

Product distribution directed modification of ZSM-5

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Abstract

Ethylene and propylene are important chemical feedstocks for the production of polyethylene and polypropylene. Ethylene and propylene can be produced by various methods including steam cracking of liquefied natural gas (LNG), naphtha or light olefin fractions. The methanol to olefin (MTO) process provides an alternative means of producing ethylene and propylene, where ZSM-5 is frequently used as catalyst due to its hydrophobicity, strong acidity, molecular sieve properties and low tendency towards coking, which makes ZSM-5 one of the most popular zeolite catalysts in the industry. The oil crisis 1973 and the second oil crisis in 1978 caused the development of a commercial MTO process. Mobil Research and Development Corporation built a fixed-bed pilot plant to demonstrate the feasibility of the MTO as well as methanol-to-gasoline (MTG) process. When the oil price dropped again during the 1980's, further developments of commercial processes were stopped for the time being. However, investigations on a bench scale are still pursued, and applications for patents are still submitted.

During this study ZSM-5 was synthesized with a hydrothermal method, which produced agglomerated polycrystalline grains with characteristic ZSM-5 morphology and a Si/Al ratio of approximately 40. The synthesis time, synthesis temperature and aging time were varied while keeping all the other synthesis parameters constant in order to determine their influence on crystallite size. The synthesis time was varied between 12-72 hours, synthesis temperature was varied between 130-170°C and aging time between 30-90 minutes. Using SEM to determine crystal size, it was found that a variation in the aging time produced the largest crystallites (average of $21.6\mu\text{m} \pm 10.8\mu\text{m}$) while also having the largest influence on crystallite size followed by synthesis temperature (average of $13.1\mu\text{m} \pm 4.9\mu\text{m}$) and finally synthesis time (average of $5.7\mu\text{m} \pm 0.4\mu\text{m}$). In all cases XRD and SEM confirmed the formation of ZSM-5.

To evaluate the as-synthesized ZSM-5 and compare it to a commercial ZSM-5 catalyst, Catalyst A using the MTO process, ZSM-5 was synthesized for 72 hours at 170°C with

an aging time of 60 minutes before synthesis. The as-synthesized as well as Catalyst A's agglomerated polycrystalline grains were sieved into three size fractions: smaller than 75µm, 75-150µm and 150-300µm. All six ZSM-5 fractions of ZSM-5 were used as catalysts for the MTO process in a fixed bed reactor at 400°C, atmospheric pressure and a 20wt% methanol to water feed. At 3.5 hours time on stream (TOS), the intermediate 75-150µm fraction had the highest light olefin selectivity for both the as-synthesized as well as Catalyst A, followed by the 150-300µm fraction and finally the smaller than 75µm fraction with the lowest light olefin selectivity. From this results it is clear that the as-synthesised ZSM-5 did not perform as well as Catalyst A.

While the intercrystalline voids of the agglomerated ZSM-5 form second-order pores where self-diffusion is enhanced, the increased diffusional barriers created by the intercrystalline boundaries reduce the diffusion rate, promoting secondary reactions at the strong Brönsted acid sites thereby reducing ethylene and propylene selectivity. Coking reduces access to the Brönsted acid sites and plays a more influential role for smaller crystallite sizes. Accordingly, the smaller than 75µm fraction had the lowest light olefin selectivity, while the 150-300µm fraction was probably least influenced by coking. The increased pathways for products and reagents in the 150-300µm fraction resulted in more secondary reactions taking place within this catalyst than the 75-150µm fraction explaining the superior performance of the 75-150µm fraction. Since the grain size determines the ratio of the external to the internal surface areas as well as the amount of intercrystalline boundaries in the catalyst, it follows that the catalytic activity and polycrystalline grain size ratio should actually be tailored when optimising the product distribution of the ZSM-5 catalysed MTO process. The as-synthesized ZSM-5 didn't perform very well when compared to Catalyst A and modification of the synthesis method is recommended.

Keywords: Zeolites, ZSM-5, Methanol to olefins, Brönsted acid, zeolite synthesis.

Table of contents

Acknowledgements	ii
Abstract	iii

Chapter

1. Introduction	1
1.1. General overview.....	2
1.2. Problem statement	3
1.3. Aim and objectives	4
1.4. Structure of dissertation.....	4
1.5. References	5
2. Literature overview: ZSM-5 as catalyst for the MTO process	7
2.1. Introduction.....	7
2.2. Zeolites	9
2.4. Synthesis parameters.....	13
2.4.1. <i>Synthesis temperature</i>	16
2.4.2. <i>Synthesis time</i>	16
2.4.3. <i>Aging time</i>	17
2.5. Methanol to olefins reaction (MTO)	17
2.6. Conclusion.....	19
2.7. References	20
3. Experimental investigation of ZSM-5 synthesis	23
3.1. Introduction.....	24

3.2. Experimental.....	24
3.2.1. <i>Synthesis of ZSM-5</i>	24
3.2.1.1. Preparation of the synthesis solution	24
3.2.1.2. Synthesis.....	25
3.2.1.3. Synthesis of ZSM-5 at varied synthesis conditions	26
3.2.2. Ion exchange of Na-ZSM-5 to H-ZSM-5	26
3.2.3. MTO reaction	26
3.3. Characterisation	28
3.3.1. <i>XRD</i>	28
3.3.2. <i>SEM and EDS</i>	28
3.3.3. <i>ICP</i>	29
3.3.4. <i>TPR-TPO-MS</i>	29
3.4. References	30
4. ZSM-5 synthesis	35
4.1. Introduction.....	32
4.2. Synthesis of ZSM-5	32
4.3. Synthesis of ZSM-5 at varied synthesis parameters.....	36
4.3.1. <i>Influence of synthesis time</i>	36
4.3.2. <i>Influence of temperature</i>	40
4.3.3. <i>Influence of aging time</i>	42
4.4. Conclusion.....	46
4.5. References	47
5. ZSM-5 as catalyst for the MTO process	49
5.1. Introduction.....	50

5.2. As-synthesised ZSM-5	50
5.2.1. <i>Smaller than 75μm</i>	50
5.2.2. <i>75-150μm</i>	56
5.2.3. <i>150-300μm</i>	59
5.2.4. <i>Effect of fraction size on the MTO product distribution</i>	62
5.3. Catalyst A	66
5.3.1. <i>Smaller than 75μm</i>	66
5.3.2. <i>75-150μm</i>	69
5.3.3. <i>150-300μm</i>	71
5.3.4. <i>Effect of fraction size on the MTO product distribution</i>	73
5.4. Deactivation and coking.....	76
5.5. Conclusion	78
5.6. References	79
6. Evaluation and recommendations	80
6.1. Introduction.....	81
6.2. Zeolite synthesis.....	83
6.3. MTO process.....	84
6.4. Evaluation.....	88
6.4. Recommendations.....	90
6.6. References	90

Chapter 1

Introduction

1.1. General overview	2
1.2. Problem statement.....	3
1.3. Aim and objectives	4
1.4. Structure of dissertation	4
1.5. References	5

Chapter 1

1.1. General overview

The coal to liquid (CTL) process produces synthesis gas and from this variety of chemicals, methanol can be synthesised. Methanol can be converted via various routes to hydrocarbons (MTHC) in the presence of an acidic catalyst (Figure 1.1) [1].

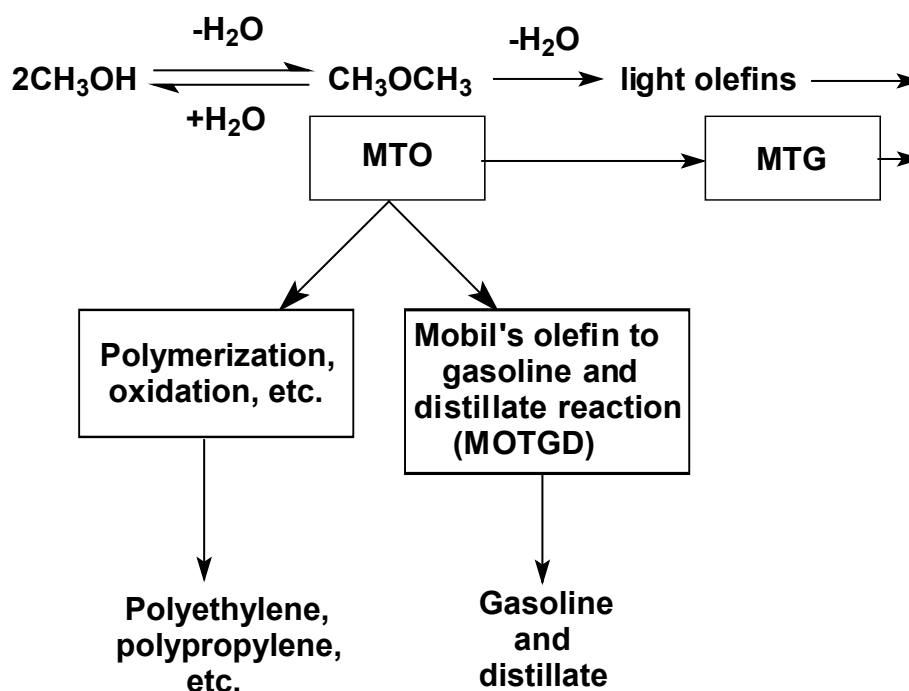


Figure 1.1: The MTO process [2].

Methanol can be converted to gasoline (MTG) or to olefins (MTO) using various catalysts and process conditions. The MTG process for example generally runs at around 400°C, using a methanol partial pressure of several bars and ZSM-5 as catalyst [2]. During the MTG process, light olefins form as intermediates which are converted to paraffins and aromatics using the appropriate catalyst. The hydrocarbons produced by the MTG process span a relatively narrow range of molecular weights, terminating at about C₁₀.

Since light olefins are very important to the petrochemical industry and the production of polyethylene and polypropylene, the methanol to olefins (MTO) process was developed. The reaction conditions were adapted from 400°C to 450°C or higher temperatures, in order to eliminate cyclisation, intermolecular hydride

transfer as well as other reactions that convert light olefins to paraffins and aromatics. The MTO process yields predominantly ethylene, propylene and butylene with high-octane gasoline as by-product [2]. ZSM-5 or SAPO-34 can be used as catalyst for the MTO process. Where light olefins are currently produced from the steam cracking of liquefied natural gas (LNG), naphtha or light petroleum fractions, the MTO process provides an alternative method [3].

Studies have been conducted to eliminate secondary reactions by modifying the ZSM-5 zeolite, for example by reducing the number and strength of the acid sites, since the acidity has an effect on the reaction path and the product distribution [4]. It has further been shown that the crystal size, as well as polycrystalline grain size in the case of intergrown crystals, influences both the catalytic and sorption properties of zeolites as well as the intracrystalline diffusion [4, 5]. The physiochemical properties of ZSM-5 can be modified by varying the type and composition of reagents as well as the alkalinity, while the size of the crystals or the agglomerated polycrystalline grains can be modified by varying the aging time, stirring tempo and temperature [4, 5].

1.1. Problem statement

Variables influencing light olefin yield include the zeolite crystal's pore geometry, acid strength and type as well as the crystal's size. In order to enhance the light olefin yield during the MTO process, the formation of paraffins and aromatics has to be reduced. This can be achieved by decoupling the secondary reactions that take place during the MTO process. The secondary reactions are influenced by the diffusional path of molecules through the zeolite, which is in turn influenced by the zeolite's size. The size of the crystals or agglomerated polycrystalline grains can be manipulated by varying synthesis parameters such as aging time, stirring tempo and synthesis temperature. While a significant amount of studies have been presented in terms of the optimisation of catalytic properties, information on the influence of ZSM-5's agglomerated polycrystalline grain size on the MTO product range is currently still lacking.

Chapter 1

1.2. Aim and objectives

The aim of the study is to compare as-synthesised ZSM-5 with a commercial catalyst (Catalyst A) as a function of particle size.

In order to achieve this goal, the synthesis time, synthesis temperature and aging time were varied to make ZSM-5 with different agglomerated polycrystalline grain sizes. The different sizes were then separated into three fractions ($<75\mu\text{m}$, $75\text{--}150\mu\text{m}$ and $150\text{--}300\mu\text{m}$) and used as catalyst for the MTO process in order to see which fraction of agglomerated polycrystalline grain sizes gives the highest light olefin yield.

1.3. Structure of dissertation

Chapter 2 covers the relevant literature about zeolites, ZSM-5 and the parameters influencing agglomerated polycrystalline grain size as well as the MTO process. Chapter 3 is an experimental chapter where detail about the experimental procedures, characterisation methods and the catalytic performance of the as-synthesized ZSM-5 is given. In Chapter 4, the results obtained from the synthesis of ZSM-5 are presented and discussed and in Chapter 5 the results obtained for the MTO reaction with different agglomerated polycrystalline ZSM-5 grain sizes as catalyst are presented and discussed. An evaluation of Chapter 4 and 5 is presented in Chapter 6 where recommendations are made for possible future studies.

1.4. References

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Chapter 2

Literature overview: ZSM-5 as catalyst for the MTO process

2.1. Introduction	7
2.2. Zeolites	9
2.3. ZSM-5	13
2.4. Synthesis parameters	15
<i>2.4.1. Synthesis temperature</i>	<i>16</i>
<i>2.4.2. Synthesis time</i>	<i>16</i>
<i>2.4.3. Aging time</i>	<i>17</i>
2.5. Methanol to olefins reaction (MTO)	17
2.6. Conclusion	19
2.7. References	20

2.1. Introduction

Zeolites are microporous crystalline aluminosilicates that have natural acidic properties that enable them to act as catalysts for various reactions. The type of zeolite used as a catalyst determines the type of reaction that will occur and the products that can be formed [1]. Zeolites have the following unique properties that make them valuable for the chemical industry [2]:

- Acidic and basic properties due to the Brönsted and Lewis acid sites with their conjugated bases.
- Ion-exchange ability
- Shape selective adsorption due to the unique channels of molecular dimensions
- High surface area due to the microporous and mesoporous structure
- Structural stability in acidic or basic media
- Thermal stability where some zeolites are able to withstand temperatures of up to 1000°C

ZSM-5 can be used as a catalyst for the conversion of methanol to olefins in the methanol to olefins (MTO) process, which yields ethylene and propylene (light olefins) as major products. The MTO process is of industrial importance as it is complimentary to the Fischer-Tropsch process for producing gasoline or an alternative for producing light olefins for polyethylene and polypropylene production [1]. The MTO process had its origins as Mobil's MTG process which was used to convert methanol to gasoline. Therefore, MTG could be seen as complimentary to the low temperature Fischer-Tropsch (FT) process which mainly produces wax and diesel while the high temperature FT process produces mainly gasoline. MTO itself is an alternative route to steam cracking technology for the production of light olefins for polyethylene and polypropylene synthesis. As the oil price increases, MTO will become more economically feasible and could also provide greater selectivity to propylene than steam crackers which produces mainly ethylene from naphtha.

ZSM-5 belongs to a well defined class of aluminosilicate zeolites of the structure type MFI (ZSM-FIVE and ZSM-5 from Zeolite Socony Mobil 5) and form part of the pentasil (5-membered ring) family of zeolites [3]. The unique catalytic properties of ZSM-5 have been attributed to its unique morphology and microporous crystal structure. The morphology of zeolites is dependent on crystal growth during zeolite synthesis. Various complex phases and reactions form during synthesis, including numerous soluble species, amorphous phases and polymerization reactions. These phases and reactions are influenced by physical effects such as stirring, aging and order of reactant addition [4]. Changes in synthesis parameters will therefore affect the zeolite's morphology and size. Smaller zeolite particles have shorter diffusional pathways through which the product and reactant molecules (when the reaction takes place inside the intercrystalline void volume) diffuse. A shorter diffusional pathway lead to a reduced amount of unwanted side-reactions taking place [5]. However, for smaller particles, the external, non-shape selective surface increase with respect to the shape selective acid sites inside the zeolite. This affects product selectivity in a negative way [6] and therefore the optimal balance between activity and selectivity will only be determined experimentally using various agglomerated polycrystalline grains sizes as catalyst for the MTO reaction [7].

2.2. Zeolites

Zeolites, derived from two Greek words *zeo* (that boils) and *lithos* (stone), are crystalline three-dimensional aluminasilicate supercages composed of TO_4 tetrahedra ($\text{T}=\text{Si}, \text{Al}$), where O atoms connect the neighboring tetrahedral [8]. When only Si atoms are present in the zeolite framework the framework is uncharged, but when some of the Si atoms are replaced by Al, the framework acquires a negative charge due the fact that Si has a +4 charge and Al only has a +3 charge. To ensure a neutral framework an extra framework cation, usually an alkaline, alkaline earth metal cation or H^+ is bound to one of the neighboring oxygens as shown in Figure 2.1 [9, 10]. These extra framework cations can easily be substituted which enables these zeolites to have ion-exchange properties [2, 8].

Chapter 2

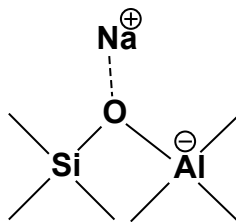


Figure 2.1: An Al containing zeolite with an extra framework cation [11].

The amount of Al in the framework can vary from $\text{Si/Al}=1$ to $\text{Si/Al}=\infty$. The Si/Al ratio cannot be below one because the placement of directly neighboring AlO_4^- tetrahedra in the framework is not favourable due to electrostatic repulsions between the negatively charged groups [3]. The amount of Si and Al in the framework is dependent on the synthesis conditions, but can also be changed by means of post-synthesis modifications. Apart from the influence on the ion-exchange properties, the Si/Al ratio influences the hydrothermal stability, hydrophobicity as well as the crystal size of the zeolite. As the Si/Al ratio increases, the hydrothermal stability as well as the hydrophobicity increases. The crystal size also increases with increasing Si/Al ratio [12]. Zeolites' thermal stability also depends on the Si/Al ratio. Low-silica zeolites are less thermally stable than high-silica zeolites [3].

Each zeolite type has a distinct pore structure formed by the way the Al-O-Si rings bind to each other. This enables zeolites to separate molecules of different sizes and shapes because of selectivity imposed by their pore structure as shown in Figure 2.2. ZSM-5 and other medium-pore zeolites impose restricted transition state as well as product selectivity [13, 14] which also gives them a high resistance to coke formation [15, 16, and 17].

The crystallinity of zeolites ensures that the pore structure is uniform throughout the crystal which enables zeolites to allow selective diffusion of molecules that differ in dimensions with less than 1 Å [1, 3, 8]. Zeolites' molecular sieve properties are applied for a variety of processes ranging from highly valuable, low flow streams that have to be separated or purified to household applications such as washing powders.

Zeolites contain both Lewis (Figure 2.3) and Brönsted (Figure 2.4) acid sites. A Brönsted acid can donate a proton, while a Lewis acid can accept an electron pair. Brönsted acids form where an OH-group links silicon and an aluminum atom in the zeolite framework (Figure 2.4). The OH-group forms because H^+ , which can be donated to a base, acts as an extra-framework cation to compensate for the negative charge caused by the Al^{3+} in the zeolite framework. Both Brönsted and Lewis acid sites enable zeolites to act as solid acid catalysts for hydrocarbon transformation reactions [19, 20, and 21]. Brönsted acid sites can change into Lewis acid sites through dehydroxylation upon heating above 773 K (Figure 2.3) and Lewis acid sites can change into Brönsted acid sites when water is present in the zeolite (Figure 2.4) [1].

Usually a Brönsted acid forms at each framework aluminum (Al_f). However, for solid acid catalysts, it is not necessarily desirable to have the maximum amount of acid sites available [20]. It would be expected that the maximum acid strength would be achieved by having the maximum amount of acid sites. However, studies have indicated that the acid strength increases with a decrease in the total amount of Al_f . This is due to the fact that the strongest acid sites are the sites where the Al has no 'next nearest neighbour' (NNN) aluminium in the framework [19]. Therefore the acid site concentration increases with aluminium content in the zeolite, while the acid strength and proton activity coefficients increase with decreasing aluminium content [3].

Another influencing factor on acidity is the presence of non-framework aluminium (NFA) [20]. When zeolites are treated with steam for example, Al_f is removed (dealumination) and a defect site is created which is eventually filled with Si atoms. NFA is therefore a source of Lewis acidity while also inducing a polarization effect which enhances the Brönsted acidity [22].

