preparation 1-E shows that a significant amount of amorphous material was found when diaminoethane was used as the principal template. By following the changes in the diffractograms while moving across from preparations 1-E to 6-E, it can be observed that as the size of the alkane group (see Table 2.5)

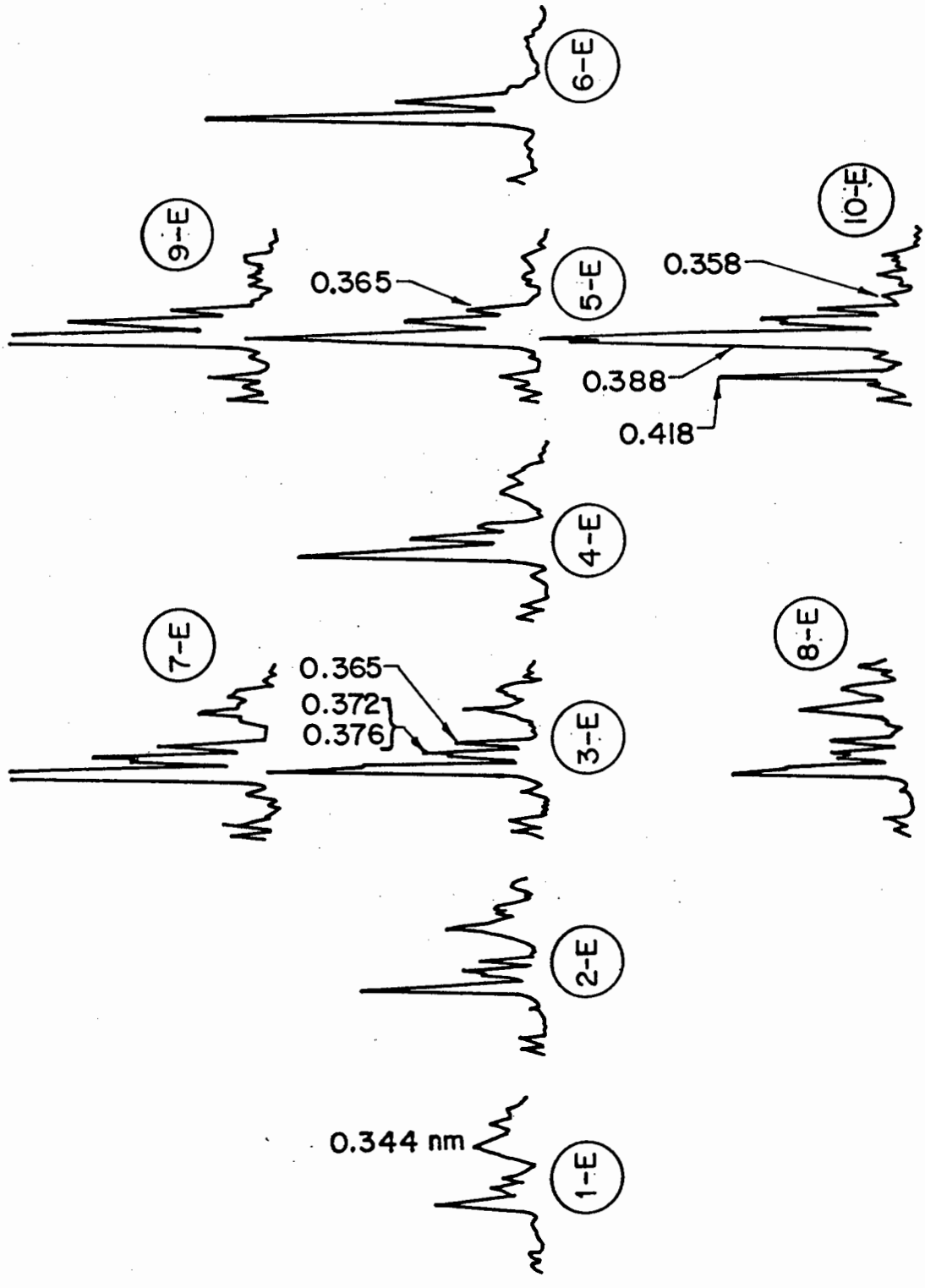

Figure 3.4. X-ray diffractograms of preparation 1-E to 10-E, showing the region between 10° and 14° θ. Radiation source from CuK_α, operating at 40 kV and 20 mA.

increased, the amount of amorphous material diminished and the crystallinity of the ZSM-5 increased.

Figure 3.4 also includes sections of the diffractograms of preparations with various silica to alumina ratios; namely samples 7-E, 3-E and 8-E when using diaminobutane, and samples 9-E, 5-E and 10-E when using diaminohexane as the main template. The X-ray diffraction intensities of the preparations made with diaminobutane were lower than those made with diaminohexane, particularly for the higher silica to alumina ratios. This shows that the products from the diaminobutane tended to yield more amorphous material in highly siliceous ZSM-5 than its hexane counterpart, and therefore, when trying to synthesise highly siliceous ZSM-5, it is preferable to use 1,6-diaminohexane. In the technique used in this work, 1,6-diaminohexane can be used with a reasonable degree of success to synthesise crystalline ZSM-5 with a silica to alumina mole ratio in the region of 250 : 1.

The intensity of the XRD peaks resulting from preparation 9-E was about the same as that obtained from the samples from the A- and B-series. This can be observed from the full diffractograms shown in Appendix B. Therefore, it can be concluded that sample 9-E is a fairly well crystalline material, but is however, not quite as good as the products from the D-series. As can be estimated from the XRD intensities, the amount of crystalline ZSM-5 of the preparations decreased as the silica to alumina ratio increased: the XRD intensity of preparation 5-E is only about 70 % of that of 9-E, while that of preparation 10-E is even less. This indicates a decrease in the amount of ZSM-5. This subject will be dealt more fully in section 3.3.1.

There are two ways to distinguish between zeolites ZSM-5 and ZSM-11 [19,192]. Firstly, the XRD doublets (where *h* and *k* have the same value) of orthorhombic ZSM-5 merge into a single peak in tetragonal ZSM-11. However, when referring to Table 3.1, it can be seen that the d spacing between these peaks of the doublets are small, and, as shown in Figure 3.1, it is difficult to actually

distinguish whether the peak is a doublet or singlet. The alternative method is to observe the extinction of the peaks where $h + k + l = 2n + 1$. For sample 3-E three XRD peaks at 0,376, 0,372 and 0,365 nm, which are associated with ZSM-5, are clearly marked. The latter peak at 0,365 nm is the (*133*) reflection (see Table 3.1) and its extinction provides evidence of the presence of tetragonal ZSM-11 instead of orthorhombic ZSM-5 [19,192]. As the length of the carbon chain in the diamine compound was increased, the height of this peak was reduced. The reduced diffraction intensity of the (*133*) peak means that the zeolite crystallised with the aid of the diaminopentane and diaminohexane compounds produced ZSM-5 with significant ZSM-11 inter-growths. Further, when diaminooctane was used in the synthesis this peak was not detected, and thus confirms that 1,8-diaminooctane is an ideal template for producing ZSM-11 [42,47,55].

Apart from the peaks identified with ZSM-5, the X-ray diffractogram of sample 1-E gave a solitary broad peak at 0,344 nm. This peak could be attributed to the presence of analcime. As this mineral was not well-crystallised it was not possible to confirm the rest of its listed diffraction peaks [193]. As the length of the alkane group of the diaminoalkane increased, the presence of "analcime" decreased; with diaminopentane it was very small, and with diaminohexane and diaminooctane it was not detected.

On the section of the diffractogram of sample 10-E peaks with d values of 0,418, 0,388 and 0,358 nm are caused by the presence of zeolite ZSM-48 [52,61]. Although smaller, these peaks were also present in preparations 5-E and 9-E.

3.2.2. CONCENTRATION OF ZSM-48

Moving along the three diffractograms of samples 9-E, 5-E to 10-E in Figure 3.4, it can be seen that the fraction of ZSM-48 increased. This increase in the amount of ZSM-48 runs parallel with the reduction in the aluminium content of the preparation. This

trend to co-crystallise ZSM-48 is in line with the results of Franklin and Lowe [53,54], where no aluminium was used in their preparation mixtures. Naturally, this increase in ZSM-48 results in a concomitant decrease in the amount of ZSM-5 in these three samples, which has already been mentioned in section 3.2.1.

The series of samples 11-E, 12-E, 5-E and 13-E, were prepared to examine what effect the concentration of sodium used in the preparation mixture had on the amount of ZSM-48 that crystallised simultaneously. With the low amount of sodium used in preparation 11-E, it appeared from the XRD intensities that the product contained similar amounts of ZSM-48 and ZSM-5. This was confirmed by visual inspection with the aid of the scanning electron microscope in section 3.2.3. Increasing the sodium oxide concentration in the reaction by moving from sample 11-E to 13-E did reduce the amount of ZSM-48 formed, but some of this mineral was still present in sample 13-E, in which the highest concentration (x = 2,90) of Na_2O was used.

Franklin & Lowe [53] have shown that the addition of small amounts of tetrapropylammonium cations to the reaction mixture suppressed the formation of ZSM-48 during the synthesis of silicalite. They used concentrations of z equal to 0,1 and 0,5, and found that as more TPA was added, the concentration of ZSM-48 was lower. Similar variations in the TPA concentrations were used in this work and the same trend was observed. The effect of the TPA variation was much smaller than those of aluminium and sodium contents of the reaction mixture. When no TPA was added (sample 14-E), about twice the amount of ZSM-48 was found as in the central preparation 5-E, while when five times as much TPA was used (sample 16-E), this amount was reduced to only half.

3.2.3. SCANNING ELECTRON MICROSCOPY

The scanning electron micrographs of the first six preparations of the E-series are to be found in Figure 3.5. It can be visually

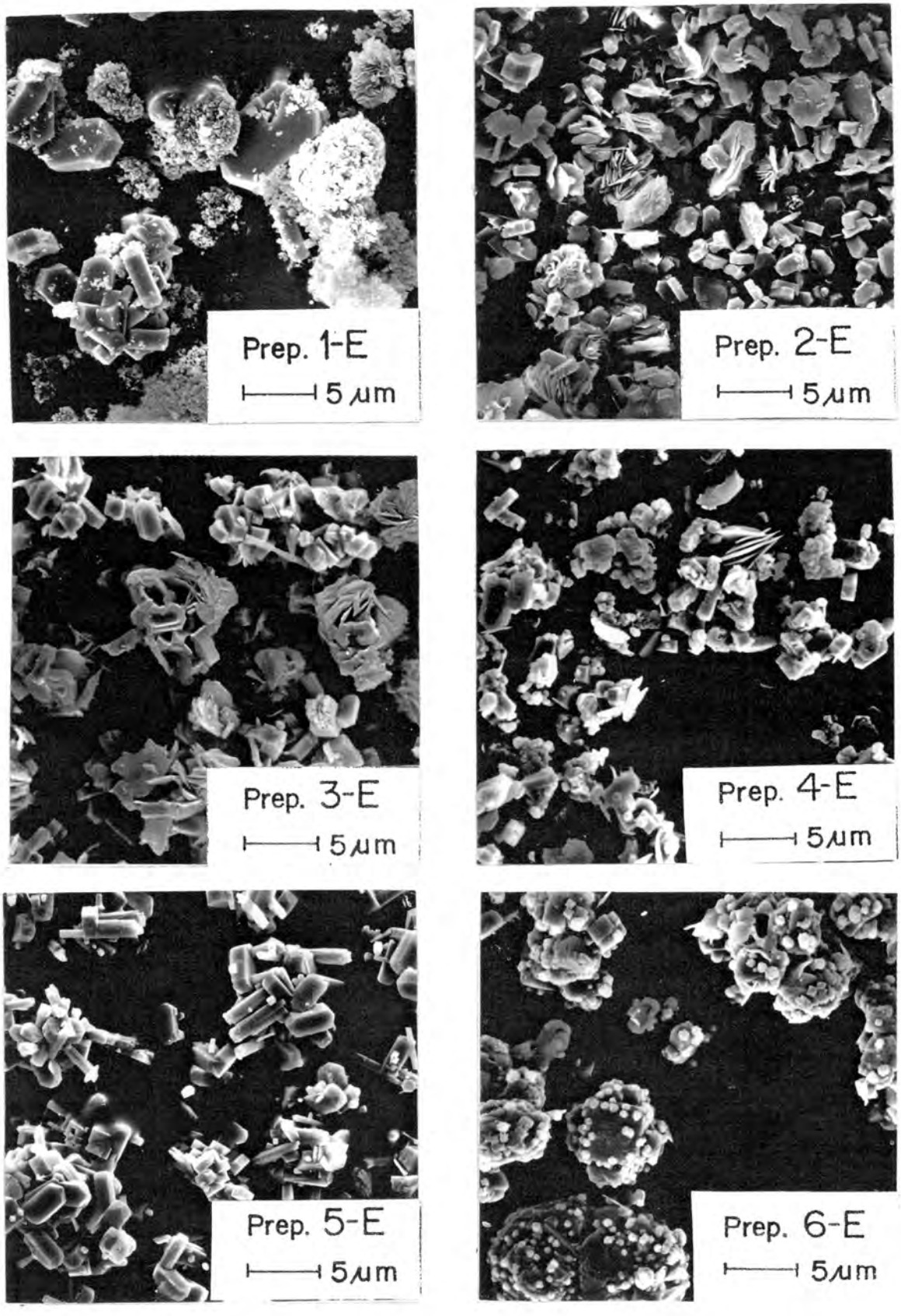

Figure 3.5. Scanning electron micrographs of preparations 1-E to 6-E.

observed in the micrographs that when moving from number 1-E onwards, the amount of amorphous material decreased while the crystallinity of the zeolite simultaneously increased. This substantiates the result that was found from X-ray diffractometry. The shape of the crystallites of sample 5-E were about 3µm in length and about 1 µm in width.

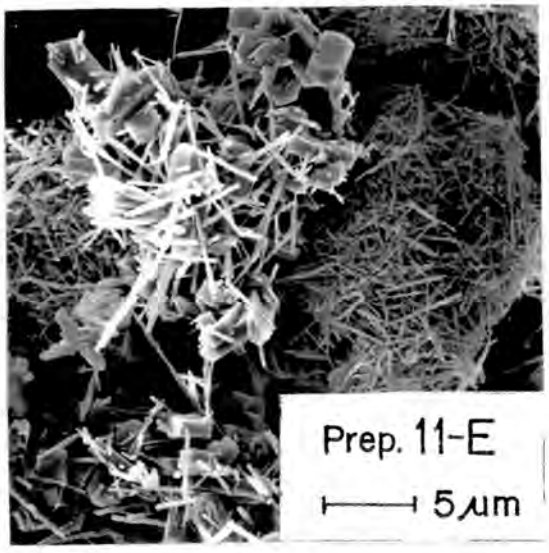

Figure 3.6. Scanning electron micrograph of preparation 11-E.

The SEM of preparation 11-E is shown in Figure 3.6, and clearly indicates that the sample contains a high proportion of the "needle" structure of ZSM-48 [21]. A quantitative determination of the amounts of materials present is difficult, but a visual observation suggests that this sample consisted of about equal amounts of ZSM-5 and ZSM-48. This substantiates the result obtained from XRD.

3.2.4. CO-ORDINATION OF ALUMINIUM ATOMS

The shifts in the ^{27}Al NMR peaks produce information on the co-ordination of the aluminium atoms. In an octahedral environment aluminium will show virtually no shift, but when it is tetrahedrally

co-ordinated, the resulting peak is to be found at between 51 and 65 ppm [194,195]. The ^{27}Al NMR spectra of preparations 1-E to 10-E are shown in Figure 3.7. The aluminium in all the preparations give a single peak around 56 ppm, which is typical for the tetrahedral co-ordination in zeolite ZSM-5. This must be the only significant location for the aluminium atoms as no other shifts were evident.

The intensity of ^{27}Al NMR peaks from preparations 1-E to 6-E grew as the size of the alkane group increased. However, as the same concentration of aluminium was used in each of these preparations (see section 2.1.2.3), and the same concentration was to be found in the final product (see section 3.2.5.1), no other significance can be attached to this increase in peak intensity. The ^{27}Al NMR spectra of preparations 7-E, 3-E and 8-E, and 9-E, 5-E and 10-E showed a decrease in peak intensity with increasing silica to alumina ratio. However, this change in intensity must be influenced largely by the aluminium content of the preparation, and all that can be concluded from this is that these preparations again showed the presence of only tetrahedrally co-ordinated aluminium in the ZSM-5.

3.2.5. CHEMICAL ANALYSIS

3.2.5.1. ALUMINIUM CONTENTS

Preparations 1-E to 6-E should all have the same concentration of Al_2O_3. From the amount of aluminium sulphate added to the synthesis mixture, the Al_2O_3 content should theoretically be 0,71 %. The actual results obtained by chemical analysis is reported in Table 3.6, and is obviously higher than what was expected. The average the Al_2O_3 concentration was found to be 0,98 %.

When the ZSM-5 was synthesised with TPA in section 2.1.1.2, allowance was made that the *Ludox* solution contained 0,04 % Al_2O_3. The specification on the silica, *Neosyl ET,* that was used when the synthesis was performed with α,ω-diaminoalkanes, stated that the

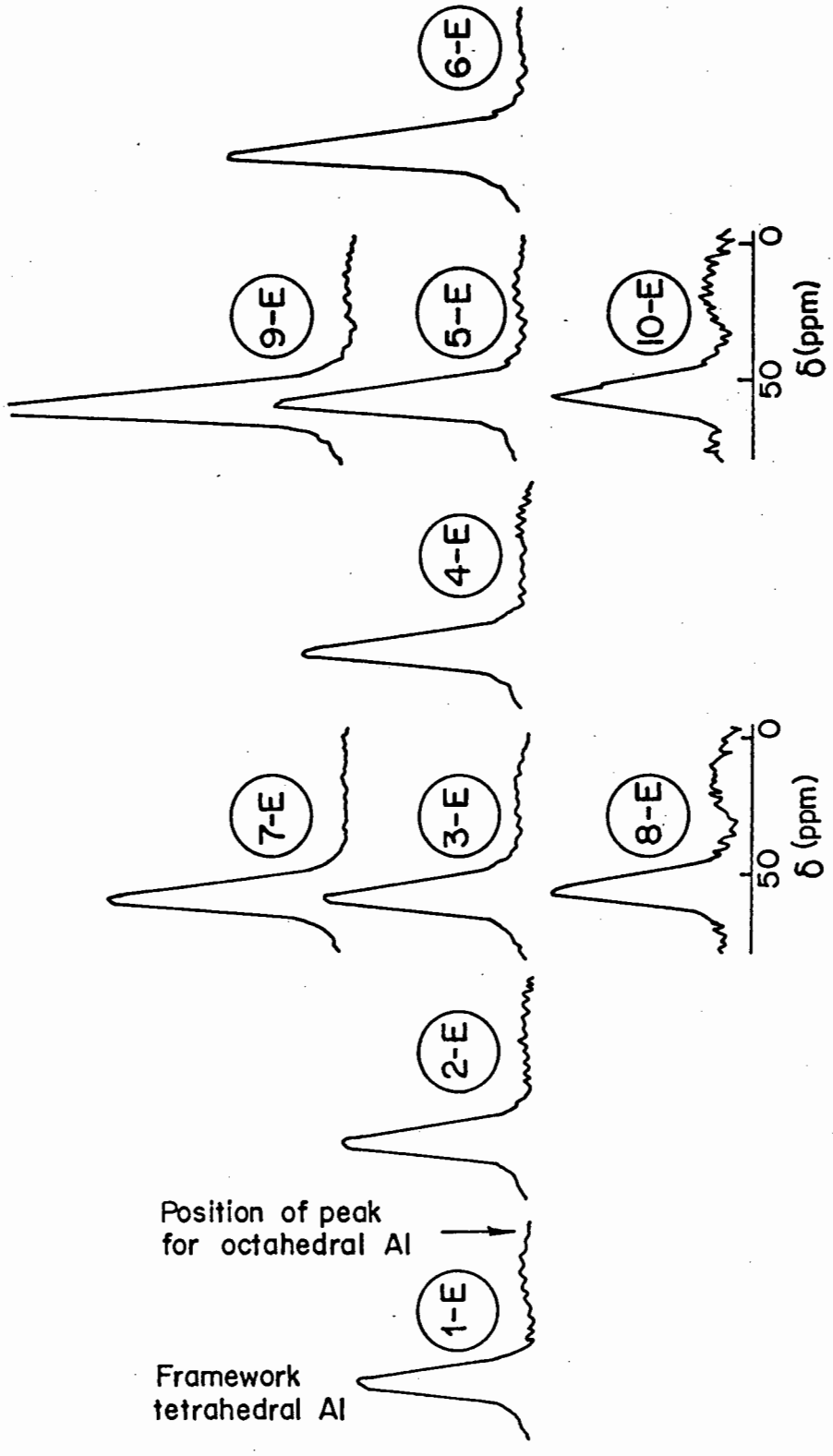

Figure 3.7. Magic angle spinning ^{27}Al nuclear magnetic resonance spectra of preparation 1-E to 10-E. Samples scanned between δ = 80 and -5 ppm.

amount of Al_2O_3 therein was negligible and consequentially no allowance was made for any of it being present (section 2.1.2.3). However, subsequent analysis showed that it did indeed contain 0,15 % Al_2O_3. By taking into account this additional source of alumina, the theoretically expected Al_2O_3 should then be 0,87 %. This value is reasonably close to that actually found when also taking into consideration that the accuracy of the determination is ±0,07 % (see section 2.2.4).

Table 3.6 Chemical analysis of the preparations 1-E to 6-E. Figures reported are given as mass percentages. Na_2O results are the amounts of this compound in the ZSM-5 after synthesis, while resid Na_2O are the residual concentrations of this chemical after its removal by cation exchange.

Prep	Parent alkane of DAA	Al_2O_3 %	Na_2O %	Resid Na_2O %
1-E	ethane	1,06	2,13	1,03
2-E	propane	0,94	2,80	0,57
3-E	butane	0,97	2,26	0,33
4-E	pentane	0,90	0,75	0,25
5-E	hexane	1,04	0,51	0,02
6-E	octane	0,99	0,45	0,19

3.2.5.2. SODIUM CONTENTS

The sodium content of ZSM-5 after synthesis gives a good indication of the purity of the product; excessive amounts of sodium generally indicate the presence of non-zeolitic material. The results on samples 1-E to 6-E are given in Table 3.6, and show that as the length of the alkane group was increased the sodium content decreased. This indicates that the amount of amorphous material

diminished while the crystallinity of the zeolite increased. When diaminopentane, diaminohexane and diaminooctane were used, the materials had sodium contents more or less equivalent to that expected of fully crystalline ZSM-5 or ZSM-11. However, in comparison to products made with only TPA as the template, preparations 4-E, 5-E and 6-E had lower sodium contents. This point will be addressed in section 3.2.7.1.

As was already mentioned in section 3.1.2.3, all the sodium in ZSM-5 ought to be cation-exchangeable, and the lower the amount of sodium remaining after cation exchange, the purer the zeolite. From the residual sodium contents given in Table 3.5, it can be seen the preparation in which 1,6-diaminohexane was used, produced the purest ZSM-5. Further, its residual Na_2O content is as low as the samples of the D-series. Although samples 4-E and 6-E, which were prepared with diaminopentane and diaminooctane respectively, had initially normal (compared to sample 5-E) sodium contents, it was not possible to decrease the level these cations to almost nothing as was in the case of sample 5-E.

3.2.6. THERMOGRAVIMETRIC ANALYSIS OF α,ω-DIAMINOALKANES WITHIN ZSM-5

3.2.6.1. THERMOGRAVIMETRIC ANALYSIS OF PRODUCTS FORMED

The thermogravimetric analyses of preparations 2-E to 6-E are given in Figure 3.8. The top portion, Figure 3.8 (A), shows the rate at which alkalis were released due to evolution of the nitrogen-bearing fragment of the organic compounds, from the zeolite. The rate is given in micromoles for an equivalent monovalent compound being released, although in the original preparation mixture the diamines are divalent. The quantity released from the sample formed with diaminopropane was low and is due to the ZSM-5 being poorly crystalline. Nevertheless, the rate of alkali release follows the same trend as that found with the two other preparations 3-E and 4-E.

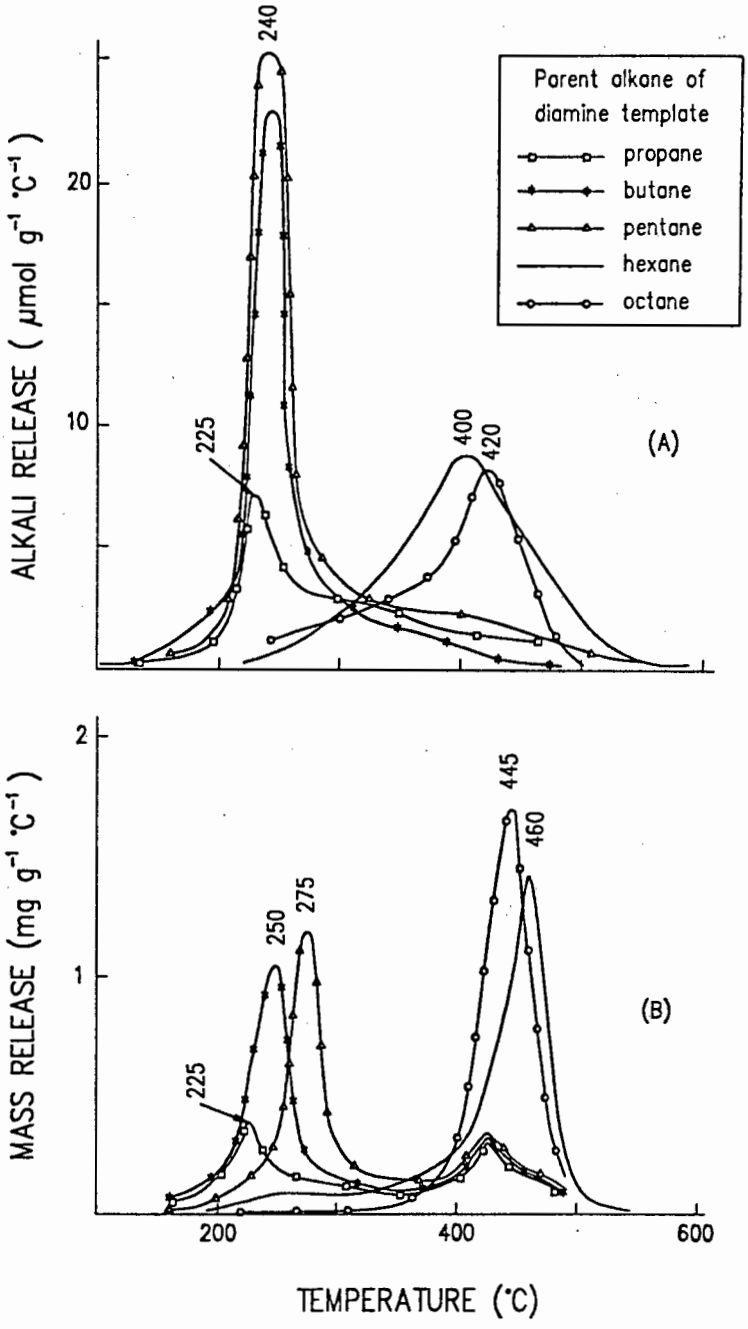

Figure 3.8. Thermogravimetric analysis on preparations 2-E to 6-E, which were synthesised with different diaminoalkanes as the organic directing agent. Identification of the parent alkane is given by the symbols on each curve as indicated in the legend.

Calcination of the synthesised samples meant that both adsorbed water and the organic template were driven from the zeolite structure. Below 160 °C most of the water was removed and the reduction in mass above this temperature is mostly attributable to loss from the template. The rate at which the total mass of the product was reduced above 160 °C, presumed to be mostly due to the template being driven off, is shown in Figure 3.8 (B).

Samples 2-E, 3-E and 4-E, synthesised with diamine compounds from propane, butane and pentane respectively, released nearly all their nitrogen portion at roughly the same temperature. This temperature is around 240 °C, and is higher than all the boiling points of these organic materials: 1,5-diaminopentane boils at 179 °C. By comparing the curves in Figure 3.8 for the ZSM-5 containing these three templates, it is clear that the thermal removal of the nitrogen- (alkaline-) containing portion took place at a lower temperature than the removal of the bulk of the template molecule. The difference between 240 and 275 °C with sample 4-E means that 1,5-diaminopentane must crack before leaving the zeolite. When diaminopropane and diaminobutane were used in the synthesis, the difference between the temperatures at which these two removals occurred was much smaller.

Figure 3.8 (B), shows that at around 425 °C samples 2-E, 3-E and 4-E had a second, but smaller, amount of template that was driven off. This remaining bulk of the organic material was equivalent to 2,5 % of the mass of the preparation. The TPA molecules are also released at this temperature [174] but would account for a mass loss of only 1,1 %. However, at around 425 °C, these samples, as shown in Figure 3.8 (A), released only small quantities of nitrogen- (alkali-) containing material. This means that some of the second mass loss must be attributed to a hydrocarbon fraction originating from the diamine and not only the TPA. This portion of the diamines is strongly held and contains little (if any) nitrogen.

When diaminohexane and diaminooctane were used as the main template (samples 5-E and 6-E respectively), the zeolites similarly released the amine portion before the bulk of the organic molecule. The cracking and subsequent release of these compounds however, took place at significantly higher temperatures, namely greater than 400 °C. Such high temperatures indicate that these organic compounds must be firmly incorporated in the zeolite structure. Since they form an intricate part of the zeolite structure, diaminohexane and diaminooctane function effectively as templates during the synthesis of ZSM-5 and ZSM-11 respectively.

To establish the effects of the presence of the small amounts of the TPA compound that were also added to the preparations, thermogravimetric determinations were also carried out on samples 14-E to 16-E. The results calculated from these experiments are given in Table 3.7, which also includes an estimate of a theoretical result in which only tetrapropylammonium cations and no diaminohexane would be used [37-39,174]. In order to calculate the number of nitrogen atoms per unit cell, it was necessary to estimate the atomic mass of the unit cell of ZSM-5. This value was taken as 6500, based on the unit cell having 96 silicon / aluminium atoms, approximately one sodium atom and that the synthesised ZSM-5 contained 11 % by mass organic material and adsorbed water. Further, it is assumed that the TPA compound was preferentially incorporated into the zeolite structure and would account for 0,4 molecule per unit cell.

Table 3.7 includes the peak temperatures at which the alkali portion and the total mass from the diaminohexane are released. When comparing the results for preparation 14-E, where no TPA was added, with those for preparations 15-E and 5-E, it can be seen that the addition of small amounts of TPA cations did not significantly shift the position of these peaks. Therefore, it can be concluded that the portion of the diaminohexane containing the nitrogen atom is released around 390 °C, while the much larger remainder of this organic compound is released only at a temperature which is 70 °C higher. The hydrocarbon portion of the organic compound is more

Table 3.7. Data and calculations on the composition of the preparations of ZSM-5 using diaminohexane as main template but with different amounts of TPA cations as seeding compound.

Prep	Filling by Pr_4N cations %	Alkali release mmol/g	Nitrogen atoms per u.c.	Temp. of alkali release °C	Mass loss >160 °C %	Temp. of mass release °C
14-E	nil	1,30	8,5	390	10,3	460
15-E	5	1,28	8,3	390	10,3	460
5-E	10	1,32	8,6	400	10,0	460
16-E	50	0,91	6,0	410	11,0	440
	100	±0,5	3,6	-	-	-

strongly attached within the zeolite structure, and would play the major role in the direction of crystallisation.

Table 3.7 also shows that samples 14-E, 15-E and 5-E produced similar amounts of alkali release and loss in mass above 160 °C. As sample 14-E contained no TPA compound, it may be deduced that the small additions of TPA had little effect on the amount of 1,6-diaminohexane filling the intersections and channels of the ZSM-5 zeolite. It was only when relatively larger amounts of TPA cations were used, such as with preparation 16-E, that the thermogravimetric analysis showed a decrease in the amount of alkali material being released. This means that there was also a reduction in the number of nitrogen atoms being incorporated into the zeolite structure. However, it must be remembered that when using TPA compounds as the template, the theoretical maximum number of cations to be found in the zeolite structure is 4 per unit cell. In practice this value is usually about 3,6 or less [37-39,174].

3.2.6.2. QUANTITY OF AMINES AND ALKANES IN ZEOLITE STRUCTURE

The total amounts of alkali released and mass loss above 160 °C of preparations wherein different α,ω-diaminoalkanes were used as the main templates (samples 2-E to 6-E) are given in Table 3.8. From this data, together with the assumption mentioned in section 3.2.6.1 that atomic mass of the unit cell was 6500, the number of nitrogen and alkane molecules per unit cell were calculated. These results are given in Table 3.8.

The theoretical permissible number of diaminoalkane molecules that can be accommodated per unit of ZSM-5 is eight. However, it was pointed out in section 1.3.2 that it is sometimes less than eight. This was found with the samples from the E-series, where it was calculated that the average number of alkane molecules per unit cell was 5,3. With the same number of diaminoalkane molecules, there ought to be 10,6 amine or nitrogen containing groups. The average number from Table 3.8 was only 7,7. This was again less than expected and this point will be analysed in section 3.2.6.3 below.

3.2.6.3. COMPOSITION OF DIAMINES IN ZEOLITE STRUCTURE

It was mentioned in section 1.3.2 that the diaminoalkanes undergo some degree of de-amination. Therefore, from the number of nitrogen atoms per unit cell and the number of alkane molecules per unit cell listed in Table 3.8, the number of nitrogen atoms per alkane molecule was calculated. The results are given in Table 3.9, and show that on average each molecule has 1,4 nitrogen bearing groups. On the assumption that the number of nitrogen bearing groups are amine groups, the results indicate that the diamine compound inside the zeolite must have undergone some de-amination during the synthesis.

From the determinations of the number of amine groups per molecule, the carbon to nitrogen ratios were calculated. These

Table 3.8. Data and calculations on the quantity and composition of organic compound from the thermogravimetric analysis done on the ZSM-5 / 11 preparations using different diaminoalkanes as the template (see Figure 3.8). Alkane molecule mentioned below the symbol DAA is only the linear hydrocarbon portion of the actual diaminoalkane.

Prep	DAA	Alkali release mmol/g	Nitrogen atoms per u.c.	Mass loss >160 °C %	Alkane molecules per u.c.
2-E	propane	0,82	5,4	5,2	4,5
3-E	butane	1,35	8,7	8,6	6,3
4-E	pentane	1,54	10,0	10,0	6,3
5-E	hexane	1,32	8,6	10,0	5,4
6-E	octane	0,92	6,0	9,9	4,2

Table 3.9. Determinations of the number of nitrogen atoms per molecule and carbon atoms occluded in zeolite. Ratios were determined from thermogravimetric analysis (Table 3.8), direct chemical analysis and taken from results of ref. 47.

DAA	Nitrogen atoms per alkane	C/N mole ratio from TG	C/N mole ratio from chem. anal	C/N mole ratio from ref. 47
propane	1,1	2,7	2,9	-
butane	1,3	3,0	2,6	± 3
pentane	1,5	3,3	3,1	2,9
hexane	1,5	3,9	4,2	4,5
octane	1,3	6,1	6,2	8,3

results are given in Table 3.9. These figures were confirmed by obtaining virtually the same values by direct chemical analysis, which are also shown in Table 3.9. Further, they are similar to published data [47], which are also included in Table 3.9.

Although chemical analysis indicates that some form of de-amination had taken place, it has been shown that the three chemical shifts at 43, 35 and 28 ppm from the MAS ^{13}C-NMR spectra 1,6-diaminohexane are also found when this compound is occluded in the ZSM-5 structure during synthesis [56]. From this it was reasoned that the organic molecule remains intact during synthesis [46,56] and would imply that no de-amination takes place.

The MAS ^{13}C-NMR spectra of preparations 5-E and 14-E, as well as that of pure 1,6-diaminohexane, are shown in Figure 3.9. The NMR spectrum of sample 5-E (preparation using 1,6-diaminohexane and tetrapropylammonium cations) shows six peaks. Peaks marked X, Y and Z at 63, 16 and 11 ppm are attributed to shifts from the TPA cations [196,197], while the three remaining shifts, marked A, B and C, are similarly located to those of the pure 1,6-diaminohexane.

If as a result of the synthesis, de-amination of the compound to a monoamine took place, shifts below 28 ppm should be evident. However, none were found. Although their absence is obscured by two peaks from the tetrapropylammonium shifts, it is clear there are no shifts in this region with sample 14-E, which contained none of the TPA compound. Although the positions of the NMR shifts indicate no alteration in the diaminoalkanes, their magnitudes, which are proportional to the amount of carbon present, did show some changes. In pure 1,6-diaminohexane, peaks A, B and C ought to be, and are, the same size. Referring to Figure 3.9, it is clearly shown that after synthesis peaks A and B are much smaller than peak C. This variation in the magnitudes of the peaks suggests that the diaminohexane has undergone some change, but it is not a simple partial de-amination to a monoamine. As it is much larger than the other, a major portion of peak C must be caused by carbon atoms that

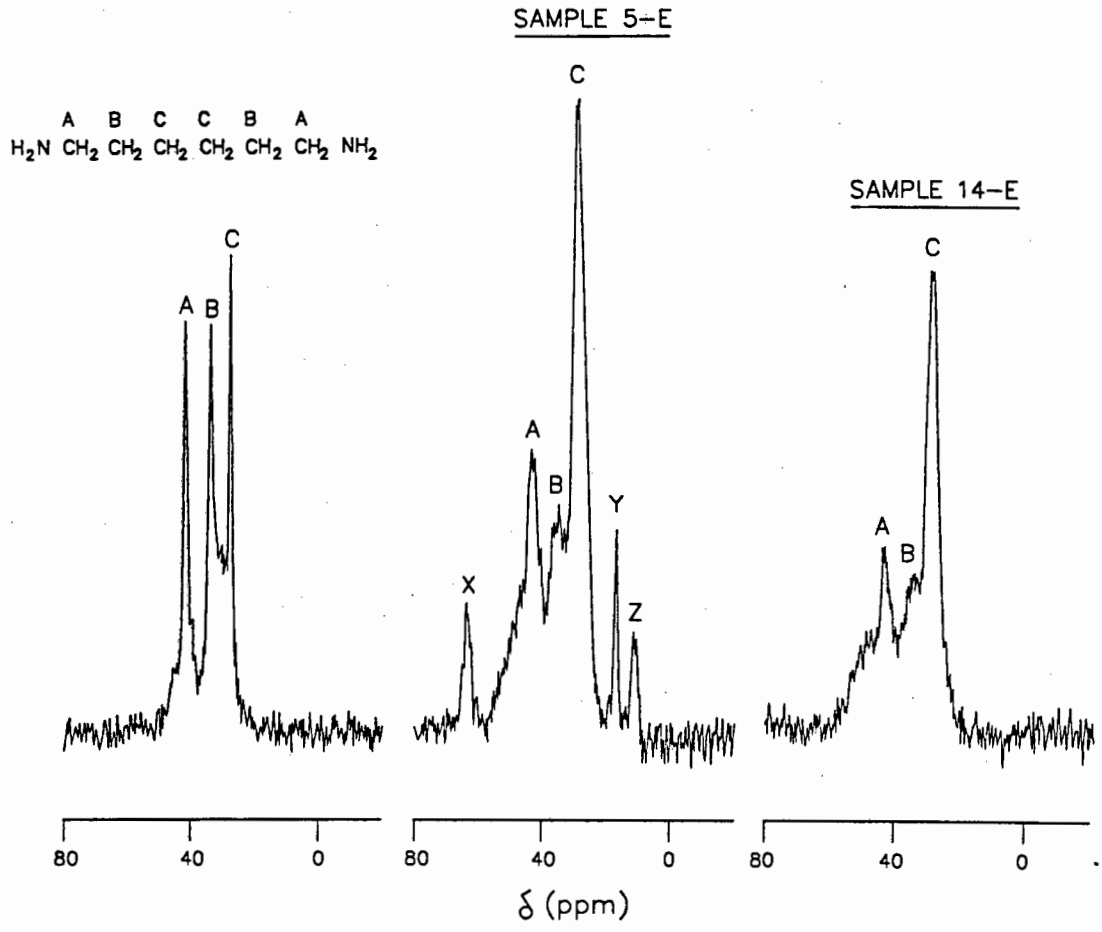

Figure 3.9. Magic angle spinning ^{13}C nuclear magnetic resonance spectra of pure 1,6-diaminohexane and samples 5-E and 14-E. Sample 5-E contains both diaminohexane and tetrapropylammonium cations as templates, while sample 14-E contains only diaminohexane.

are in an environment that is not part of a diamine, or a monoamine or a normal hydrocarbon.

A similar result was found with sample 6-E, which was made with 1,8-diaminooctane, giving a large prominent shift at 32 ppm. The other three samples, 2-E, 3-E and 4-E, also appeared to produce a new peak, but this was difficult to identify as they were much smaller than the normal peaks from the pure diaminoalkanes. These spectra are included in Appendix C.

The NMR of the excess 1,6-diaminohexane remaining in the filtrate gave the same spectrum as the pure compound, and not like that within the zeolite. This means that de-amination takes place as a result of the compound being incorporated into the zeolite structure.

3.2.7. CATION CONCENTRATION IN ZSM-5 SYNTHESISED WITH 1,6-DIAMINOHEXANE

3.2.7.1. AMOUNT OF SODIUM IN SYNTHESISED ZSM-5

In their preparation mixture, all the samples of the D-series had the same concentration of aluminium, but the amount of sodium hydroxide used was varied. Similarly samples 11-E, 12-E, 5-E and 13-E had the same aluminium, but different amounts of sodium hydroxide (see Table 2.5). The chemical analysis for aluminium and sodium (expressed as their oxides) of the products are given in Table 3.10. The results show that as was previously found in section 3.1.3.1, the Na_2O of the ZSM-5 is not related to its aluminium content.

Table 3.10. Chemical analysis of the preparations from the E-series wherein the aluminium concentration was kept constant, but that of the sodium was varied. Figures reported are given as mass percentages.

Prep	Al_2O_3 %	Na_2O %
11-E	0,98	0,25
12-E	0,98	0,27
5-E	1,05	0,52
13-E	1,10	0,50

The Na_2O contents in the crystalline ZSM-5 of the above samples of the E-series are plotted in Figure 3.10 against the amount of Na_2O, expressed as the mole fraction x in the formula used during synthesis. Also in the figure are the results obtained on the samples from the D-series. The preparations of the E-series, where 1,6-diaminohexane was used, contained less sodium than those of the D-series, which were synthesised with tetrapropylammonium cations.

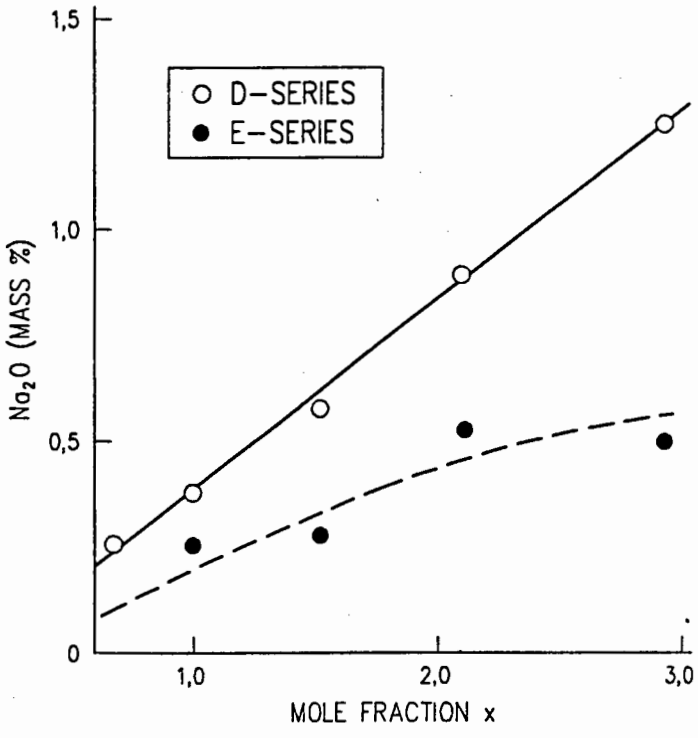

Figure 3.10. The Na_2O content of the crystalline ZSM-5 in relation to the concentration used during synthesis. Samples from the D-series were made with tetrapropylammonium cations, while those from the E-series were made with 1,6-diaminohexane.

3.2.7.2. CATION EXCHANGE CAPACITY

As done in section 3.1.3.2, the cation exchange capacity of the ZSM-5 was carried out to determine the concentration of aluminium

atoms that are tetrahedrally co-ordinated and are responsible for the active sites in the zeolite [178,187]. The results are given in Table 3.11, which also includes the total aluminium concentration derived from the determinations in Table 3.10. The results show that only about 65 % of the aluminium atoms present are located in the zeolite framework, and the rest must be in some amorphous phase. It should be noted that with the D-series (section 3.1.3.2) 84 % of the aluminium was in the zeolite structure.

Table 3.11. Ammonia contents and cation exchange capacities of the ammonium exchanged samples of the E-series. Included also is the total aluminium concentration taken from Table 3.10.

Prep	NH_3 %	NH_3 mmoles/g	Al_2O_3 %	Al mmoles/g
11-E	0,182	10,68	0,98	19,22
12-E	0,208	12,21	0,98	19,22
5-E	0,222	13,03	1,05	20,60
13-E	0,245	14,38	1,10	21,58

3.3. ANALYSIS OF PRODUCTS FORMED WHEN REUSING FILTRATE (SAMPLES FROM THE F-SERIES)

3.3.1. CRYSTALLINITY AND ZEOLITES FORMED

The X-ray diffractograms of the preparations from the F-series identified the presence either of only zeolite ZSM-5, or a mixture of zeolites ZSM-5 and ZSM-48. The heights of the main ZSM-5 diffraction peak at θ = 11,56° (d value = 0,384 nm) were measured for each sample, and were normalised against the average value for the central sample F-13 being equal to 100. The values of these normalised intensities of preparation F-10, and the averages of

those determined for preparations F-35, F-34, F-13 and F-15 are plotted in Figure 3.11 against the silica to alumina mole ratio used in the reaction mixture.

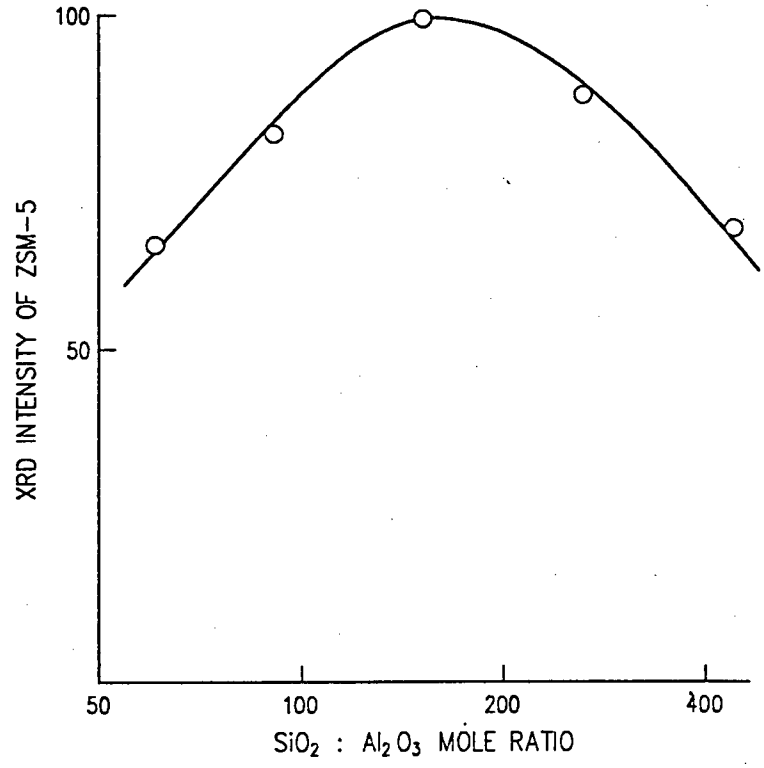

Figure 3.11. X-ray diffraction intensities of the products formed from the F-series in relation to the silica to alumina mole ratio of the reaction mixture when using 1,6-diaminohexane as the template.

It was stated in section 3.2.1 that sample 9-E has an XRD intensity similar to the zeolite made with TPA, which is assumed to consist entirely of pure ZSM-5. As it is made via a similar method to sample 9-E and gave a similar XRD intensity, preparation F-13 therefore, except for small amounts ZSM-48 and possibly some amorphous material, consisted also virtually of pure ZSM-5. As the XRD intensity is proportional to the concentration of ZSM-5 [176], the graph gives a clear indication of the concentration of ZSM-5 in

each mixture, and shows that the purest product is obtained when the silica to alumina mole ratio is in the region of 120 to 200 : 1.

The diffractograms also showed that several samples contained significant amounts of zeolite ZSM-48. As no reference material was available, the concentration of ZSM-48 in preparation F-10 was taken as the remainder of material which was not ZSM-5. It was estimated the amount of ZSM-48 present in this preparation was about 30 %. Further determinations were done by comparing the intensity of the main XRD peak due to the ZSM-48 at θ = 10,64° (d value = 0,418 nm) from sample F-10 with those from the other preparations. The concentration of ZSM-48 in samples F-15 and F-13 was found to be about 10 % and 5 % respectively. The presence of ZSM-48 is the reason for the decrease in the concentration of ZSM-5 in the product shown in Figure 3.11, when higher silica to alumina ratios were used in the reaction mixture.

The XRD results showed that neither preparation F-35 nor F-34 contained any ZSM-48. However, as can be seen in Figure 3.11, neither of these two preparations produced pure ZSM-5. It was shown in Figure 1.4 that as the aluminium concentration in the synthesis mixtures is increased, the amount of crystalline ZSM-5 product decreased and would naturally lead to a concomitant trend to form more amorphous material [30]. As the concentration of aluminium decreased, the amount of amorphous material decreased, and naturally more ZSM-5 is formed. With a silica to alumina mole ratio in the region of about 150 : 1, it can be assumed that little amorphous material was formed and that the product consisted mainly of zeolite ZSM-5.

3.3.2. CATION EXCHANGE CAPACITY

As done in sections 3.1.3.2 and 3.2.7.2, the cation exchange capacity of the ZSM-5 was carried out to determine the concentration of aluminium atoms that are tetrahedrally co-ordinated in the zeolite, and result in active sites [178,187]. The results are

given in Table 3.12, which also include the theoretical aluminium concentrations determined from the amounts used in Table 2.6.

The results in Table 3.12 show that about half the aluminium atoms that were added to the reaction mixtures of preparation F-34 and F-35 became incorporated into the zeolite structure. The remainder would be in the amorphous phase mentioned in section 3.3.1. With the other three preparations the concentration of aluminium atoms resulting in active sites is about the same as that expected from the amount of aluminium sulphate added to the synthesis mixture. However, it should be remembered that when the expected aluminium concentration in the zeolite product was calculated no allowance was made for the presence of some of it in the *Neosyl ET* silica. As mentioned in section 3.2.5.1, this material contained 0,15 % Al_2O_3, and would therefore increase the actual concentration in the ZSM-5 product by about the same amount.

Table 3.12. The theoretical Al_2O_3 contents samples of the F-series (determined from the formulae in Table 2.6), the ammonia contents of the ammonium exchanged samples, the equivalent Al_2O_3 from these CEC results and a calculation of the SiO_2 : Al_2O_3 mole ratio of the ZSM-5 present in the product.

Prep	Nominal SiO_2:Al_2O_3 mole ratio	Theoret. Al_2O_3 %	NH_3 %	Al_2O_3 from CEC %	Calculated SiO_2:Al_2O_3 mole ratio
F-35	60 : 1	2,95	0,487	1,46	80 : 1
F-34	90 : 1	1,93	0,363	1,09	130 : 1
F-13	150 : 1	1,15	0,319	0,96	180 : 1
F-15	250 : 1	0,71	0,233	0,70	230 : 1
F-10	425 : 1	0,41	0,152	0,46	280 : 1

On the assumption that all the aluminium atoms resulting in sites which have cation exchange capacity are part of the ZSM-5 present with none in the ZSM-48, and from the concentrations shown in Figure 3.11, the silica to alumina mole ratio of the ZSM-5 in the product was calculated. These results are given in Table 3.12. As can be judged from Table 3.12, these calculated ratios for samples F-35, F-34, F-13 and F-15, are reasonably close to the nominal ratios. It is only with the remaining preparation, F-10, that a certain degree of error is evident.

When these samples were used in the catalytic experiments in chapter 4, their composition was expressed according to the nominal silica to alumina mole ratio used in the synthesis mixture. As nearly all the work in the catalytic experiments was focused on the three central samples (F-34, F-13 and F-15), it appears quite acceptable to use and to express their nominal mole ratio as an accurate reflection of their actual compositions.

3.3.3. EFFECT OF REUSING FILTRATE

Amongst the first syntheses with each formula, only samples F-10 contained ZSM-48. None of the other initial preparations from F-15, F-13, F-34 or F-35 contained a detectable amount of this zeolite. With the second crystallisation using the same filtrate, it was found with samples F-15 and F-13 that some zeolite ZSM-48 was present, and it was estimated that the concentrations were about 13 % and 8 % respectively. However, the amount of ZSM-48 was about the same with subsequent crystallisations using the old filtrate. With the remaining two preparations F-34 and F-35, which had the higher concentrations of aluminium, no ZSM-48 was formed in the any of the subsequent crystallisations.

The increase in the amount of ZSM-48 formed could also be noticed by the decrease in the bulk density (mass per volume) of the product, caused by the presence of its needle-like crystallites.

3.3.4. REACTION TEMPERATURE

In section 1.3.3 it was pointed out that for the synthesis of ZSM-5 with 1,6-diaminohexane, the use of lower temperatures favours the formation of ZSM-5 above ZSM-48. It was thus to be expected that with sample F-150, which had the same composition as preparation F-13 but was allowed to crystallise at a lower reaction temperature of 150 °C, would give less ZSM-48. Although also showing no ZSM-48 in the initial synthesis, the second and third syntheses with the same filtrate, gave the same amount (around 9 %) of ZSM-48 that was recorded in the subsequent preparations of F-13. Because only the initial crystallisation was done at 130 °C, the amounts of ZSM-48 in subsequent crystallisations were not determined.

The crystallinity, as estimated from the XRD intensity, of the products, increased slightly as the crystallisation temperature was decreased. However, by carrying out the synthesis at 150 °C the period required for crystallisation had to be increased to three days. When the crystallisation was done at 130 °C, completion was achieved only after a period of approximately eight days, which does seem rather unnecessarily long for this type of operation.

3.4. EXTRUSION OF ZSM-5 WITH PSEUDO-BOEHMITE

3.4.1. SELECTION OF PSEUDO-BOEHMITE

Samples of the type of pseudo-boehmite suitable for co-extruding catalyst were obtained from a few of the well-known manufacturers. A list of the sources of products are shown in Table 3.13. A micro-sieve analysis was carried out on each of the samples, and the results are included in Appendix D. From these results, the median particle size was determined and this is included in Table 3.13. When using pseudo-boehmite as a binder, it must be fine enough to fit between the crystallites of the ZSM-5. It has already been established from the micrographs in Figure 3.5,

Table 3.13. List of various samples of pseudo-boehmite, and their median particle size and loss in mass on being calcined.

Manufact.	Country	Brand name	Median size µm	Loss on ignition %
LaRoche	USA	Versal 250	6,9	33,1
Dyson Ref.	UK	Dycat 052	7,2	20,9
Condea	Germany	Pural SCF	14,3	22,7
Akzo	Netherland	Ketjen H	20	29,1
Condea	Germany	Pural SB	33	22,3
LaPorte	UK	Actal KH	35	29,8

that the average size of the ZSM-5 crystallites were about 3 µm in size. As can be seen in Table 3.13, that regarding particle size of the samples being examined, the product Versal 250 is the closest to the ZSM-5 and would therefore be the most suitable for binding the zeolite that had been synthesised.

The loss on ignition by calcining the samples at around 800 °C, was determined on each of the samples. Obviously the higher this value the more hydrated is the pseudo-boehmite, which gives the Versal 250 type two distinct advantages. Firstly, it will make the paste more gelatinous and easier to extrude. Secondly, it will give a more porous product after calcination, which means that reactants and products can diffuse easier through the catalyst agglomerate.

3.4.2. TESTING OF EXTRUDATES

Very small additions of acetic acid started to make the paste workable. However, the best results were found when between 0,5 % and 2,5 % acetic acid relative to the amount of pseudo-boemite, were

used. These additions hardly altered the pH of the paste which was between 6 and 7. Larger additions decreased the pH, made the mixture "watery", and was thus incapable of being extruded.

Extrudates were made wherein the amount of acetic acid being used as peptiser, ranged between 0,38 and 2,5 %. They were then calcined at 550 °C. The average crushing strengths of these extrudates were determined, and the results are shown in Figure 3.12. When packed into a fixed-bed reactor, the catalyst extrudates are naturally compressed by material above, and must be strong enough to withstand such loads. To meet this requirement, catalyst manufacturers have learnt from experience, that extrudates should be capable of withstanding a crushing force of 5 to 10 N / mm. It is

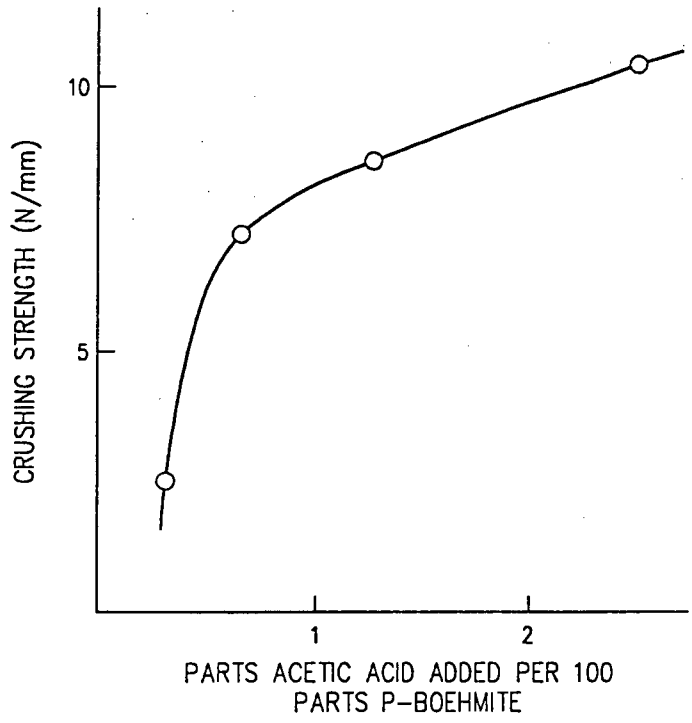

Figure 3.12. Crushing strength of calcined extrudates made with different concentrations of acetic acid being used as a peptising agent.

clear that the addition of slightly less than 1 % acetic is enough to produce extrudable material, which is adequately strong after calcination.

It was decided that 0,63 % acetic acid was the optimum amount of peptiser to use, and as shown in Figure 3.12, this gave a crushing strength of 7,2 N / mm. Calcination of the same extrudates at higher temperatures of 600 °C and 650 °C increased the crushing strength to 7,3 and 7,7 N / mm respectively. These increases are small and therefore it seemed there was little advantage in increasing the crushing strength by raising the calcination temperature.

A final criterion of an extrudate is that as a result of being crushed, the broken product should be fragments rather than a powder. In this aspect, the extrudates made with the aid of Versal 250 and calcined at any of these three temperatures, were satisfactory.

3.5. SOURCES AND COSTS OF RAW MATERIALS

For producing the ZSM-5 catalyst on an industrial scale it is necessary that commercial grade raw materials be used. Commercial grades of silica and 1,6-diaminohexane have already been successfully used in the method of synthesis. The remaining raw materials are also commercially available, and suggested suppliers are listed in Table 3.14. The *Neosyl ET* silica from Crosfield contains, after drying, 98 % silica. The 1,6-diaminohexane from BASF is 99,7 % pure. The aluminium sulphate from AECI Ltd should preferably low in iron, while the sodium hydroxide ought be low in both calcium and magnesium. The ammonium nitrate from AECI Ltd is 99,6 % pure.