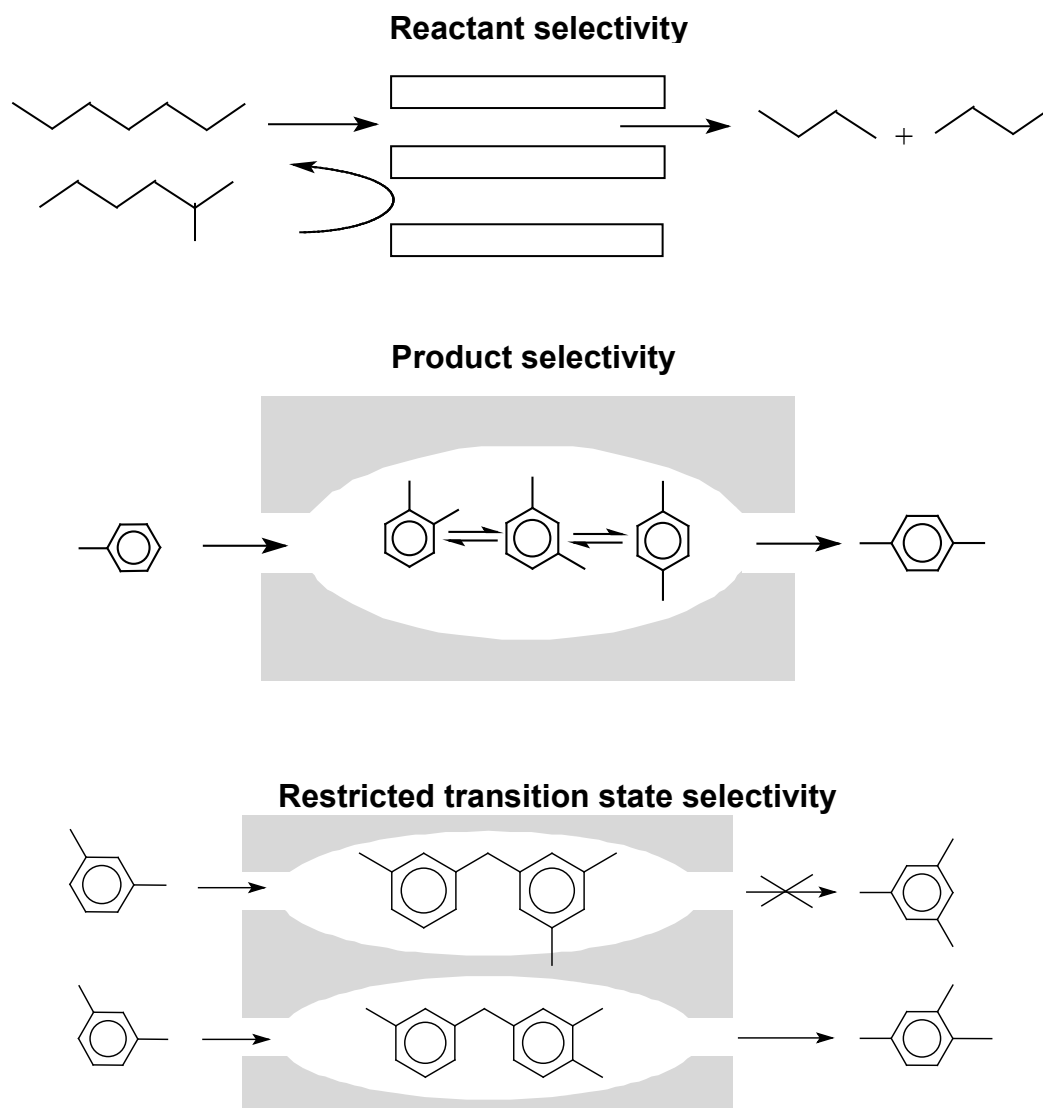


Figure 2.2: Types of selectivity found in zeolites [18]

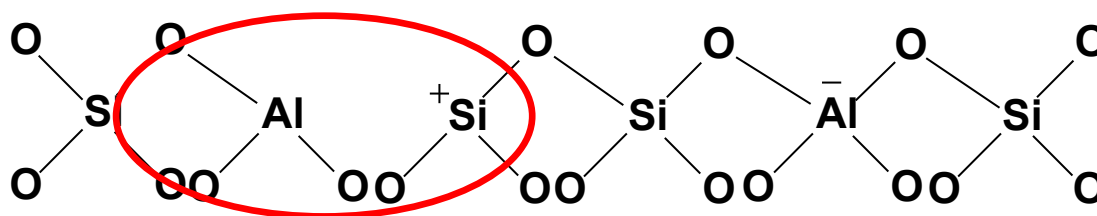


Figure 2.3: Lewis acid site [2].

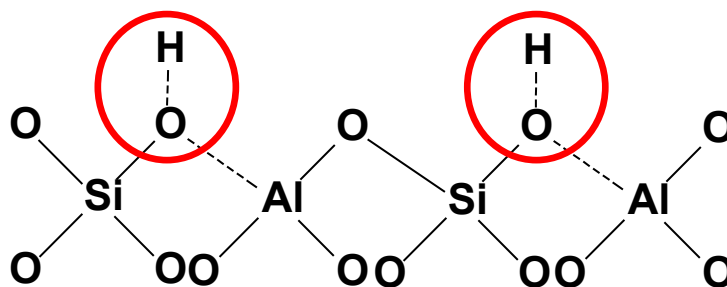


Figure 2.4: Brønsted acid sites [2].

Zeolites' extensive channel system creates a high surface area as well as a big pore volume which can adsorb a significant amount of molecules including hydrocarbons. During catalysis, the reactant has to diffuse through the pores until it reaches an active acid site within the channels and cages of the zeolite. Adsorption onto the active site occurs next followed by a chemical reaction to form the product. The product desorbs and diffuses out through the channels and cages [19]. Diffusion occurs within the crystal because of concentration gradients as well as electrical potential gradients caused by charge density differences. Diffusional effects can reduce the selectivity of methanol conversion for desired intermediate products (light olefins), causing an increased selectivity towards paraffins and aromatics. Therefore light olefin selectivity could be improved if diffusional limitations are minimized [23]. Some zeolites such as ZSM-5 display molecular traffic control properties because ZSM-5 has two types of intersecting channels. Reactants preferentially enter the catalyst through the one channel system while the products diffuse out through the other. Molecular control limits counterdiffusion effects inside the catalyst [24].

2.3. ZSM-5

ZSM-5, which is the zeolite of interest in this study, belongs to a well defined class of alumino-silicate zeolites that consist of a three dimensional structure built from tetrahedral units linked by oxygen atoms [25]. The SiO_4 tetrahedron is neutral, while the AlO_4 carries a negative charge on the ZSM-5's framework and thus requires an extra framework cation to ensure a neutral framework (Figure 2.5). The extra framework cations are located in the zeolite's pores and on its surface and are

Chapter 2

electrostatically bonded to aluminium, which give ZSM-5 its ion exchange properties [26].

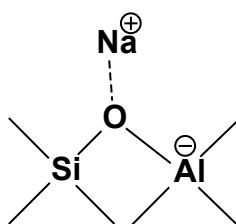
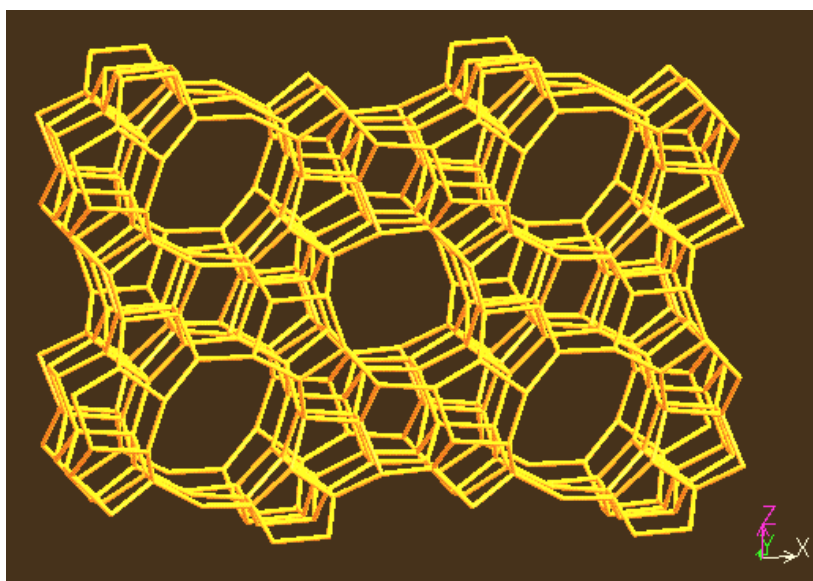


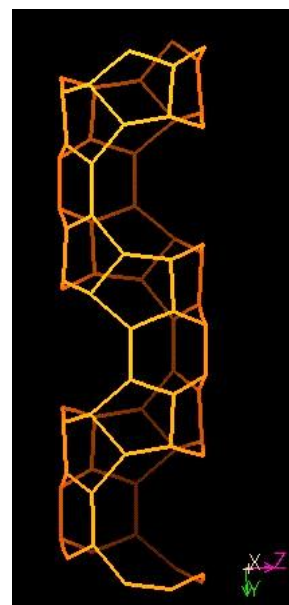
Figure 2.5: Extra framework cation in Na-ZSM-5 [26].

ZSM-5 has the general formula $\text{Na}_n[\text{Al}_n\text{Si}_{96-n}\text{O}_{192}] \cdot 16\text{H}_2\text{O}$ (where $n < 27$), with an orthorhombic symmetry [26]. ZSM-5 has two dimensional channels, one running parallel to (010) (Figure 2.6a) and one running perpendicular to the straight channel system in a sinusoidal shape (Figure 2.6b) [26].

The channels are ellipsoidal with ten ring openings with approximate dimensions of $5.4 \times 5.6 \text{ \AA}$ viewed along the straight channels (010) and $5.1 \times 5.4 \text{ \AA}$ viewed along the sinusoidal channels (100) [27]. The pores of ZSM-5 are wide enough to allow cyclisation, intermolecular hydride transfer and other reactions that convert light olefins to paraffins and aromatics [28].



(a)



(b)

Figure 2.6: ZSM-5's straight channels (a) and sinusoidal channels (b) [26].

The crystallographic pore dimensions of ZSM-5 can however not be used to predict which molecules will form as products. Molecules larger than the calculated channel and cage size of ZSM-5 sometimes form, e.g. durene (1,2,4,5-tetramethylbenzene that has a 6.1Å diameter) which is readily formed and able to diffuse through ZSM-5 [29, 30]. It has even been reported that 1,2,3,5-tetramethylbenzene with a 6.7Å diameter is formed inside ZSM-5, which reacts further to form the even bigger 1,1,2,4,6-pentamethylbenzenium cation [31]. According to the hydrocarbon pool mechanism (Figure 2.7), 1,1,2,4,6-pentamethylbenzenium cation is an intermediate to the formation of olefins [31, 32]. The hydrocarbon pool mechanism predicts that light olefins form from larger organic molecules inside zeolite cages and channels that act as catalytic scaffolds to which methanol/dimethyl ether is added and from which alkenes and water are split off. These large organic, catalytic scaffolds form during an induction period. The olefins that form from the organic molecules usually undergo chain growth and cracking reactions [31, 32].

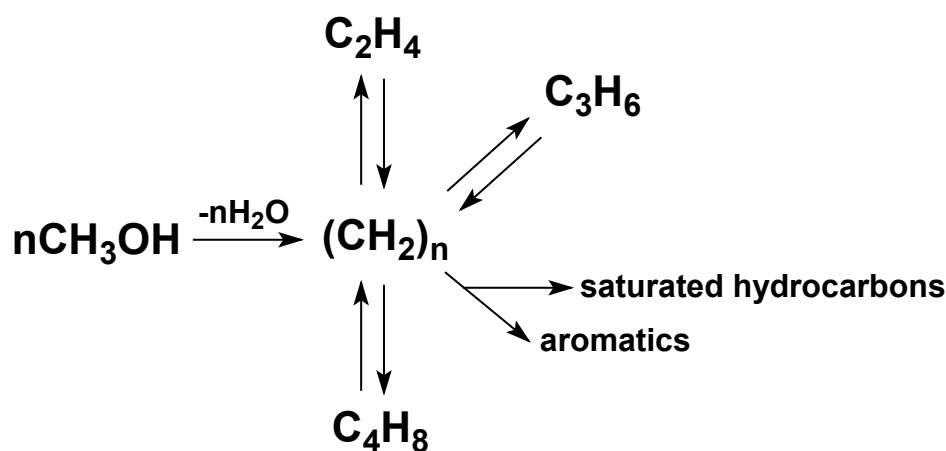


Figure 2.7: Kolboe's schematic hydrocarbon pool mechanism [3].

2.4. Synthesis parameters

ZSM-5 synthesis is a hydrothermal process which requires a silica source, alumina source, mineralizing agent as well as structure-directing agents [3]. The presence of various soluble species, an amorphous phase and polymerization reactions cause zeolite synthesis to be dependent on physical effects such as stirring, aging and

Chapter 2

order of reactant addition. The purpose of this study is to determine the influence of crystal/agglomerated polycrystalline grain size on the MTO product distribution and therefore variables that have a significant influence on crystal/agglomerated polycrystalline grain size, such as synthesis temperature, synthesis time and aging time will be discussed in this section.

2.4.1. *Synthesis temperature*

Previous studies showed that with increasing temperature, the induction period for crystal formation decreases and the crystallisation rate increases with increasing temperature but fewer crystals form at high temperatures [31, 32]. At higher temperatures and shorter crystallization time, higher crystallinity is reached and temperatures above 130°C are required for crystal formation [33, 34]. The aspect ratio (length of crystal/width of crystal) also increase with increasing temperatures [35]. Zeolite crystal growth is a complex process in which numerous soluble species are involved in the presence of various amorphous phases. A variety of polymerization and depolymerization reactions occur during crystal growth. It is a process of repeated addition of precursor structures to formed nuclei [36]. Therefore, physical parameters like stirring, aging and the order of adding reagents will have an influence on the crystal growth [37]. When the temperature is increased, the species' activity and concentration increase and this will lead to faster nucleation which in turn influences the crystals' size. A small number of nuclei will lead to a smaller amount of larger crystals while a large number of nuclei leads to a lot of crystals with smaller size. Crystal growth can be divided into four stages [38]:

- a) Initial tetrahedral monomeric aluminosilicates form, which are the primary building blocks of the zeolite. These monomers form not only during aging but also at elevated synthesis temperatures [39, 40].
- b) The monomers combine to form clusters (embryo) via condensation reactions.
- c) Nucleates which are aggregates with a well ordered core, form due to precipitation of the clusters.
- d) Once a critical nucleus size is reached, crystallization occurs where monomers and clusters condensate onto the formed nucleates.

2.4.2. *Synthesis time*

It was shown that by extending the synthesis time, whilst maintaining the same temperature, the average crystallite size increased [41]. This was ascribed to the Ostwald ripening phenomenon which entails the dissolution of small crystals and the redeposition of the dissolved species on the surfaces of larger crystals over a period of time [41].

2.4.3. *Aging time*

When the reagents for zeolite synthesis are mixed together, a primary amorphous phase which contains the initial as well as intermediate products forms [40]. During aging, partial hydrolysis and depolymerization of these species occur, forming monomers that eventually agglomerate to form polycrystalline particles (the secondary phase). These particles have a larger surface area than single crystallites and will therefore incorporate nutrients easier and will cause augmented crystalline growth during hydrothermal synthesis [40].

2.5. Methanol to olefins reaction (MTO)

Methanol can be converted to various hydrocarbons (MTHC), such as gasoline and olefins, in the presence of an acidic catalyst (Figure 2.9). As stated previously, both Brönsted as well as Lewis acid sites are present in zeolites, which make zeolites suitable catalysts for hydrocarbon transformation reactions [34, 35]. The choice of catalyst and process conditions used determine which hydrocarbons are formed [12].

The process of methanol conversion to hydrocarbons using ZSM-5 as catalyst was accidentally discovered by Mobil researchers while trying to find a route to manufacture hydrocarbons from natural gas. A research group tried to convert methanol to other oxygen-containing compounds over ZSM-5, but instead hydrocarbons were obtained. Later another research group tried to alkylate isobutene with methanol over ZSM-5 but instead paraffins and aromatics in the

Chapter 2 ng range formed.
was discovered [12].

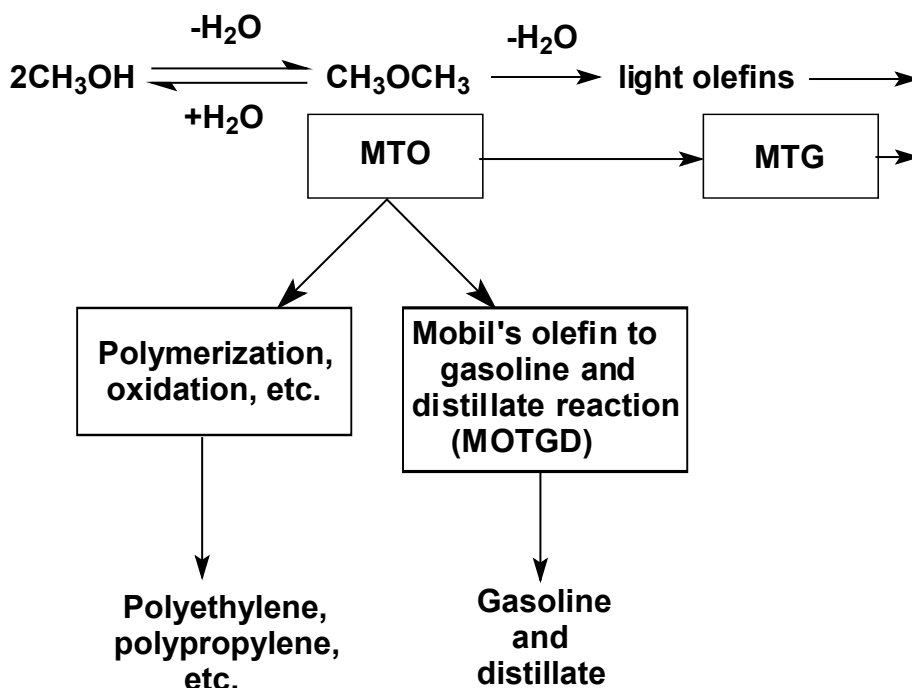


Figure 2.9: A diagram of methanol conversion to hydrocarbons [12].

During the MTG process (which is carried out at 400°C using ZSM-5 as catalyst) light olefins are intermediate products that are converted to aromatics and paraffins [12]. Because of the worldwide demand for light olefins, the MTG process was modified (for example by raising the temperature [12]) to increase the light olefin yield. The methanol to olefins (MTO) process generates mostly C₂-C₄ olefins [12].

Methanol is dehydrated to form an equilibrium mixture of methanol, dimethyl ether (DME) and water and this mixture is then converted to light olefins. Hydrogen transfer, alkylation and polycondensation reactions then convert light olefins to paraffins, aromatics, naphthenes and other higher olefins [12]. The intermediate in the dehydration of methanol to DME over a solid acid catalyst is a protonated surface methoxyl, which is subject to a nucleophilic attack by methanol [39]. According to the hydrocarbon pool mechanism olefin formation takes place on larger organic molecules (1,1,2,4,6-pentamethylbenzenium cation) located inside the zeolite's pores. These larger organic molecules are formed during an induction period and act as catalytic scaffolds to which methanol is added and from which light olefins are split off. The light olefins that form also undergo cracking and chain

Chapter 3

growth reactions to form other light olefins mostly in the C₂-C₄ range [31]. The conversion of light olefins to paraffins, aromatics, naphthenes and higher olefins proceeds via a carbenium ion mechanism with concurrent hydrogen transfer [38]. The hydrocarbons produced by ZSM-5 for MTO and MTG are limited between C₁ and C₁₀ [41].

Gasoline produced via the MTG process is higher in yield and quality to the gasoline produced by the Fischer-Tropsch process however, MTHC reactions are used complimentary to the Fischer-Tropsch process [3]. The MTO reaction is thus an alternative way to produce C₂-C₄ olefins for use in the chemical industry. Currently light olefins are produced from steam cracking of liquefied natural gas (LNG), naphta or light fractions of petroleum. In order to produce the optimal light olefin yield it is necessary to inhibit secondary reactions.