The relative amounts of materials needed for the first synthesis in Table 3.14 are the same as for sample F-13 in Table

Table 3.14. Details of the sources and prices (prevailing March 1993) of commercial raw materials used in synthesising ZSM-5 extrudates, and the cost of the amounts needed to make 2 tonnes of this catalyst.

Material	Source	Price	Price in South Africa	Amounts for first synth. Kg	Amounts for subsequent syntheses Kg	Amounts for first and 4 sub. synth. Kg	Total cost raw material R
$Al_2(SO_4)_3.16H_2O$	AECI Ltd	R1252 / tonne		25,7	25,7	128,5	161
NaOH	Holpro-Lovasz	R2.81 / Kg		46,6	± 20	126,6	356
H_2O				1463			
Pr_4NBr	Rhone Poulenc,UK	£16.03 / Kg	R90 / Kg	6,83	6,83	34,2	3 078
1,6-diaminohexane	BASF, Germany	DM 6.48 / Kg	R14 / Kg	177,8	35,6	320,2	4 483
H_2O				926			
Neosyl ET	Crosfield, UK		R4400 / tonne	417,3	375,6	1919,7	8 447
H_2O				1991			
NH_4NO_3	AECI Ltd	R1476 / tonne		± 100	± 100	± 500	738
Versal 250	LaRoche, USA	$1745 / tonne	R6200 / tonne	157,3	157,3	786,5	4 876
						TOTAL	22 139

2.7, except that one thousand times more by mass are used. This preparation should therefore give a yield of 360 Kg ZSM-5. After calcination, cation exchanging, extrusion with Versal 250 pseudo-boehmite and second calcination, this amount of ZSM-5 should, allowing for small material loses, give around 400 Kg catalyst extrudates. Subsequent syntheses using the same filtrate would naturally also produce 400 Kg each.

An initial preparation together with four subsequent ones using the same filtrate, should therefore give two tonnes of catalyst. From the cost for each component given in Table 3.14, it was calculated that the total cost of the raw materials to produce one tonne of catalyst is about R11 000.

CHAPTER 4

RESULTS OF CATALYTIC ACTIVITY MEASUREMENTS ON SYNTHESISED ZSM-5

4.1. CONVERSION OF METHANOL TO LIGHT OLEFINS

4.1.1. INFLUENCE OF REACTION CONDITIONS ON SELECTIVITY

In the second stage of the work the practical performance of the catalyst was evaluated, and this meant using conditions where there is a high conversion of methanol. Naturally for this, there would several factors regarding the conditions being used that have an effect on the light olefin selectivity, and all of them ought be identified so that they can be specified in the final results. They will therefore include some previously reported data which was briefly tested on the samples of this work.

4.1.1.2. REDUCED PARTIAL PRESSURE OF METHANOL

The first real success reported in increasing the light olefin selectivity was by reducing the partial pressure of the methanol feed [124]. Two samples of ZSM-5, 3-B and 5-B which were prepared with only tetrapropylammonium cations and which, calculated from their chemical analysis for Al_2O_3 in Table 3.2, had silica to alumina mole ratios of 605 : 1 and 170 : 1 respectively, were tested under these conditions. To reduce its partial pressure to below one atmosphere, the methanol being fed into the reactor was diluted with nitrogen. The results of these tests, where complete conversion of the methanol took place, are given in Figure 4.1, and it is clear that, irrespective of the composition of the ZSM-5, in order to obtain a good olefin selectivity, the methanol feed obviously has to have a relatively low partial pressure. These conditions were therefore used in rest of this work.

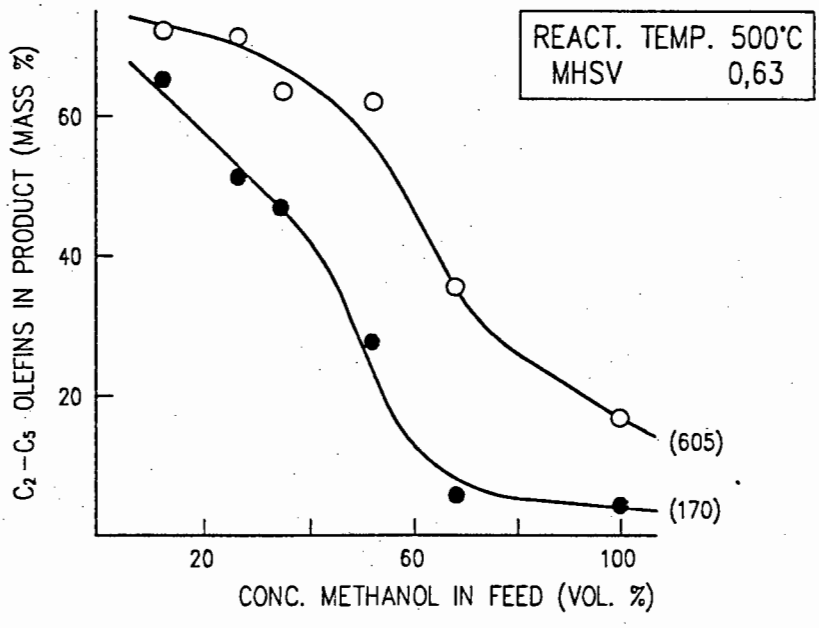

Figure 4.1. Light olefin selectivity in relation to concentration of the methanol feed. Complete conversion to hydrocarbons was obtained using the conditions in the legend. Silica to alumina mole ratios of catalysts are given in brackets.

4.1.1.2. MASS HOURLY SPACE VELOCITY (MHSV)

This parameter was studied during the initial investigations by Chang and Silvestri [14], and their results are shown in Figure 1.7. It can be seen that approximately half the hydrocarbon product can be in the form of light olefins if the MHSV is around 20. In their work the reaction was carried out at a pressure of several atmospheres.

Having already decided that the reaction should preferably be done at a relatively low pressure, the effect of the variation in the MHSV under these conditions was examined on sample 5-E. The results after about three hours on stream are given in Figure 4.2. While it appears that the highest selectivity to olefin was obtained with a MHSV of around 2, it was also found that under these conditions the selectivity decreased the longer the reaction

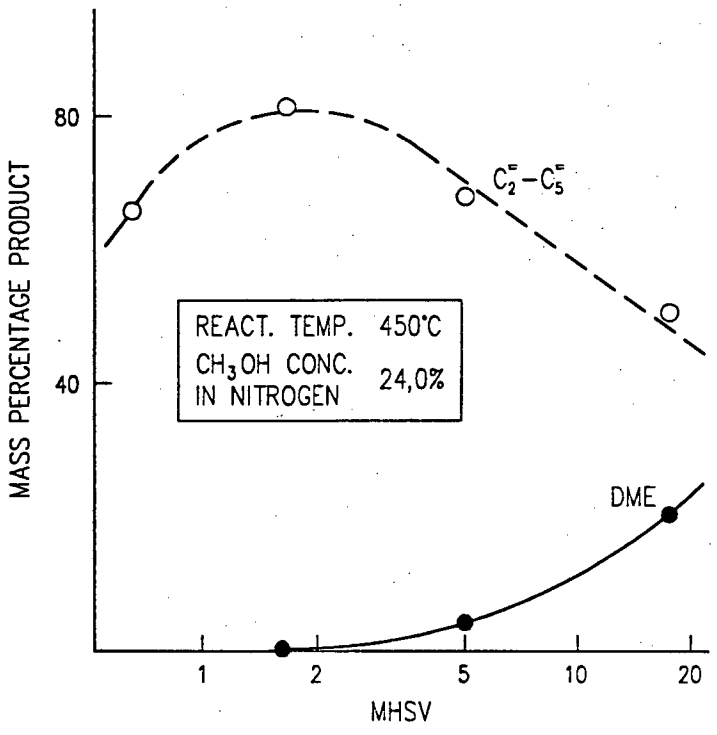

Figure 4.2. Light olefin selectivity in relation to MHSV of the methanol feed. Catalyst was made from preparation 5-E and the remaining conditions used are listed in the legend.

proceeded. This is attributed to the deactivation of the catalyst and it was found that this was more prevalent when even higher MHSVs were used. With a MHSV of 17,3 the catalyst was completely inactive after about seven hours. On the other hand when a MHSV of 0,66 was used the olefin selectivity was constant, and as will shown in Figure 4.5 that under these conditions the catalyst remained active for several days (219 hours). Therefore, it was decided to keep the MHSV to less than one for the rest of the work. Further, these conditions also gave complete conversion of the methanol, and which unless otherwise stated, was maintained in all the MTO experiments.

The catalyst utilisation value (CUV) when the MHSV was 17,3 was 136 gram feed per gram ZSM-5 catalyst, while with the MHSV of 0,66, this value of 121 g / g. These results are similar, and show that the amount of feed converted by the catalyst is not influenced by the MHSV.

4.1.1.3 REACTION TEMPERATURE

Raising the reaction temperature is known to increase the proportion of light olefins obtained [14,128], and the effect of this parameter is shown in Figure 4.3. The conversion was studied with a low methanol concentration and a low MHSV. The result confirmed that by increasing the temperature to around 530 °C, the olefin selectivity increased, but at higher temperatures it actually decreased as the rate of cracking increased.

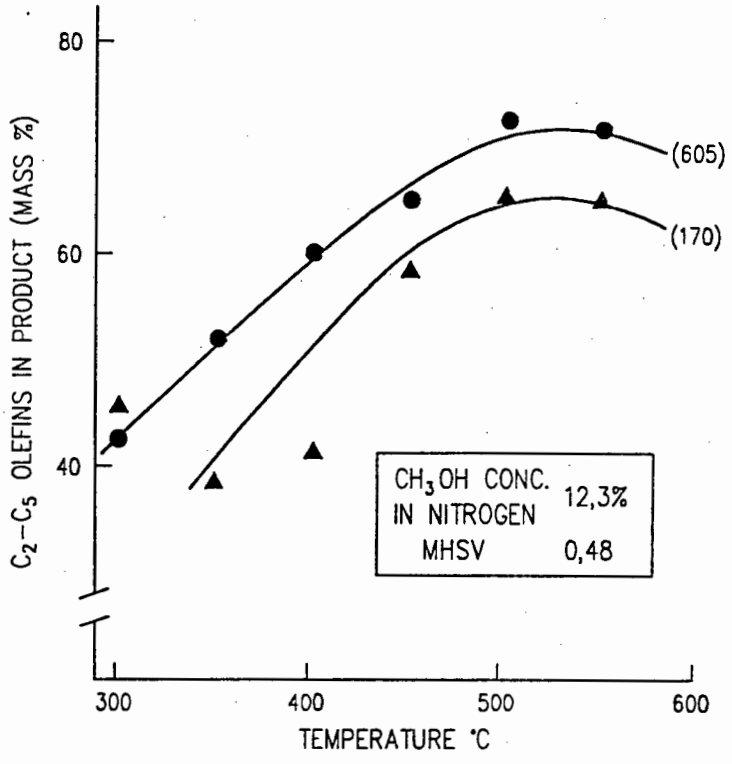

Figure 4.3. Total light olefin selectivity in relation to reaction temperature, using the conditions in the legend. ZSM-5 catalysts were taken from the B-series which were prepared with TPA as the template and their silica to alumina mole ratios are given in brackets.

As an aim of this work was to establish what the overall role of ethene was in the sequence of reactions, it was decided that the

ethene selectivity should be analysed separately from that of the other light olefins, namely propene to pentene. The results of the selectivities of the two separate fractions, obtained from using the two catalyst samples over the same range of reaction temperatures, are shown in Figure 4.4. While the results obviously still show an

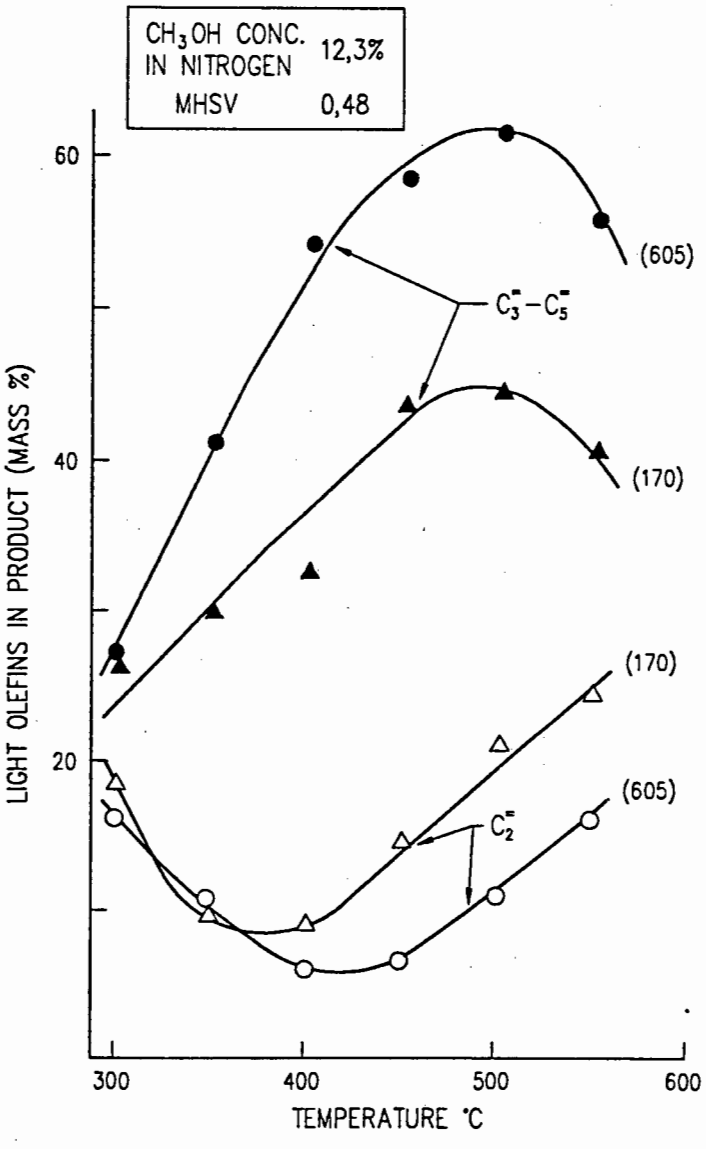

Figure 4.4. Ethene and other light olefin selectivities in relation to reaction temperature. Catalysts and reaction conditions are the same as in Figure 4.3.

overall increase of olefins with increasing temperature, the individual components showed different behaviours. The C_3 to C_5 olefin fraction increased as the reaction temperature was increased, and had a maximum value just below 500 °C. The individual compounds in this fraction, which consisted of about 65 % propene, 25 % butenes and 10 % pentenes, all gave similar trends. However, the ethene fraction behaved completely differently, and actually had a minimum value at around 400 °C.

The amount of methane formed was quite low, with the highest concentration being about 2,5 % obtained at a reaction temperature of 550 °C. This low result is attributed to the reaction been kept on stream for a only a few hours. As will be shown in section 4.1.1.4, the yield of methane increased the longer the reaction proceeded.

With the ZSM-5 made with tetrapropylammonium cations, a good olefin selectivity was obtained with a reaction temperature in the region of 450 °C to 500 °C. When determining the results given in Figure 4.4, the methanol feed was diluted with nitrogen, but in practice the feed entering the reactor would consist of a mixture of methanol and water. The next questions to be simultaneously addressed were whether similar results could be achieved with a catalyst made with 1,6-diaminohexane, and by reducing the partial pressure of the methanol with steam. Therefore, extrudates of sample F-13, which had a silica to alumina mole ratio of 150 : 1, were used with a methanol-water mixture as feed. The results are shown in Figure 4.5.

As can be seen in Figure 4.5, throughout the duration of the reaction at temperatures of 450 °C and 480 °C, there were only small changes in the olefin selectivity. It was only when the temperature was increased to 510 °C that noticeable changes in the olefin selectivity took place the longer the reaction remained on stream. Further, the catalyst itself was very stable under these

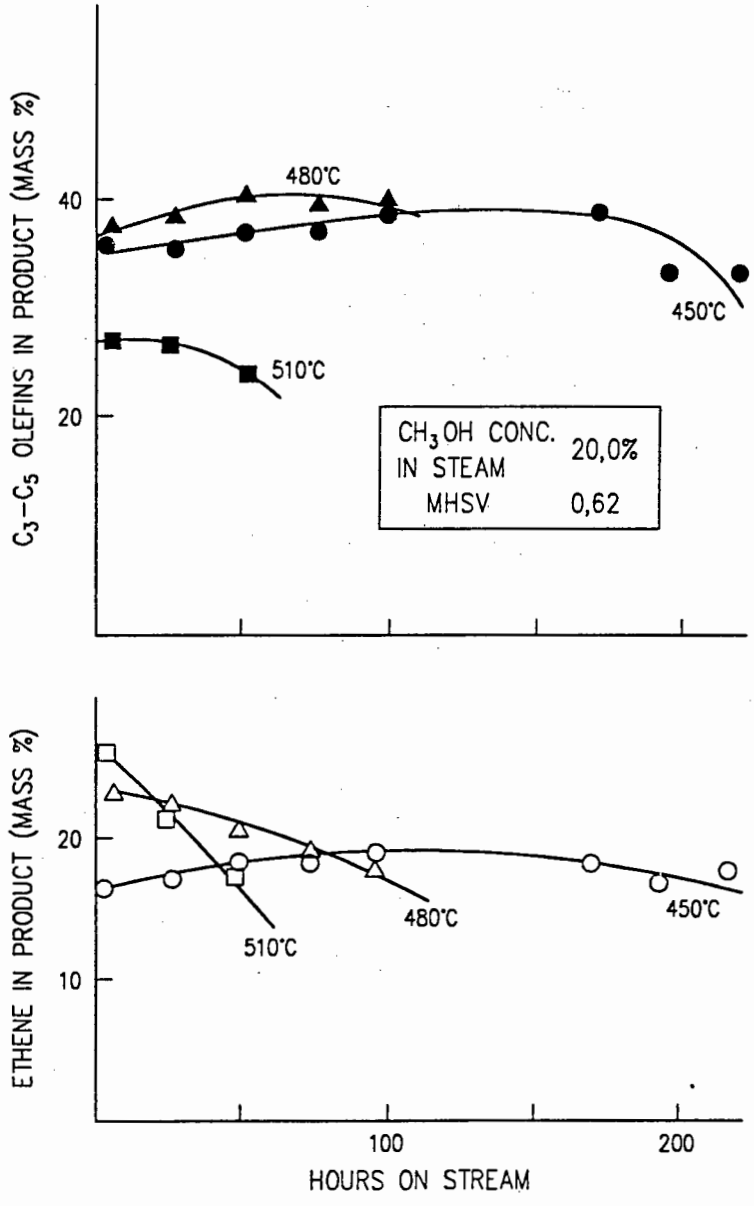

Figure 4.5 Light olefin selectivity over a long period. Reaction conditions are given in the legend and different temperatures indicated on the curves. ZSM-5 catalyst was made from sample F-13, which was prepared with 1,6-diaminohexane as the main template, and had a silica to alumina mole ratio of 150 : 1.

conditions: after testing, the samples that had been reacted at 480 °C and 510 °C were regenerated and then re-examined under the same conditions. The product selectivities and lifetimes were

almost identical to those obtained originally, which indicated that the catalyst was virtually unaltered during the reaction or regeneration.

Besides light olefins and methane, the remainder of the product consisted of light alkanes and aromatics. The alkanes are simultaneously formed roughly in the ratio of 3 : 1, with aromatic compounds [86]. The aromatic fraction was found to consist of a mixture of which p-xylene was the largest component together with smaller amounts of the other xylenes, toluene and trimethylbenzenes. There was only very small fraction of a C_{10} aromatic compound, and no detectable amount of any heavier hydrocarbons. This subject will be discussed in more detail in section 4.2.1.

4.1.1.4 DEACTIVATION

Changes in selectivity are usually caused by the build-up of coke. The samples for which the results are given in Figure 4.5 were left in the reactor until the yield of light olefin began to decrease significantly. It was found from subsequent calcination in air, that the amount of coke deposited on all three samples was about 5 % by mass. By comparing the three curves, it is obvious that the rate of coke deposition and the period of reaction before necessary regeneration are adversely affected by use of reaction temperatures in the region of 500 °C. This criterion appears to set the maximum temperature (around 450 °C) at which this type of reaction could take place.

Although the percentage of C_3 to C_5 olefins showed only a small variation throughout the duration of the reaction, it was found, as shown in Figure 4.6, that the concentration of methane formed increased, particularly at the two higher temperatures of 480 °C and 510 °C. This result therefore also sets the same upper limit for the temperature at which it is advisable to conduct the reaction. As mentioned above this is around 450 °C.

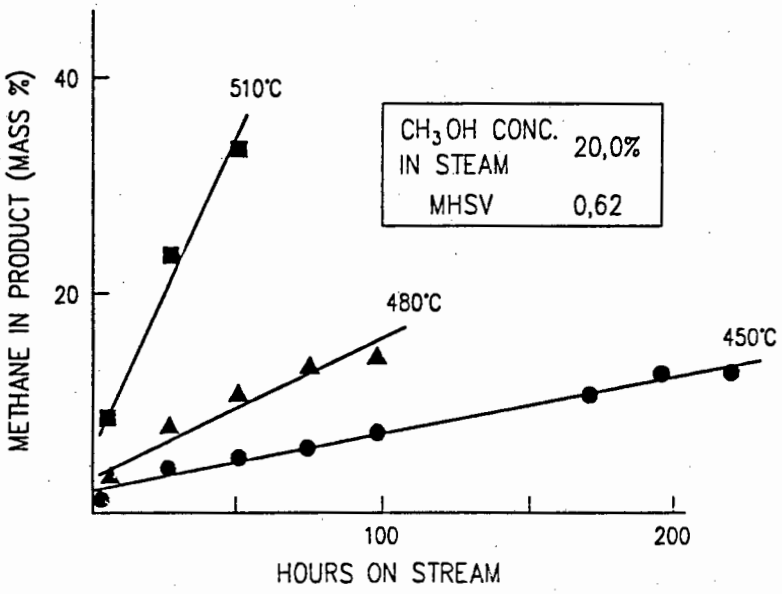

Figure 4.6. Changes in methane selectivity with time on stream, using conditions given in the legend and different reaction temperatures indicated on the straight lines. Catalyst was made from sample F-13.

4.1.2. INFLUENCE OF CATALYST COMPOSITION ON SELECTIVITY

Besides the different conditions used during the reaction, the composition of the ZSM-5 catalyst naturally also has an effect on the light olefin selectivity. All these factors must also be identified.

4.1.2.1. CRYSTALLITE SIZE AND SHAPE

As was shown in Figure 3.2, sample 1-D had much larger crystallites than the other preparations from this series. The olefin selectivities of samples 1-D and 5-D were measured, and their results are shown in Table 4.1. These results indicate that by

reducing the crystallites from 30 to 2 µm, the ethene selectivity is increased, while the selectivity for the other light olefins have concomitantly decreased.

Table 4.1. Effect of crystallite size and shape on the light olefin selectivity. Reaction temperature was 450 °C, MHSV was 0,66 and the concentration of the methanol was 24,0 vol. % in nitrogen.

Prep	Cryst. size µm	$C_2^=$ %	$C_3^=$-$C_5^=$ %
1-D	30	5,9	70,1
5-D	2	11,0	64,9
16-E	3	15,4	57,0
5-E	3 x 1	14,9	49,7
14-E	3 x 1	15,6	54,6

As will be discussed in section 5.3.2, the shape of the crystallite depended on whether tetrapropylammonium cations or 1,6-diaminohexane was used in the synthesis. In preparation 16-E a relatively large amount of tetrapropylammonium compound was used in its synthesis, and the crystallites were similar to those of sample 5-D. As the amount of TPA in the synthesis was reduced, with preparations 5-E and 14-E (where no TPA was used) more elongated crystallites were obtained, which were about 3 µm long and had a diameter of 1 µm. The olefin selectivities of extrudates of these three samples were measured, and the results are also given in Table 4.1. This difference in the shape does not have a large effect on the olefin selectivity that was obtained.

4.1.2.2. SOURCE OF ALUMINA BINDER

In section 3.4.1, various different types of pseudo-boehmite were tested for their suitability as extrusion binders. These extrudates were tested for their olefin selectivity for the conversion of methanol, and the results are given in Table 4.2. The results show that similar selectivities were obtained irrespective of which type of pseudo-boehmite was used as the binder.

Table 4.2. Effect of different types of pseudo-boehmite used as binder on the light olefin selectivity. ZSM-5 was a composite of preparations from the D-series. Reaction temperature was 450 °C, MHSV was 0,66 and the concentration of the methanol was 24,0 vol. % in nitrogen.

Type of p-boehmite	$C_2^=$ %		$C_3^= - C_5^=$ %	
Versal 250	12,1		60,7	
Dycat 052	12,2		62,4	
Pural SCF	12,4	12,2	60,8	61,5
Ketjen H	11,1		63,8	
Pural SB	12,8		58,6	
Actal KH	12,8		62,8	
No binder	11,6		69,1	

Also included is the result of the pure catalyst: the powder was compressed into granules without any additive. The olefin selectivity of the pure catalyst was slightly higher than when pseudo-boehmite had been added. However, this benefit cannot be realised as the use of a binder is absolutely necessary.

4.1.2.3 SILICA TO ALUMINA RATIO OF THE ZSM-5

In section 1.7.2 it was established that the best method to increase the olefin selectivity was to use ZSM-5 with higher silica to alumina mole ratios. This statement is base on work by Chang *et al* [128], who synthesised ZSM-5 with the aid of tetrapropylammonium cations. This work was repeated here using the samples from the B-series. The olefin selectivity of these preparations are shown in Figure 4.7, which confirmed an increase in the results as the silica to alumina ratio is increased up to 400 : 1.

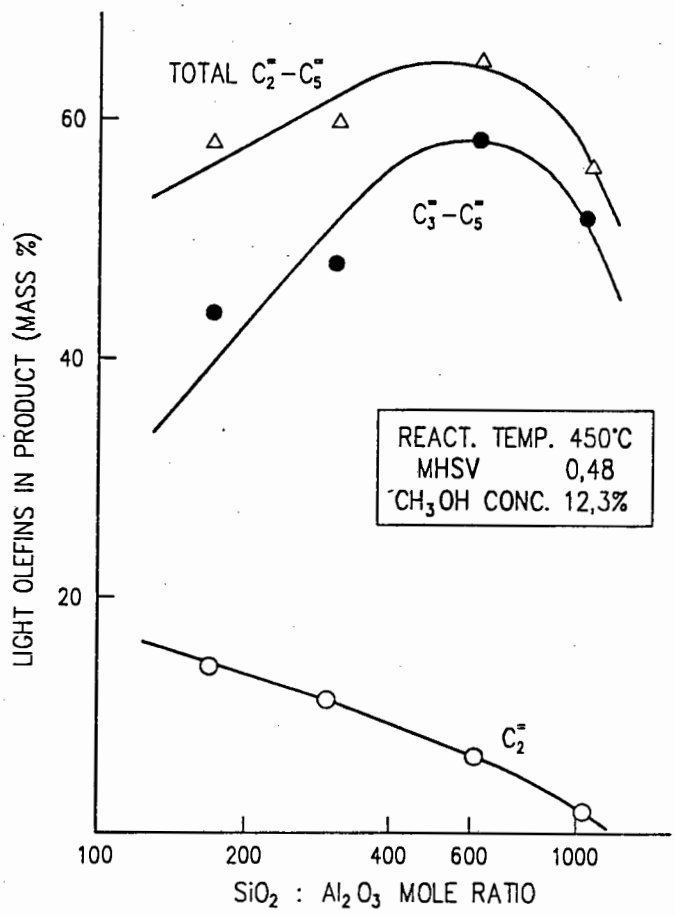

Figure 4.7. Light olefin selectivity in relation to silica to alumina mole ratio of the ZSM-5 catalyst, using the conditions in the legend. ZSM-5 were taken from the B-series, wherein TPA was used as the only template. Methanol feed was diluted with nitrogen.

While the overall result confirmed that as the silica to alumina ratio is increased the olefin selectivity is increased, there is a difference between the separate results of ethene and the other light olefins, $C_3^=$ to $C_5^=$. It was found that as the silica to alumina ratio increased, the C_3 to C_5 olefins increased as the total selectivity increased, but that the ethene selectivity actually decreased.

With very high silica to alumina ratios, the olefin selectivity began to decrease and dimethyl ether was detected in the product spectrum. This obviously meant there was incomplete conversion, which was due to insufficient residence time for the reactant under the prevailing conditions where the catalyst has a limited density of active sites.

By examining the four most siliceous preparations of the F-series, the variation in the olefin selectivity caused by changes in the silica to alumina ratios of the ZSM-5 prepared with 1,6-diaminohexane, is shown in Figure 4.8. Over the silica to alumina ratio range depicted in Figure 4.8, the same change in the light olefin selectivity was found with the ZSM-5 synthesised with 1,6-diaminohexane as that made using TPA. This is exemplified by both types of preparation giving a propene to pentene selectivity of 50 % to 55 % when the silica to alumina ratio mole was around 300 : 1. The ethene selectivity also produced the same pattern in that it decreased from about 20 % to 15 % as the silica to alumina ratio increased.

4.1.2.4. PRESENCE OF ZSM-48

It was established in the previous chapter on synthesis that due to the co-crystallisation of ZSM-48, the upper limit of the silica to alumina mole ratio that could be attained with ZSM-5 when using 1,6-diaminohexane as the template is about 250 : 1. The results in Figure 4.8 show that the olefin selectivity continued to increase as the silica to alumina mole ratios were extended

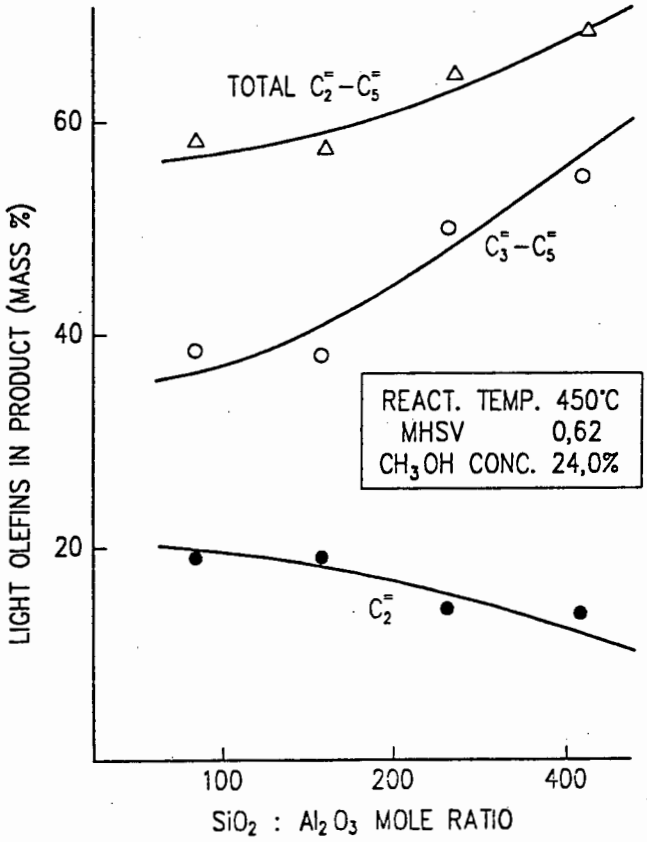

Figure 4.8. Light olefin selectivity in relation to silica to alumina mole ratio of ZSM-5 catalyst from the F-series, wherein 1,6-diaminohexane was used as the main template. Complete conversion of the methanol was obtained under the reaction conditions given in the legend. Methanol feed was diluted with nitrogen.

above 400 : 1, but it was not as pronounced as the trend shown in Figure 4.7, where the ZSM-5 had been prepared with TPA. The reason for this is at this level of silica to alumina ratio, the catalyst samples made with 1,6-diaminohexane contained some ZSM-48.

With 1,6-diaminohexane as the main template, a number of samples in the E-series were made wherein the concentration of ZSM-48 could be studied by variations in the synthesis mixture. With 9-E, 5-E and 10-E the aluminium content was decreased, while

with 11-E, 12-E, 5-E and 13-E the sodium content was increased, and with samples 14-E, 15-E, 5-E and 16-E the concentration of tetrapropylammonium cations used as a seeding agent was also increased. As was shown in section 3.2.2, the concentration of ZSM-48 that co-crystallised in the product increased as the amount of aluminium was decreased, but the concentration of ZSM-48 decreased as the amount of sodium oxide or TPA was increased. The effect of the concomitant variations in the concentration of ZSM-48 on the olefin selectivities from the conversion of methanol are given in Table 4.3.

It can be seen that as the silica to alumina ratio is increased, namely preparations 9-E, 5-E and 10-E, the normal decrease in ethene and simultaneous increase in C_3 to C_5 olefin selectivity took place. As was to be expected, these results were similar to those obtained with the samples from the F-series shown in Figure 4.8. However, it was found that the increase in olefin selectivity achieved with preparations when the silica to alumina mole ratio used in the synthesis mixture was increased above 250 : 1 with both the E-series in Table 4.3 and the F-series in Figure 4.8, was much smaller than could have been expected. This is attributed to the presence of ZSM-48, which because of its siliceous nature [21] means that the crystallised ZSM-5 has a lower silica to alumina ratio than that used in the synthesis mixture. In section 3.3.1 it was estimated that there was about 30 % ZSM-48 in preparation F-10, and probably the same concentration would be present in sample 10-E as it had been similarly prepared. As a result of the presence of ZSM-48, it was calculated for preparation F-10, and is therefore also valid for sample 10-E, that the ZSM-5 had a silica to alumina mole ratio of about only 280 : 1 instead of the anticipated 425 : 1 (see Table 3.12).

Sample 11-E was prepared where there was a low concentration of sodium in the synthesis mixture, and it was shown in section 3.2.2 that it contained large amounts of ZSM-48. As more sodium was used in this set of samples, the ZSM-48 concentration decreased. This decrease in the concentration of ZSM-48 is responsible for the

increase in the olefin selectivity with this set of samples. However, this increase is not as large as that found by decreasing the aluminium content of the preparation mixture.

Table 4.3. Variations in the synthesis mixture when using 1,6-diaminohexane as the template, and the effect that the product has on the light olefin selectivity. Reaction temperature was 450 °C, MHSV was 0,66 and the concentration of the methanol was 24,0 vol. % in nitrogen.

Prep	Variation studied	ZSM-48 change	$C_2^=$ %	$C_3^=-C_5^=$ %
9-E	decrease	increase	19,7	37,8
5-E	in	in	14,9	49,7
10-E	Al	ZSM-48	13,9	54,9
11-E	increase	decrease	17,8	48,2
12-E	in	in	18,0	51,0
5-E	Na	ZSM-48	14,9	49,7
13-E			15,2	56,1
14-E	increase	decrease	15,6	54,6
15-E	in	in	16,0	52,6
5-E	TPA	ZSM-48	14,9	49,7
16-E			15,4	57,0

Increasing or decreasing the small amounts of tetrapropyl-ammonium cations used in the synthesis mixture caused a corresponding increase or decrease in the concentration of ZSM-48 that was co-crystallised. These changes were small, and are reflected by the small improvement in the olefin selectivity shown in Table 4.3.

4.1.2.5. STEAM DE-ALUMINATION

It has already been stressed that to maximise the olefin selectivity the ZSM-5 catalyst should preferably have a silica to alumina mole ratio of around 400 : 1 [128]. However, due to the problems of co-crystallising ZSM-48, it is not possible to directly synthesise suitable ZSM-5 when using 1,6-diaminohexane. With this material as the template, ZSM-5 is prepared with a ratio of around 200 : 1, which must then subsequently be increased by calcination in the presence of steam [132,133]. Although thermal steaming does remove aluminium atoms from the ZSM-5 framework, they remain within the zeolite matrix, and it was therefore not possible to determine by chemical analysis to what level the silica to alumina ratio had actually increased. The effect of steam calcination has to be evaluated from changes in the catalytic performance of the ZSM-5 catalyst.

Firstly, the extent of de-alumination at different calcination temperatures was studied with sample F-13, which had an initial silica to alumina mole ratio of approximately 150 : 1. Extrudates were steam-calcined at 400 °C, 450 °C and 500 °C for 50 hours. Their olefin selectivities from the conversion of methanol, tested in a similar manner as for the samples synthesised with different silica to alumina ratios, are given in Figure 4.9. The shape of the selectivity curve indicated that the rate of de-alumination becomes significant only when the steaming temperature approaches 500 °C.

Secondly, the extent of de-alumination on the duration of the steam calcination was also done on the same preparation. Extrudates were de-aluminated in steam at 500 °C for various periods of time. The same testing technique was used, and the resulting olefin selectivities are illustrated in Figure 4.10. It is clear that about 20 to 50 hours steaming under these conditions are required to produce sufficient de-alumination to give a significant change in the olefin selectivity. Shorter periods would not produce a worthwhile change, while further prolonged steaming would not increase the selectivity much more.

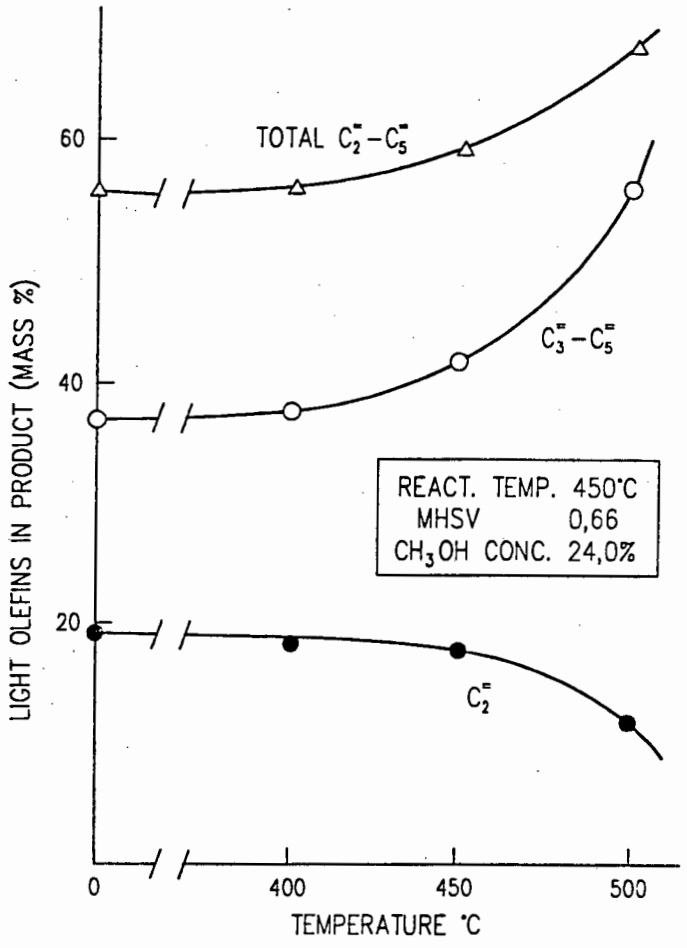

Figure 4.9. Light olefin selectivity in relation to temperature at which the ZSM-5 catalyst from sample F-13 was steamed for 50 hours. Conditions used in the test reaction are given in the legend, where the methanol was diluted with nitrogen.

Since no difference could be detected between the performance of a ZSM-5 synthesised directly with a low aluminium content and that in which this content had been reduced through steaming, it can be concluded that the technique of steaming is quite acceptable for arriving at a suitable catalyst for the MTO process.

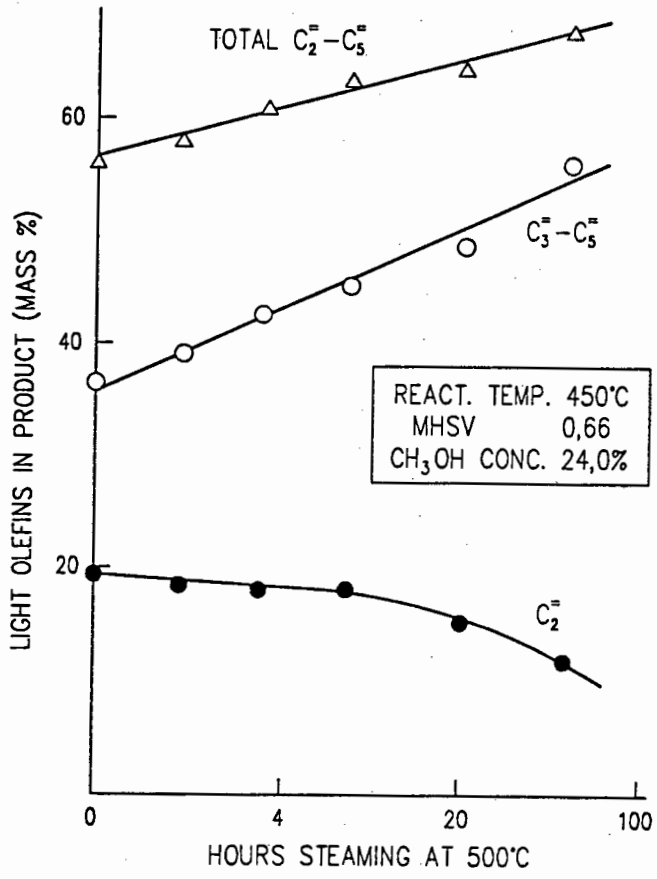

Figure 4.10. Light olefin selectivity in relation to the duration of steaming at 500 °C of the ZSM-5 catalyst from sample F-13. Conditions used in the test reaction are given in the legend, where the methanol was diluted with nitrogen.

4.1.2.6. THERMAL RE-INSERTION OF ALUMINIUM

While the presence of steam at high temperatures de-aluminates ZSM-5, this is tempered with the caution that in dry conditions aluminium atoms could be thermally re-inserted into the zeolite structure [134,135]. Thus, to gauge the magnitude of this problem it was decided to calcine extrudates of preparation 15-E at temperatures higher than the usual 550 °C, and to measure the olefin

selectivity of these samples. The results are given in Figure 4.11, and show a small decrease in the C_3 to C_5 olefin yield that would be expected from a catalyst wherein the amount of aluminium had been increased. However, contrary to expectations caused by increasing the silica to alumina ratio through re-alumination, the ethene selectivity also decreased. This could probably mean that the catalyst had suffered some thermal destruction at these higher temperatures.

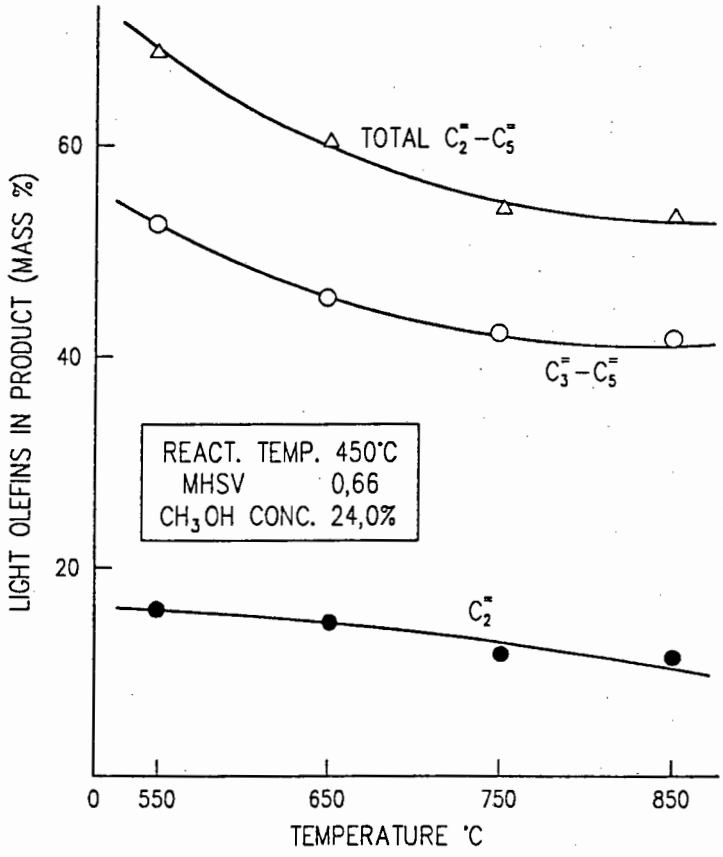

Figure 4.11. Light olefin selectivity of extrudates of sample 15-E after calcination at various temperatures. Conditions used in the test reaction are given in the legend, where the methanol was diluted with nitrogen.

4.1.2.7. POISONING OF CATALYST WITH SODIUM

An alternative method of reducing the number of active sites is to poison some of them. For example, this can be done by cation exchanging with phosphorus compounds or sodium [126-128]. Samples of preparation 5-B were only partially exchanged, leaving some sodium behind. The silica to alumina mole ratio was calculated from the remaining (non-poisoned) sites and the resulting catalysts were tested for their conversion of methanol; the results are shown in Figure 4.12. For comparison, results from the other preparation from the B-series, that were synthesised directly with higher silica to alumina mole ratios, are also included. The findings confirm

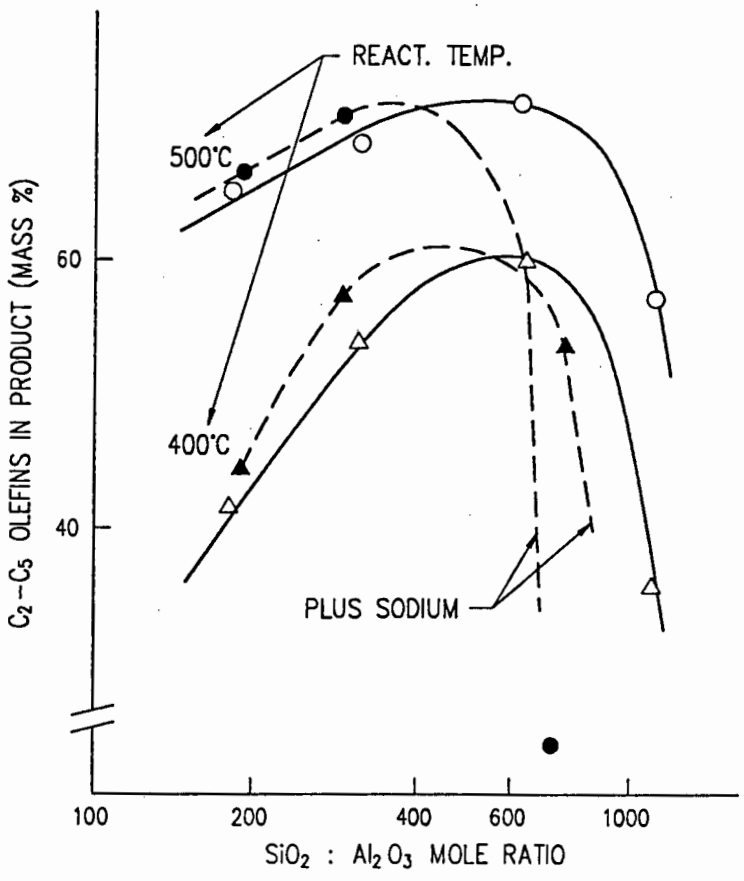

Figure 4.12. Comparison of product from catalyst partially poisoned by sodium and that using higher silica to alumina ratios.

that this technique of poisoning does indeed increase the olefin selectivity.

However, the problem with having significant concentrations of sodium cations in the catalysts was that the catalyst deactivated rather rapidly, particularly at higher temperatures. Deactivation was coupled with the deposition of coke, which appears to be readily formed by the presence of the sodium. The use of poisons to improve olefin selectivity seems therefore restricted to low levels of conversion and low reaction temperatures. This approach would therefore be unsuitable in industrial practice.

4.1.3 APPLICATION OF RESULTS TO OBTAIN OPTIMUM OLEFIN SELECTIVITY

In the preceding sections the various parameters regarding the conditions in the reactor and properties of the catalyst, were identified to give the highest selectivity of light olefins. It therefore remains to combine as much of these parameters as possible into a single experiment to arrive at a result which would be the optimum olefin selectivity that could possibly be attained. A summary of the best parameters concerning the reaction conditions are that the MHSV should be between 0,5 and 1, the partial pressure of the methanol should be about 0,2 bar and the temperature of the reactor should be around 450 °C. Regarding the ZSM-5 catalyst, it should preferably have a silica to alumina mole ratio of around 400 : 1, naturally be fairly pure and have a low sodium content.

When using 1,6-diaminohexane as the organic structure directing agent in the synthesis of ZSM-5, the highest feasible silica to alumina mole ratio is around 150 to 200 : 1. Although this latter figure is somewhat low, calcining the ZSM-5 in saturated steam at temperature in the region of 500 °C does increase the silica to alumina ratio by removing aluminium atoms from the zeolite framework. However, as mentioned in section 4.1.2.5, the modified silica to alumina ratio could not be determined.

The preparation selected as the most suitable for this section of the investigation was sample F-150, which was crystallised at 150 °C and had a silica to alumina mole ratio of 150 : 1. The crystallites were fairly small, being about 3 µm in size. The Na_2O after synthesis was 0,49 %, and was easily reduced to 0,01 % through cation exchanging, before being formed into extrudates. The extrudates were calcined in saturated steam at 500 °C for 16 hours to produce the final catalyst. The catalyst was placed in the larger reactor and pre-conditioned at 450 °C for 3 hours while passing nitrogen through the system.

The reactant feed consisted of 30 mass % methanol in water. This concentration is equivalent to 19,4 mole % methanol, and would therefore give the same volume concentration in the gaseous form. The MHSV of the methanol feed was 0,67 with respect to the ZSM-5 portion of the catalyst extrudates. The temperature of the reaction was maintained at 450 °C and virtually complete conversion was

Table 4.4. Optimum olefin selectivities obtained with extrudates of preparation F-150, using a reaction temperature of 450 °C, a feed of 19,4 vol. % methanol in steam and a MHSV of 0,67.

Product	Fresh catalyst mass %		Regenerated catalyst mass %	
ethene	14,3		11,0	
propene	40,7	78,1	40,5	75,1
butene	18,3		17,6	
pentene	4,8		6,0	
C_1 - C_5 alkanes	13,3		13,7	
C_{6+}	8,5		10,6	

obtained throughout. The product spectrum from the experiment is given in Table 4.4. The catalyst remained active for 100 hours. After the initial experiment, the catalyst sample was regenerated by removing the coke through calcination at 550 °C in air, and then tested a second time under the same conditions. The results on the regenerated catalyst are also given in Table 4.4, and show that the product spectrum is nearly the same as in the original test. In the second experiment the catalyst remained active for 166 hours.

4.2. SUBSEQUENT REACTIONS OF LIGHT OLEFINS OVER ZSM-5

In converting methanol to the maximum amount of light olefins, subsequent reactions which these olefins may themselves undergo must be kept to the minimum. As discussed in chapter 1 there are two types of reaction which do take place. Firstly, the olefins can form aromatics and alkanes, such as gasoline production in the MTG process (section 1.7.1) or the specific production of aromatics in the M2 forming process (section 1.7.3). Secondly, the light olefins can oligomerise to give longer olefins, such as the production of raw diesel in the MOGD process (section 1.7.4). In this section of the work emphasis will be placed on understanding these two reactions, so that in knowing under what conditions they operate, they can be best avoided in order to keep the light olefin selectivity high.

4.2.1. CONVERSION OF 1-OCTENE TO AROMATICS

In section 1.7.3 it was shown in order to increase the yield of aromatics from olefins, a bi-functional catalyst should be used that consists of ZSM-5 and a promoter. Kanai and Kawata [153] studied the effect of various additions of zinc oxide on the conversion of n-hexene. Figure 4.13 shows the results of this work where the same amounts of ZnO were added to sample F-34, but the conversion was carried out on 1-octene. The effect that the addition of zinc oxide

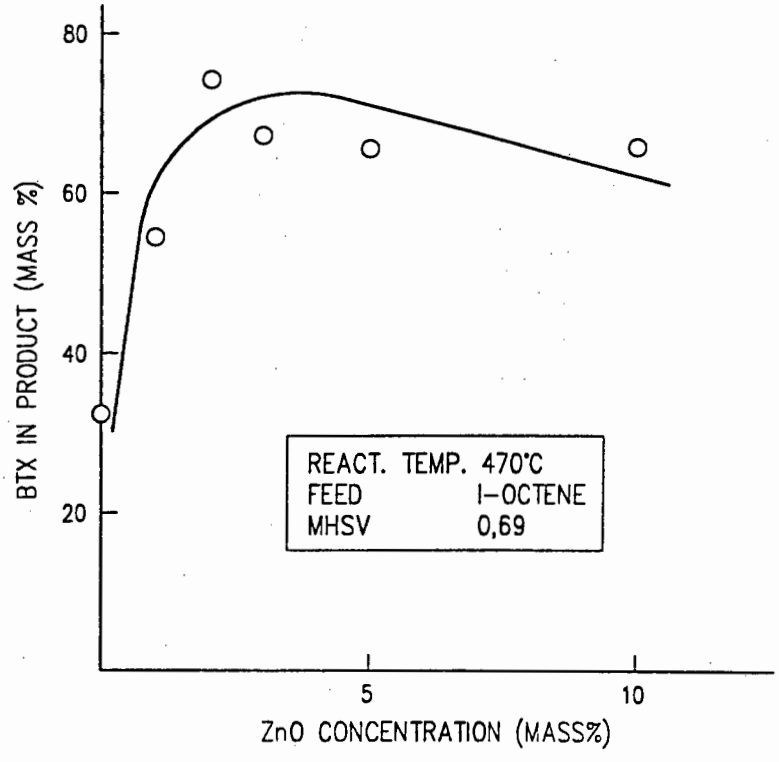

Figure 4.13. Conversion of 1-octene to BTX when using ZSM-5 promoted with ZnO. Catalyst extrudates were made from ZSM-5 preparation F-34 and various amounts of ZnO. 1-octene feed was diluted by 20 % with nitrogen and the MHSV is expressed with respect to only the ZSM-5 / ZnO portion.

as a promoter has on the yield of BTX is as expected virtually identical to that of Kanai and Kawata [153], namely that the total amount of benzene, toluene and xylene (BTX) that was produced increased significantly through the addition of 2 % to 3 % ZnO, but that further additions of ZnO actually give a slight decrease in the yield.

The examination of both the pure and promoted catalyst over a large temperature range is given in Figure 4.14. The results show that the addition of the ZnO promoter almost doubles the selectivity of BTX aromatics, but it is necessary that the reaction temperature is in the range between 450 °C and 550 °C.

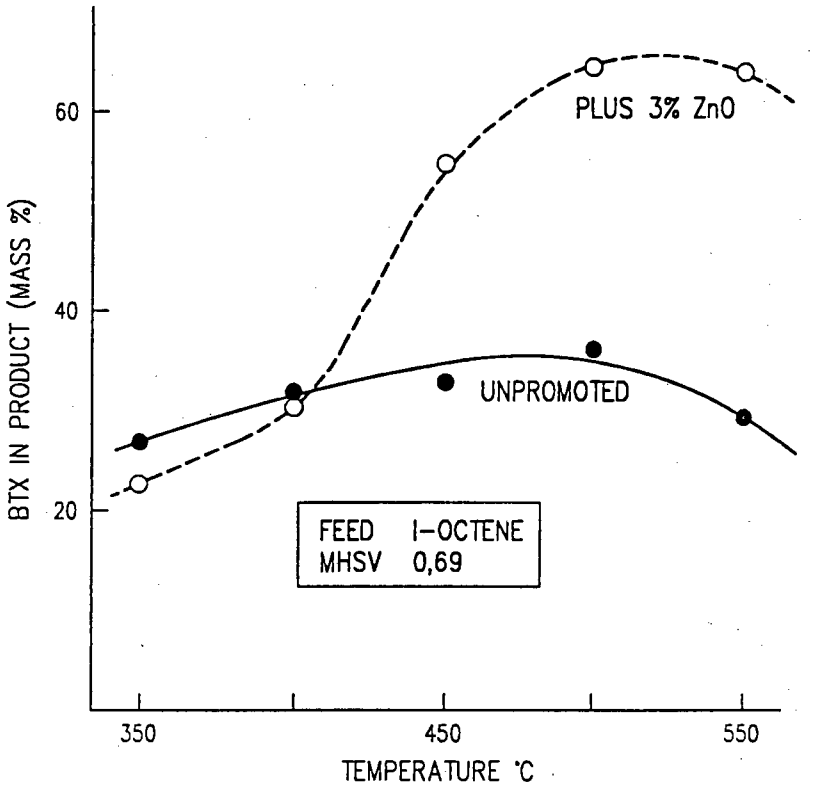

Figure 4.14. Conversion at different temperatures of 1-octene to BTX over unpromoted ZSM-5 and ZSM-5 promoted with 3 % ZnO. Catalyst extrudates were made from ZSM-5 preparation F-34 and ZnO. Feed was diluted by 20 % with nitrogen and the MHSV is expressed with respect to only the ZSM-5 / ZnO portion.

As summarised in section 1.7.3, 1-octene is converted into aromatics through a sequence of reactions. The initial reaction is the cracking of the 1-octene feed, which would give mostly C_3 to C_5 olefins. The yields of the non-aromatic products formed are given in Figure 4.15, and show at the lower reaction temperatures, which gave low yields of aromatics, the product spectrum contained large amounts of these C_3 to C_5 alkenes. In the study of the MTO process in section 4.1, it was established these are the main alkenes found during the selective conversion of methanol, and is desired that these compounds do not react further. Therefore an analysis of the conditions that increase their chances of subsequent reaction is the

important information to be gained from this section of the investigation.

In Figure 4.14 it is shown that at a reaction temperature in the region of 350 °C to 400 °C the BTX selectivity was not increased by the presence of the ZnO promoter, and it is therefore not surprising that the composition of the non-aromatic fractions given in Figure 4.15, were also similar. By increasing the temperature to between 450 °C and 550 °C, the BTX selectivity increased through the presence of the ZnO, and this was simultaneously accompanied by a significant decrease in the concentration of C_3 and C_{4+} fractions. This mean that these fractions, consisting of both olefins and alkanes, are the main reactants from which the aromatic compounds are formed.

Without the presence of the promoter, the amounts of C_1 and C_2 products, especially ethene, formed as a result of the conversion was found to increase as the reaction temperature was increased up to 550 °C. At 550 °C the product spectrum contained 34 % of these light materials, of which 22 % was ethene.

It was found that the conversion produced only small amount of hydrogen, which were about 1 % or lower, irrespective of the temperature used. Using a reaction temperature of 500 °C together with the presence of the ZnO promoter (roughly optimum conditions for BTX selectivity), it can be seen in Figure 4.15 that the non-aromatic fractions contained a large fraction of methane and ethane, being around 3 % and 4 % respectively. As will be discussed in section 5.5.3.1, methane, ethane and to lesser extent propane are the favoured by-products when striving for a highly aromatic selectivity.