2.6. Conclusion

From the literature presented, it is clear that due to ZSM-5's shape selectivity, solid activity, ion exchangeability, pore size, thermal stability and structural network, it has widely been used as catalyst in the petroleum and petrochemical industry [43]. One of the factors that influence the light olefin yield during the MTO process is the size of the ZSM-5 crystals. The crystal size is dependent on many synthesis parameters including synthesis temperature, synthesis time and aging time and thus by altering these parameters different crystal sizes can be obtained.

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Chapter 3

Experimental investigation of ZSM-5 synthesis

3.1. Introduction	24
3.2. Experimental	24
3.2.1. <i>Synthesis of ZSM-5</i>	24
3.2.1.1. <i>Preparation of the synthesis solution</i>	24
3.2.1.2. <i>Synthesis</i>	25
3.2.1.3. <i>Synthesis of ZSM-5 at varied synthesis conditions</i>	26
3.2.2. <i>Ion exchange of Na-ZSM-5 to H-ZSM-5</i>	26
3.2.3. <i>MTO reaction</i>	26
3.3. Characterisation	28
3.3.1.1. <i>XRD</i>	28
3.3.1.2. <i>SEM and EDS</i>	28
3.3.1.3. <i>ICP</i>	29
3.3.1.4. <i>TPR-TPO-MS</i>	29
3.4. References	30

3.1. Introduction

ZSM-5 was synthesised by a hydrothermal method inside an autoclave with a Teflon insert [1]. Non-acidic ZSM-5 is formed by this method and the synthesised crystals have to be ion exchanged to form acidic H-ZSM-5. As explained in Chapter 2, zeolite crystal growth is sensitive to changes in the synthesis parameters (temperature, aging and stirring tempo) and these parameters were varied to investigate the influence that each parameter has on the crystallite/agglomerated polycrystallite grain size. The as-synthesised ZSM-5 was then used as catalyst in a fixed bed reactor and the light olefin selectivity of different crystallite/agglomerated polycrystallite grain sizes was investigated.

3.2. Experimental

3.2.1. Synthesis of ZSM-5

3.2.1.1. Preparation of the synthesis solution

The synthesis solution was prepared using 6.63g tetrapropyl ammoniumbromide (TPA-Br, Merck) and 28.53g tetrapropyl ammoniumhydroxide (TPA-OH, Fluka) which was dissolved in 84.12g deionised water in a 500ml PE bottle. TPA-Br and TPA-OH's geometry and charge enable these molecules to act as templating agents during crystal growth and synthesis of ZSM-5 [1].

The template/water solution was stirred for 10 minutes to ensure proper dispersion of the template and was then split into two equal amounts, each in their own 500ml PE bottle. To the first bottle, 8.70g tetraethylortosilicate (TEOS, Merck) was added as silica source, while 0.09g sodium aluminate (Saarchem) was added to the second bottle as source of aluminium. These values correspond to a Si/Al ratio of 45 with a molar composition of $100 \text{ SiO}_2 : 123 \text{ TPA}^+ : 63.7 \text{ OH}^- : 14200 \text{ H}_2\text{O} : 2.22 \text{ Al}_2\text{O}_3$.

Both solutions were allowed to age for one hour under constant stirring. After this initial ageing process, the aluminum solution was added dropwise to the silica solution over the course of 15 minutes under constant stirring. When the two solutions are added together the precursor structures, essential to formation of the

Chapter 3

zeolite, starts to form. These structures form the building blocks for the zeolite's supercage structure [4, 5]. The synthesis solution was aged for another hour to ensure that the process had run to completion [1].

3.2.1.2. *Synthesis*

The synthesis solution was transferred into a Teflon insert. The Teflon insert was closed with a lid and placed in a stainless steel autoclave (Figure 3.1) which was properly sealed and placed in an oven fitted with a rotating arm. The oven was preheated to 170°C and the rotation arm was set to rotate at 75 rpm for a total synthesis time of 72 hours. After 72 hours, the as-synthesised ZSM-5 was removed, washed with distilled water and placed in an ultra-sonic bath for 30 minutes after which the supernatant was separated from the precipitate using a centrifuge. In order to remove the organic template trapped in the ZSM-5 pores the as-synthesised zeolite was calcined at 550°C for 360 minutes in air. In order to determine the reproducibility of the synthesis method, as well as the standard deviation between the sizes of the crystallites/agglomerated polycrystalline grains synthesised in different autoclaves, the synthesis solution was divided into five autoclaves and synthesised at 170°C for 72 hours.



Figure 3.1: Stainless steel autoclave with Teflon insert used for ZSM-5 synthesis.

3.2.1.3. *Synthesis of ZSM-5 at varied synthesis conditions*

Experimental investigation of ZSM-5 synthesis

In order to determine the influence of the synthesis parameters on the crystallite size, the synthesis time was varied (12 to 72 hours) using a temperature of 170°C and an aging time of 60 minutes. The synthesis temperature was also varied (130°C, 150°C and 170°C) with a synthesis time of 72 hours and an aging time of 60 minutes. Finally the aging time (30, 60 and 90 minutes) was varied with a synthesis time of 72 hours and a synthesis temperature of 170°C. The synthesised ZSM-5 was then calcinated at 550°C for 360 minutes in air.

3.2.2. Ion exchange of Na-ZSM-5 to H-ZSM-5

In order to convert the synthesised crystals to the acidic H-ZSM-5 form, Na-ZSM-5 was ion exchanged with 1 mol.dm⁻³ NH₄NO₃(aq) (ACE Acechem) at room temperature (23°C) for 12 hours under constant stirring with a zeolite-to-solution ratio of 1g zeolite/10 cm³ solution. The crystals were washed thoroughly with deionised water and placed in an ultra sonic bath for 30 minutes after which the water and crystals were separated using a centrifuge. During ion exchange, NH₄-ZSM-5 formed which was then converted to H-ZSM-5 by heating the zeolite to 550°C for 240 minutes in air to decompose the ammonium ions to produce the hydrogen form of ZSM-5. The as-synthesised ZSM-5 was characterised with X-ray diffraction (XRD) and scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS).

3.2.3. MTO reaction

The process studied and evaluated at bench scale was based on Lurgi's methanol to propylene (MTP) reaction which uses ZSM-5 as catalyst [6]. During this reaction a fixed bed reactor was operated adiabatically (Figure 3.2). The fixed bed reactor was used because of ease of scale up, lower investment costs while providing uniform residence time for reactants resulting in the ability to maximise light olefin selectivities. The as-synthesised ZSM-5 as well as Catalyst A, were used as catalyst and control catalyst respectively during the MTO reaction. ZSM-5 with different crystallite/agglomerated polycrystallite grain sizes were separated using a sieve into three fractions, <75µm, 75-150µm and 150-300µm for both as-synthesised as well as Catalyst A. The 16mm ID × 24 cm long stainless steel tubular reactor hot zone was loaded with 1-5g catalyst. The void space was filled with coarse carborundum

Chapter 3

and glass wool (Figure 3.2). The catalyst was not diluted and the catalyst bed-length was between 7 and 10 cm. The reaction temperature for all reactions was 450°C and the feed composition was 12:88 (mol %) methanol and water. The feed mixture was pumped into the reactor at a rate of 0.1 ml/min for 1g synthesised ZSM-5 and 0.5 ml/min for 5g of Catalyst A. The catalyst was activated by heating to 450°C and leaving it overnight under 1 bar nitrogen flow. The liquid products were collected in a catch pot that was cooled to 5°C from where samples were collected hourly. The water and the oils were separated, weighed and analysed in an off-line GC-FID (Agilent 7890A equipped with an Agilent 7693 autosampler). Gaseous products were also collected hourly and manually injected into an off-line GC-FID (Agilent 6890N) as well as an off-line GC-TCD (Agilent 6850). The temperature programs for the GC's are shown in Table 3.1. The components in the product stream were identified using GC-MS.

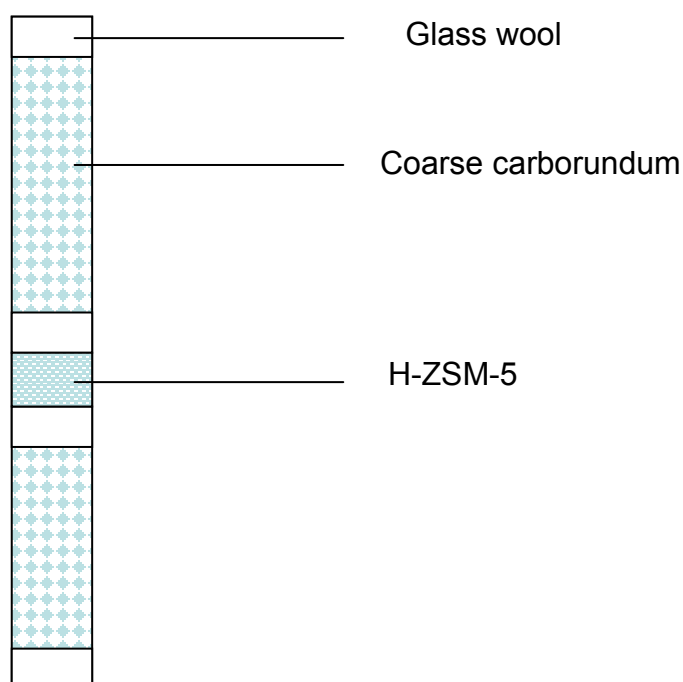


Figure 3.2: Tubular reactor for MTO reaction

Table 3.1: Temperature programs of the GC's

Detector	TCD		FID	
GC analysis	CO, CO ₂ , CH ₄	Water	Oil	Gas
Column	Shincarbon packed column	HP-INNOWAX	HP-PONA	CP-Sil 5 CB
Initial temperature (°C)	36	50	35	35
Hold time (min)	4	0	5	2.4
Ramp rate (°C/min)	10	4	4	10
Final temperature (°C)	200	220	300	260
Hold time (min)	1	10	14	1
Total program (min)	21.4	52.5	85.25	25.9

3.3. Characterisation

3.3.1.1. XRD

XRD is a well established zeolite characterisation method and was used to verify that the zeolite formed was H-ZSM-5 and to determine the crystallinity, purity and crystal size of the synthesised crystals. The as-synthesised ZSM-5 was characterised using a Röntgen PW3040/60 X'Pert Pro equipped with a Cu tube working at a generator potential of 40kV and a generator current of 45mA.

Chapter 3

3.3.1.2. SEM and EDS

SEM was used to obtain information about the type of zeolite (through the crystal form), crystal size as well as crystal size distribution phenomena, for example, aggregation, twinning, intergrowth and whether other zeolite types were present. Energy dispersive X-ray analysis (EDS) is a method used to identify the inorganic elemental composition of a sample or small area of a sample. During EDS analysis, a sample is exposed to an electron beam inside a scanning electron microscope (SEM). The electrons collide with the electrons within the sample. Some of the electrons of the sample will then get knocked out of their orbits. The empty positions are filled by higher energy electrons and x-rays are emitted in the process. By analysing the emitted x-rays, the inorganic elemental composition of the sample can be determined. The Si/Al ratio of the samples were analysed with EDS. SEM as well as the EDS characterisation was performed on a FEI Quanta ESEM instrument.

3.3.1.3. ICP

ICP is probably the most widely used technique for the determination of the elemental composition of zeolites and was used to determine the bulk silica/alumina ratio of the synthesised ZSM-5, to determine the degree of ion exchange and to detect contaminants. A Thermo Scientific iCAP 6000 series was used for ICP analyses.

3.3.1.4. TPR-TPO-MS

Coke deposited on MTO catalysts has been investigated by continuously monitoring the H₂ consumption during temperature-programmed reduction (TPR). If a reduction takes place at a certain temperature, hydrogen is consumed [8]. Coke deposition on MTO catalysts was also investigated by monitoring the CO and CO₂ evolved during temperature-programmed oxidation (TPO) in a 1% O₂/N₂ mixture. In order to quantify the amount of polymeric carbon, TPR-TPO-MS spectra of the spent catalyst were recorded on an Autochem 2910 (Micromeritics) instrument coupled with a Cirrus Mass spectrometer. Approximately 100 mg of sample was placed in a U-shaped quartz tube fitted with a thermocouple for continuous temperature measurements. The sample was dried under argon flow (50 ml/min) by increasing the temperature from room temperature at a heating rate of 10°C/min to 100°C and held at 100°C for 30 min. The sample was then cooled to room temperature and subsequently heated

to 280°C with a heating rate of 10°C/min and held at 280°C for 60 minutes in a flow of pure H₂ (50 ml/min). This step was performed in order to remove the surface carbidic carbon. The amount of hydrogen consumed during reduction was measured with a thermal conductivity detector (TCD) and the off-gas was analysed using the MS for all masses between 1 and 50. The sample was then cooled down to room temperature and flushed for two hours with argon. The next step was the TPO measurement, which included switching of the gases to 10% O₂/He (50 ml/min), heating to 900°C with a heating rate of 10°C/min, a hold time at 900°C of 60 minutes and cooling down to room temperature. The amount of oxygen consumed was again monitored with a TCD on the Autochem and the off-gases were analysed using the MS.

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Chapter 4

Discussion of ZSM-5 synthesis

4.1. Introduction	32
4.2. Synthesis of ZSM-5	32
4.3. Synthesis of ZSM-5 at varied synthesis parameters ..	36
<i>4.3.1. Influence of synthesis time</i>	<i>36</i>
<i>4.3.2. Influence of temperature</i>	<i>40</i>
<i>4.3.3. Influence of synthesis on aging time</i>	<i>42</i>
4.4. Conclusion.....	46
4.5. References	47

Chapter 4

4.1. Introduction

ZSM-5 was synthesised by a crystallisation method in an autoclave system as developed by Vorster [1]. The synthesis parameters used from this method were varied to determine their influence on crystal/agglomerated polycrystalline grain size. As-synthesised ZSM-5, as well as Catalyst A was used as catalyst in a fixed bed reactor and the light olefin selectivity of different agglomerated polycrystalline grain size ranges was investigated and is presented in Chapter 5.

4.2. Synthesis of ZSM-5

ZSM-5 was synthesised under standard conditions (aged for 60 minutes and synthesised for 72h at 170°C) in five different autoclaves to obtain adequate quantities of each batch for the fixed bed reactor. SEM images, EDS (Energy-dispersive X-ray spectroscopy) analysis and XRD spectra of the as-synthesised ZSM-5 were obtained. From the SEM images (shown in Figure 4.1), it is clear that the ZSM-5 crystals were intergrown forming bigger agglomerated polycrystalline grains. Hay and co-workers [2] studied intergrown ZSM-5 and found that often adjacent crystals are rotated 90° around a common *c*-axis which is caused by nucleation at the small areas on the (010) faces of growing crystals. Previous studies found that zeolites with compositions of $a\text{M}_2\text{O} \cdot b\text{Al}_2\text{O}_3 \cdot 15\text{SiO}_2 \cdot 49\text{H}_2\text{O}$ with $\text{M}=\text{Li}, \text{Na}$ or K ; $0.9 \leq a \leq 8.82$ and $1.66 \leq b \leq 15$, formed agglomerated polycrystalline grains [3], which is similar to the molar ratio that was used in this study. Sigmoid nucleation-growth crystallisation kinetics characterise this type of ZSM-5 synthesis [4] during which a large number of nuclei are formed which leads to the formation of polycrystalline aggregates. Different templating agents form ZSM-5 crystals with different morphologies and crystal sizes [5]. The shape of the crystals forming the intergrown agglomerated polycrystalline grains is consistent with that of ZSM-5 found in literature where TPA derivatives were used as templating agent [5].

Discussion of ZSM-5 synthesis

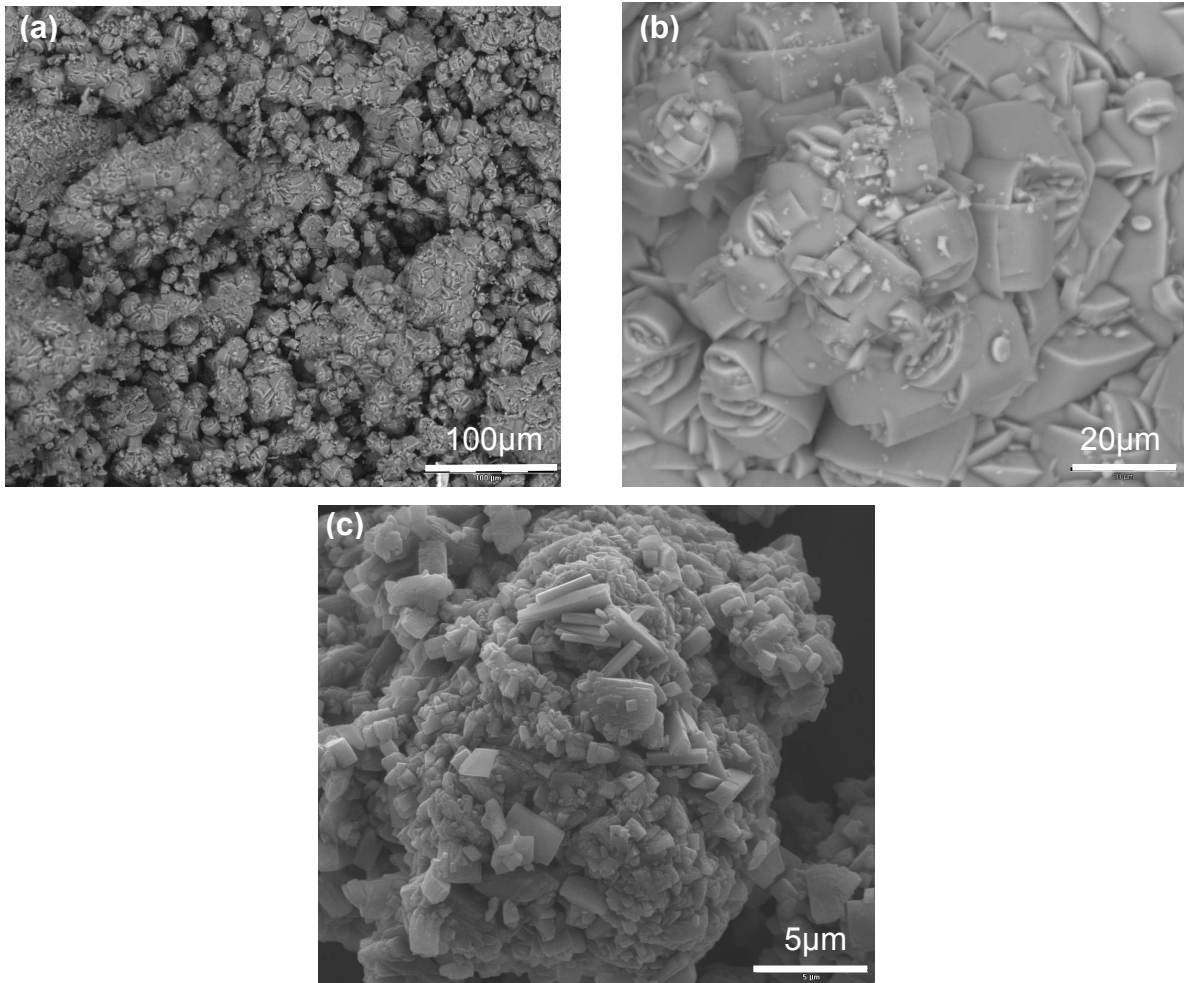


Figure 4.1: SEM images of as-synthesized ZSM-5 (a and b) with Si/Al= 45, aged for 60 minutes and synthesized at 170°C for 72 hours and Catalyst A (c) with Si/Al=90.

During synthesis, crystallisation occurred both on the surface of the Teflon inserts as well as in the synthesis solutions forming agglomerated polycrystalline grains with a widespread size distribution (Figure 4.1). Both the observed morphology, as well as the difference in the agglomerated polycrystalline grain sizes of the obtained ZSM-5 can be attributed to the rapid nucleation in the supersaturated environment found during synthesis as spontaneous nucleation is common when the synthesis solution is supersaturated. The free energy of formation of a nucleus has a negative value under these conditions and when a critical degree of supersaturation is reached, nucleation occurs spontaneously, followed by crystallisation of the formed nuclei while the nutrients are abundant [6]. However, some of the clusters grow onto larger crystals to form larger agglomerated polycrystalline grains [7, 8, and 9]. The size

Chapter 4

distribution in batch crystallisation strongly depends on the number of nuclei formed during crystallisation and on the rate of crystallisation. Since the crystallisation process in zeolites is very sensitive to changes in the synthesis parameters, reproducibility is often difficult [10].