It has previously been shown [142,143] that without a promoter, the ZSM-5 should contain a relatively high concentration of active sites; i.e. it should have a low silica to alumina ratio. Therefore, besides the sample made from preparation F-34, which had a silica to alumina mole ratio of 90 : 1, samples made from F-35 and F-13, which had ratios of 60 : 1 and 150 : 1 respectively, and

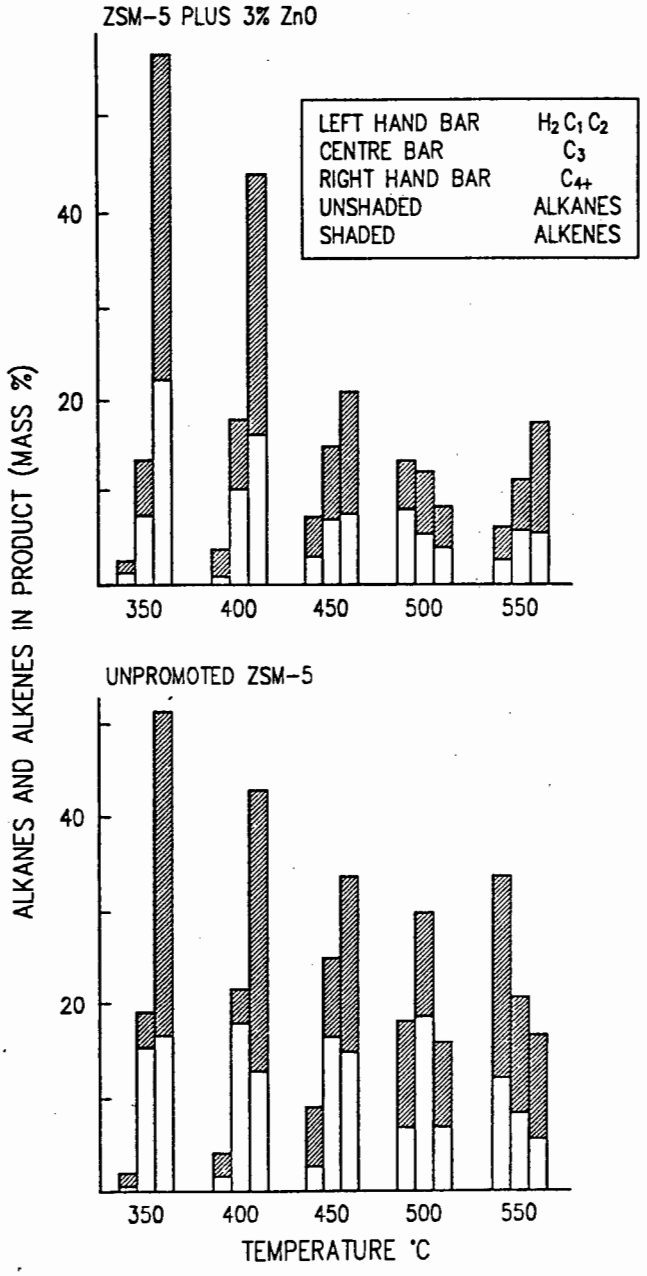

Figure 4.15. Non-aromatic products formed at different reaction temperatures during the conversion of 1-octene over unpromoted ZSM-5 and ZSM-5 promoted with 3 % ZnO. Catalyst extrudates were made from ZSM-5 preparation F-34 and ZnO. BTX yields are given in Figure 4.14.

together with 3 % ZnO as a promoter, were also tested to investigate the relationship between the silica to alumina ratio of the ZSM-5 and the amount of BTX formed. The results are given in Figure 4.16, and show that under the conditions mentioned in the legend, even with the promoter present, the ZSM-5 has to have sufficient active sites to achieve the best conversion to aromatics.

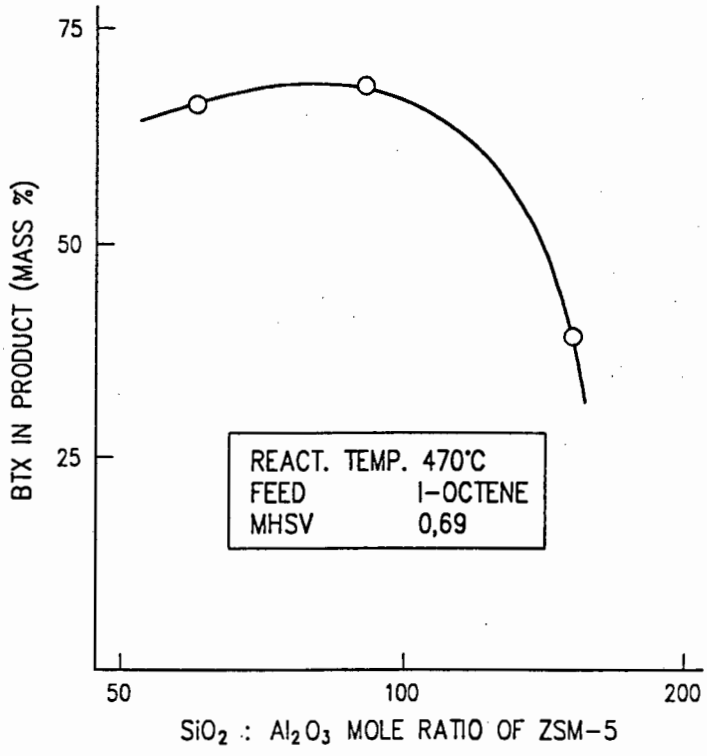

Figure 4.16. Conversion of 1-octene to BTX aromatics using ZSM-5 having different silica to alumina ratios and 3 % ZnO as promoter.

4.2.2. CONVERSION OF PROPENE TO DIESEL

It was mentioned in section 1.7.4 that the optimum conditions to be used in the MOGD process have been established by workers at Mobil [159,160,162]. The operation requires a pressure of 50 bar, a reaction temperature of between 290 and 300 °C and an MHSV of around 1. An example of the performance of a catalyst made in this work, sample F-34, is shown in Figure 4.17. The reaction was very

exothermic, and to maintain the correct temperature the controllers had to be set at a lower temperature of 270 °C.

As defined in section 2.3.3.2, the conversion was the amount of propene feed that was converted to liquid product, and of this condensate, the raw diesel was the fraction with a boiling point greater than 180 °C. Over the period of testing, both the conversion and concentration of heavy fraction showed only relatively small variations, and it was only when the catalyst deactivated that the yields from both fractions were simultaneously reduced. The reaction was continued until the the catalyst had deactivated, at this point the test was terminated: this was usually in the region of 100 hours or longer. 100 hours on stream gives a catalyst utilisation value of 138 g / g.

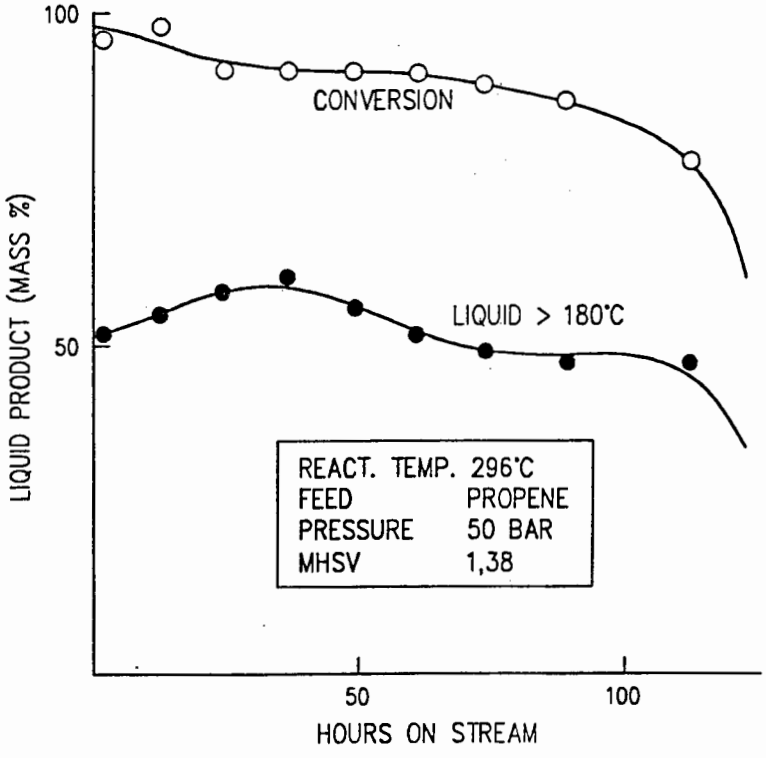

Figure 4.17. Conversion of propene to liquid products using catalyst extrudates made from preparation F-34 and the conditions given in the legend.

Besides the sample made from preparation F-34, which had a silica to alumina mole ratio of 90 : 1, samples made from F-35 and F-13, which had ratios of 60 : 1 and 150 : 1 respectively, were also tested using the same conditions. Their results, although showing different magnitudes, gave the same trend as that shown in Figure 4.17.

The yields of the liquid product, after 24 hours on stream, on the initial samples in relation to their silica to alumina ratios are shown in Figure 4.18. As shown in the figure, the catalysts with the lower silica to alumina ratios gave almost complete conversion, and that hardly any gas was found. As the silica to

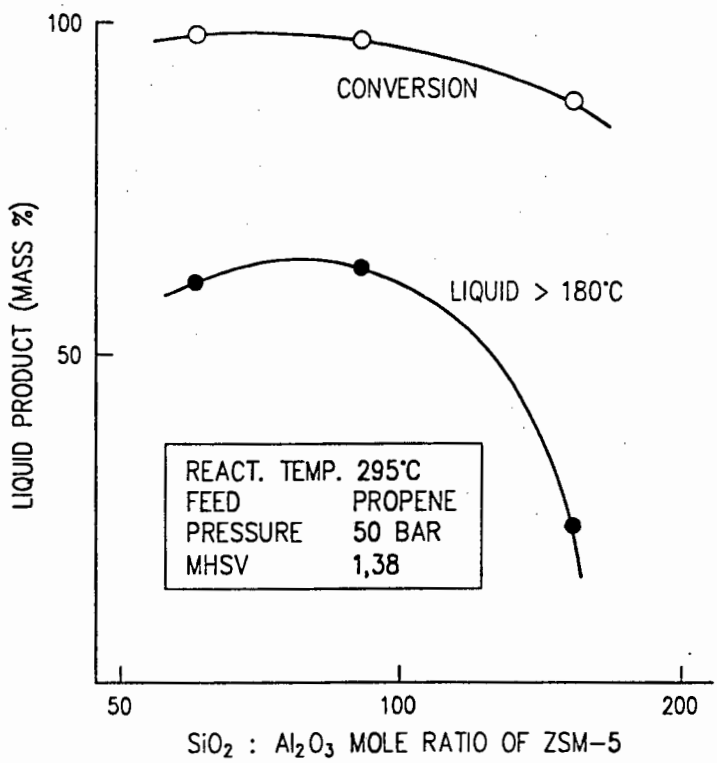

Figure 4.18. Conversion and petrol-diesel fraction after 24 hours on stream from MOGD catalysts having different silica to alumina ratios. Reaction conditions used are given in the legend.

alumina mole ratio of the ZSM-5 increased, the conversion decreased, and the preparation which had a silica to alumina mole ratio of 150 : 1 gave only 88 % liquid product.

Figure 4.18 also gives the fraction of heavy liquid that was simultaneously produced. By selecting a "cut-off" temperature of 180 °C, the product would only contain hydrocarbons having more than about ten carbon atoms, and was found to consist of material with mainly twelve or fifteen carbon atoms. The samples of catalysts made from preparations F-35 and F-34, which had silica to alumina mole ratios of 60 : 1 and 90 : 1 respectively, delivered roughly the same amount of raw diesel, which was slightly above 60 %. However, when the silica to alumina ratio was increased, as was done when using preparation F-13, there was a significant decrease in the concentration of raw diesel produced. This reduction in the amount of oligomerisation taking place must be attributed to there being, under the prevailing conditions, insufficient active sites within the catalyst.

After deactivation as a result of being tested in the reactor, the sample made from preparation F-34, was regenerated by calcining it in air at 550 °C before being retested twice. The actual durations of the first and each subsequent experiment are given in Table 4.5, and shows that the catalyst remained active for longer periods after regeneration.

The bromine number of the light liquid fraction, boiling between ±25 °C and 180 °C, was determined on three samples. The results are included in Table 4.5. As pure hexene and nonene should have bromine numbers of 190 and 127 respectively, it indicated that the light liquid fraction consisted mainly of hydrocarbon molecules oligomers containing around six to nine carbon atoms. Similarly, the bromine number of the heavy liquid fraction, boiling above 180 °C, was determined on two samples. The results are also included in Table 4.5. Pure dodecene has a bromine number of 95, and as the heavy liquid fraction gave a similar value, it indicated that it consisted of oligomers containing about twelve carbon atoms.

On completion of three of the experiments, the hydrocarbon liquid boiling above 180 °C was hydrogenated to convert the raw diesel to the finished product, which requires lowering the bromine number to a value of less than 10. The cetane numbers were then measured on the finished material, and the results are listed in Table 4.5. The cetane values are slightly low as the SABS specification states that for diesel it should be at least 45 [183]. This can be attributed to the product not containing enough large molecules; it was mentioned above that these products had on average only about twelve atoms, whereas cetane has sixteen carbon atoms.

Table 4.5. Catalyst performance in the MOGD experiments and the bromine numbers of the light and heavy liquid fractions. Included is the bromine number of the heavy fraction after hydrogenation, and its corresponding cetane number.

Preparation	F-35	F-34	F-34	F-34	F-13
SiO_2 : Al_2O_3 mole ratio	60 : 1	90 : 1			150 : 1
Regeneration	fresh	fresh	first	second	fresh
Hours on stream	269	83	124	162	69
Bromine number of					
light fraction	163	-	169	-	140
heavy fraction	99	94	-	-	-
after hydrogen.	2	6	-	8	-
Cetane number	43,6	42,3	-	40,4	-

CHAPTER 5

DISCUSSION

5.1. SYNTHESIS FORMULA

Based on the original method of preparing zeolite ZSM-5 by Argauer and Landolt [10], sections 1.3.1 and 1.3.2 outlined modifications that were recommended for the composition of the reactants to be used in the synthesis. The optimum formula should be:

$$x\ Na_2O \quad 3 - 5\ \textit{template molecules} \quad y\ Al_2O_3 \quad 20\ SiO_2 \quad \pm 1000\ H_2O$$

The ZSM-5 catalyst for the methanol-to-olefins process needs a high silica to alumina ratio, and this means that the value of *y* should be low. In the initial recipe, tetrapropylammonium cations were used as the template, but were then subsequently changed to α,ω-diaminoalkanes to fulfil one of the aims of this work. The recommended concentration for the sodium oxide gives *x* a value between 0,5 and 3.

5.2. SYNTHESIS IN THE PRESENCE OF TPA

5.2.1. ALUMINIUM CONTENT OF SYNTHESIS FORMULA

It has been established by Derouane *et al* [37,40] that during the synthesis of ZSM-5 there is a preference to include silicon rather than aluminium atoms in the zeolite structure. Therefore it is possible to make ZSM-5 with low amounts of aluminium [20], and to ultimately synthesise silicalite which has virtually no aluminium [17].

In order to ensure the incorporation of aluminium into the zeolite structure, it was necessary, as found with the samples of

the A-series and most of those of the D-series, that the synthesis mixture had to have a minimum amount of sodium oxide. When the concentration of sodium oxide was reduced so that the value of x in the above formula was less than about one, there was a tendency for a large fraction of the aluminium not to be incorporated into the zeolite. This was illustrated with all the samples from the B-series as well as preparation D-1. The importance of the sodium content will be discussed later in section 5.2.2.

When using tetrapropylammonium cations as the template, there is no limit as to the extent to which the aluminium could be reduced. Samples with about 0,15 % Al_2O_3 were prepared, giving a silica to alumina mole ratio in the region of 1000 : 1. It was found in section 3.1.3.2 that most (84 %) of the aluminium in the product was incorporated into the zeolite structure. However, due to reluctance to incorporate aluminium in the ZSM-5 structure, the highest possible concentration is in the region of about 3 %, and which is equivalent to a silica to alumina mole ratio of around 50 : 1.

5.2.2. SODIUM CONTENT OF SYNTHESIS FORMULA

For the synthesis of zeolites it is necessary that the reaction mixture have a certain degree of alkalinity to make the product crystallise [23,25]. In the above formula, the alkalinity is directly related to the sodium oxide concentration. Regarding the Na_2O concentration for the synthesis of ZSM-5, Fegan and Lowe [32,33] found that if the value of x in the formula was less than 0,5, ZSM-5 did not crystallise.

The value for x in the B-series of samples of this work was 0,48, and therefore, it was not surprising that additional time at a higher temperature was needed for their crystallisation to take place. As has already been discussed in section 5.2.1, the use of a low sodium content in the reaction mixtures also caused related problems in that there is a tendency not to include aluminium atoms

in the crystallisation process, and thus less aluminium is ultimately incorporated into the ZSM-5 structure than was added to the reaction mixture. Finally, as was shown in section 3.1.2.2, the use of a low Na_2O results in relatively large crystallites. This confirmed an earlier observation of Fegan and Lowe [33]

The work by Erdem and Sand [31] established the limit to the amount of sodium oxide that ought to be used. It was shown that when x has a value of three or higher, there is the tendency to co-crystallise mordenite. The highest alkali concentration that was used in this work was with sample 6-D where the value of x was 2,90, and it was found that the product did include a small amount of mordenite.

Having reconfirmed the lowest and highest concentration for Na_2O in the synthesis formula, namely that $0,5 < x < 3,0$, it can be assumed that ideally it should be between these limits, and a value of 2,10 was thus generally used. This gave the reaction mixture a pH of between 12,0 and 12,7 (see sections 2.1.1.3 and 2.1.1.4) and it would have the required degree of alkalinity needed for the crystallisation of ZSM-5.

5.2.3. SODIUM CONTENT OF PRODUCT

If the sodium content of the crystallised product is abnormally high, it probably means that it contains some amorphous material as well as the ZSM-5 formed. In order to answer the question whether the product is reasonably free of amorphous material, it is necessary to ascertain what is the expected Na_2O content of pure ZSM-5.

The relationship between the amount of Na_2O used in the synthesis mixture and the content that is ultimately found in silicalite was established by Fegan and Lowe [32]. In section 3.1.3.1 it was shown that the highly siliceous ZSM-5 made in this work gave the same results as that of silicalite. Based on this relationship, when the value of x in the synthesis formula is 2,10,

the expected Na_2O of the final ZSM-5 should be around 1 %. The actual results obtained on all the relevant samples were approximately this amount, and were thus fairly pure ZSM-5. It should be noted that if all the sodium (x = 2,10) were to be included in the final product, its Na_2O content would be about 10 %.

Based on the relationship first established by Fegan and Lowe [32], and confirmed here, the Na_2O content of the product is dependent on the amount added to the synthesis mixture. It followed that the Na_2O content is not related to the tetrahedral co-ordinated aluminium in the zeolite ZSM-5, nor to the cation exchange capacity of the zeolite. However, there is a relationship between the last two parameters; namely that the cation exchange capacity is directly proportional to the aluminium concentration in the zeolite structure.

It has been stated in section 3.1.1.2, that with pure ZSM-5 it should be possible to remove all the sodium via cation exchanging. Therefore any sodium remaining after this treatment (residual sodium) would be indicative of the presence of impurities such as amorphous material. With the preparation of the samples from the B-series relatively low concentrations of sodium were used in the static reactor, and only moderately successful results were obtained regarding the ability to remove all the sodium cations. With the samples from the D-series however a wide range of Na_2O contents were used during synthesis, but the reaction mixtures were stirred while the ZSM-5 was crystallising. It was found that the residual sodium in all the samples of the D-series, irrespective of the Na_2O content in the synthesis mixture, were low, being around 0,01 %. This shows that it is beneficial for the mixture to be stirred while crystallisation is taking place. It increased the crystallinity of the product and thus simultaneously decreased the amount of amorphous material. Although its use is generally recommended [24,25], this result clearly illustrated an advantage of stirring during the preparation of a zeolite.

Finally, stirring the reaction mixture during synthesis gives

a product having a uniform size of crystallites, and if the correct amount of alkalinity is present, these are around 1 to 3 μm.

5.3. SYNTHESIS IN THE PRESENCE OF α,ω-DIAMINOALKANES

From the preceding discussion it was established that to have the best conditions for synthesis, the concentration of sodium oxide in the reaction mixture should have a value of around 2,1 for *x* in the standard formula, and that the contents should be slowly stirred while crystallisation takes place. These conditions must therefore continue to be applied when using α,ω-diaminoalkanes as the organic structure directing agents. This section will then focus on which would be the best alternative template to use when wishing to make highly siliceous ZSM-5, and then concentrate on what could be the expected silica to alumina ratio of such a product.

5.3.1. SELECTION OF MOST SUITABLE DIAMINOALKANE

It was stated in section 1.3.2 that in published work where α,ω-diaminoalkanes had been used as the synthesising template, the silica to alumina mole ratio of the reaction mixture was in the region of 50 to 90 : 1 [46-51,55]. Further, when using 1,6-diaminohexane as the template, van der Gaag *et al* [50] found that when they increased the silica to alumina mole ratios of the reaction mixture to around 200 : 1, ZSM-5 did not crystallise.

However, for the MTO process, the ZSM-5 has to have a relatively high silica to alumina mole ratio, and therefore when considering whether any of the alternative templates from the α,ω-diaminoalkanes could be suitable, results would focus on attempts to make products where this ratio has a minimum value around 200 : 1. Therefore, in this work when initially considering the suitability of a template, the silica to alumina mole ratio of the reaction mixture was 250 : 1. This was done with samples 1-E to 6-E.

With this requirement placed on the synthesis mixture, it was found that when diaminoethane, diaminopropane, diaminobutane and to a lesser extent diaminopentane were used, they were inclined to give large amounts of amorphous material and probably some analcime, and therefore none of these organic compounds would be suitable. It was only when the large molecules such as diaminohexane and diaminooctane were used that it appeared from XRD results, that the product consisted of only crystalline zeolite.

As was mentioned in section 1.3.2, the diamine being used as templates determines which zeolite is formed. With diaminopentane and diaminohexane, it was found that the product did not consist of pure ZSM-5, but also contained significant amounts of ZSM-11. The presence of ZSM-11 however, should not be considered deleterious because its structure and properties are very similar to those of ZSM-5. Thus, 1,6-diaminohexane appears to be a good template when preparing siliceous ZSM-5. Diaminooctane itself leads to the crystallisation of pure ZSM-11.

However, Jacobs and Martens [42] have felt that in the absence of tetrapropylammonium cations, seeding is necessary for ZSM-5 to crystallise. In an autoclave where ZSM-5 had been synthesised before, it was felt that irrespective of how well it was cleaned there would always be sufficient small crystals remaining behind which would act as the seeding agent. As has been recommended by Calvert and Rollmann [57], small amounts of tetrapropylammonium cations were added to the mixtures of this work to function as a seeding agent to propagate the crystallisation of ZSM-5. However, when none of this material was added (preparation E-14), it was found that ZSM-5 still crystallised, and this could have been due to seeds remaining from previous crystallisations. Although this last result indicates that the small addition of TPA could be unnecessary, it would be safer to continue including it especially as only a small amount is recommended.

Araya and Lowe [51] have stated that tetrapropylammonium cations are the only true template for the synthesis of ZSM-5,

and that 1,6-diaminohexane does not function as effectively. The most common template used for the synthesis of ZSM-48 is 1,6-diaminohexane itself [52-54,62]. Therefore, it should not be surprising that the presence of ZSM-48 was to be found in preparations where little or no aluminium is added to the reaction mixture, such as in samples 5-E and more particularly 10-E. As the aim is to prepare ZSM-5 as pure as possible, precautions must be made to reduce the likely co-formation of ZSM-48. This will be discussed in more detail in section 5.3.8.

5.3.2. SHAPE AND SIZE OF CRYSTALLITES

Different shapes have been reported for the crystallites of ZSM-5. The materials made by Derouane and co-workers [37,40] were mostly agglomerates. A second shape is like intergrown discs, having a "hum-bug" appearance [33,35,36,40,198,199]. This shape has found to be prevalent when using alkali cations other than sodium in the reaction mixture [40,174,198,200]. Von Ballmoos and Meier [41] formed elongated or "coffin" shape crystallites when making their relatively large crystals of ZSM-5. Gabelica *et al* [40] showed that certain of their agglomerates consisted of these elongated crystallites.

As shown in Figure 3.2, the crystallites formed when using tetrapropylammonium cations as the template had the disc or "hum-bug" shape, and with preparations 2-D to 6-D were about 2 µm in size. The crystallites obtained from the preparation where the diaminoalkanes were used as the template are shown in Figure 3.5. Samples 1-E to 4-E clearly contained amorphous matter, but samples 5-E and 6-E consisted of only crystalline material. Preparation 5-E, when 1,6-diaminohexane was used, was the most uniform of all the samples of the E-series, and showed that it was single clear crystallites and not agglomerates of smaller ones. The type of crystallites formed with sample 5-E indicated that after the initial formation of ZSM-5 seeds there is then a steady growth wherein both the organic compound and silicon or aluminium atoms from the aqueous

gel, participate simultaneously. The crystallites of sample 5-E had the elongated or "coffin" type, and were about 3µm in length with a cross section of about 1 µm, and were therefore about the same size as those made with TPA.

The large crystallites found with sample 1-D were formed as there was a low Na_2O concentration in the synthesis mixture [33]. Because it has already been decided not to employ low concentrations of Na_2O in order to enhance crystallisation and, as will be discussed in section 5.3.8, to also reduce the tendency to co-crystallise ZSM-48, large crystallites should not be encountered when using 1,6-diaminohexane as the template.

5.3.3. ROLE OF α,ω-DIAMINOALKANES IN SYNTHESIS

From the thermogravimetric analysis shown in Figure 3.8, the calcination temperature required to remove a particular α,ω-diaminoalkanes included in ZSM-5 during synthesis, varied considerably. When this organic compound contained between three and five carbon atoms they could be removed at a relatively low temperature of around 250 °C. But the diaminohexane and diaminooctane compounds required a much higher temperature of around 450 °C for their removal. As was mentioned in section 1.3.2, and as was indicated with the XRD results in section 5.3.1, the size of the diaminoalkane plays an important role in the synthesis of ZSM-5.

From the dimensions of the unit cell given in section 1.2, it was calculated that the distance between the centres of successive intersections of ZSM-5, along the straight and sinusoidal channels are about 1,0 and 1,2 nm respectively. The length of a carbon-carbon bond is 0,154 nm, while a carbon-nitrogen bond is 0,147 nm [201]. These values were taken to draw Figure 5.1, which shows molecules of 1,6-diaminohexane located in either type of channel. The terminal amine groups would naturally protrude into the intersections.

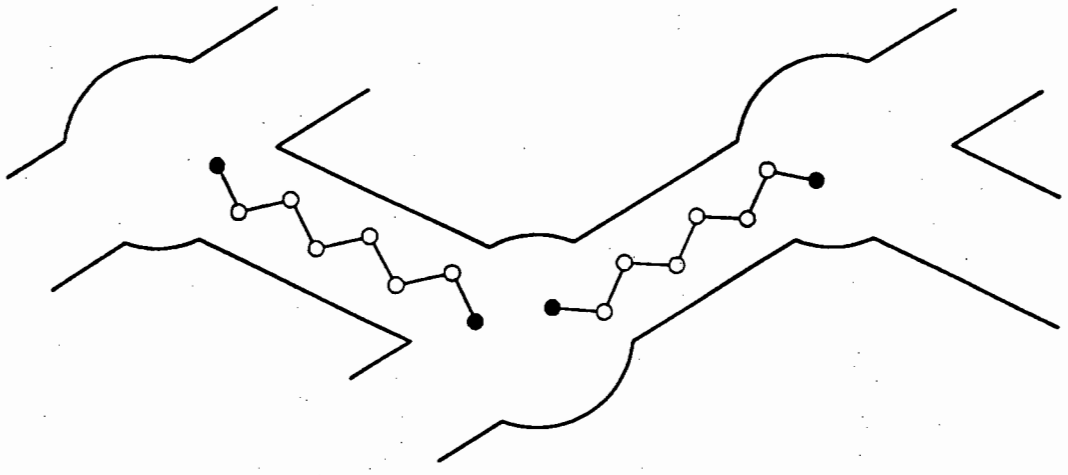

Figure 5.1. Location of molecules of 1,6-diaminohexane in the channel system of zeolite ZSM-5. Open spheres are carbon while the shaded ones are nitrogen; hydrogen atoms have not been drawn. Longer sinusodial channel is on the left, and shorter straight one is on the right.

Figure 5.1 shows how the 1,6-diaminohexane molecules fit neatly into the ZSM-5 channels. Jacobs and Martens [42] have said that the slightly smaller 1,5-diaminopentane molecules should fit even better. However, the relatively low temperature needed for its removal, indicates that this template is actually too small and is therefore not strongly held in the zeolite structure, and does not function as an ideal structure directing agent. The diaminopropane and diaminobutane are obviously too small. Due to their matching size and as indicated by the high temperature required to remove them, the larger diaminohexane and diaminooctane molecules are more firmly held by the zeolite structure. It can therefore be deduced that this secure locating in the zeolite took place as a result of the synthesis, and diaminohexane and diaminooctane must have good templating effects.

It has already been shown in section 5.3.1, that the size

of the organic molecule would play an important role in whether ZSM-5 or ZSM-11 are formed. As can be judged from the preceding paragraph, the molecules of diaminobutane are small enough and are easily located within either channel of ZSM-5. However, the molecules of diaminooctane are too long to fit comfortably in the channels thereby inhibiting the formation the sinusoidal channels and favouring the straight ones of ZSM-11. The molecules of diaminopentane and -hexane are of an intermediate size, and therefore give products consisting of both ZSM-5 and ZSM-11.

Valyocsik and Rollmann [47] and Lowe and co-workers [51,53] found that the number of organic templates that were located in the unit cell of the ZSM-5 structure was around eight. Jacobs and Martens [42] and Gabelica *et al* [46], however, obtained a lower value which showed that there were only about five molecules per unit cell. In this work, as shown in Table 3.8, the average number of molecules included in the zeolite was 5,3 per unit cell. Jacobs and Martens [42] attributed their lower values to the use of a low concentration of the organic compound in the preparation mixture. However, in this work a similar concentration to that of Valyocsik and Rollmann [47] was used and a lower degree of filling was still found. These variations must be caused by differences in each individual's synthesis. Consequently, it can be concluded that during crystallisation, although diaminoalkanes function as templates, some of the ZSM-5 zeolite can also form without the aid of these compounds.

The amino-groups of the compounds are at the intersections of the channels, and are more exposed than the rest of the molecule. Therefore, during calcination this portion of the molecule cracks from the diaminoalkane molecule and is driven from the zeolite structure before the remaining fragment of organic material. This implies that the amino-groups are not as firmly located in the zeolite structure as the main alkane building agent. The highest difference in temperature between which the amine portion is driven off before the main alkane section, was 70 °C, which occurred when 1,6-diaminohexane was used as the template.

5.3.4. COMPOSITION OF DIAMINE TEMPLATES

Valyocsik and Rollmann [47] and Jacobs and Martens [42] have found via chemical analysis that as a result of forming ZSM-5, the diaminoalkanes undergo some degree of de-amination. The latter workers suggested that de-amination was severe enough for the template remaining in zeolite to become a monoaminoalkane. However, this observation conflicts with reported NMR experiments [46,56], which show that the template is unchanged.

As shown in Table 3.9, the average number of amine groups per molecule was 1,4, confirming the same degree of de-amination determined by Valyocsik and Rollmann [47], but less than the de-amination equivalent to leave the compound as only a monoaminoalkane found by Jacobs and Martens [42]. The partial de-amination should not cause undue problems, because monoaminoalkanes themselves have been used to prepare ZSM-5 [43].

The argument that the NMR spectra showed that no change had occurred in the diaminoalkanes was based on the fact that the position of peaks of the material within the zeolite was the same as that of the pure compound [46,56]. In this work it was shown that the position of the peaks were also unchanged, but what was important was that their magnitudes had altered significantly.