When comparing the SEM micrographs of the as-synthesised ZSM-5 (Si/Al=45) to those of Catalyst A (Si/Al=90), it is clearly visible that the as-synthesised ZSM-5 has a more round crystal form than Catalyst A. Previous studies by Čížmek and co-workers as well as Aiello and co-workers [10, 11] determined that a decrease in the Si/Al ratio of the zeolite has a rounding effect on the morphology of the crystals. Similarly, ZSM-5 with a high Si/Al ratio has a longer length than width, while for the lower Si/Al ratio the aspect ratio (crystal length/crystal width) is usually smaller [10].

It is also notable that the crystal size of Catalyst A is significantly smaller than the as-synthesised ZSM-5, which can probably be ascribed to different synthesis conditions used for Catalyst A. However, this could not be confirmed as the synthesis conditions of Catalyst A have not been disclosed.

The surfaces of the ZSM-5 synthesised in the five different autoclaves were analysed by EDS and the results presented in Table 4.1. The amounts of reagents used during synthesis were calculated to produce ZSM-5 with a Si/Al of 45. The average Si/Al obtained by EDS was 42.48 with a standard deviation of 6.68 which means that the obtained Si/Al ratio was in the same range as was initially planned. The actual Si/Al variation could probably be improved by adding the Al-source solution more slowly to the Si-source solution which will enhance the incorporation of Al into the zeolite framework [12]. However, for the purpose of this study the average Si/Al ratio and its variation were within acceptable boundaries.

The as-synthesised ZSM-5's XRD spectra (Figure 4.2) showed sodium peaks which were present due to the fact that the synthesised ZSM-5 has not yet been ion exchanged to replace the extra-framework Na^+ with H^+ to form acidic H-ZSM-5. The as-synthesised ZSM-5's XRD spectrum was compared to Catalyst A's spectrum which was used as a reference (Figure 4.3). The synthesised ZSM-5, showed only

Discussion of ZSM-5 synthesis

the characteristic ZSM-5 peaks at $2\theta=7-10^\circ$ and $23-25^\circ$ [6] which indicated that the method used to synthesise ZSM-5 was successful and ZSM-5 of high purity were obtained [5]. The intensity of the peaks is determined by the arrangement of atoms in the crystal. The as-synthesised ZSM-5 and Catalyst A were synthesized using different methods and therefore the XRD peak intensity of these catalysts will vary.

Table 4.1: The elemental composition of as-synthesised ZSM-5 as determined by EDS.

Sample	[O] (wt%)	[Al] (wt%)	[Si] (wt%)	[Na] (wt%)	Si/Al
1	55.55	1.14	42.32	0.99	37.12
2	55.63	0.99	42.48	0.90	42.91
3	55.15	1.21	42.65	0.99	35.25
4	54.72	0.96	43.35	0.97	45.16
5	54.05	0.85	44.17	0.93	51.96
Average	55.02	1.03	42.99	0.96	42.48
Std. deviation	0.65	0.14	0.76	0.04	6.68
Max.	55.63	1.21	44.17	0.99	51.96
Min.	54.05	0.85	42.32	0.90	35.25
Target	50.00	1.00	45.00	0.00	45.00

Chapter 4

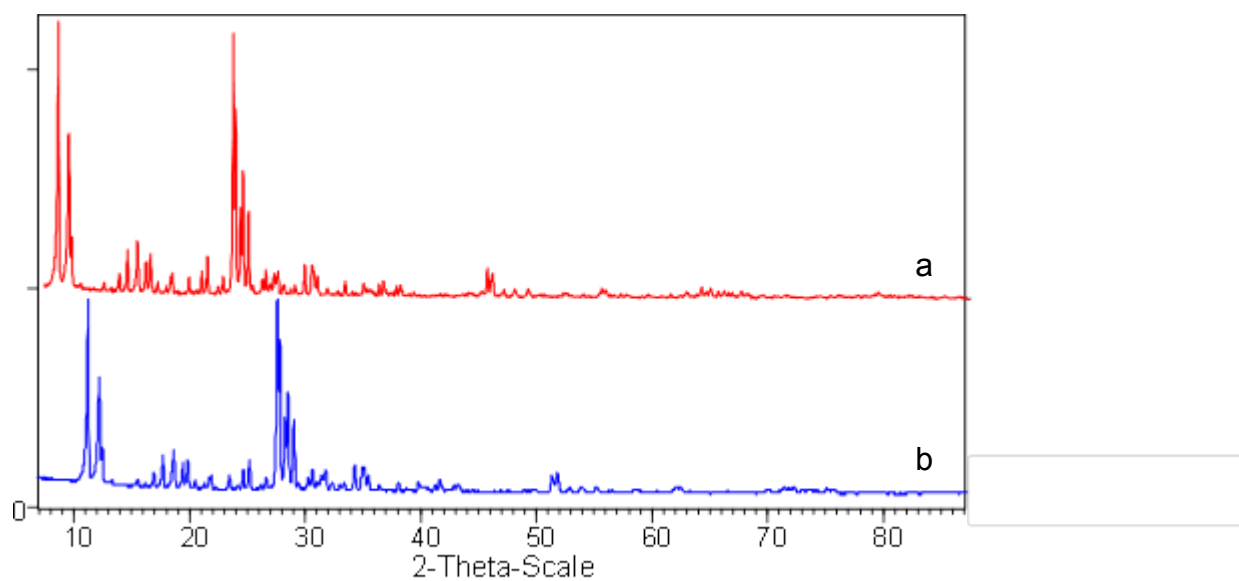


Figure 4.2: XRD spectrum of (a) ZSM-5 with characteristic ZSM-5 peaks at $2\theta=7-9$ and 22-25 and (b) reference Catalyst A.

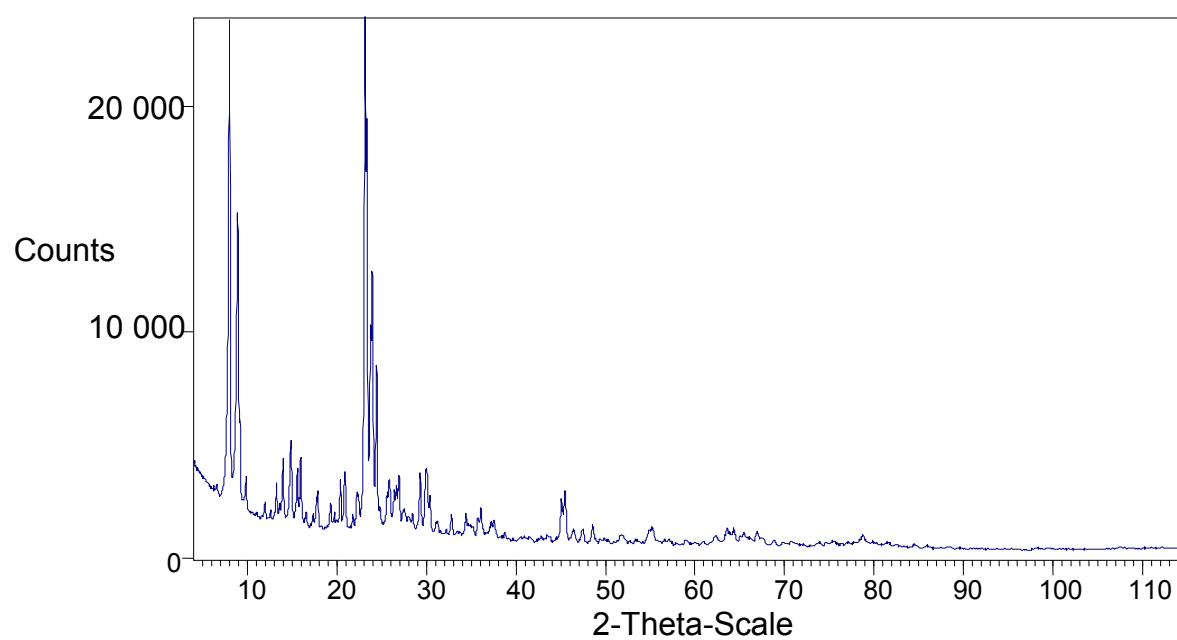


Figure 4.3: Reference XRD spectrum (Catalyst A).

4.3. Synthesis of ZSM-5 at varied synthesis parameters

4.3.1. Influence of synthesis time

The synthesis time was varied from 12 to 72 hours, while keeping the aging time and synthesis temperature constant at 60 minutes and 170°C respectively, to evaluate the influence of synthesis time on the ZSM-5 agglomerated polycrystalline grain size. According to the SEM images (Figure 4.4), the synthesised ZSM-5's morphology contained intergrown polycrystallite grains or agglomerated particles with different sizes while maintaining the characteristic ZSM-5 morphology observed for ZSM-5 synthesised using TPA derivatives as templating agents [3].

XRD spectra showed only the characteristic ZSM-5 peaks at $2\theta=7-9$ and 22-25 which confirms that highly pure ZSM-5 formed (Figure 4.5) [5]. Figure 4.5 shows the characteristic ZSM-5 peaks from as early as 12 hours synthesis time. The relatively short time necessary for the synthesis of ZSM-5 with a Si/Al ratio of 45, is due to the fact that the crystallite growth rate increases with decreasing Si/Al ratio, resulting in aluminous zeolites requiring relatively short preparation times [14].

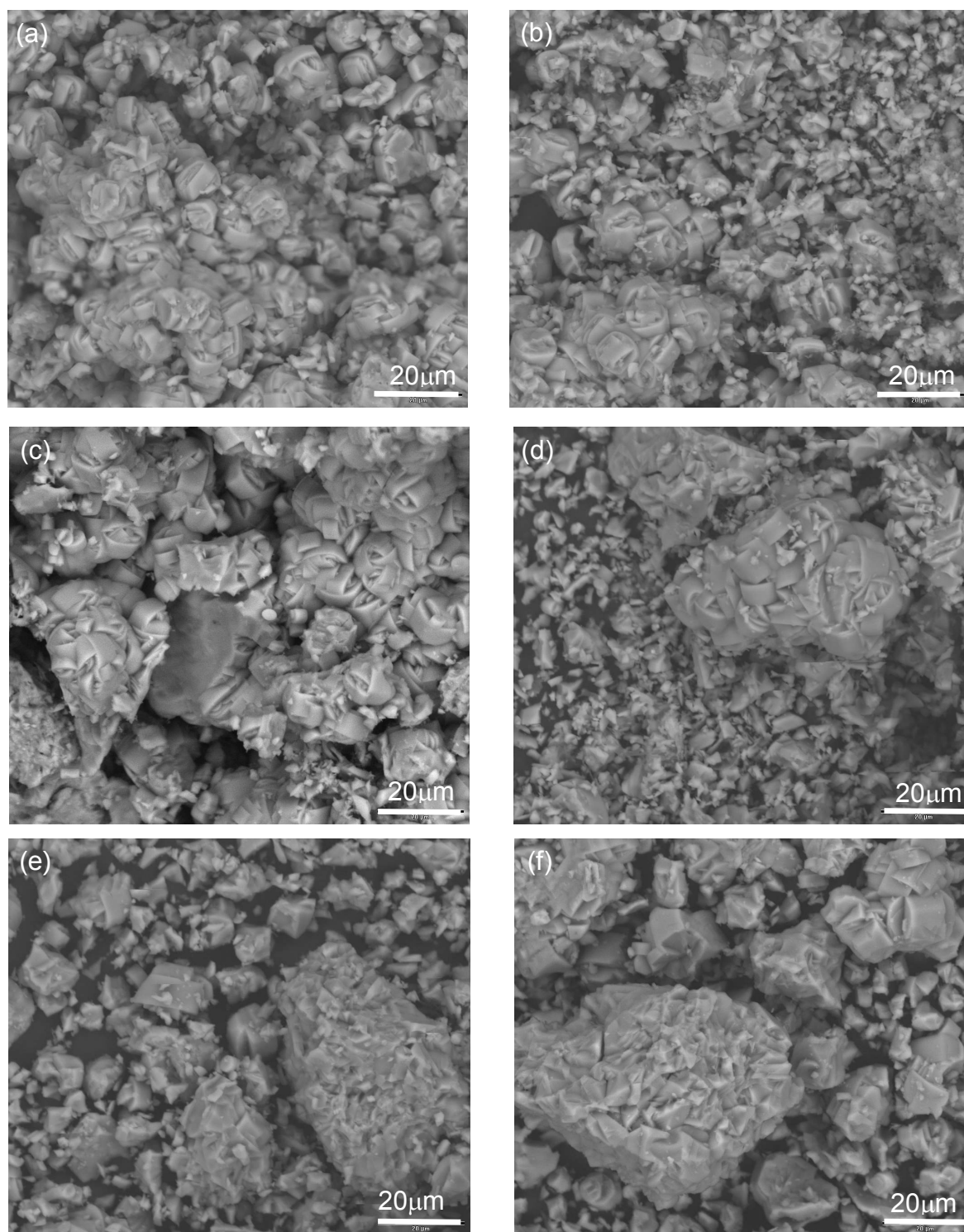


Figure 4.4: SEM images of ZSM-5 synthesised for (a) 12 hours, (b) 24 hours, (c) 36 hours, (d) 48 hours, (e) 60 hours and (f) 72 hours.

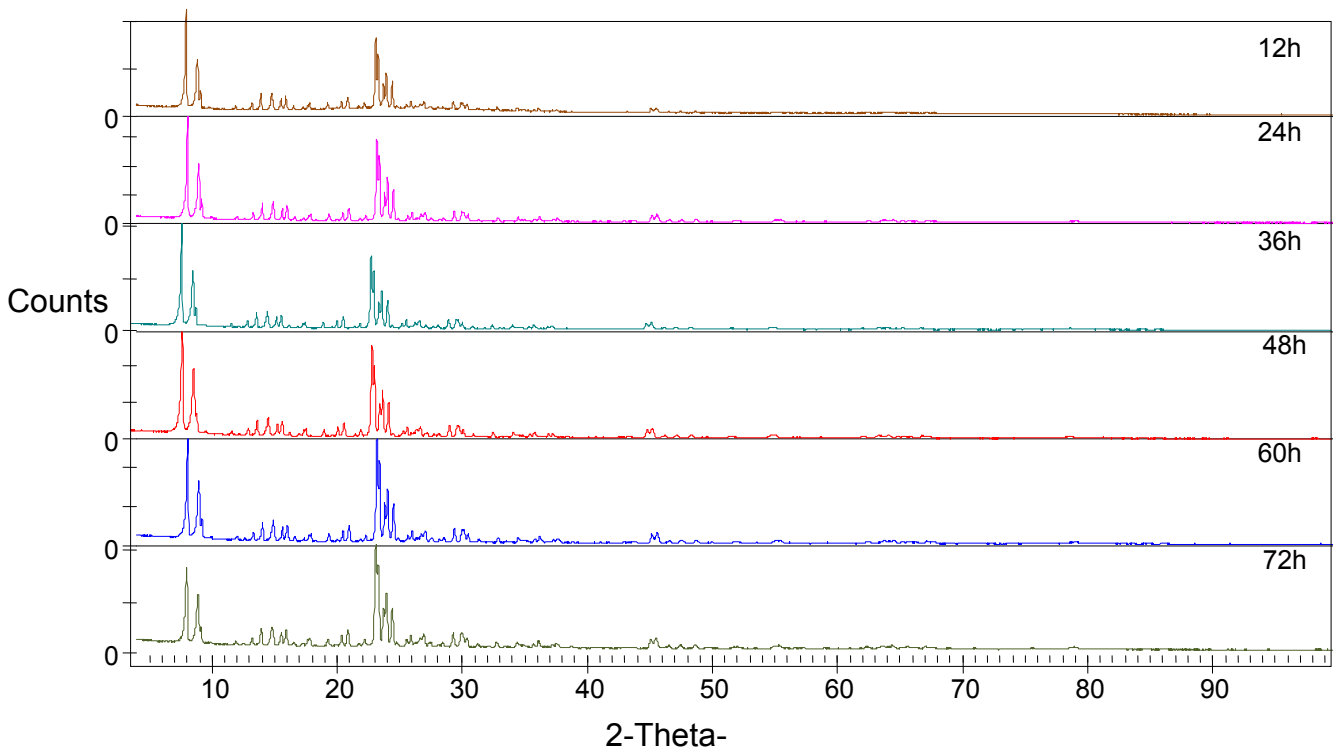


Figure 4.5: XRD spectra of ZSM-5 at different synthesis times.

Since the ZSM-5 crystals were intergrown, the crystals' sizes of the intergrown agglomerated polycrystalline grains were physically measured using SEM images as shown in Figure 4.6 for the ZSM-5 synthesised for 60 hours. In an attempt to exclude the effect of clustering and intergrowth, only single crystal sizes were measured. Eighty SEM measurements (Figure 4.6) were used to obtain an adequate crystal size and standard deviation which is presented as a function of synthesis time in Figure 4.7. The standard deviation was $3.8\mu\text{m}$, $2.5\mu\text{m}$, $2.6\mu\text{m}$, $2.0\mu\text{m}$, $2.0\mu\text{m}$ and $3.2\mu\text{m}$ for the 12 h, 24 h, 36 h, 48 h, 60 h and 72 h treatment respectively. The y-axis in Figure 4.7 was set at $30\mu\text{m}$ for comparative purposes when discussing the influence of synthesis temperature and aging time.

A slight decrease in crystallite size can be observed from an average crystallite size of $6.2\mu\text{m}$ when synthesised for 12 hours to $5.4\mu\text{m}$ crystallites after 72 hours of synthesis. A standard deviation of $0.4\mu\text{m}$ between the average crystallite sizes shows that the synthesis time didn't have a profound influence on the average crystallite size of ZSM-5. The Scherrer equation was used to calculate crystal size [13] and from XRD data and a slight decrease in crystal size was confirmed.

Chapter 4

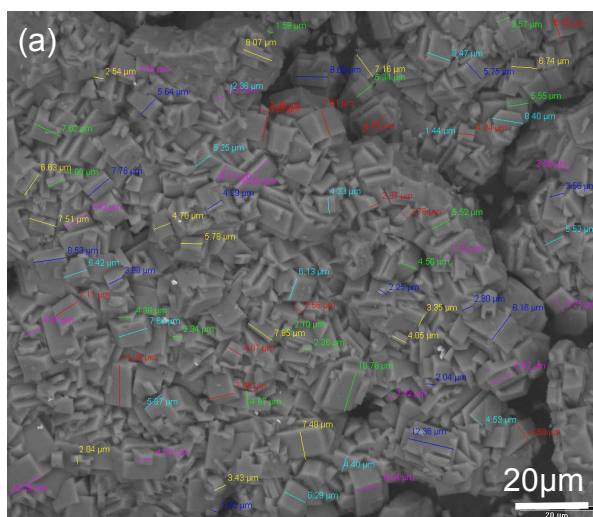


Figure 4.6: Determining particle size of ZSM-5 synthesised for 60h (at 170°C and aged for 60 minutes) using a SEM image.

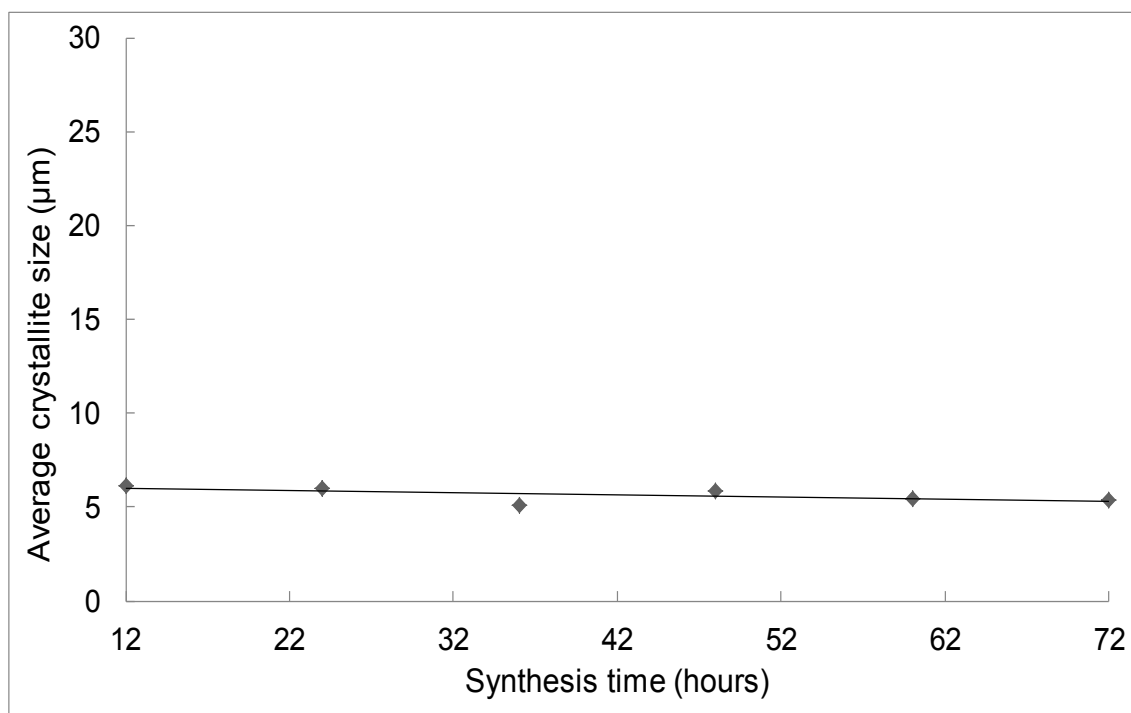


Figure 4.7: The effect of synthesis time on crystal size.

Mohamed and co-workers [13] found that longer synthesis times at constant temperature decreased crystallite size. Cundy and co-workers [14] also observed a decrease in crystal mass with synthesis time. Our results therefore suggests that more than one nucleation mechanism was in effect. During the first part of the reaction, heterogeneous nucleation probably occurred. At a later stage of the reaction, when there was crystalline material present, additional crystals nucleated

Discussion of ZSM-5 synthesis

via a secondary mechanism or by release of heteronuclei from dissolving amorphous material resulting in the observed decrease in crystal size with increasing synthesis time [13].

4.3.2. Influence of synthesis temperature

The influence of temperature on crystal or agglomerated polycrystalline grain size was investigated by synthesising ZSM-5 at 130°C, 150°C and 170°C while keeping the aging time and synthesis time constant at 60 minutes and 72 hours respectively. At all three temperatures, the crystals were intergrown (Figure 4.8), with the ZSM-5 morphology displaying the characteristic ZSM-5 peaks on its XRD spectra (Figure 4.9) irrespective of the synthesis temperature.

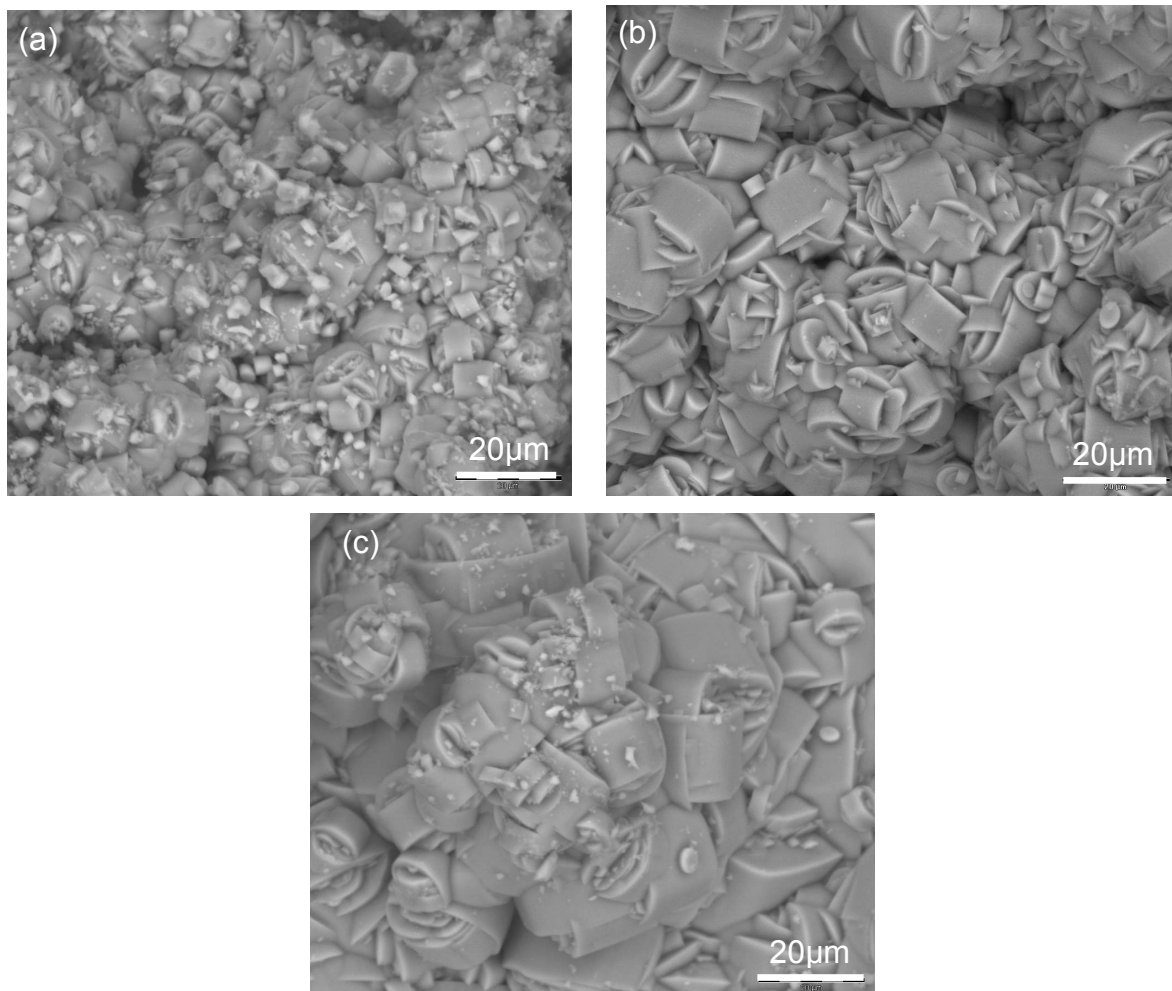


Figure 4.8: Intergrown ZSM-5 crystals synthesised at (a) 130°C, (b) 150°C and (c) 170°C for 72 hours and aged for 60 minutes.

Chapter 4

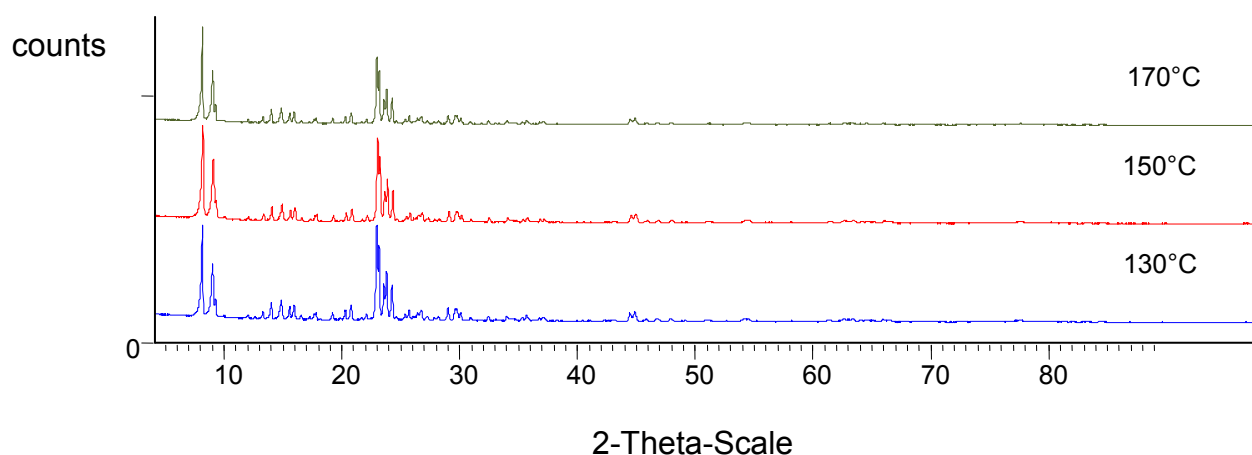


Figure 4.9: XRD spectra of ZSM-5 synthesised at 130°C, 150°C and 170°C respectively (aged for 60 minutes and synthesised for 72 hours).

The crystal sizes as a function of synthesis temperature were measured using SEM images and in an attempt to exclude the effect of clustering and intergrowth, only single crystal sizes were again measured. Eighty measurements were used to obtain an adequate crystal size and standard deviation. At 150°C the largest average crystals, 17.3µm, were observed (Figure 4.10) with a standard deviation of 2.7µm. At 130°C an average crystal size of 7.7µm and a standard deviation of 1.9µm was observed and at 170°C an average crystal size of 14.2µm with a standard deviation of 5.1µm was obtained.

The average crystal size increased from 7.7µm at 130°C to 17.3µm at 150°C from where the crystal size decreases to 14.2µm at 170°C. Figure 4.10 shows that the crystal size increased with increasing temperature confirming results that have been reported by Mintova and co-workers [15]. From their studies, they have shown that an increase in temperature decreases the induction period for crystal growth and increases the crystallisation rate. The growth mechanism however, is independent from the synthesis temperature [16]. Fewer but larger crystals form at higher temperatures and this can be attributed to the Ostwald ripening phenomenon [15]. This phenomenon leads to small crystals slowly disappearing while the larger crystals continue to grow bigger. The smaller crystals act as "nutrients" for the bigger crystals [16]. From Figure 4.10, which confirms previous studies [12], it is clear that temperature had a larger influence on crystal size than synthesis time had.

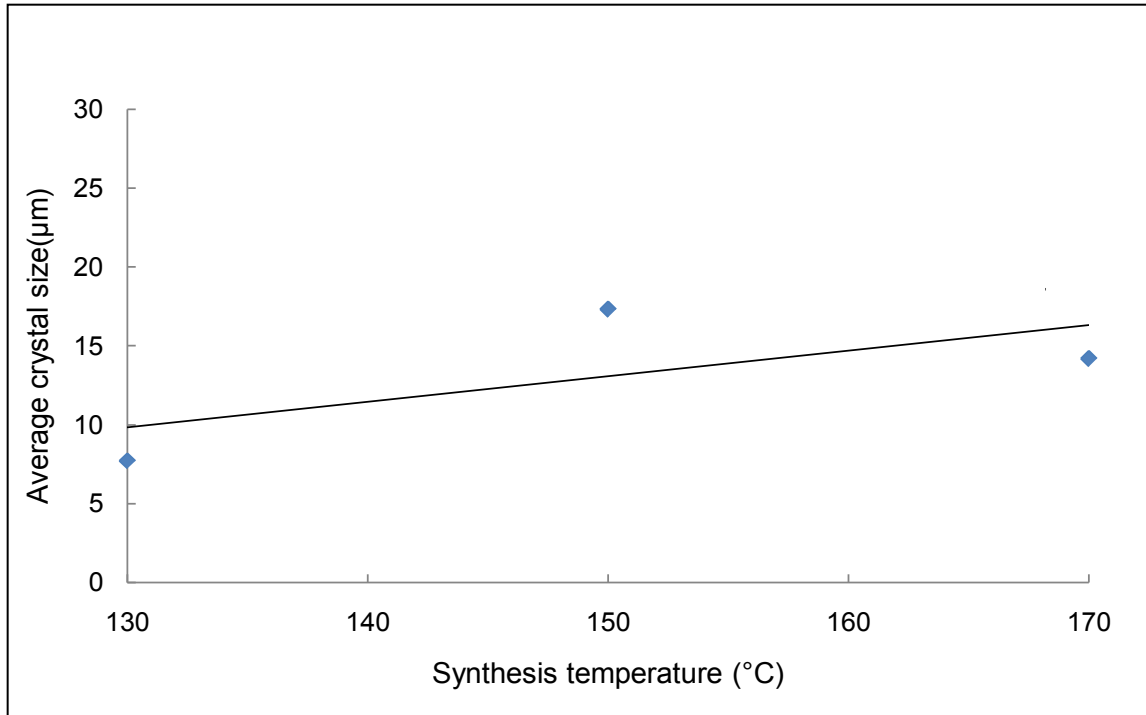


Figure 4.10: The effect of synthesis temperature on average crystal size for ZSM-5 synthesised for 72 hours and aged for 60 minutes.

4.3.3. Influence of aging time

The synthesis solution is often aged for a period of time before hydrothermal synthesis in order to form the so called primary amorphous phase [9]. This phase consists of the initial and intermediate products. During aging, partial hydrolysis and depolymerisation of these species occur and monomers form. These monomers (during crystal growth) form the secondary amorphous phase. The particles that form during this phase have a larger surface area than single crystallites and have planar faces that can incorporate nutrients more readily causing increased crystallite growth during hydrothermal synthesis [9]. For this study, the aging time was varied using 30, 60 and 90 minutes, while keeping the synthesis time and synthesis temperature constant at 72 hours and 170°C respectively. SEM images (Figure 4.11) again show intergrown crystals with the characteristic morphology while the XRD spectra confirmed that ZSM-5 was synthesised by displaying the characteristic ZSM-5 peaks at $2\theta=7-9$ and 22-25 (Figure 4.12).

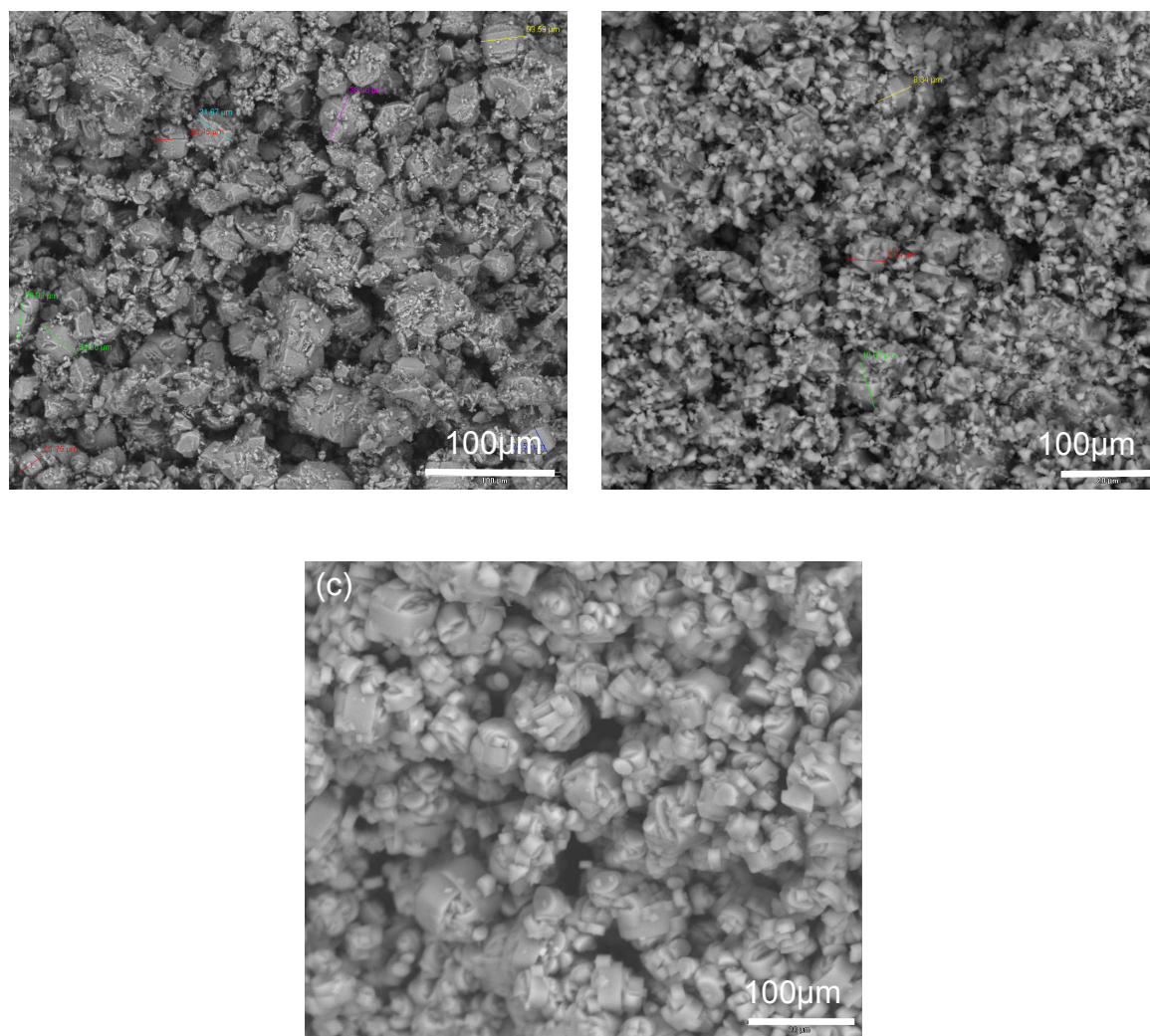


Figure 4.11: ZSM-5 aged for (a) 30 minutes, (b) 60 minutes and (c) 90 minutes.

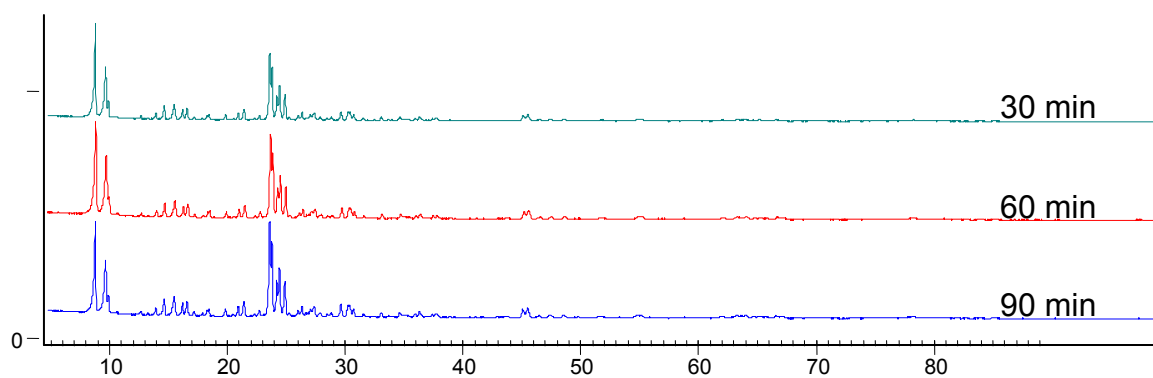


Figure 4.12: XRD spectra of ZSM-5 aged for 30, 60 and 90 minutes respectively (synthesized for 72 hours at 170°C).

Discussion of ZSM-5 synthesis

An aging time of 90 minutes produced the largest average crystals ($29.3\mu\text{m}$) (Figure 4.13) with a standard deviation of $4.1\mu\text{m}$. At an aging time of 60 minutes, an average crystal size of $9.3\mu\text{m}$ and a standard deviation of $1.4\mu\text{m}$ was observed while an aging time of 30 minutes yielded an average crystal size of $26.1\mu\text{m}$ with a standard deviation of $5.5\mu\text{m}$. It is clear that a significant variation in size was obtained with varying aging times. This variation was however confirmed by the SEM images (Figure 4.11), i.e. average intergrowth at 30 minutes, least intergrowth at 60 minutes and most intergrowth at 90 minutes. The smaller crystals obtained after 60 minutes aging could be a result of more rapid nucleation which led to a large number of smaller crystals [12]. Previous studies have confirmed that a prolonged aging time, increases the number of nuclei as well as the growth rate and the formation of polycrystalline grains because more germ nuclei are present for further growth [12]. From Figure 4.11, it is clear that the longest aging period (90 minutes) produced the most intergrown crystals.