Referring to the spectra of samples 5-E and 14-E in Figure 3.9, it can be seen that shifts causing peaks A and B from the diaminohexane are still present, and this naturally implies that its third peak at around 28 ppm, and which must be of similar size to those of A and B, is also be present. However, where it is to be found, there is the much larger peak C, and this peak must therefore be comprised of two components: namely a small portion due to the third peak resulting from the presence of diaminohexane, and the remainder caused by carbon atoms in another environment. It is therefore proposed that the template inside the zeolite consists of two components; diaminohexane and a new component. Although this section of the investigation was focused on 1,6-diaminohexane, an identical arrangement seems to exist where 1,8-diaminooctane was

used in the synthesis of ZSM-5. With the other diaminoalkanes examined, this arrangement did not appear to be well developed.

This new component of the template is neither a diamine nor a monoamine. Further, the single peak means that all the carbon atoms of this compound are in identical arrangements, like a normal alkane. However, normal hexane would record hardly any shift and the shift which was found must therefore be due to some uniform interaction between all the carbon atoms of the organic compound and the atoms of the zeolite structure.

5.3.5. SODIUM CONTENT OF PRODUCT

As was discussed in section 5.2.3, Figure 3.3 showed that the relationship between the amount of Na_2O that is ultimately found in the product synthesised with TPA is proportional to the concentration added to the reaction mixture [32]. When the concentration of Na_2O is 2,10 in the synthesis formula, all the products have a Na_2O content of around 1,0 %. However, when α,ω-diaminoalaknes are used as the template, it has been reported that the ZSM-5 contains hardly any sodium [42,47-49,51,55]. It has been argued that as a result of the filling of the channels with diaminoalkanes, sodium cations are excluded from the product.

When using the same Na_2O concentration, namely x = 2,10, in the preparation mixture, but using diaminopentane, -hexane and -octane for the synthesis, the ZSM-5 product contained on average 0,57 % Na_2O. This is less than the amount obtained when the ZSM-5 was made with TPA, but is higher than that reported previously in the literature [42,47-49,51,55]. As discussed in section 5.3.3, the channels of the ZSM-5 made with these templates contained only 5,3 molecules, instead of the anticipated eight. This means that the channels were only about 70 % filled with diaminoalkanes, and consequentially only partially forced the exclusion of sodium cations.

In Figure 3.10 the relationship between the concentration of Na_2O that was added to the reaction mixture and the amount that is ultimately found in the synthesised product, when using 1,6-diaminohexane is compared to that when using TPA. It appears that the results obtained with diaminohexane is influenced by two components. Firstly, the Na_2O content is controlled by the amount added to the synthesis mixture similar to that with TPA as shown with the D-series in the figure. Secondly, through the filling of the channels by the diaminohexane, the greater the extent of the filling, the lower the amount of sodium in the zeolite product.

The Na_2O contents of the preparations 1-E, 2-E and 3-E that were made with diaminoethane, -propane and -butane respectively, were excessively high. This attributed to these products containing large amounts of amorphous matter, that were originally identified by XRD and SEM results.

It was mentioned in section 5.2.3, that when tetrapropyl-ammonium cations were used to synthesise ZSM-5, the Na_2O bore no relationship to the cation exchange capacity or aluminium content of the product. In the case where 1,6-diaminohexane was used as the template an additional factor of the degree of filling also influenced the Na_2O content of the synthesised ZSM-5, and it should therefore not be surprising that again it was not related to the cation exchange capacity or aluminium content of the product. This can be seen in Table 3.10 where preparations with the same aluminium content had different amounts of Na_2O.

It has already been stated before that with pure ZSM-5 it should be possible to remove virtually all the sodium by cation exchange. In this aspect, as shown in Table 3.6, the only diaminoalkanes tested that met this criterion was the sample made with 1,6-diaminohexane. It was possible to remove nearly all the sodium from the product by cation exchanging, and to obtain a residual Na_2O level with sample 5-E of 0,02 %, which is comparable to the good results achieved when using TPA as the template (see Table 3.4).

Some idea of the importance of having a low sodium content in a ZSM-5 catalyst was demonstrated in section 4.1.2.7, where it was shown that its presence led to rapid deactivation. However, it should be remembered that the sodium ions in this experiment were cation exchangeable, whereas the residual sodium in the ZSM-5 mentioned above, were probably located in an amorphous phase.

5.3.6. PERMISSIBLE RANGE OF SILICA TO ALUMINA RATIO

In the preceding sections, particularly regarding crystallinity and the low levels to which the sodium content could be reduced, it was shown from the α,ω-diaminoalkanes group of compounds that 1,6-diaminohexane was the most suitable template when aiming to make highly siliceous ZSM-5. The question that now needs to be addressed is to what extent the silica to alumina ratio can be increased using this template. It has already been mentioned in section 5.3.1 that in all previous reported work [46-51,55] when 1,6-diaminohexane was used as the synthesising template, the silica to alumina mole ratio was in the region of 50 to 90 : 1, and never in excess of 200 : 1.

Referring to the results shown in Figure 3.11, which gave the XRD intensity of preparations made with 1,6-diaminohexane as the template, there was a limited range for the silica to alumina ratio wherein a fairly pure ZSM-5 is obtained. The ideal range for the silica to alumina mole ratio is from 120 : 1 to 200 : 1. This range is quite different, being somewhat higher, than those of previous reported results. Therefore when using this template, this seems an unique way when considering making a ZSM-5 catalyst for the MTO process.

Under the synthesis conditions being used in this work, when the silica to alumina mole ratio was less than 120 : 1, it was shown in section 3.3.1 that the product will contain relatively high levels of amorphous material. On the other hand when the silica to alumina mole ratio of the reaction mixture was raised beyond

200 : 1, the product contained significant amounts of ZSM-48. This is in contrast to when using tetrapropylammonium cations, where there is little restriction on the upper silica to alumina ratios that can employed (this was emphasised in section 5.2.1). As mentioned earlier, methods to keep the level of ZSM-48 to a minimum when using 1,6-diaminohexane, will be discussed later in section 5.3.8

Due to the aluminium impurity in the source of the silica, it was found (see Table 3.6) that the products from the preparations of the E-series contained higher amounts of aluminium than was expected. Logically the same trend should be found with the samples of the F-series where 1,6-diaminohexane was the main template as the composition of the ZSM-5 was varied. This would mean that the actual silica to alumina ratios of these samples were lower than the nominal values depicted in Figure 3.11 and Table 3.12. However, although the product contained more aluminium, it was shown in section 3.2.7.2, that only 65 % of the total amount of the aluminium was functioning actively in the ZSM-5 structure. Secondly, as shown in Figure 3.11, not all the product consisted of ZSM-5. When taking all these factors into account (see section 3.3.2), the upper silica to alumina mole ratio for pure ZSM-5 is about 200 : 1, but it can be about 300 : 1 if the presence of some ZSM-48 is acceptable.

Although Chang *et al* [128] indicated that for the maximum olefin selectivity, the silica to alumina mole ratio for an MTO catalyst should preferably be around 400 : 1, and which was further confirmed by activity measurements in section 4.1.2.3, this was beyond the range found with the products synthesised in this work. As mentioned above, the practical limit for pure ZSM-5 was found with a silica to alumina mole ration of about 200 : 1. However, as will be shown in section 5.3.7, that subsequent hydrothermal treatment can increase the silica to alumina mole ratio of the preparation to the required level.

The aluminium included in the ZSM-5 structure is tetrahedrally co-ordinated [194,195]. The NMR data in Figure 3.7 showed that

all the aluminium in the product was located in a tetrahedral environment. Therefore, the remaining aluminium, which must be in an amorphous phase, was also tetrahedrally co-ordinated. This means that it is not possible from NMR results to estimate what fraction of the aluminium is located in the zeolite.

5.3.7. STEAM CALCINATION

As was discussed in section 5.3.6, when 1,6-diaminohexane is used to prepare ZSM-5, the highest practical silica to alumina mole ratio with ZSM-5 is about 200 : 1, and that this is too low for an MTO catalyst. In section 1.7.2 it was reported that calcination in steam removes some of the aluminium from the zeolite structure [132,133], thereby increasing the silica to alumina ratio of the ZSM-5. Sano *et al* [133] found that the rate of de-alumination depends on the calcination temperature, duration of the treatment and the aluminium content of the ZSM-5.

The first of these parameters, the effect of temperature, was studied in section 4.1.2.5. As has already been mentioned in section 4.1.2.5, although thermal steaming does strip aluminium atoms from the ZSM-5 framework, they may still remain within the catalyst matrix, and the increased silica to alumina ratio could not be easily determined by chemical analysis. Therefore, changes in the ZSM-5 due to steam calcination had to be evaluated from improvements in its catalytic performance. It was found that improved olefin selectivity, which must have stemmed from increasing the extent of de-alumination, became significant only when the temperature of the steaming approached 500 °C. The second parameter was the duration of the treatment and this was also studied in section 4.1.2.5. It is clear that about 20 hours steaming at 500 °C was required to produce sufficient de-alumination to give a product selectivity of about 55 % C_3 to C_5 olefins, which, as shown in Figure 4.7, is obtained from a sample of ZSM-5 with a silica to alumina mole ratio of about 400 : 1.

The third parameter identified by Sano *et al* [133] was that the rate of de-alumination also depended on the concentration of aluminium in the zeolite. Referring to Figure 4.10, it can be seen that the duration of steaming is plotted on a logarithmic scale, yet it produced only a linear increase in the olefin selectivity. It logically follows that hydrothermal de-alumination proceeds easier when there is a high concentration of aluminium, and conversely, when the concentration is low it is more difficult to remove the aluminium.

It was mentioned in section 1.7.2 that re-insertion of aluminium also takes place [134,135]. Naturally, this is undesirable as it would be decreasing the silica to alumina ratio of the ZSM-5. However, this fear that a simultaneous re-insertion of aluminium into the zeolite framework takes place seems exaggerated. Even under the most adverse conditions of a dry atmosphere, strong presence of alumina from the binder and a temperature of 850 °C, only little re-alumination occurred as can be gauged from the decrease in olefin selectivity measured in Figure 4.11.

5.3.8. CONTROL OF THE CONCENTRATION OF ZSM-48

It has already been shown in sections 5.3.1 and 5.3.6 that when 1,6-diaminohexane was used as the structure-directing agent in the synthesis of ZSM-5 with relatively high silica to alumina ratios, the product was inclined to co-crystallise ZSM-48. As ZSM-48 contains very little aluminium [21], its presence meant that the ZSM-5 has relatively more, giving it a lower silica to alumina ratio. This is counter-productive to the aim of this work when making a catalyst for the MTO process, where the ZSM-5 should contain low amounts of aluminium. As it appears that when using 1,6-diaminohexane as the template, it is unlikely to completely avoid co-crystallisation of ZSM-48, every effort should be made to keep its concentration as low as possible.

Syntheses with 1,6-diaminohexane as the template in reaction mixtures with no or low amounts of aluminium have shown that ZSM-48 is crystallised preferentially to ZSM-5 [52-54]. Further, the crystallisation of ZSM-48 is enhanced by using higher synthesis temperatures, but is reduced through the addition of some TPA [53].

Using the particular synthesis formula with 1,6-diaminohexane in this work, it was found that the concentration of ZSM-48 formed in the products was influenced by three factors; namely the silica to alumina ratio, and the amounts of sodium and tetrapropylammonium cations that were in the reaction mixtures. There were two other factors which also favour the formation ZSM-48, namely seeds which would exist in an area where syntheses had previously taken place, and the use of high temperatures for crystallisation.

As indicated in the literature and confirmed in section 5.3.6, the largest effect on the formation of ZSM-48 is the silica to alumina ratio. It was shown that under the conditions being used here that if the silica to alumina mole ratio is more than 200 : 1, some ZSM-48 also crystallises, with the higher the ratio the more ZSM-48 being formed. Therefore with this preparation technique the maximum permissible silica to alumina mole ratio is about 250 : 1.

It was shown that low amounts of sodium oxide in the synthesis formula favoured the formation of ZSM-48. This is clearly illustrated by the micrograph in Figure 3.6 of preparation 11-E, which was made with a low amount of sodium oxide and contained a large proportion of ZSM-48. However, as mentioned at the beginning of section 5.3, in order to facilitate crystallisation, low concentrations of sodium oxide in the synthesis mixture should be avoided. At the recommended level of Na_2O, the concentration of ZSM-48 is still controlled mostly by the silica to alumina ratio.

Naturally the addition of more TPA will favour the formation of ZSM-5 and thereby the reduce the amount of ZSM-48. However, as first found by Franklin and Lowe [53] and confirmed in section 3.2.2, this has only a limited effect on the concentration of ZSM-48 formed in the product.

As shown in section 3.3.3. when the filtrate was reused for a second synthesis the level of ZSM-48 increased, which is probably caused by seeds in the filtrate which preferentially crystallised ZSM-48. When the same filtrate was used for successive syntheses, the same concentration of ZSM-48 as in the second preparation, was again found. The problem of preferential seeding for ZSM-48 is permanent, and can therefore not be avoided.

Although reduction in the the synthesis temperature should decrease the amount of ZSM-48 that is formed [53], this is offset by the fact that longer periods are required for crystallisation. Therefore in this work it was only possible to reduce the reaction from 170 °C to 150 °C. However, this did not lead to a lowering of the concentration of ZSM-48 that co-crystallised. This means that variation in the synthesis temperature is not really a practical option to reduce ZSM-48.

From the above discussion it can be concluded that the main parameter to ensure that the product is predominantly ZSM-5 with little ZSM-48 present, is to have a synthesis mixture wherein the silica to alumina mole ratio is that which was recommended in section 5.3.6: namely, that the practical limit is a value of around 200 : 1, and that a ratio of 250 : 1 should definitely never be exceeded.

5.4. INDUSTRIAL SYNTHESIS

An aim of this work was that the accumulated data could be practically applied. This section therefore summarises the information that could possibly be used to do the synthesis on an industrial scale.

When using 1,6-diaminohexane as the principal organic directing agent for the synthesis of ZSM-5, the best formula for

the preparation mixture is

2,10 Na_2O 0,084 Pr_4NBr 5 DAHX 0,1-0,133 Al_2O_3 20 SiO_2 ±800 H_2O

In the formula 1,6-diaminohexane is abbreviated DAHX. In this mixture the silica to alumina mole ratio is between 150 and 200 : 1, which would keep the amount of unwanted ZSM-48 that can co-crystallise to an acceptably low level.

For an industrial scale of synthesis, the chemicals have naturally to be commercially available. Commercial grade 1,6-diaminohexane was successfully used with the F-series of preparations, while a precipitated silica was used with both the E- and F-series of samples. Table 3.14 lists these two chemicals, as well as giving a single source of all the others raw materials needed. Except for the pseudo-boehmite, no alternative sources for the other materials were examined in any detail, and therefore, it naturally would be possible to use products from alternative suppliers.

It was established that the best temperature range for crystallisation to take place was between 150 °C and 170 °C. Further, the aqueous mixture should be slowly stirred throughout this process. The process leads to a fairly pure ZSM-5 and it was possible to reduce its sodium content through ammonium cation exchanging to 0,02 %. The synthesis requires a large industrial autoclave wherein the contents can be stirred, and the cation exchanging needs a counter-flow belt-filter system. Both these procedures are accepted practice on an industrial scale of operation.

In the above synthesis formula virtually all the aluminium and tetrapropylammonium compound are consumed during synthesis. However, a small portion of the silica, more than half the sodium hydroxide and about 80 % of the 1,6-diaminohexane remain in the filtrate. Further, as shown in section 3.2.6.3, this excess 1,6-diaminohexane does not undergo decomposition such as de-amination, as happened to the fraction that becomes incorporated into the ZSM-5

zeolite. Therefore, in section 3.3, the work focused on extending the synthesis technique so that these raw materials in the filtrate could still be used. While a obvious purpose of this technique was be to cut the costs of the raw materials, it would also reduce the necessity of treating or disposing of the effluent containing the chemicals in the filtrate.

The major problem found when reusing the filtrate containing the excess chemicals was that because of preferential seeding, it increased the concentration of zeolite ZSM-48 in the crystallised product. However, on the second and subsequent reuses, the level of ZSM-48 did not increase any further. With a silica to alumina mole ratio of about 200 : 1, the concentration was about 5 to 10 %. It seems that this is the amount of ZSM-48 that will most likely be found in the product, and at this level appears to be acceptable. In this work it was shown that it was possible for the filtrate to be reused four times, and still produce a satisfactory product. However, it cannot be continued for ever due to the increase in concentration of sodium sulphate and sodium bromide in the filtrate, and at some point it will have to be discarded.

The preparation of extrudates from a mixture of ZSM-5 and pseudo-boehmite, and the subsequent calcination at 550 °C to give the product its strength, are routine industrial procedures. After calcination it is necessary that the extrudates be exposed to steaming at 500 °C, which strips the ZSM-5 of some of its aluminium atoms (the purpose and necessity of steaming were discussed in section 5.3.7). These two steps are carried out consecutively in the calcination furnace without allowing the extrudates to cool down.

The price of the raw materials are also included in Table 3.14, and apart from the tetrapropylammonium compound, all are relatively inexpensive. In working out the cost of the raw materials, it was decided to base it on reusing the filtrate four times. It was calculated in Table 3.14 that the total costs of the raw materials required to make one tonne of catalyst extrudates would be about

R11 000. The final cost of ZSM-5 extrudates made by Mobil is $30 / lb. [202], which converted to local currency is about R180 000 / tonne. This means that the raw material cost only about 6 % of the final overall price of the catalyst.

5.5. SELECTIVE CONVERSION OF METHANOL TO LIGHT OLEFINS

The dehydration of methanol leads to water and olefins, after which the olefins themselves react further.

$$CH_3OH \text{ -----> } H_2O + (CH_2)_n \text{ -----> }$$

The stoichiometry of the reaction shows it is theoretically possible to attain a light olefin selectivity of 100 %, provided the olefins do not themselves react. Therefore, to obtain the maximum olefin selectivity conditions must be chosen for the reaction not to proceed far beyond that shown above. These would include optimising the reaction conditions and the composition of the ZSM-5 catalyst. Secondly, it is an advantage to know how the olefins proceed further to form aromatics and oligomers so that these reactions can be minimised.

It should however be stressed that in this work the optimum olefin selectivity meant that which could possibly be achieved in practical circumstances, and this requires simultaneously a high level of methanol conversion. It is well known that by using lower conversion levels (which are normally used when studying reaction mechanisms) very high selectivities of a particular component are attained, which here would be the light olefins.

5.5.1. REACTION CONDITIONS

Chang *et al* [124] have shown that a low partial pressure is needed for the formation of light olefins. A product spectrum of light olefins has a high volume, and according to *La Chatelier's*

principle increasing the pressure will cause these products to react further to form the heavier products that occupy a lower volume. Therefore it is necessary that one of the conditions to ensure a high olefin selectivity is that the partial pressure of the methanol feed be kept at 0,2 bar, or even lower. As shown in Figure 4.1, this pressure would give a product containing about 70 % light olefins.

The effect of using different mass hourly space velocities, but operating at several atmospheres, was studied by Chang and Silvestri [14]. By increasing the MHSV the chances of secondary reaction taking place were reduced, and naturally, the olefin selectivity is increased. However, in this work the partial pressure of the methanol was much lower, and this itself, as discussed above, reduced the secondary reaction of the olefins. Therefore by increasing the MHSV at low reaction pressures as shown in Figure 4.2, would only have a limited effect in improving the olefin selectivity.

As shown in section 4.1.1.2, a more pertinent problem encountered by increasing the MHSV was that the catalyst deactivated. Even a MHSV of around 2 caused deactivation, and therefore it is essential that the MHSV be kept below one.

Together with highly siliceous ZSM-5 as the catalyst, Chang *et al* [128] recommended that the reaction temperature required for a good olefin selectivity is 500 °C. As can be seen from Figure 4.3, the same temperature gave optimum results with the preparations of this work. However, by then referring to Figure 4.5, it can be seen that although a temperature of around 500 °C gave a good selectivity, the catalyst deactivated rather rapidly. Therefore it is advisable to reduce the reaction temperature to 450 °C, where the catalyst remains active much longer, although giving slightly inferior selectivity.

The reason for this deactivation of the catalyst was examined in section 1.5 where it was mentioned that above 400 °C coke forms on the outside of the ZSM-5 [79-81] and blocks the entrance to the

pores [77,80,82]. Schulz *et al* [80] and Echevskii *et al* [88] have shown that the rate at which the coke forms increases as the temperature of the reaction is increased, and the results in Figure 4.5 are in agreement with this observation. This meant that although increasing the temperature of the reaction increased the olefin selectivity, it unfortunately simultaneously increased the rate of catalyst deactivation, and that whereas reducing the temperature decreased the olefin selectivity, it increased the life of the catalyst. Therefore, when selecting the best reaction temperature a compromise has to be met between these two trends, and it appears that this is about 450 °C.

Schulz *et al* [113] have postulated that during the dehydration of methanol the formation of coke leads to the formation of methane, and the more coke formed the more methane is produced. As the reactions progressed in the experiments reported in Figure 4.6, more coke would have been produced and it can be seen that more methane was formed. This supports the above theory that the production of methane is coupled to the formation of coke. Further, it was stated in section 4.1.1.4 that irrespective of the temperature of the reaction, the same amount of coke (about 5 %) was deposited on the catalyst, and yet as the temperature was increased so did the yield of methane increase. This means that the temperature also influences the rate of methane formation, with the higher the temperature the higher the rate. By not exceeding a temperature of 450 °C the rate of both coke and methane formations are kept low, and the concentration of unwanted methane is kept to a minimum.

5.5.2. COMPOSITION OF ZSM-5 CATALYST

It can be seen from sample 1-D in Table 4.1, that if the crystallites are rather large there is a variation in the type of light olefins produced. However, as this sample was made from a composition with an unrecommended low amount of sodium oxide (see section 5.2.2), crystallites, whether they be made with TPA or 1,6-diaminohexane, should all be a few microns in diameter. As

this is not a possible variation in the physical nature of the ZSM-5 catalyst, neither it nor its shape, as shown in section 4.1.2.1, has a significant influence on the yield and spectrum of light olefin formed. Similarly, although the addition of an alumina binder lowered the yield of light olefins, it is impractical to consider making an industrial catalyst without a binder, and therefore the small drawback that is caused is unavoidable, and will therefore be a permanent characteristic of the catalyst.

During the reaction of methanol to light olefins, the reaction must be curtailed to prevent complete conversion. This is done by balancing the number of active sites in the catalyst against the amount of reactant passing over it. As mentioned in section 1.7.2, the initial attempts to reduce the number of active sites was to poison a certain fraction of them. This approach was tried and confirmed with the use of sodium in section 4.1.2.7. However, it was found that although poisoning did increase olefin selectivity, it also caused the catalyst to deactivate rapidly, and is therefore not a recommended practice.

Undoubtedly Chang *et al* [128] showed that the best way to reduce the number of active sites was to synthesise ZSM-5 wherein there were relatively few sites. Using tetrapropylammonium cations in the synthesis, suitable ZSM-5 was prepared, and as shown in Figure 1.9, produced a high olefin selectivity. The results seem to indicate that ideally the silica to alumina mole ratio of the ZSM-5 should be around 400 : 1. This conclusion was confirmed in this work, as shown by the results in Figure 4.7 and by extrapolation of the trend shown in Figure 4.8. The samples of Figure 4.7 were synthesised with the aid of TPA, while those of Figure 4.8 were made with 1,6-diaminohexane. This means that the olefin selectivity obtained is dependent on the composition of the ZSM-5 catalyst, and not on the method in which it was prepared.

Although the ZSM-5 should have a silica to alumina mole ratio of 400 : 1, this was not directly possible when it was prepared with 1,6-diaminohexane. In section 5.3.6 it was pointed out that when

aiming to make the ZSM-5 with this composition, it would co-produce large amounts of ZSM-48. Although it was mentioned in section 1.8 that the catalytic activity of ZSM-48 itself is low enough to have little effect on the reaction, the major problem caused by its presence was that it restricts the maximum silica to alumina mole ratio of the ZSM-5, and to ensure a pure product this value should not exceed about 200 : 1. Fortunately, subsequent calcination at about 500 °C in the presence of steam causes de-alumination of the zeolite, and as shown in section 5.3.7, this treatment increased the silica to alumina ratio sufficiently to give a satisfactory olefin selectivity.

5.5.3. UNDESIRED SIDE REACTIONS

5.5.3.1. FORMATION OF AROMATICS

In the conversion of methanol over ZSM-5 where no attempt is made to have a high olefin selectivity, such as in the MTG process, the product spectrum consists mainly of alkanes and aromatics [14,114]. As discussed in section 1.4, the shape selectivity properties of ZSM-5 means that the aromatics are restricted to mono-cyclic compounds.

In studying the specific formation of aromatics in section 4.2.1, it was shown that the aromatics are mostly formed from C_{4+} compounds. Where these compounds are alkanes they will undergo dehydrogenation in the presence of the promoter to give alkenes, whence the aromatics are formed [143,146,153] and which means that the main reactant are olefins. Although propene, due its higher standard heat of formation than that of the larger olefins, is less reactive, it has also been shown to form aromatics [144,147-149]. In the MTO process the C_3 to C_6 olefins formed the bulk of the product, and they could thus naturally be further converted to aromatics. The reaction temperature of 450 °C being recommended in section 5.5.1, for the selective conversion to olefins in the MTO process, it is only slightly below the 450 °C to 550 °C range which,

as shown in Figure 4.14, gave a significant increase in the yield of aromatics from the conversion of olefins.

Olefins contain two hydrogen atoms for every carbon atom, and although the ratio of hydrogen to carbon in aromatics vary, it is invariably less than two. Thus when converting olefins to aromatics, there must be a transfer of hydrogen to another product that is relatively richer in hydrogen. Hydrogen itself is naturally the ideal by-product, with the next highest hydrogen rich by-product being methane, followed in order by ethane, propane and the other paraffinic compounds. The formation of other olefins as the by-product does not favour the production of aromatics. In section 1.7.3 it was pointed out that the addition of a promoter meant that the catalyst is bi-functional, and that the role of the promoter was to facilitate hydrogen transfer as aromatics and alkanes are simultaneously formed [143,144,146,148,149,153].

Ono *et al* [156] have shown, when converting propene and butene with the aid of zinc as a promoter, that maximum aromatic selectivity is coupled to high yields of methane and ethane, and low yields of propane. This was confirmed when the highest BTX yield was obtained by using 3 % ZnO promoter and a reaction temperature of 500 °C (see Figure 4.14), and concomitantly gave a non-aromatic fraction wherein the largest fraction consisted of methane and ethane (see Figure 4.15). The high yield of ethene produced from 1-octene with pure ZSM-5 as the catalyst is caused by cracking due to the zeolite [143,153]. The higher the temperature, the higher the cracking and consequentially, as shown in Figure 4.15, the higher the concentration of ethene. In the absence of a promoter little hydrogen transfer takes place and this meant that the ethene itself did not react any further.

In this work zinc oxide was added as a promoter to the catalyst. The results confirmed that it did indeed increase the yield of aromatics, and simultaneously produced higher than normal amounts of light alkanes. The addition of the ZnO promoter was

used to exemplify the reaction in which aromatics are formed from olefins. However, as shown in Figure 4.14, although the absence of a promoter does not enhance the reaction, some degree of aromatisation still takes place. Therefore, it was not surprising that, as mentioned in section 4.1.1.3, while the MTO process gave an olefin selectivity in the region of 75 %, it unfortunately also produced additional products, which consisted of light alkanes and aromatics, and that the latter aromatic fraction consisted mostly of C_7 to C_9 compounds.

Besides needing a promoter to increase the yield, the ZSM-5 catalyst for aromatisation needs to be fairly active [149,153], and this can simply be achieved by using a catalyst which has a low silica to alumina ratio [142,143]. This observation was confirmed by the results given in Figure 4.16. Therefore, when striving to reduce the amount of aromatics formed, the ZSM-5 should have a relatively low activity, which is best achieved by having a high silica to alumina ratio. As this is already a prerequisite for the type of the catalyst described in this work for the MTO process, all the possible conditions to minimise the formation of aromatics have been met. However, even under these conditions a small amount of aromatics are still formed, and their presence is therefore unavoidable.

5.5.3.2. FORMATION OF METHANE

As a result of the aromatisation discussed in section 5.5.3.1, small amounts of methane are formed. However, the largest quantities of methane are caused by the formation of coke on the surface of the ZSM-5 catalyst. This point has already been handled in section 5.5.1.

5.5.3.3. FORMATION OF OLIGOMERS

When feeding small olefins over a ZSM-5 catalyst at the relatively high pressure of about 50 bar but low temperature of less than 300 °C, the molecules of the feed are joined together to form longer olefins [159,160,162]. These results were confirmed in this work where propene was examined under the same conditions (section 4.2.2). From the determination of bromine numbers it was calculated that the products were mostly dimers, trimers, tetramers and some pentamers. It was further found that the heavier tetramers and pentamers, after hydrogenation, gave a good cetane number indicating a fairly linear product.

While it has been reported that the larger olefins in the conversion of methanol occur as a result of methylation of smaller olefins [99,100,104,112], Dejaifve *et al* [111] found that butenes are also formed via the dimerisation of ethene. To enhance the linear coupling of olefins, it is necessary to have a high pressure. In section 5.5.1 it was recommended in the MTO process to use a partial pressure of 0,2 bar, which is very different to the 50 bar mentioned above. Therefore, the chances that a significant amount of polymerisation of olefins taking place is low.

In order to reduce the cracking of oligomers the temperature required for the MOGD process is around 290 °C [160]. The reaction temperature recommended in section 5.5.1 for the MTO process was 450 °C, and therefore if any oligomers are formed they are likely to be cracked back to light olefins.

None the data or publications supplied by Mobil mention what the silica to alumina ratio of the ZSM-5 catalyst ought to be for the MOGD process, but the work by Schwarz *et al* [164] showed that it should be around 96 : 1. This is supported by the results in Figure 4.18, where it was found that the silica to alumina mole ratio of the ZSM-5 should be in the region of 100 : 1. This means that the ZSM-5 catalyst for the MOGD reaction needs to be fairly active (this is the same as the catalyst needed for aromatisation mentioned in section 5.5.3.1 above). The requirement of a ZSM-5 catalyst with a

low silica to alumina ratio is obviously different to that specified for the MTO process, and this is a third reason why there is little likelihood of oligomerisation taking place during the conversion of methanol to light olefins described in this work.