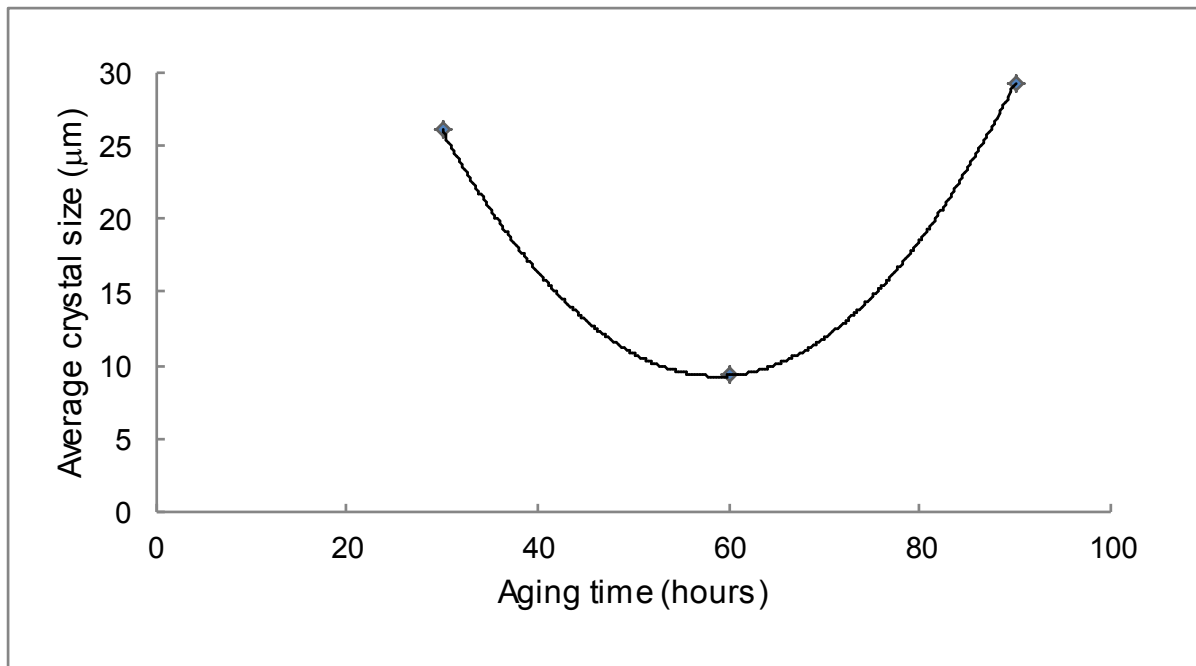


Figure 4.13: The effect of aging time on average crystal size.

In a final comparison, the average of the average crystal sizes was calculated for each set of experiments (synthesis time, synthesis temperature and aging time) and presented in Figure 4.14. Similarly, the average of the standard deviations for each set of experiments was determined (Figure 4.15). It is clear from Figure 4.14, that the

Chapter 4

largest crystal size was obtained by varying the aging time, which is understandable considering the significant influence of the aging time on the nucleation and growth of the crystals during the subsequent hydrothermal synthesis. Synthesis temperature, although smaller than aging time, also resulted in larger crystal than synthesis time which can again be related to the effect the temperature has on the nucleation and growth as explained in Section 4.3.2. The smallest crystals were obtained by varying the synthesis time, which is understandable, since the synthesis time has the least influence on the nucleation and growth rate.

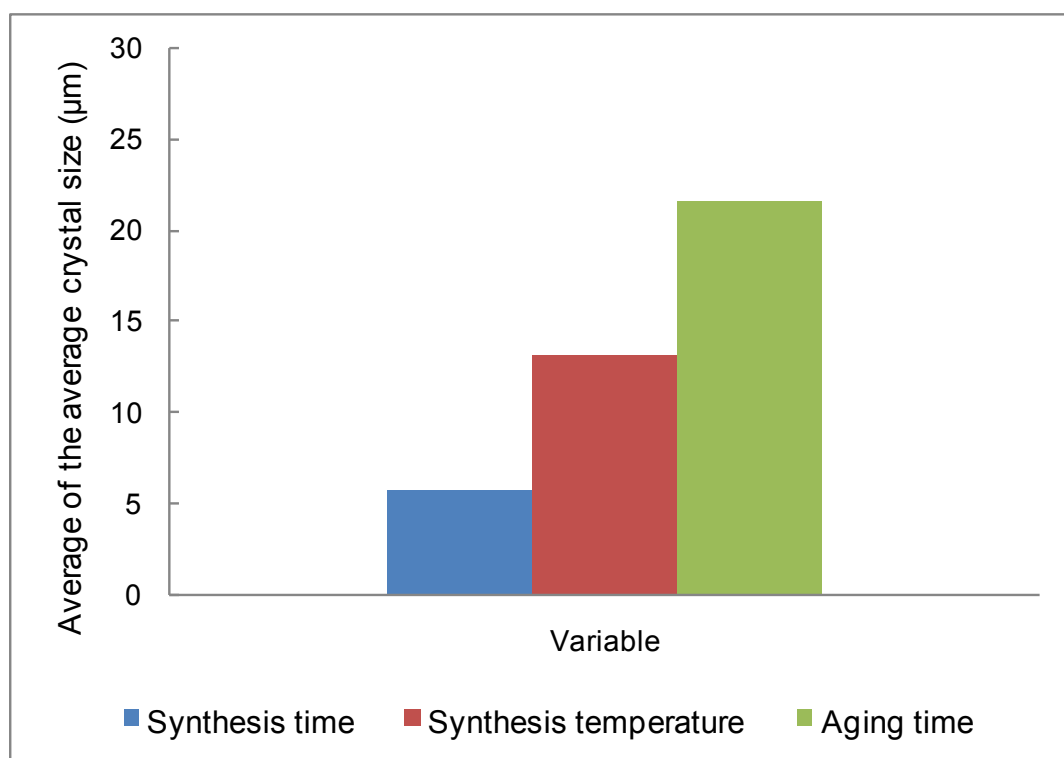


Figure 4.14: The influence of synthesis time, synthesis temperature and aging time respectively, on the average crystal size of ZSM-5.

According to Figure 4.15, aging time not only yielded the largest crystals, but also resulted in the largest variation of crystal sizes. Similar to the average crystal sizes (Figure 4.14), the average standard deviation decreased in the order: aging time>synthesis temperature>synthesis time, which confirms that the influence on crystal growth and subsequent variation decreased in the order aging time>synthesis temperature>synthesis time. Although larger crystals would have been obtained had the synthesis time and temperature experiments been conducting using an aging

Discussion of ZSM-5 synthesis

time of 30 or 90 minutes, the fact remains that aging had the larger influence on crystal size.

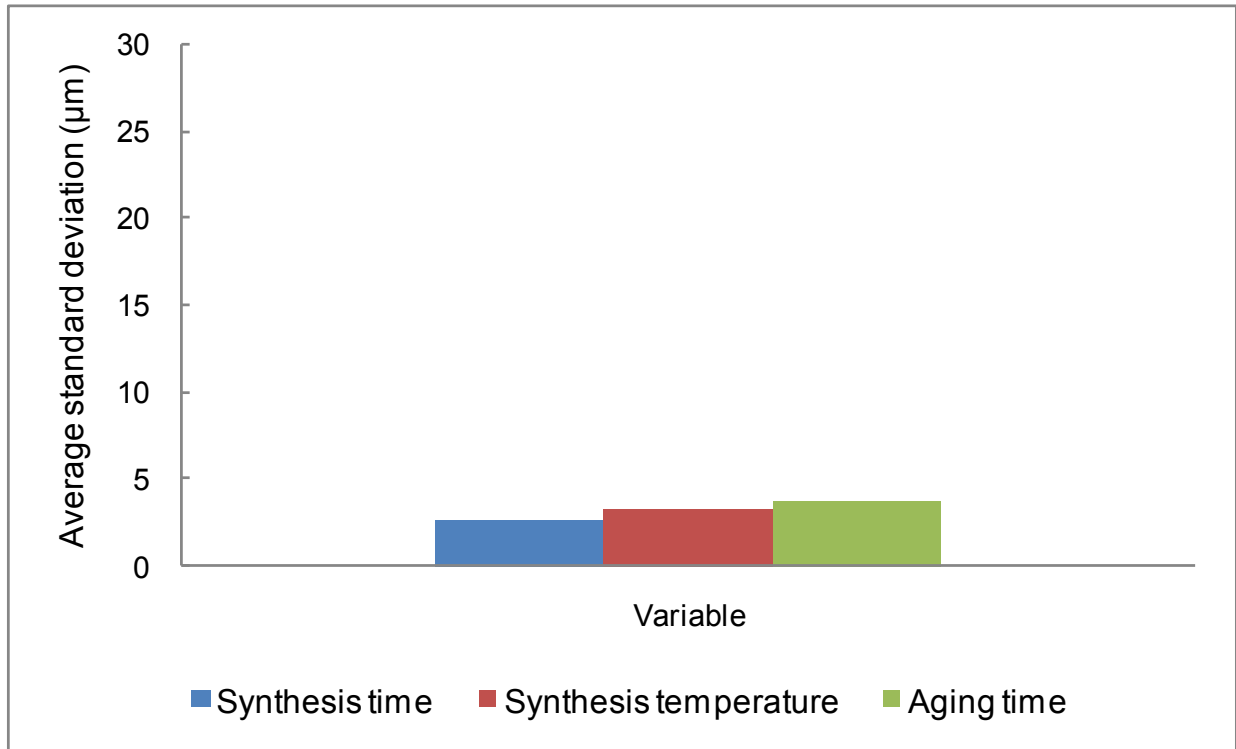


Figure 4.15: The influence of synthesis time, synthesis temperature and aging time respectively, on the average crystal size of ZSM-5.

4.4. Conclusion

XRD spectra confirmed that the hydrothermal synthesis method used to synthesise ZSM-5 was successful. ZSM-5 obtained from this method were intergrown and formed agglomerated polycrystalline grains that varied considerably in size. The influence of synthesis time, synthesis temperature as well as aging time on the size of the crystallites that form the agglomerated polycrystalline grains were investigated using SEM and XRD. From the results, it is clear that aging time had the biggest influence on the crystallite size. During the aging time, germ nuclei form which later become active in the crystal growth process. With increasing aging time, more germ nuclei and therefore more crystals form at different stages during the crystal growth process resulting in different crystallite sizes.

Chapter 4

In spite of the variation observed in the crystal sizes, all experimental variations yielded crystals that were highly intergrown. Therefore, it was not possible to separate the agglomerates to yield single crystals at different sizes for use as catalyst in the MTO process. Furthermore, usually the ZSM-5 used commercially is also highly intergrown. Therefore instead of using ZSM-5 with various crystallite sizes based on varied synthesis conditions, zeolites were all grown using a synthesis time of 72 hours at 170°C and aged for 60 minutes. In order to obtain separate particle sizes, the agglomerates then were sifted to obtain three batches, one containing agglomerated polycrystalline grains smaller than 75µm, one between 75 and 150µm and the third batch consisting of particles between 150 and 300µm.

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Discussion of ZSM-5 synthesis

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Chapter 5

ZSM-5 as catalyst for the MTO process

5.1. Introduction	50
5.2. As-synthesised ZSM-5	50
5.2.1. <i>Smaller than 75μm.....</i>	50
5.2.2. <i>75-150μm</i>	56
5.2.3. <i>150-300μm</i>	59
5.2.4. <i>Effect of fraction size on the MTO product distribution</i>	62
5.3. Catalyst A.....	66
5.3.1. <i>Smaller than 75μm</i>	66
5.3.2. <i>75-150μm</i>	69
5.3.3. <i>150-300μm</i>	71
5.3.4. <i>Effect of fraction size on the MTO product distribution</i>	73
5.4. Deactivation and coking.....	76
5.5. Conclusion.....	78
5.6. References	79

Chapter 5

5.1. Introduction

The as-synthesised ZSM-5 described in Chapter 4, as well as Catalyst A were used as catalysts for the MTO reaction in a fixed bed reactor as described in Chapter 3. The as-synthesised ZSM-5 was synthesised for 72 hours at 170°C and aged for 60 minutes. A wide range of polycrystalline grain sizes were obtained. The as-synthesised ZSM-5 as well as the Catalyst A were sieved into three fractions of polycrystalline grain sizes: smaller than 75µm, 75-150µm and 150-300µm. Although the same synthesis conditions were used to manufacture the ZSM-5 for the MTO process the syntheses were done in different batches. Therefore, SEM, XRD and ICP analyses were performed on all the ZSM-5 fractions prior to its use as catalysts in the MTO reaction. Conversion (equation 5.1) and selectivity (equation 5.2) is defined as [1]:

$$\text{Conversion} = \frac{\text{reactant input to process} - \text{reactant output from process}}{\text{reactant input to process}} \quad (5.1)$$

$$\text{Selectivity} = \frac{\text{mass of desired product}}{\text{mass of undesired product}} \quad (5.2)$$

5.2. As-synthesised ZSM-5

5.2.1. Smaller than 75µm

5.2.1.1. SEM

SEM images (Figure 5.1) of the fraction smaller than 75µm showed intergrown agglomerated polycrystalline grains, which is commonly observed for ZSM-5 [2] with the characteristic morphology of ZSM-5 when using TPA derivatives as template [1]. From the SEM micrographs a rounded form of the polycrystalline grains can be seen, which is characteristic of ZSM-5 with a lower Si/Al ratio [2] as previously discussed in Chapter 4.

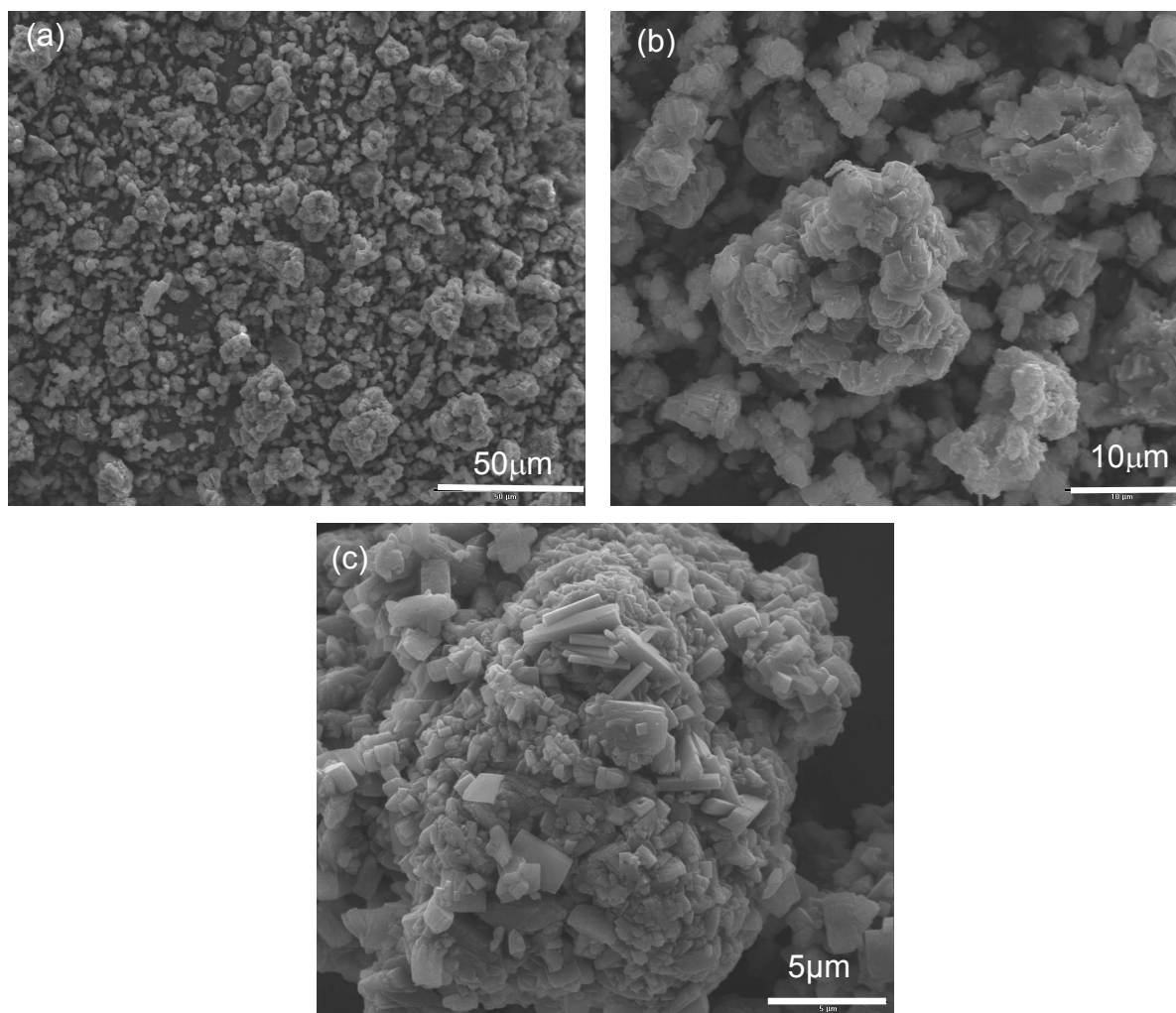


Figure 5.1: Intergrown agglomerated polycrystalline grains of as-synthesised ZSM-5 with particle sizes of smaller than 75μm (a), a closer view of the agglomerated particles (b) and Catalyst A.

5.2.1.2. XRD

The XRD pattern of the as-synthesised ZSM-5 (Figure 5.2) with polycrystalline grain sizes smaller than 75μm showed the characteristic ZSM-5 peaks at $2\theta = 7-9$ and $23-25$, confirming that ZSM-5 of high purity was synthesised [3]. The smaller than 75μm fraction's XRD pattern was also compared to the XRD spectra of Catalyst A (Si/Al=90) which was used as reference XRD spectra (Figure 5.3). The reference ZSM-5 XRD spectra also exhibited the characteristic ZSM-5 peaks as obtained for the as-synthesised ZSM-5.

Chapter 5

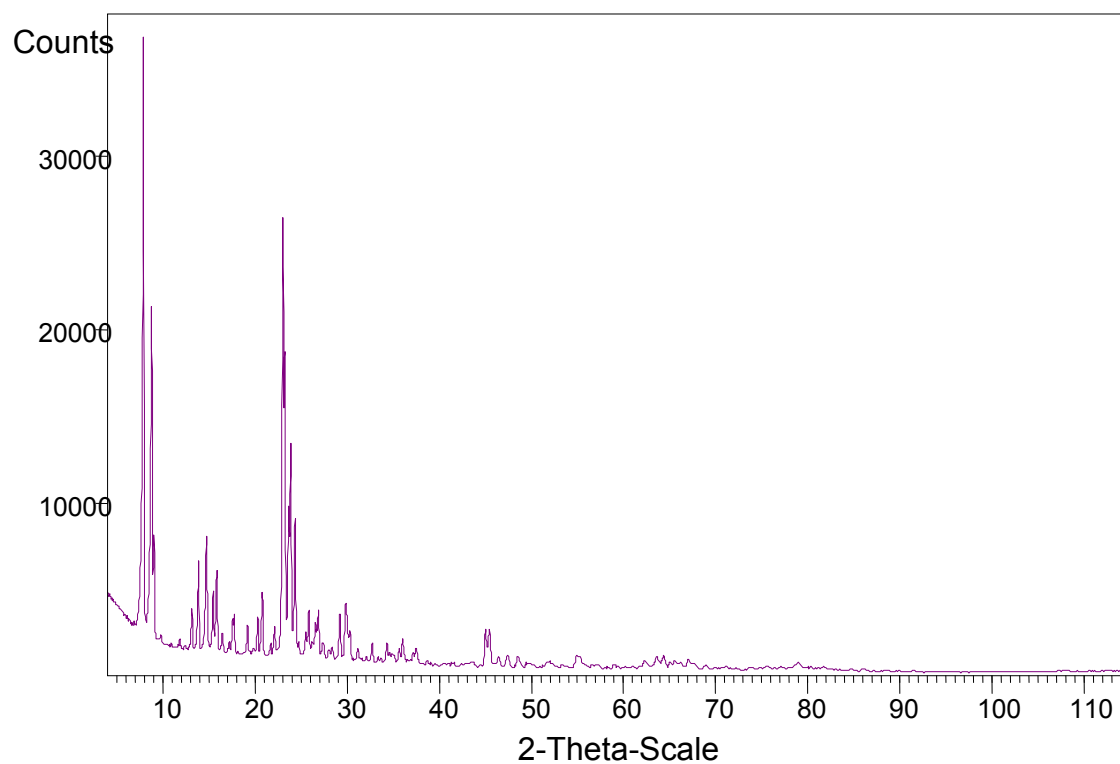


Figure 5.2: The XRD spectra of as-synthesised ZSM-5 with polycrystalline grain sizes smaller than $75\mu\text{m}$.

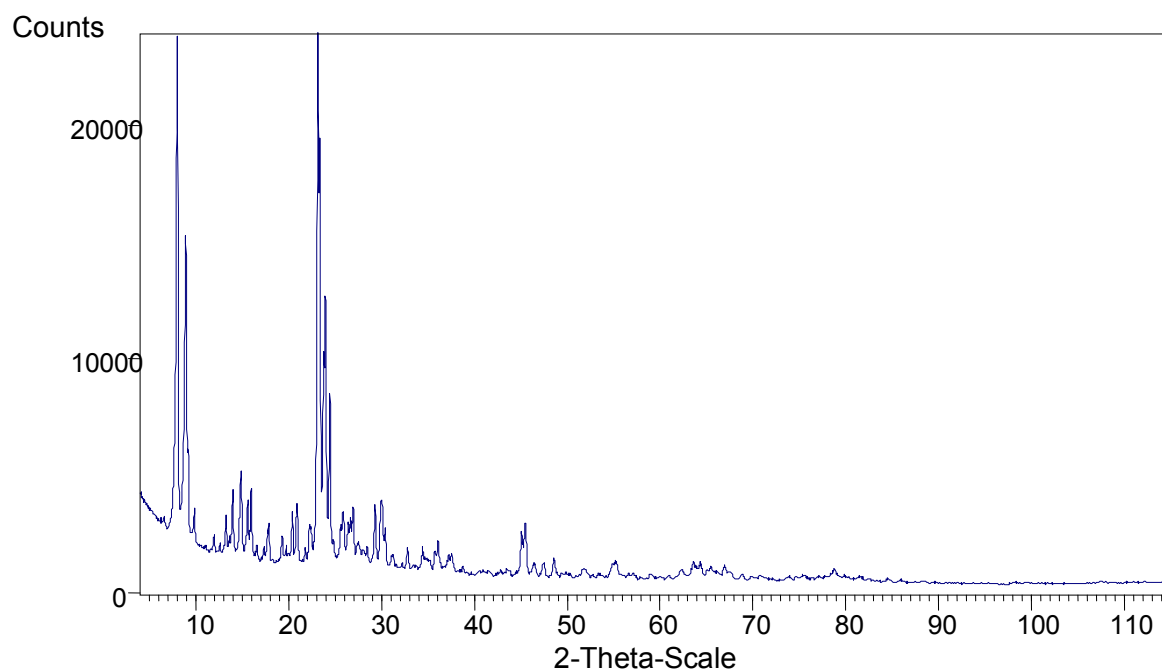


Figure 5.3: The reference XRD spectra for ZSM-5 (Catalyst A).

5.2.1.3. ICP

According to the ICP analysis, the as-synthesised ZSM-5 with polycrystalline grain sizes smaller than $75\mu\text{m}$ showed particles have a Si/Al ratio of 40.8, which is within the range of the intended Si/Al ratio of 45.

5.2.1.4. Light olefin selectivity

For the MTO reaction, 1g of the as-synthesised ZSM-5 with polycrystalline grain sizes smaller than $75\mu\text{m}$ was loaded into the fixed bed reactor with a feed consisting of 20wt% methanol in water and a flow rate of 0.1 ml/min, WHSV of 5.77 h^{-1} at atmospheric pressure and 450°C . The obtained product distribution is shown in Figure 5.4.

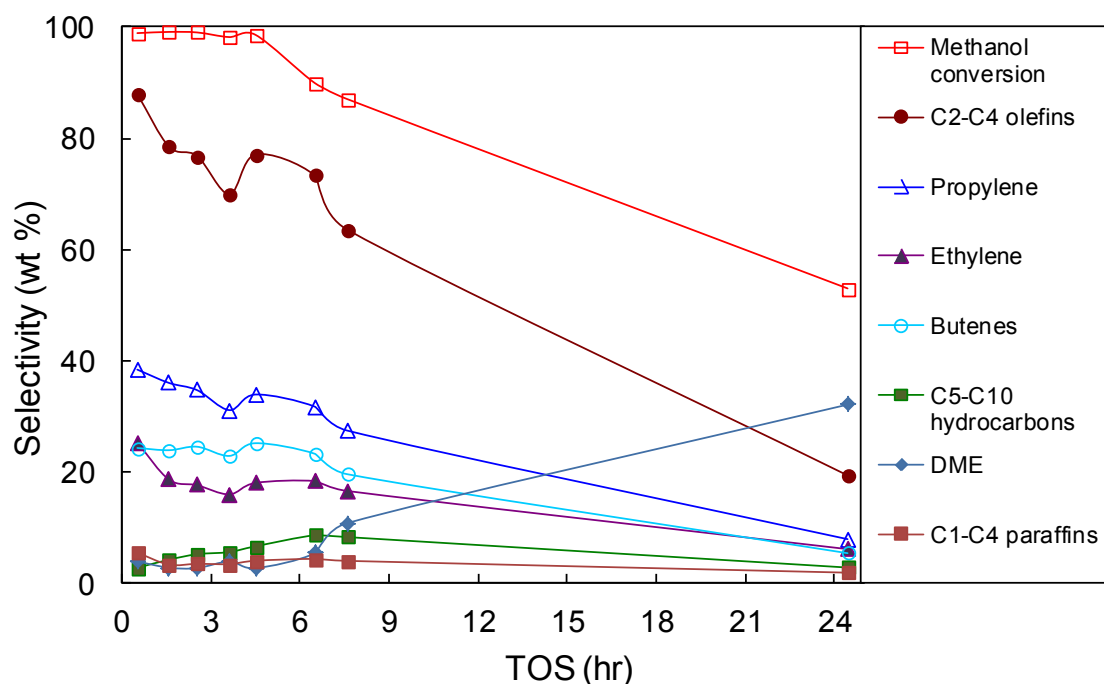


Figure 5.4: The product distribution of as-synthesised ZSM-5 with polycrystalline grain sizes smaller than $75\mu\text{m}$.

During the MTO process, methanol is first dehydrated to form an equilibrium mixture of DME, water and methanol. Freshly activated catalysts exhibit a short induction period before primary olefin, paraffin and aromatic products are formed. The equilibrium mixture is then converted to primary olefin products (ethylene and

Chapter 5

propylene). Strongly acidic zeolites like H-ZSM-5, convert the primary olefin products via secondary reactions to paraffins, aromatics and higher olefins [3].

When considering the individual products, the following was observed. A methanol conversion of almost 100% was achieved for the first 5 hours of the reaction after which the conversion decreased to 53% after 24 hours. The decrease in conversion could be caused by water formed during the reaction as well as water in the feed, which adsorbed on the Brönsted acid sites preventing methanol molecules from adsorbing on the acid sites as well as possible deactivation of the Lewis acid sites by water [2]. However, the contribution of Lewis acidity during methanol conversion is considered negligible in comparison to the Brönsted acidity, although cracking reactions could be favoured by the mutual effect of neighboring Brönsted and Lewis acid sites [4].

Experimental and theoretical studies conducted by Haw and co-workers [6] and Cui and co-workers [7], found that the MTO process could only take place in zeolites that have transition-state shape selectivity in order for the hydrocarbon pool mechanism to occur. The hydrocarbon pool mechanism proposes that methanol and DME react on cyclic organic species inside the cages and channels of ZSM-5. These organic species form during the induction period and act as scaffolds to which methanol and DME add and ethylene is split off. The cyclic organic species form via secondary reactions and will eventually become polycyclic aromatic hydrocarbons (coke) which deactivates the ZSM-5 catalyst [6]. Svelle and co-workers [8] proposed that the MTO process proceeds through dual cyclic reaction. Ethylene forms through the hydrocarbon pool mechanism and propylene, butenes and higher olefins form via an olefin methylation-cracking cycle [9].

The C₂-C₄ selectivity of the reaction initially was at 88% but gradually decreased to 19% after 24 hours. The decrease in C₂-C₄ selectivity is probably a result of the increase in unconverted dimethyl ether (DME) as active sites are blocked by coking as TOS increase. The decrease in light olefin selectivity can also be a reflection of the fact that ZSM-5's channel intersections provide enough space for cyclisation reactions and intermolecular hydride transfer reactions to convert C₂-C₄ olefins to paraffins and aromatics [5].

ZSM-5 as catalyst for the MTO process

Propylene is the primary olefin product with the highest selectivity (38% at TOS=0.52 hours). Ethylene, which had an initial selectivity of 25%, dropped to 19% after an hour. Previous studies showed that during methanol conversion, ethylene is methylated to propylene [6]. The extent of this and other secondary reactions depends on the acid strength, acid site density, catalyst topology as well as crystallite size and process conditions [6].

The butenes' selectivity increased to reach a maximum selectivity of 25% at 2.53 hours followed by a gradual decrease in selectivity. The typical increase to a maximum selectivity followed by a gradual decrease in selectivity of the MTO olefinic products is indicative of their intermediate character [5].

From Figure 5.4 it is clear that small amounts of C_1 - C_4 paraffins and C_5 - C_{10} hydrocarbons formed during the reaction. The channel intersections of ZSM-5 provide enough volume for cyclisation reactions and intermolecular hydride transfer reactions by which a mixture of olefins can be converted into paraffins and aromatics [6].

The ratio of acid sites on the external surface to intracrystalline acid sites plays a very important role in the selectivities towards certain MTO products. The smaller the crystallites, the higher the ratio and a sufficient acid site concentration on the non-selective outer surface lead to aromatics and branched isomers being formed [5].

The DME selectivity increased after a few hours TOS which indicates a decrease in active acid sites as well as coke being forming in the intracrystalline and intercrystalline voids of the catalyst [5].

In conclusion, it was shown that the product selectivities of the MTO reaction with agglomerated polycrystalline grain sizes smaller than $75\mu\text{m}$ were comparable to results of previous studies with similar process conditions [5]. A detailed discussion on the possible effect of the various fractions on the product distribution is discussed in Section 5.2.4.

Chapter 5

5.2.2. 75-150 μm

5.2.2.1. SEM

SEM images (Figure 5.5) again showed intergrown agglomerated polycrystalline grains with the characteristic morphology of ZSM-5 synthesized with TPA derivatives as templating agent. The relatively low Si/Al ratio of 40.9 (as determined by ICP analysis) decreased the crystallites' length/width aspect ratio which caused the ZSM-5 crystals to be rounded [2].

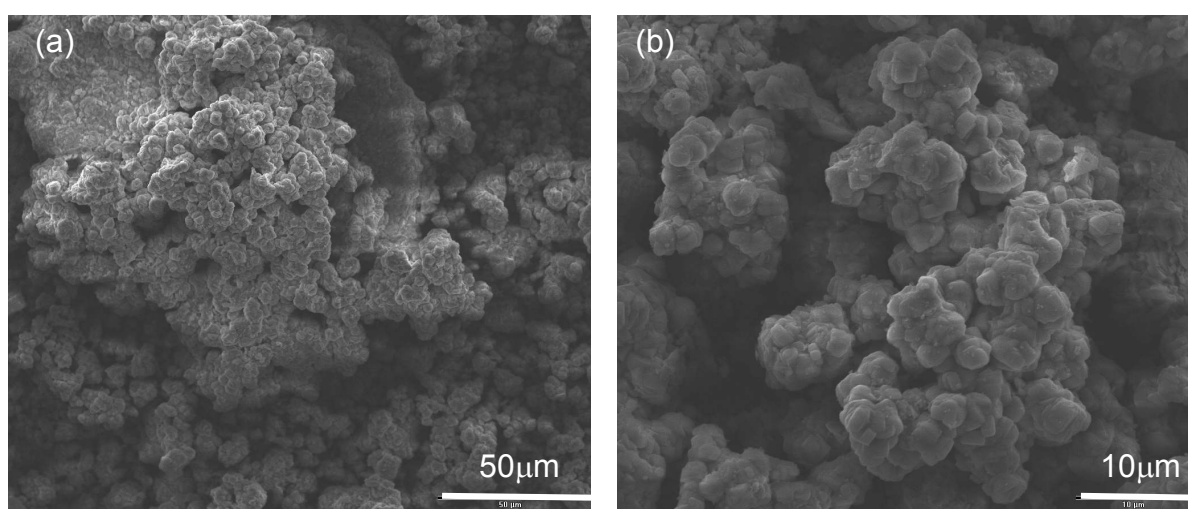


Figure 5.5: Intergrown polycrystalline grains of as-synthesised ZSM-5 with sizes 75-150 μm (a) and a closer view of the same zeolite fraction (b).

5.2.2.2. XRD

The XRD pattern of the as-synthesised 75-150 μm fraction (Figure 5.6) displayed the characteristic ZSM-5 peaks at $2\theta = 7-9$ and $23-25$. No other peaks formed which means that highly pure ZSM-5 was synthesised and that the hydrothermal synthesis method was successful.

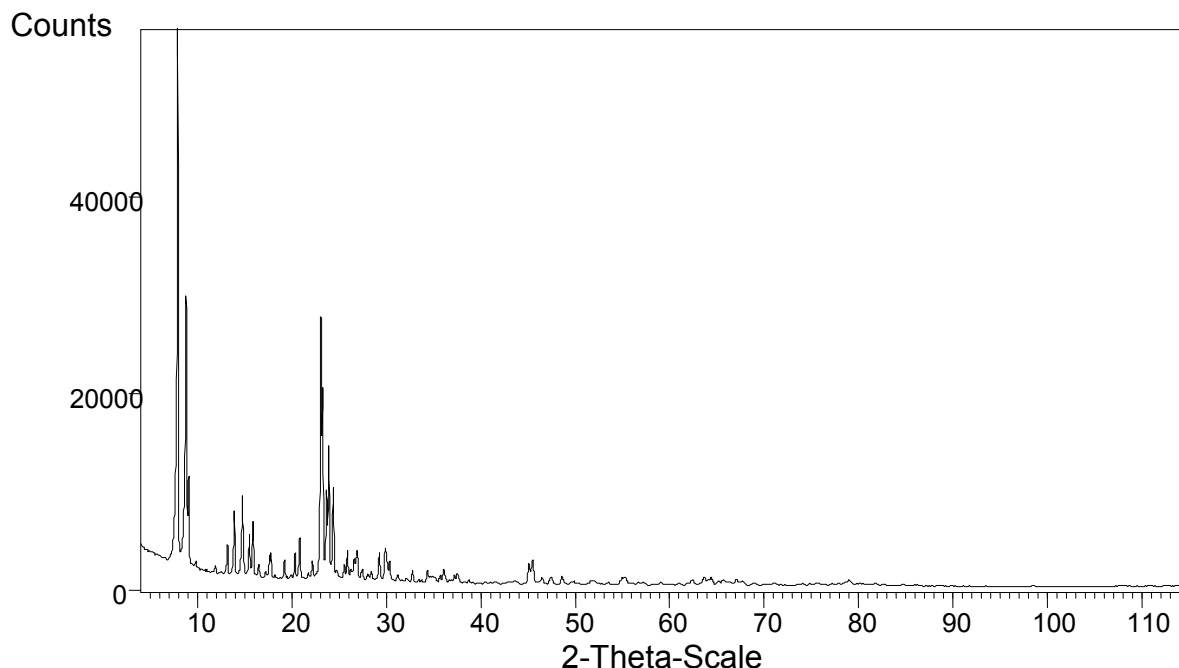


Figure 5.6: XRD spectra of as-synthesised ZSM-5 with polycrystalline grain sizes of 75-150 μm .

5.2.2.3. ICP

ICP analysis of the 75-150 μm fraction of as-synthesised ZSM-5 reported a Si/Al ratio of 40.9. This is the ratio as obtained for the smaller than 75 μm fraction, which is understandable since both fractions come from identical batch reactions. This also confirms the repeatability of the zeolite synthesis batch process.

5.2.2.4. Light olefin selectivity

For the MTO reaction, 1.16g of as-synthesised ZSM-5 with agglomerated polycrystalline grain sizes of 75-150 μm was loaded into the fixed bed reactor with a feed consisting of 20 wt% methanol in water and a flow rate of 0.1 ml/min, WHSV of 4.97 h^{-1} at atmospheric pressure and 450°C. The results are shown in Figure 5.7.

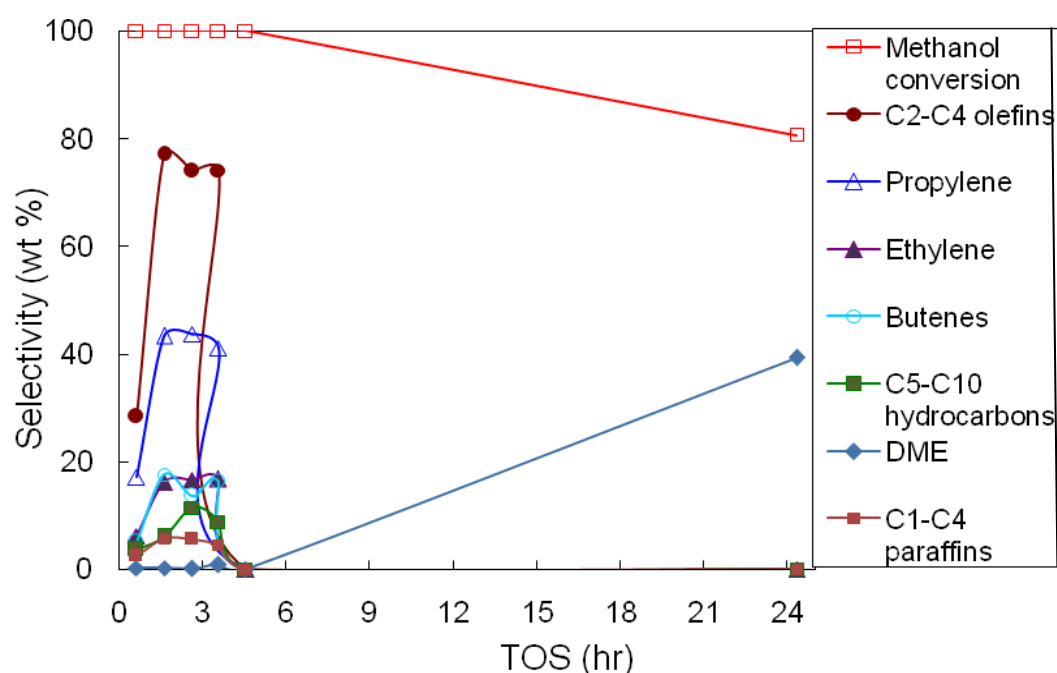


Figure 5.7: The product distribution of as-synthesised ZSM-5 with polycrystalline grain sizes of 75-150 μ m used as catalyst during the MTO process.

Methanol conversion followed the same trend as the smaller than 75 μ m fraction, i.e. there was a 100% methanol conversion for 5 hours after which the conversion decreased in this case to 81% after 24 hours because of the reasons previously mentioned in Section 5.2.1.4. An induction period was observed which is to be expected from literature as well as previous studies [6].

The C₂-C₄ selectivity reached a maximum of 77% after 1.63 hours TOS and remained high for 3 hours after which it decreased to zero selectivity for the rest of the reaction. This is probably due to an experimental error that occurred because of a gas leakage, causing the gaseous products to escape from the sampling container.

As observed for the smaller than 75 μ m fraction, propylene was the primary olefin product with the highest yield (44% at 2.63 hours TOS). The 75-150 μ m fraction produced an ethylene selectivity of 17% at 2.65 hours TOS and a butene selectivity of 18% at 1.63 hours TOS. The primary olefin products displayed the characteristic intermediate trend of increasing selectivity to a maximum value followed by a gradual decrease in selectivity as discussed in Section 5.2.1.4.