Finally, the low likelihood of oligomers to be found during the conversion of methanol are confirmed by the product spectrum obtained in sections 4.1.1.3 and 4.1.3, wherein the presence of none of these chemicals could be identified.

5.5.4. OPTIMUM OLEFIN SELECTIVITY

In the work of Chang *et al* [128] shown in Figure 1.9, a C_2 to C_5 olefin selectivity of about 85 % was obtained. The integration of all the best conditions that were derived in this work, were applied in section 4.1.3, and led to results wherein a selectivity in the region of 75 % was attained. For the latter result a similar reaction temperature and silica to alumina ratio of the ZSM-5 catalyst were used. However, the recommended MHSV of less than one is lower than that used in Figure 1.9, where it was approximately 5. It was stated in section 4.1.1.2 that with a MHSV of about 5 the olefin selectivity would decrease with time. The catalyst tested in section 4.1.3 remained active for long period, having a life of more than 100 hours on stream. Therefore it appears that a selectivity of 75 % light olefins would be about the best that could be practically attained, and it is doubtful whether it would be possible to obtain better results.

It is well-known that in this reaction that there is a connection between the product yield and olefin selectivity, and by using milder conditions a higher olefin selectivity could be obtained but the yield would be lower. This practice is often adopted when studying reaction mechanisms. However, in this work the aim was to illustrate what could be achieved in practical circumstances, and this meant getting both a good yield (in this

case virtually complete conversion of the methanol) and an acceptable (even if this meant a slightly lower) olefin selectivity.

The fact that the catalyst used in section 4.1.3 was synthesised with 1,6-diaminohexane instead of tetrapropylammonium cations does not seem to make any difference. This can be judged from the results in Figures 4.1, 4.3, and 4.7, where the catalyst being used was ZSM-5 synthesised with TPA, and the olefin selectivities thus obtained were no different than when 1,6-diaminohexane was used as the template.

Apart from the olefins formed, the remainder of the product spectrum, which under the best conditions should not exceed 25 %, would consist of mono-cyclic aromatics and light alkanes. As has been discussed in section 5.5.3.1, the conditions used in section 4.1.3 for optimum olefin selectivity make it unavoidable to simultaneously form some aromatics and light alkanes.

Of the amount of light olefins produced, more than half was propene, and thus the process is well suited for making this specific chemical. However, the concentration of ethene formed was far less, with the product spectrum giving around 13 %. Therefore the MTO process, wherein ZSM-5 is used as the catalyst, is not highly suitable for the production of ethene.

5.6. SEQUENCE BY WHICH THE OLEFINS ARE FORMED IN THE MTO PROCESS

In section 1.6 on the conversion of methanol, it was mentioned that the popular view was that the initial olefin to be formed from the dehydration of dimethyl ether, was ethene [99-101,104]. Debates on the validity of this observation arose because under certain conditions no ethene could be detected, and under others ethene can be formed via cracking from propene [107-109]. Reasons for the disputes probably stem from the vast differences in conditions used by various researchers. Another problem in these reports was that often the product spectrum contained low amounts of olefins. In

this aspect this work was therefore more capable of clarifying the issue: by producing large amounts of olefins it was possible to separate the determination of the concentration of ethene formed from that of the other light olefins.

The results in Figure 4.4, where a wide temperature range of 300 °C to 550 °C was used, showed vast changes in the ethene and C_3 to C_5 olefin yields. Secondly, these concentrations do not run parallel to each other. This means that the temperature at which the reaction temperature is carried out is a major parameter controlling the product spectrum obtained.

At 300 °C the concentration of ethene is about half that of the total amount of olefins, and if the graphs in Figure 4.4 were extrapolated to lower temperatures, the ethene concentration would even be higher. This supports the work of van den Berg *et al* [100] who, by producing high concentrations of ethene at these relatively low reaction temperatures, concluded that the initial hydrocarbon formed was ethene.

The higher olefins are formed through the methylation of ethene [99,100], and by raising the temperature there is an increase in the rate of methylation and consequently an increase in the C_3 to C_5 olefin concentration. Propene must be formed by this way, but butenes can be formed either through a double methylation or via dimerisation of ethene [111]. The C_3 to C_5 olefin fraction, as shown in Table 4.4, consisted of about 63 % propene and 28 % butenes. As the single methylation product, propene should be twice as plentiful as the double methylation product, butene, it is probable that most of the butenes are formed this way, and only a small amount are derived from dimerisation.

Naturally as a result of the methylation to form propene and other olefins, there must be a simultaneous concomitant decrease in the concentration of ethene. This is obvious in Figure 4.4 over the temperature range of 300 °C to about 400 °C, and that in this temperature range ethene is predominantly a reactant. At around 400 °C, the ethene yield was at its minimum, and when conditions

are not conducive to producing olefins, it is easy to understand why little ethene is detected, as occurred in the case of the experiments by Anderson *et al* [91].

Figure 4.4 shows that as the reaction temperature is increased beyond 400 °C, the ethene selectivity starts to increase. This can only mean that under these conditions the ethene is now a product being formed by another reaction. Working at these temperatures Dessau *et al* [107-109] found that the cracking of propene back to ethene becomes significant; the higher the temperature, the faster the cracking. This was confirmed by the results in Figure 4.4, where as the reaction temperature was increased the concentration of ethene in the product began to rise, and this trend was found to be valid as the temperature was increased up to 550 °C.

The cracking activity of ZSM-5 increases as its aluminium content increases [95]. By moving from right to left in Figures 4.7 and 4.8, the silica to alumina ratios of the ZSM-5 are decreased (i.e. its aluminium contents were increased), and meant that their cracking activities were increased. Under these circumstances, and with a reaction temperature of 450 °C, the amount of ethene being produced increased, and this was due to more severe cracking of propene and other olefins. The same conclusion can derived from the data in Figure 4.4, where two samples of ZSM-5 having different silica to alumina mole ratios of 605 : 1 and 170 : 1, were examined over a large temperature range.

As mentioned above, increasing the temperature increases the rate of methylation and an increase in the C_3 to C_5 olefin concentration. Referring to Figure 4.4, it can be seen that up to a temperature of 500 °C, the proportion of C_3 to C_5 olefins did increase due to faster methylation taking place. However, beyond this temperature the concentration of C_3 to C_5 olefins eventually start to decrease as the cracking of these olefins back to ethene began to predominate.

CONCLUSIONS

The zeolite ZSM-5 that would be suitable for the conversion of methanol to light olefins, should have a low concentration of active sites. This means it should contain a relatively low concentration of aluminium atoms. It has been shown that the concentration, expressed in terms of its silica to alumina mole ratio should be around 400 : 1.

If ZSM-5 is synthesised with the aid of tetrapropylammonium compounds, there are no problems in preparing a product with this composition. A search for an alternative organic structure directing agent that could still lead to siliceous ZSM-5, found that 1,6-diaminohexane was successful. A disadvantage when using 1,6-diaminohexane is that it simultaneously forms unwanted zeolite ZSM-48, unless certain precautions are taken. This is mainly that the silica to alumina mole ratio be restricted to a narrow range of about 150 to 200 : 1. The product naturally contains too much aluminium for the ideal catalyst, which then has to be subsequently partially de-aluminated through calcination at 500 °C in the presence of steam, to increase its silica to alumina ratio.

The configuration of the ZSM-5 crystals synthesised with α,ω-diaminoalkanes has the amine groups located at intersections of the channels of the zeolite, and the hydrocarbon chain themselves are in the channels. Of all diamines, the size of 1,6-diaminohexane makes it fit neatly into this arrangement. It requires a temperature in the region of 450 °C to remove it, and therefore 1,6-diaminohexane must act as a good template during crystallisation of ZSM-5. As a result of being incorporated into the ZSM-5 structure, 1,6-diaminohexane undergoes partial de-amination. With the remaining part of the organic compound there is some interaction between the carbon atoms and the zeolite.

Molecules of 1,6-diaminohexane are not as effective as tetrapropylammonium compounds in causing the crystallisation of ZSM-5. Therefore, it is preferable that the synthesis mixture also include a small amount of tetrapropylammonium cations which would initiate or "seed" the crystallisation of ZSM-5. No other special conditions had to used to prepare ZSM-5 with the aid of 1,6-diaminohexane, and therefore it would be possible to carry out the synthesis process on an industrial scale. It was further shown that it could include the recycling of the filtrate which contains the excess chemicals not used in the formation of the crystallites. This would naturally reduce both the subsequent effluent control and amount of raw materials required. Under these conditions the raw materials required, including the alumina binder needed to make extrudates, form only about 6 % of the total cost of the finished catalyst.

A suitable catalyst for the selective conversion of methanol to light olefins can be made from ZSM-5 synthesised with 1,6-diaminohexane. Before being used, the synthesised ZSM-5 has to be detemplated, freed of sodium cations, formed into extrudates with alumina and finally steam calcined to decrease its aluminium content. In the conversion of methanol with the catalyst just mentioned, the main conditions needed in the reaction to give a high selectivity of light olefins, are that the temperature should be around 450 °C and that the partial pressure of the methanol feed should be about 0,2 bar. The latter requirement is readily obtained by using a aqueous feed containing 30 % methanol. Under these conditions, light olefin selectivities in excess of 70 % are obtained.

The remainder of the product spectrum for the conversion of methanol consisted of aromatics and light alkanes. The conditions specified above were optimised for the conversion of methanol to olefins, and included the reaction temperature of 450 °C. This temperature is also conducive to the subsequent formation of aromatics from the olefins already formed. Therefore, it is unavoidable to prevent the simultaneously formation of small amounts

of aromatics, and a certain fraction will always be encountered in the process. However, the high temperature and low pressure being used are not favourable for forming long chain oligomers, and consequentially few of these compounds are to be found in the product.

An initial dehydration of methanol gives dimethyl ether. The next stage of the reaction consists of the formation of ethene, and it is clearly the primary olefin formed. The other larger light olefins are mainly formed through methylation of ethene, with the rate of methylation increasing as the reaction temperature raised. Opposing this reaction is the cracking of these products back to ethene, with again the rate increasing with temperature. At the operating temperature of 450 °C mentioned above, the rate of cracking is not too severe and methylation predominates. Consequently, the biggest portion of the product spectrum would be propene, and to a lesser extent butene. The process gives only around 15 % ethene.

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APPENDICES

A. ANALYSIS OF RESULTS FROM GAS CHROMATOGRAPHS

1. GC RESULTS FROM CONVERSION OF METHANOL

The temperature programme for the GC column filled with *Porapak Q* (mesh 80 /100) and nitrogen as the carrier gas, was initially isothermally kept at 70 °C for 3 min., followed by heating at 10 °C / min. until reaching 220 °C, and then being maintained at this final temperature until no more products were detected. An example of the results obtained on the GC trace from preparation 15-E being reacted at 450 °C, is shown in Figure 6.1.

The temperature programme for the second GC column filled with F-1 grade active alumina (mesh 80 / 100) and nitrogen as the carrier gas, was initially kept isothermally at 70 °C for 3 min., followed by heating at 2 °C / min. until reaching 120 °C, and then being maintained at this temperature for 10 min. At this point all the relevant information regarding products up to C_4 had been obtained, and the temperature of the column was then ramped a second time by heating at 10 °C / min. until reaching 300 °C and then been kept at this high temperature to clear the column. The GC trace from the same experiment on sample 15-E is shown in Figure 6.2.

The identification of the products responsible for the presence of a particular peak were determined and are shown in Table 6.1. Only hydrocarbons were in the product and as these compounds have a similar response factor [181], the normalised area measured by the integrator under each peak is directly proportional to the mass of the particular component present. From these values the concentration of each component was either read directly or calculated, and the results are also given in the table.

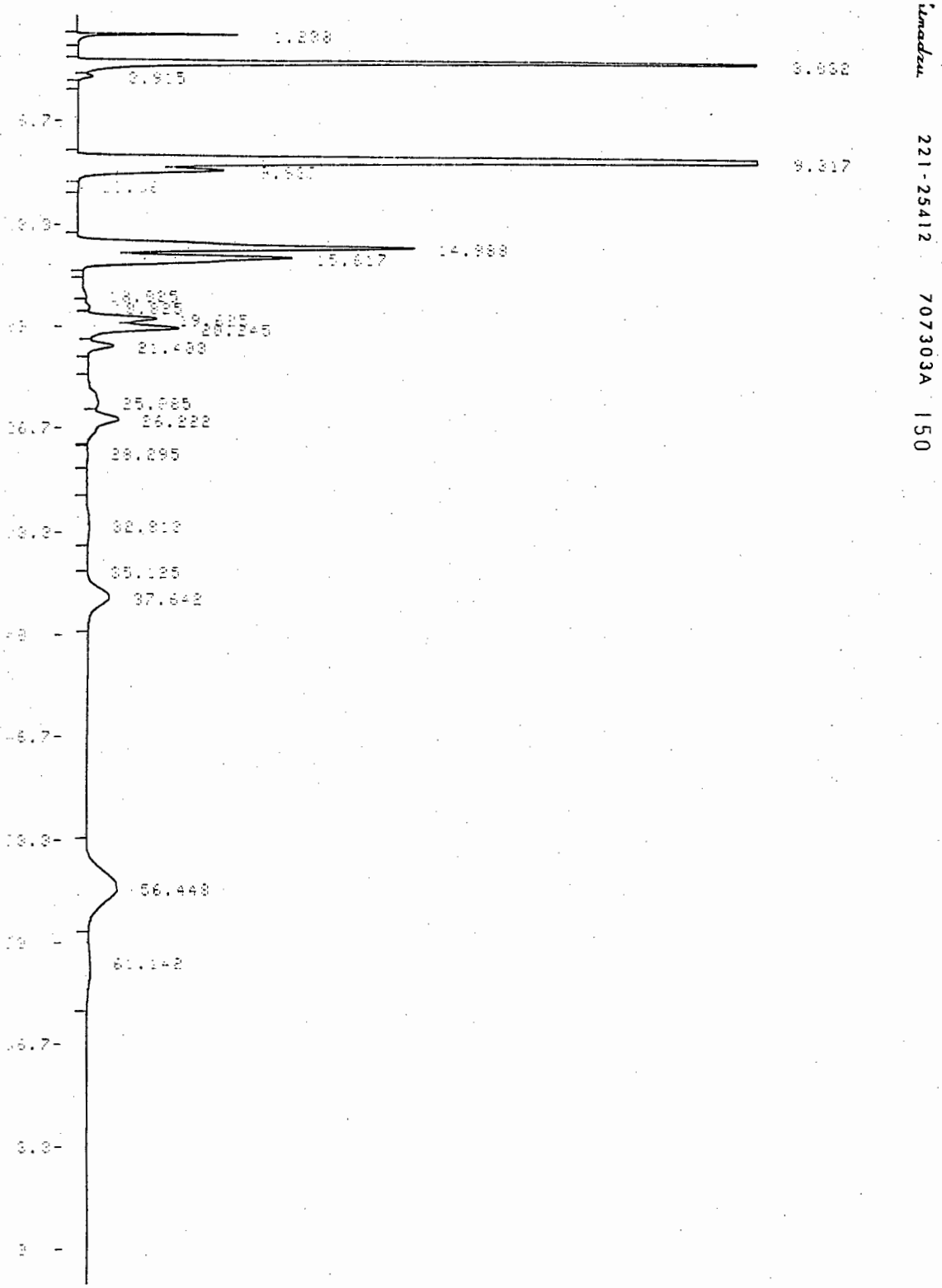


Figure 6.1. Porapak Q column gas chromatograph showing the products obtained from the conversion of methanol using the catalyst made from preparation 15-E.

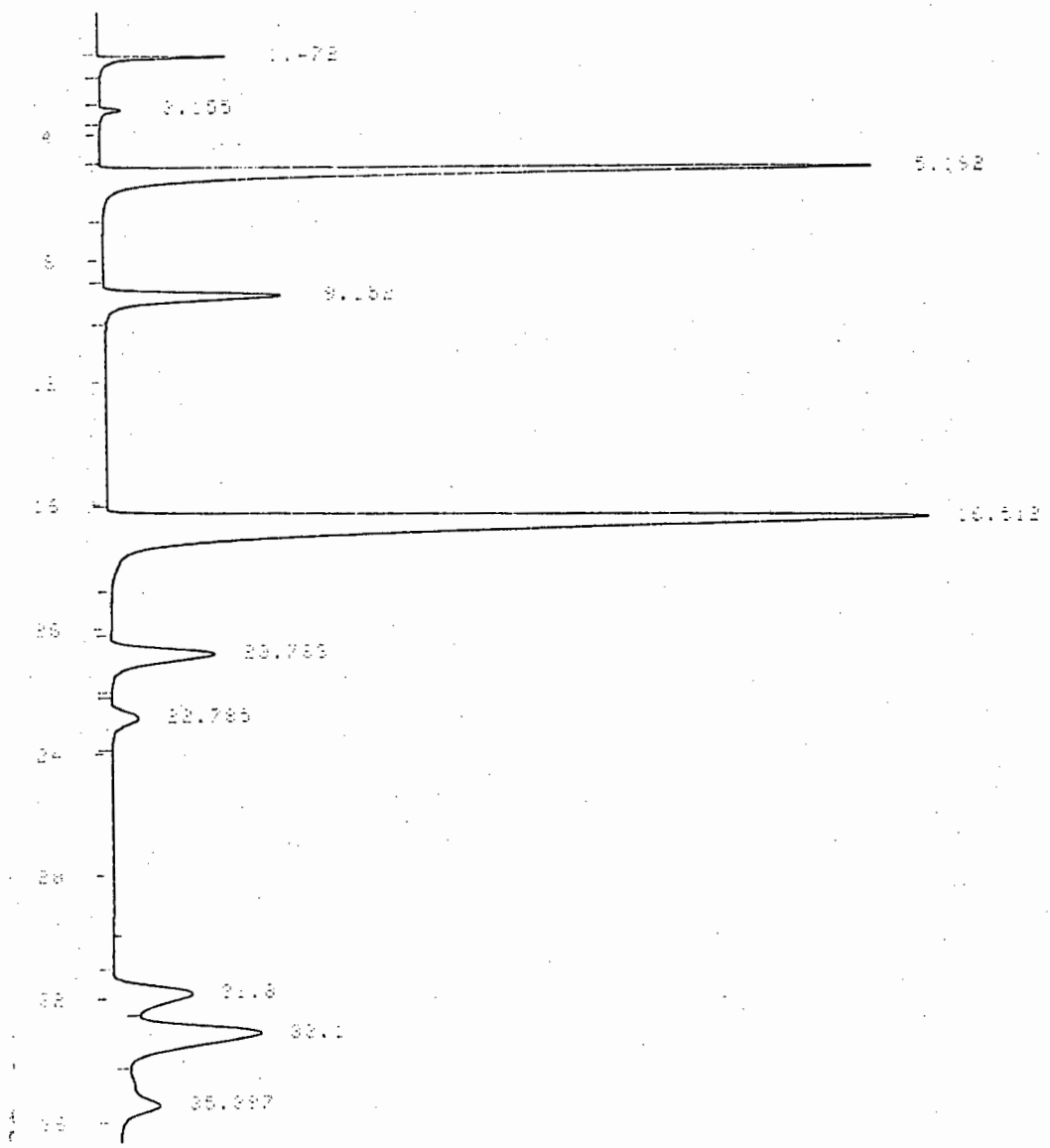


Figure 6.2. F-1 active alumina column gas chromatograph showing the products obtained from the conversion of methanol using the catalyst made from preparation 15-E.

Table 6.1. Identification of the peaks from the gas chromatographs and determination of the quantities of products formed from the conversion of methanol to light olefins.

Product	Porapak Q column		Alumina F-1 column		Average value %
	Retention time min.	Concent. %	Retention time min.	Concent. %	
methane	1,24	1,22	1,47	0,94	1,08
ethene	3,03	16,88	5,19	15,10	15,99
ethane	3,92	0,17	3,16	0,25	0,21
propene	9,32	35,34	16,51	31,64	33,49
propane	9,94	4,61	9,15	4,19	4,40
i-butene	14,99	12,43	31,80	4,05	16,13
n-butene			33,10	8,59	
t-2-butene					
c-2-butene			35,38	3,49	
i-butane	15,62	8,54	20,78	3,76	4,84
n-butane			22,79	1,08	
Total C_4		20,97		20,97	
pentene	18,03	3,02			
	18,83				
	19,63				
pentane	20,25	4,87			
	21,40				
C_6	25,09	1,18			
	26,22	2,32			
C_7	37,64	2,49			
C_8	56,45	6,12			
	61,14	0,98			

2. GC RESULTS FROM CONVERSION OF 1-OCTENE

The temperature programme for the main GC column filled with 3 % silicone OV-101 on Chromosorb W-HP (mesh 100 / 120) and nitrogen as the carrier gas, was initially isothermally kept at 50 °C for 1 min., followed by heating at 2 °C / min. until reaching 80 °C, then a second ramping of the temperature by heating at 10 °C / min. to reach 220 °C, and being maintained at this final temperature for a further 10 min. The total time for the programme was 40 min. An example of the results obtained on the GC trace from preparation F-34 with 3 % ZnO being reacted at 470 °C, is shown in Figure 6.3.

Both the off-line GC columns were filled with with *Porapak Q* (mesh 80 / 100) and nitrogen was used as the carrier gas. The temperature programme for the determination of the light hydrocarbon gases, was initially kept isothermally at 70 °C for 3 min., followed by heating at 10 °C / min. up to 220 °C and being maintained at this temperature for about 12 min. An example of the results obtained on the GC obtained from same experiment with preparation F-34 with 3 % ZnO is shown in Figure 6.4. For the determination of hydrogen, the column was isothermally controlled throughout at 50 °C.

The identification of the products responsible for the presence of a particular peak were determined and are shown in Table 6.2. Only hydrocarbons were in the product and as these compounds have a similar response factor [181], the normalised area measured by the integrator under each peak is directly proportional to the mass of the particular component present. From these values the concentration of each component was either read directly or calculated. The amount of hydrogen present was measured from a direct calibration. The determination of all the concentrations are given in Table 6.2.

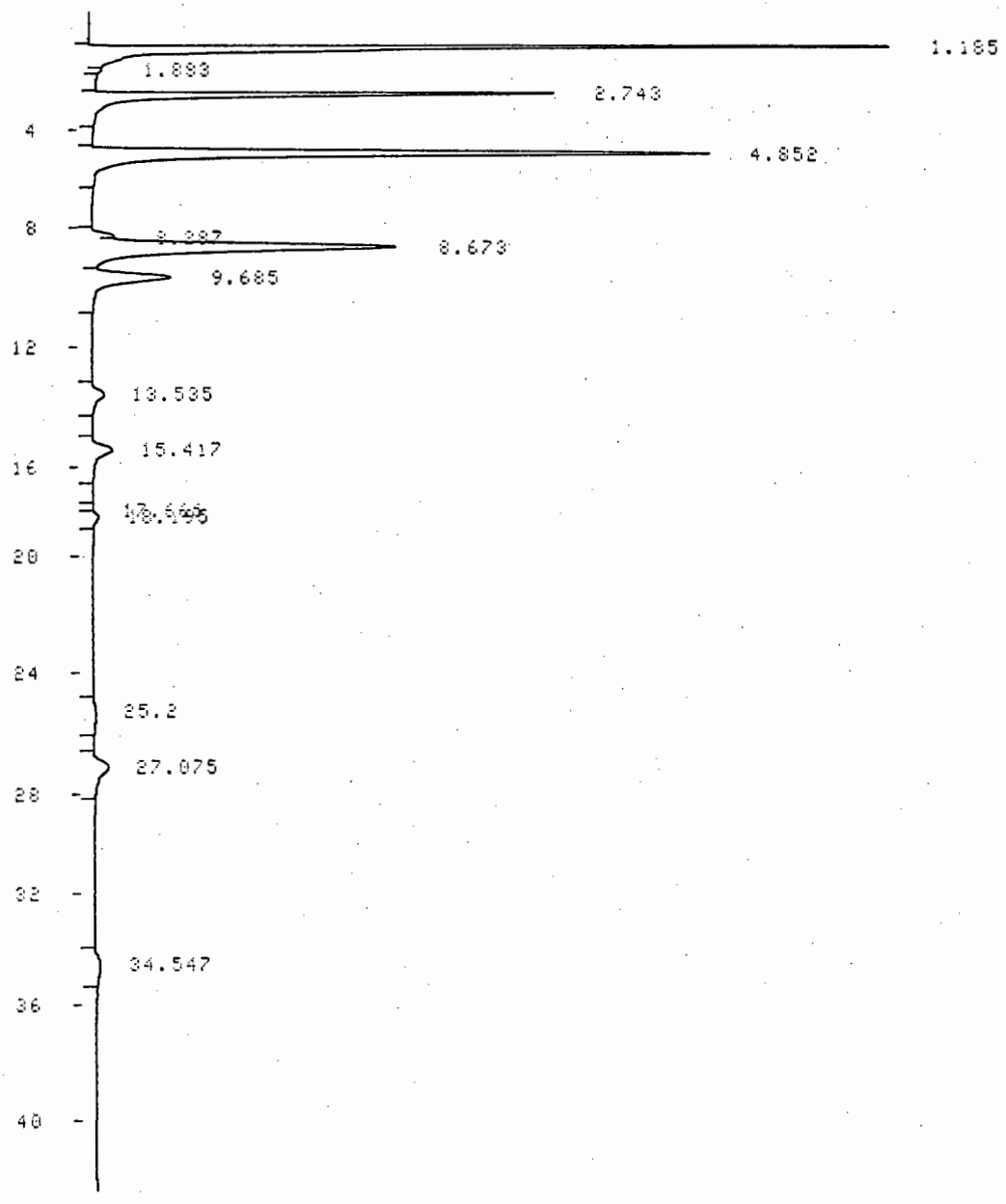


Figure 6.3. 3 % silicone OV-101 column gas chromatograph showing the products obtained from the conversion of 1-octene using the catalyst made from preparation F-34 and 3 % ZnO.

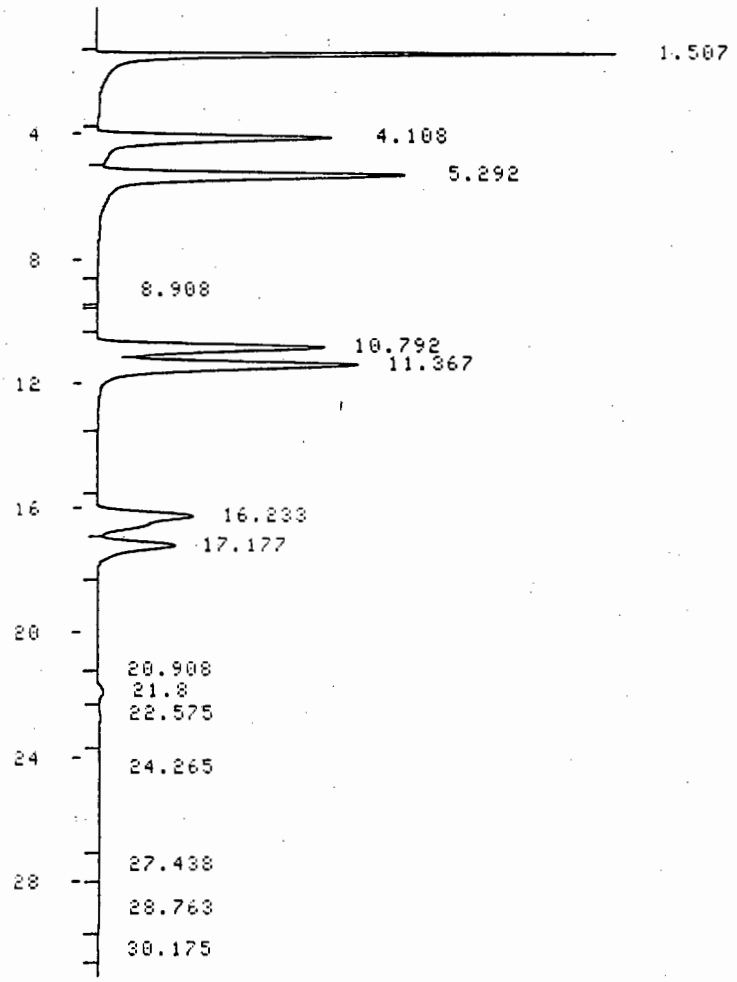


Figure 6.4. Porapak Q column gas chromatograph showing the light hydrocarbons products obtained from the conversion of 1-octene using the catalyst made from preparation F-34 and 3 % ZnO.

Table 6.2. Identification of the peaks from the gas chromatographs and determination of the quantities of products formed from the conversion of 1-octene to BTX.

Product	3 % sil. OV-101 column		Porapak Q column		Average value %
	Retention time min.	Concent. %	Retention time min.	Concent. %	
hydrogen					1,16
methane			1,51	4,28	
ethene			4,12	3,71	
ethane			5,29	5,38	
propene			10,79	3,76	
propane	1,19	26,75	11,38	4,97	26,75
butene			16,23	2,47	
butane			17,18	1,63	
pentene			21,80	0,33	
pentane			22,58	0,22	
C_6	1,88	0,04			
Benzene	2,74	13,91			
Toluene	4,85	27,29			67,04
o-Xylene	8,29	0,86			
p-Xylene	8,67	19,35			
m-Xylene	9,69	5,63			

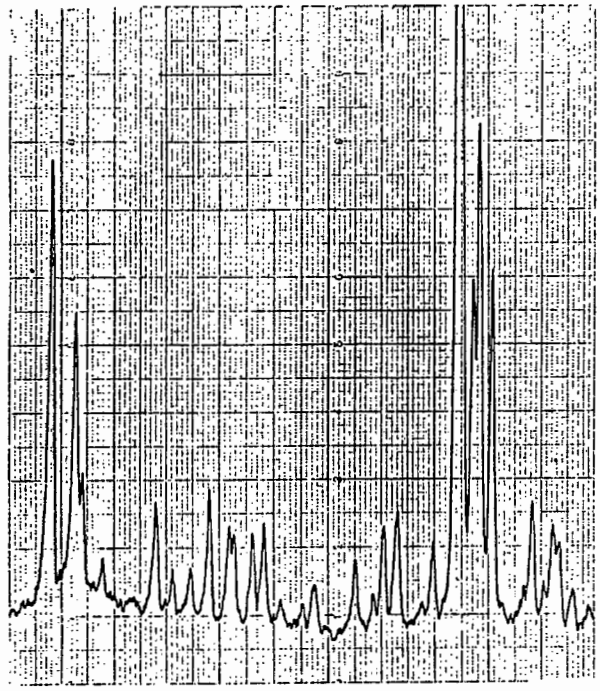
B. X-RAY DIFFRACTOGRAMS

The X-ray diffractions were determined by using CuK_{α} radiation generated from an X-ray tube at 40 kV and 20 mA, and scanning the samples from 14° to 3° θ. The diffractograms of typical examples and all the key preparations are reproduced in the appendix B, and they are:

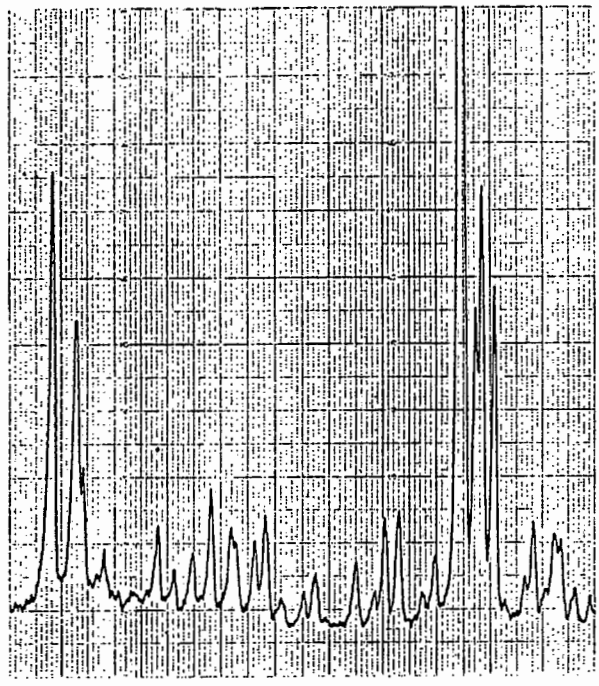
2-A and 4-A
2-B and 4-B
2-D and 4-D

1-E, 2-E, 3-E, 4-E, 5-E and 6-E
9-E and 10-E
11-E and 13-E

For the preparations from the A, B and D series, the sensitivity of the diffractometer was set to give a full scale deflection at 2000 counts per second (cps). For the samples from the E-series, the sensitivity of the diffractometer was set to give a full scale deflection at 4000 counts per second (cps). As the sensitivity in the case of the E-series was halved, equivalent diffraction peaks would be half the size as those measured with the preparation from the other three series.



Sample 2-A



Sample 4-A

3 14

Degrees θ

Figure 6.5. XRD of preparations 2-A and 4-A. Sensitivity 2000 cps.

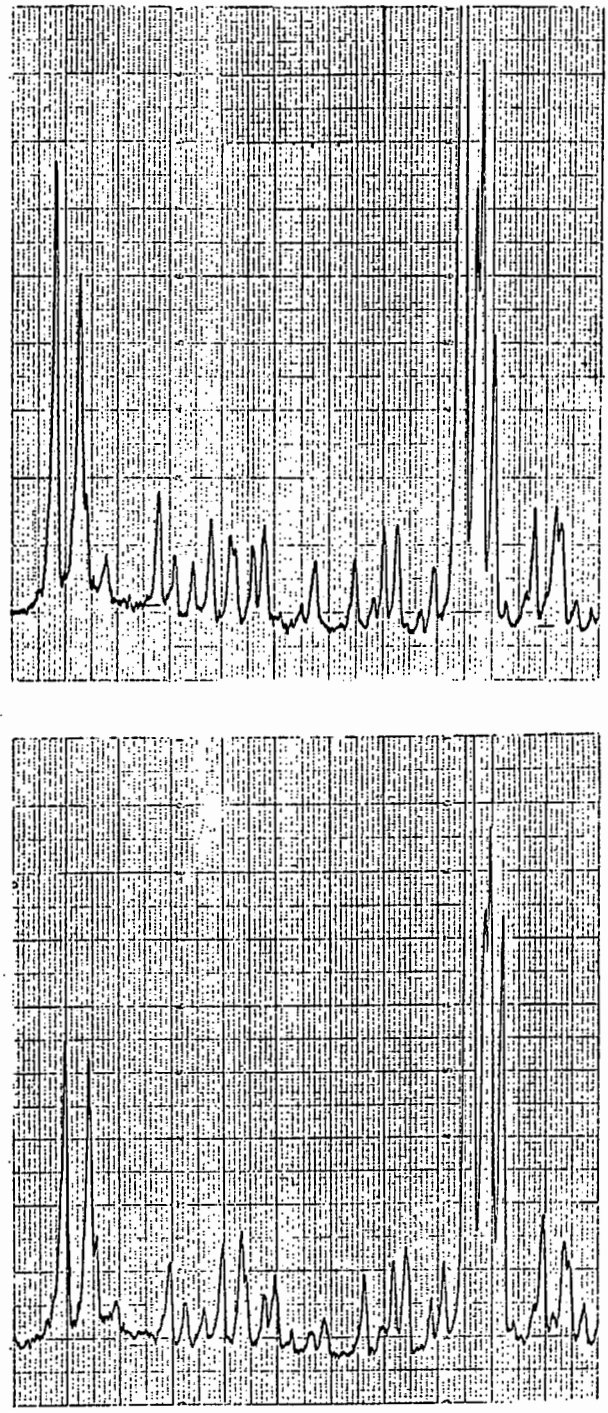
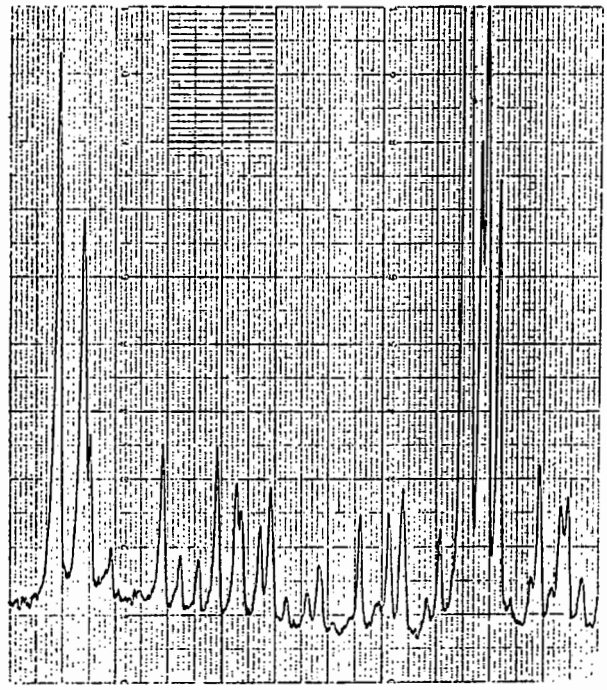
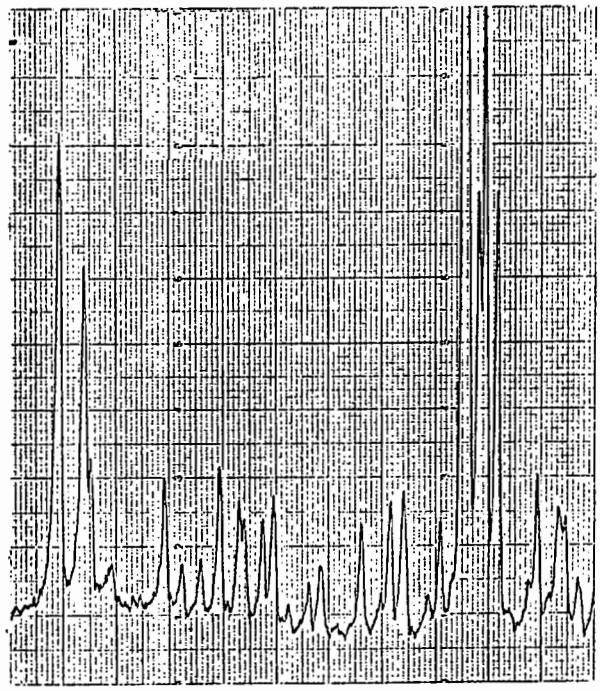


Figure 6.6. XRD of preparations 2-B and 4-B. Sensitivity 2000 cps.



Sample 2-D



Sample 4-D

3 14

Degrees θ

Figure 6.7. XRD of preparations 2-D and 4-D. Sensitivity 2000 cps.

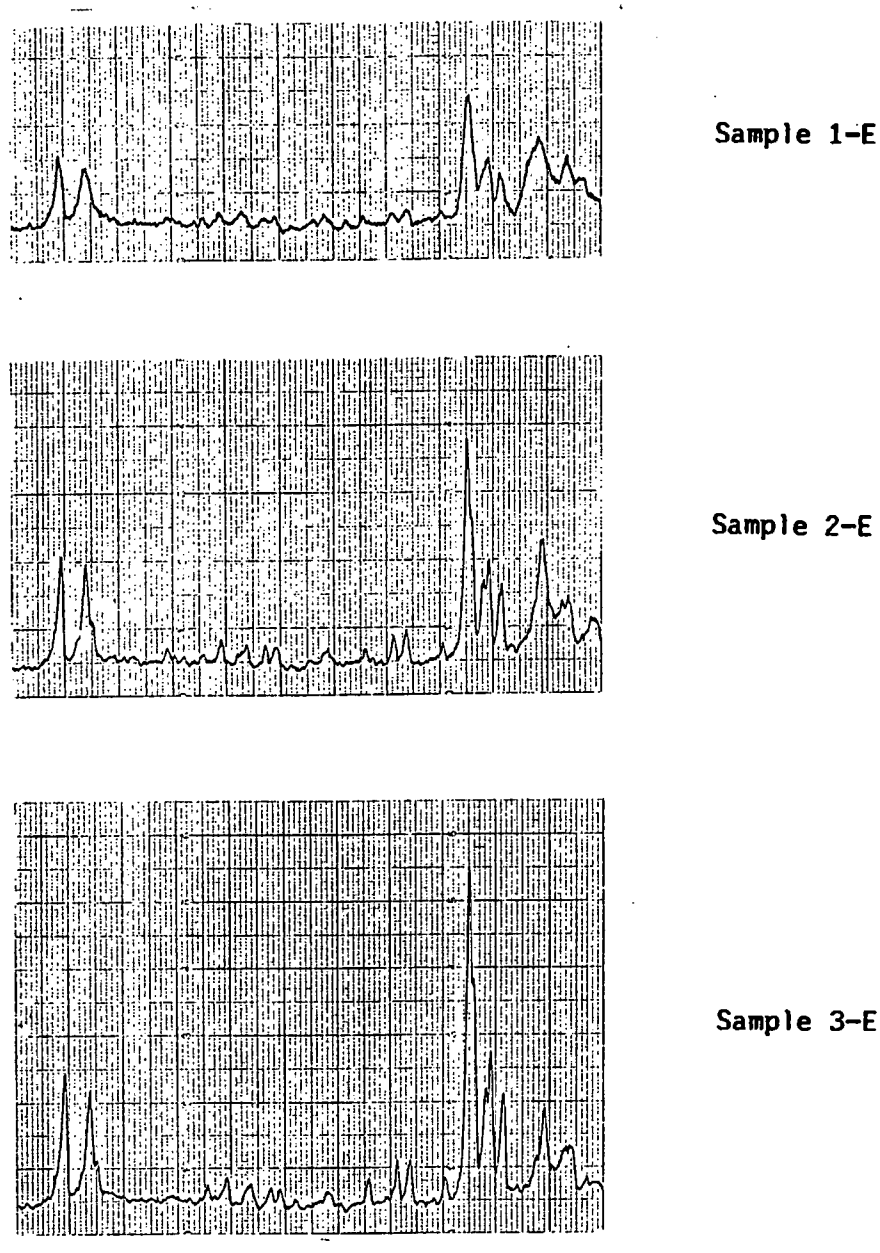


Figure 6.8. XRD of preparations 1-E, 2-E and 3-E. Sensitivity 4000 cps.

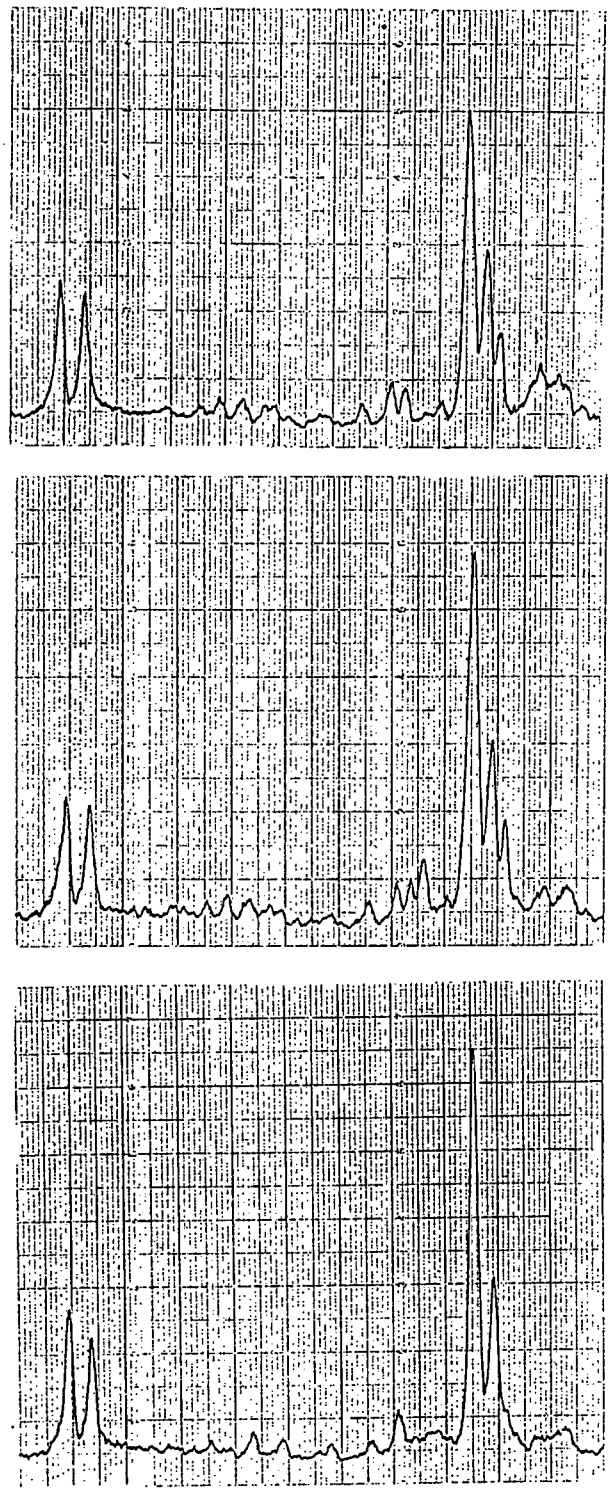


Figure 6.9. XRD of preparations 4-E, 5-E and 6-E. Sensitivity 4000 cps.

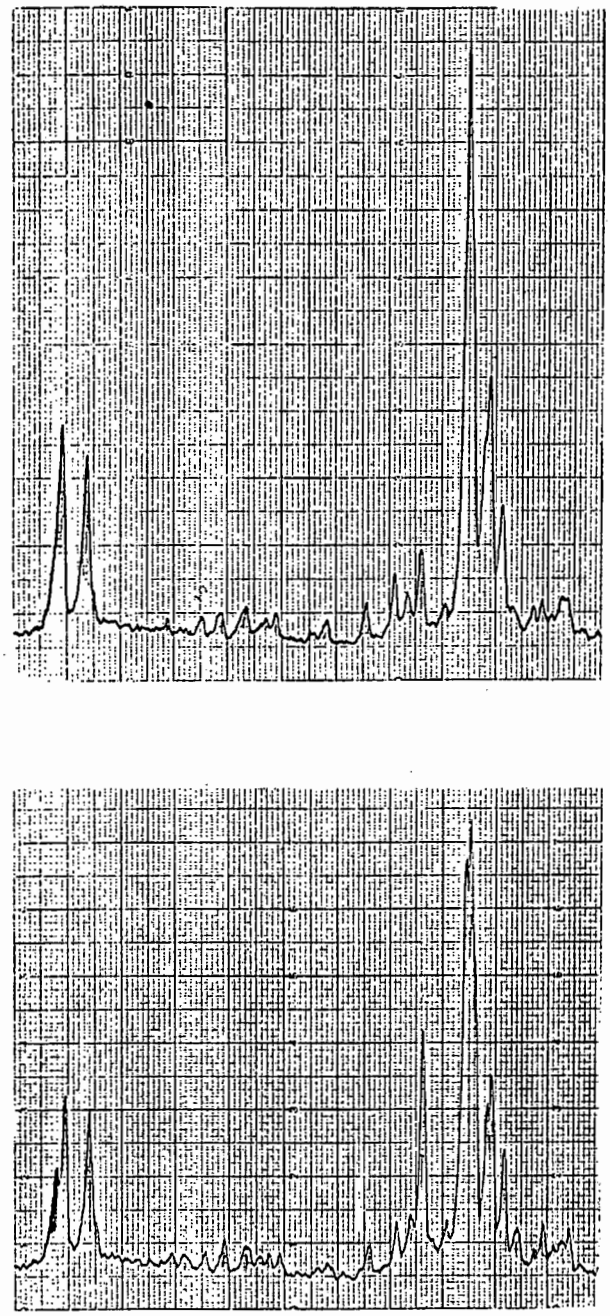
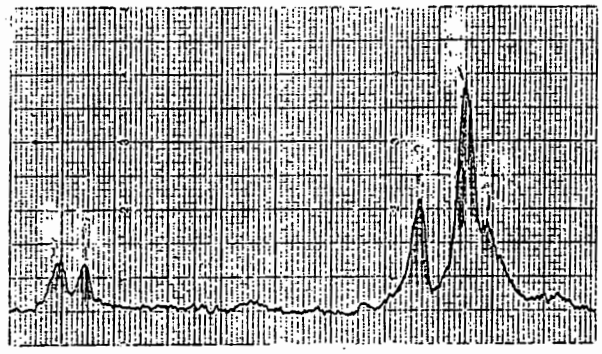
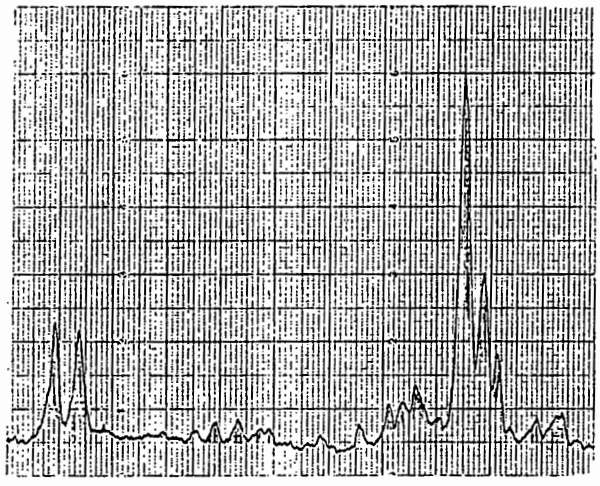


Figure 6.10. XRD of preparations 9-E and 10-E. Sensitivity 4000 cps.



Sample 11-E



Sample 13-E

3 **14**

Degrees θ

Figure 6.11. XRD of preparations 11-E and 13-E. Sensitivity 4000 cps.

C. MAGIC ANGLE SPINNING ^{13}C NUCLEAR MAGNETIC RESONANCE SPECTRA

The nature of the α,ω-diaminoalkanes in samples 2-E to 6-E were determined by MAS ^{13}C NMR. The spectra were recorded on the instrument operating at a frequency of 75,5 MHz, and spinning was carried out at 4 kHz. The C shifts were measured with respect to adamantane, which was used as an external standard.

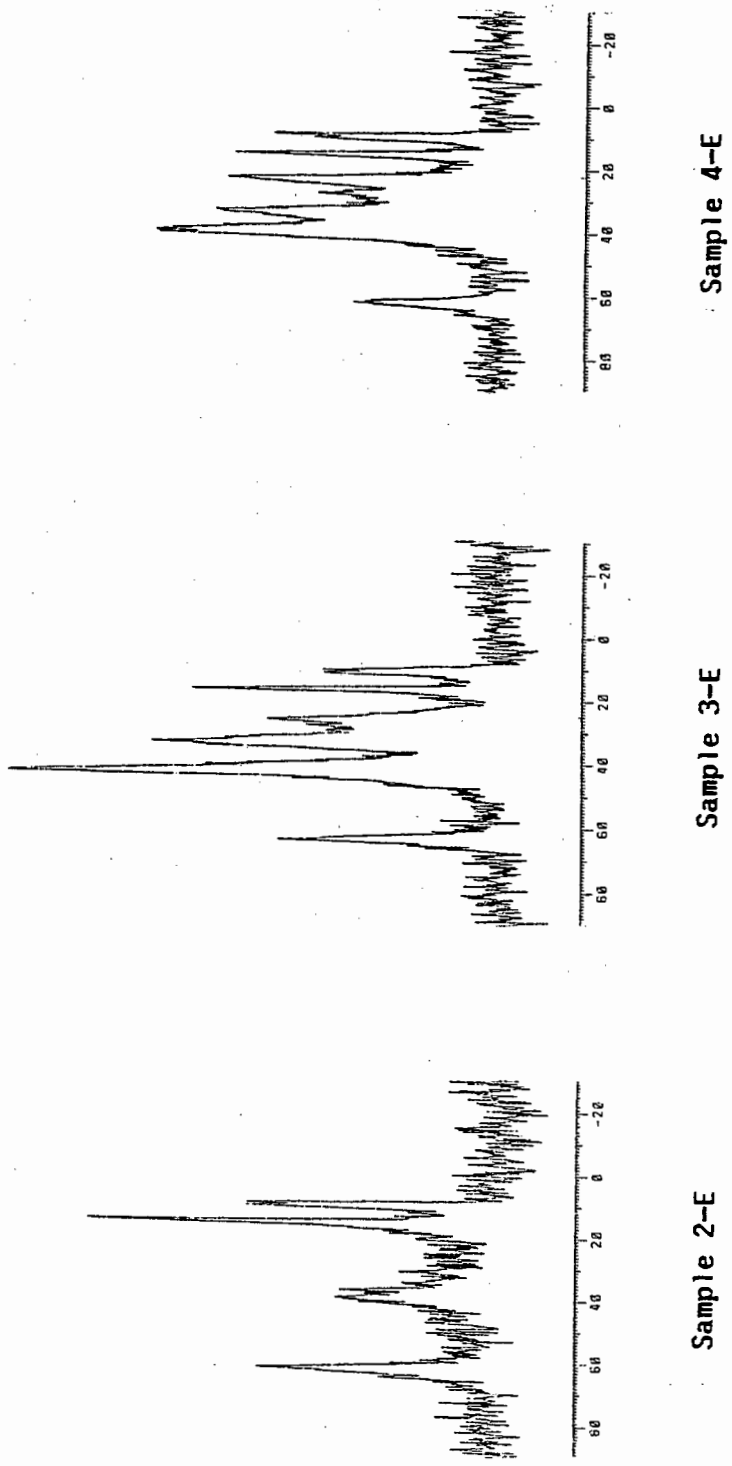


Figure 6.12. MAS ^{13}C NMR of preparations 2-E, 3-E and 4-E.

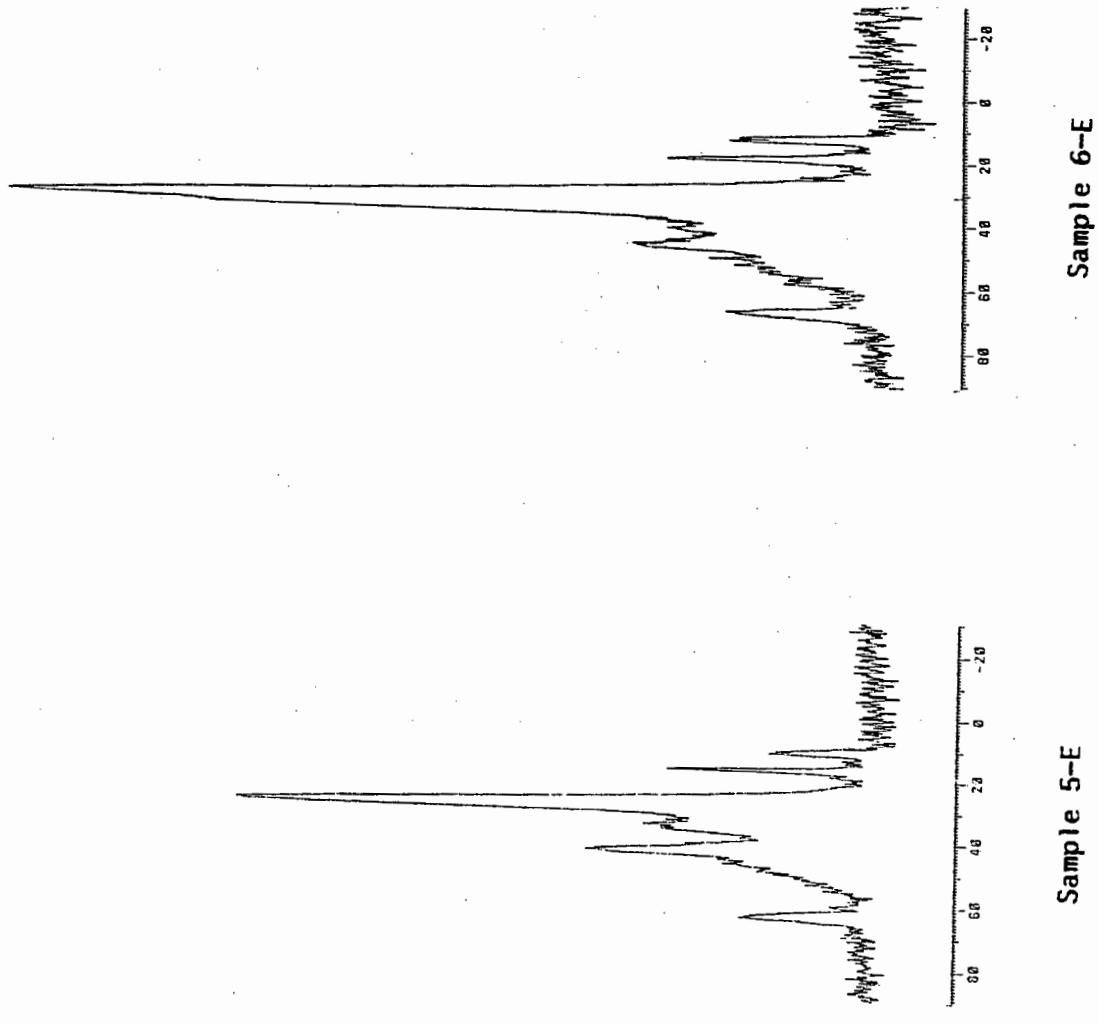


Figure 6.13. MAS ^{13}C NMR of preparations 5-E and 6-E.

D. MICRO-SIEVE ANALYSIS OF PSEUDO-BOEHMITE

The results of the micro-sieves analysis of the six sources of pseudo-boehmite that were investigated are shown in Table 6.3. These results were plotted on a log-probability graph, which is shown in Figure 6.14, to give the particle size distribution.

Table 6.3. Micro-sieve analysis of samples of pseudo-boehmite

Sieve size µm	Cumulative percentage by mass finer than stated size					
	LaRoche Versal 250	Dyson Dycat 052	Condea Pural SCF	Akzo Ketjen H	Condea Pural SB	LaPorte Actal KH
75					86,0	88,0
40	99,6	89,5	98,0	81,0	53,5	60,0
20	96,0	73,5	58,5	44,5	21,5	14,0
10	64,0	58,5	25,0	19,5	11,5	3.5
5	28,0	44,5	6,0	7,0		

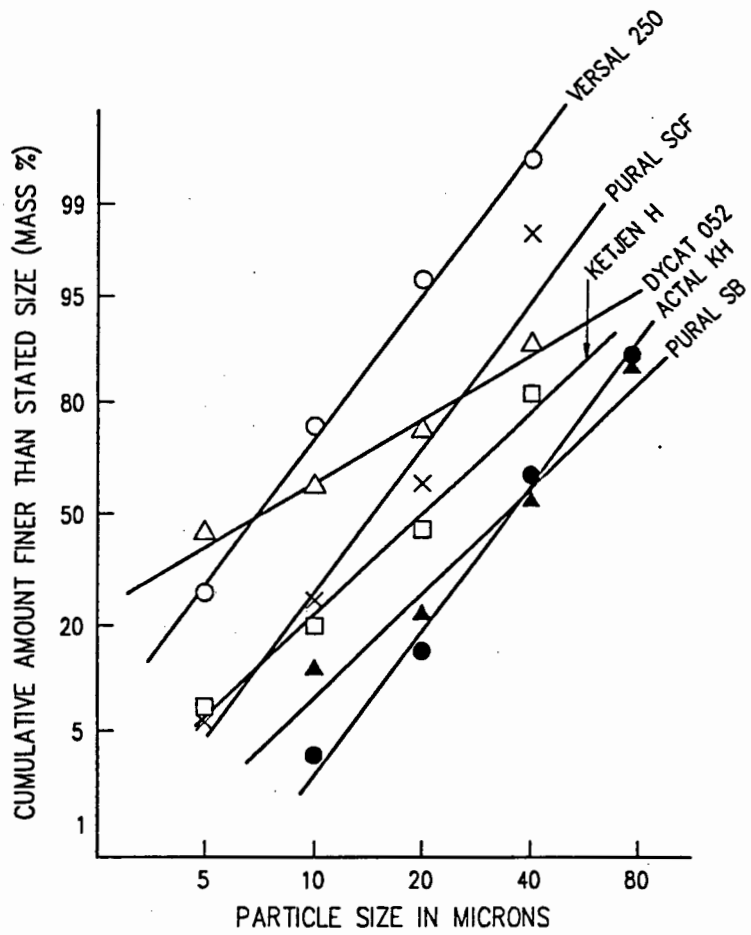


Figure 6.14. Particle size distribution of samples of pseudo-boehmite.