Similarly to the smaller than 75 μ m fraction, the DME selectivity increased with TOS and 39% unconverted DME was present after 24 hours. This is an indication that coking and therefore deactivation increased with TOS resulting in less DME being converted to products. A temperature loss in the reactor will also cause a higher DME yield due to the fact that light olefins form at higher temperatures (above 450°C) while DME forms at temperatures lower than 450°C [6].

The acid strength of the as-synthesised ZSM-5 was sufficient to convert primary olefin products to C₁-C₄ paraffins and C₅-C₁₀ hydrocarbons with a maximum of 11% at 2.63 hours TOS via secondary reactions [6]. High product selectivities during a very short induction time can be observed for the MTO products in Figure 5.6. When compared to the smaller than 75 μ m fraction, as well as results for MTO product selectivities in literature [7], the high selectivities of MTO products reached after such a short induction time as seen in Figure 5.6 is probably not accurate and could have been caused by an experimental error that occurred because of the above mentioned gas leakage. The selectivities obtained at 3.5 hours TOS is however comparable to the previously discussed results as well as literature and therefore will be compared to the other ZSM-5 fractions' selectivities at 3.5 hours TOS. The effect of the various fractions on the product distribution is discussed in Section 5.2.4.

5.2.3. 150-300 μ m

5.2.3.1. SEM

SEM images (Figure 5.8) showed intergrown agglomerated polycrystalline grains with the characteristic morphology of ZSM-5 when TPA derivatives are used as template. A relatively low Si/Al ratio of 41.3 (as determined by ICP analysis), was the cause of the rounded form of the crystals [2]. The crystallites formed on different parts of the Teflon insert have different shapes e.g. the crystallites that did not form on the Teflon insert but remained in the synthesis solution.

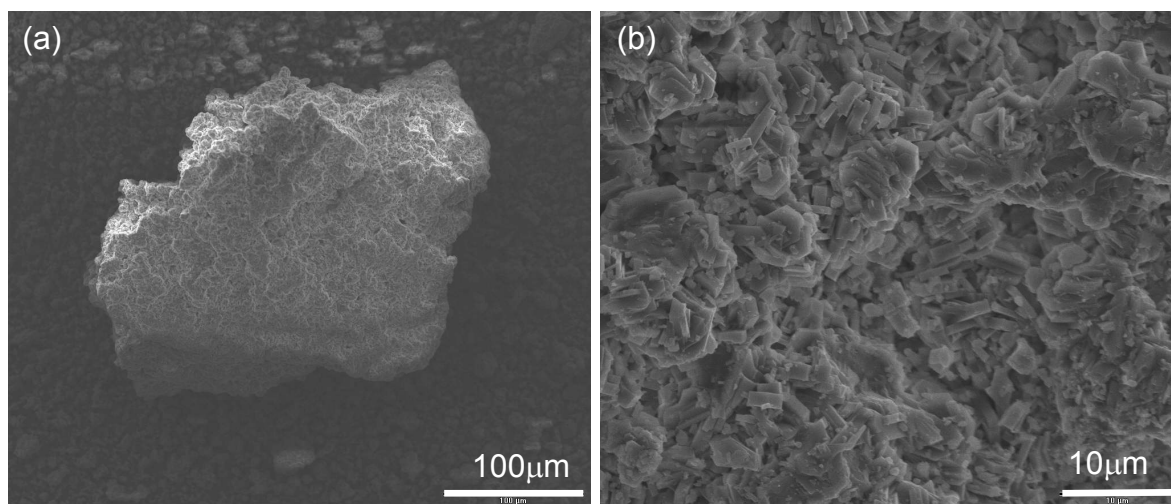


Figure 5.8: Intergrown polycrystalline grains of as-synthesised ZSM-5 with sizes of 150-300 μm (a) and a closer view of the agglomerated particles (b).

5.2.3.2. XRD

XRD confirmed the 150-300 μm fraction as ZSM-5 (2θ= 7-9 and 23-25 peaks were present). The XRD results as presented in Figure 5.9, also confirmed that only ZSM-5 and no other zeolites formed.

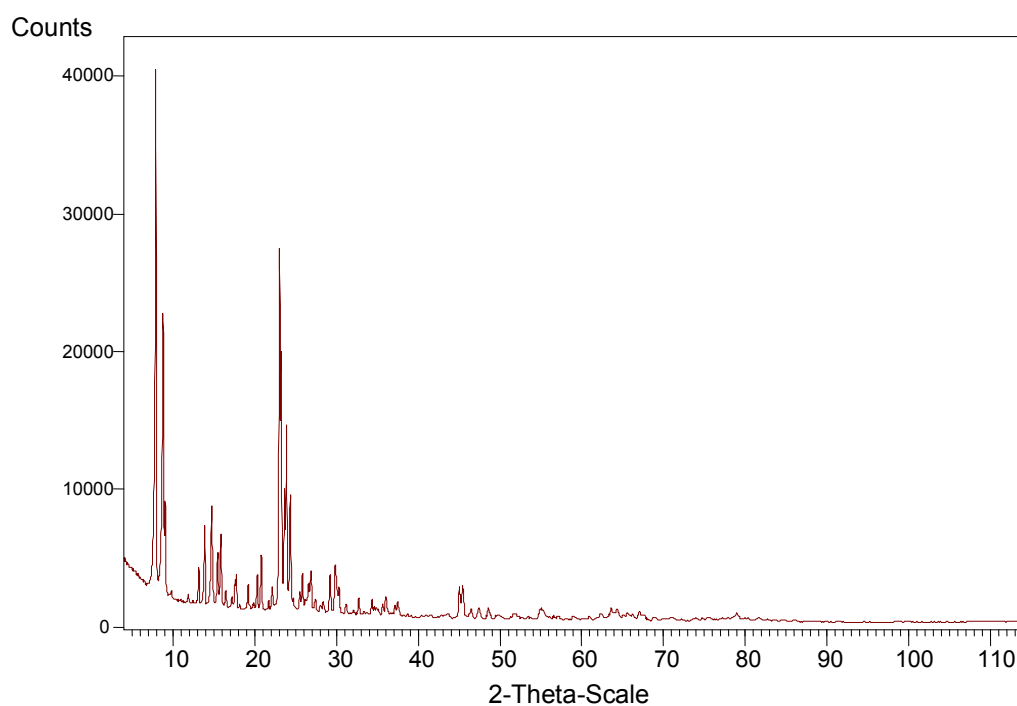


Figure 5.9: XRD spectra of as-synthesised ZSM-5 with polycrystalline grain sizes of 150-300 μm.

5.2.3.3. ICP

ICP analysis confirmed a Si/Al ratio of 41.3, which is slightly higher than the ratio obtained for the <75 μm and 75-150 μm fractions, but still falls within the acceptable boundaries of the small errors possible when using various batches.

5.2.3.4. Light olefin selectivity

For the MTO reaction, 1.02g of as-synthesised ZSM-5 with polycrystalline grain sizes of 150-300 μm was used as catalyst in the fixed bed reactor with a feed consisting of 20 wt% methanol in water and a flow rate of 0.1 ml/min, WHSV of 5.65 h⁻¹ at atmospheric pressure and 450°C. The results obtained are shown in Figure 5.10.

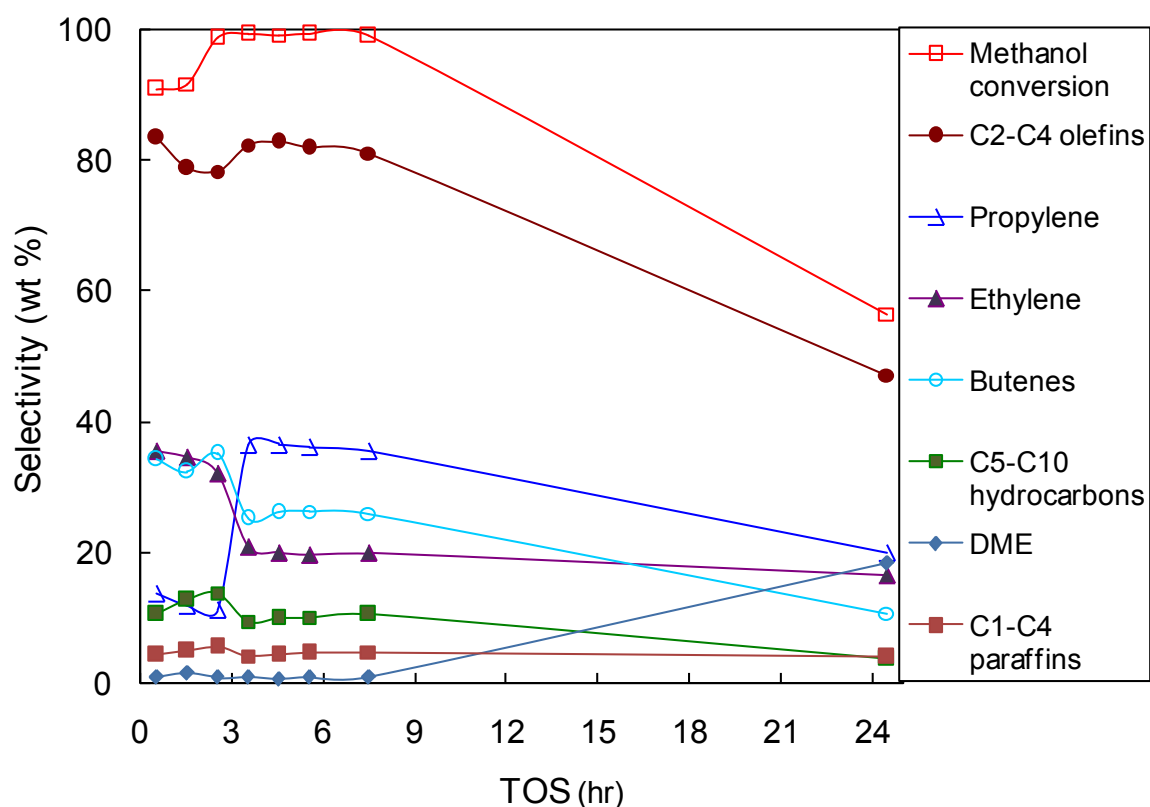


Figure 5.10: The product distribution of as-synthesised ZSM-5 with polycrystalline grain sizes of 150-300 μm .

A methanol conversion of 100% was achieved from 3 to 5 hours TOS, after which the conversion decreased to 57% after 24 hours which again correlated both with the <75 μm and the 75-150 μm fractions previously discussed in Sections 5.2.1.4. and 5.2.2.4.

Chapter 5

The C₂-C₄ selectivity started at 83% but gradually decreased to 47% after 24 hours. Propylene has the highest selectivity of the olefin products and reached a maximum of 37% after 4.5 hours TOS before decreasing to 20% after 24 hours. The propylene selectivity started off with a lower than 20% selectivity for the first 2.5 hours TOS after which the selectivity drastically increased at 3.5 hours TOS. The MTO process is characterised by an induction period during the first few hours of the reaction where the cyclic organic species are formed and therefore olefin product selectivity is low. When ample cyclic organic species are formed to produce enough ethylene for the methylation-cracking cycle to convert to higher olefins, the olefin product selectivity will increase to a maximum that will later decrease due to coking and catalyst deactivation [9]. This trend is observed for all olefin products. Ethylene had an initial selectivity of 35% which dropped to 17% after more than 24 hours TOS.

The C₁-C₄ paraffins and C₅-C₁₀ hydrocarbons' selectivity also increased to form a maximum of 6% and 14% respectively at 2.5 hours TOS after which both products' selectivity steadily decreased to 4% after 24 hours TOS. ZSM-5's Brönsted acid sites are strong enough to convert primary olefin products to paraffins and aromatics via secondary reactions. However, with increasing TOS, less strong Brönsted acid sites are available (because of coking and catalyst deactivation) and therefore the C₅-C₁₀ hydrocarbon selectivity will decrease with TOS [6]. The product selectivities of the MTO reaction with agglomerated polycrystalline grain sizes of 150-300µm were comparable to results of previous studies with similar process conditions [5]. Similarly DME's selectivity increased with TOS as the conversion to hydrocarbons decreased due to coking and catalyst deactivation [5].

5.2.4. Effect of fraction size on the MTO product distribution

In Figure 5.11, the methanol conversion as well as C₂-C₄ selectivities obtained for the three fractions are presented. From 2.5 to 5.5 hours TOS, all three MTO reactions with different polycrystalline grain sizes had a methanol conversion of 100%. The selectivities of the products formed by the three differently sized fractions can therefore be compared to each other in this region. For comparative purposes 3.5 hours TOS was chosen. In Table 5.1, the selectivities obtained for the C₂-C₄,

ZSM-5 as catalyst for the MTO process

ethylene, propylene and butane fractions after 3.5 hours TOS is presented. A detailed representation of ethylene and propylene selectivity as function of TOS is given in Figure 5.12. From Figures 5.11 and 5.12 and Table 5.1, it is clear that the 150-300 μm fraction produced the largest light olefin yield at TOS=3.5 hours, followed by 75-150 μm and the lowest yield from the smaller than 75 μm fraction. Only the light olefin selectivity ($\text{C}_2\text{-C}_4$ olefins) of the different fractions was compared because of the commercial importance of light olefins as raw materials for polyethylene and polypropylene production [7]. The three fractions' light olefin selectivity was between 70-82%. MTO product selectivities of the as-synthesised particles compared well to results from previous studies with similar process conditions [5].

When comparing the three catalysts' products at 3.5 hours TOS, all three catalysts had a higher selectivity towards propylene (31%, 41% and 36% for the <75 μm , 75-150 μm and 150-300 μm fractions respectively) than towards ethylene (16%, 17% and 21% for the <75 μm , 75-150 μm and 150-300 μm fractions respectively). A higher propylene yield is expected and can be explained by the fact that ethylene undergoes methylation while butene undergoes cracking reactions inside ZSM-5 forming propylene [6]. The intermediate 75-150 μm fraction produced the highest propylene selectivity. However, the larger 150-300 μm fraction produced the highest ethylene selectivity as seen from Figure 5.11. Smaller single crystals give better light olefin selectivities than larger single crystals [3]. Smaller crystals have shorter diffusional paths and thus less opportunity for secondary reactions at strong Brönsted acid sites to convert the primary olefin products to paraffins and aromatics as well as reducing the reaction rate [7, 8 and 9]. The external crystal surface/internal crystal surface ratio increases for small crystals and this has a negative effect on shape selectivity [7].

Chapter 5

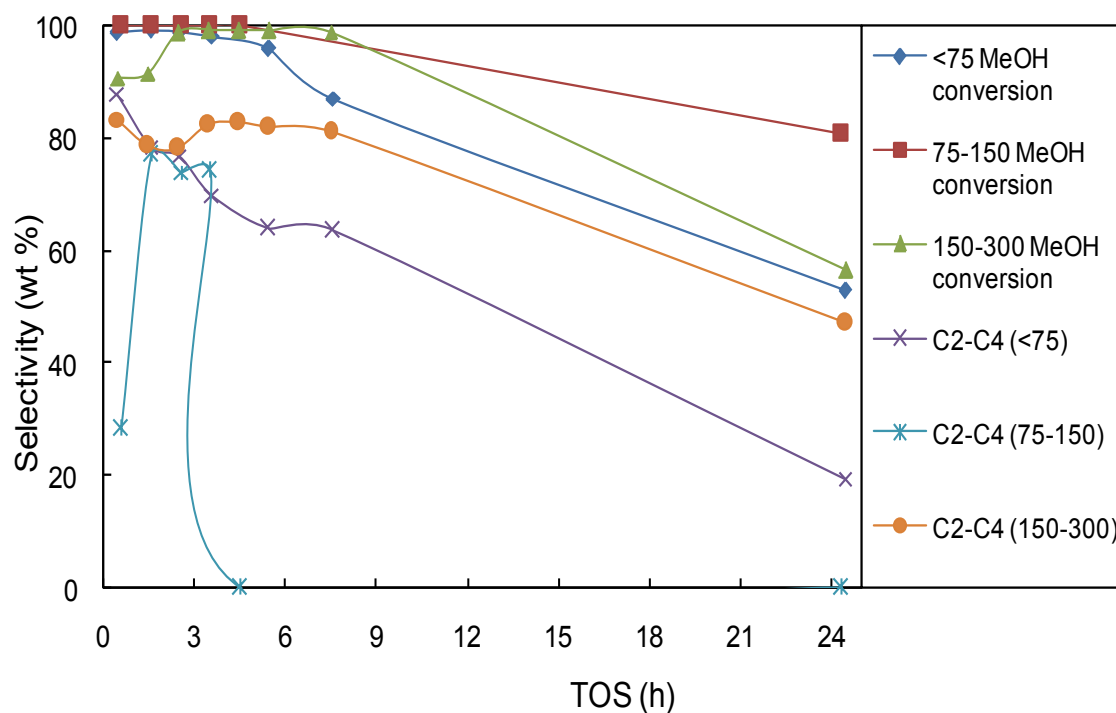


Figure 5.11: Methanol conversion and C₂-C₄ selectivity for MTO reactions with as-synthesised ZSM-5 of varying polycrystalline grain sizes as catalyst.

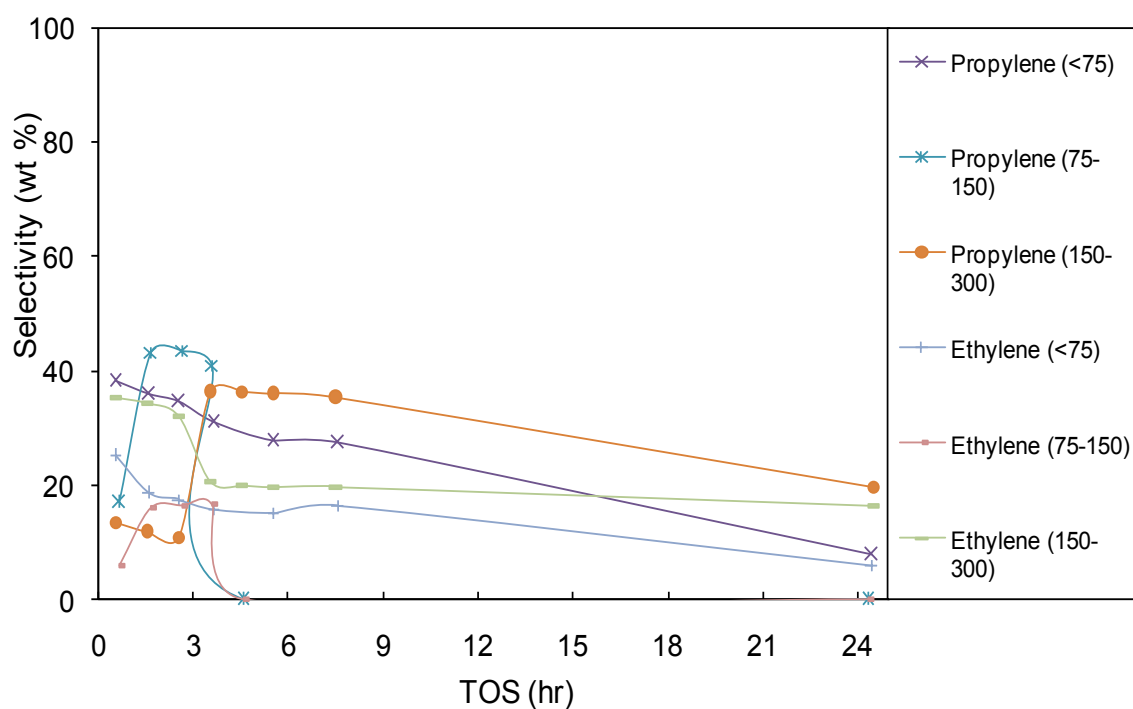


Figure 5.12: Ethylene and propylene selectivity for MTO reactions with as-synthesised ZSM-5 as catalyst.

ZSM-5 as catalyst for the MTO process

Table 5.1: Primary olefin product selectivities (3.5 hours TOS) obtained from various as-synthesised ZSM-5 polycrystalline grain fractions.

Olefin products	Selectivity(wt%)		
	<75µm	75-150µm	150-300µm
C ₂ -C ₄ olefins	70	74	80
Ethylene	16	17	21
Propylene	31	41	36
Butenes	23	17	25

However, when the catalyst used for MTO consists of intergrown agglomerated polycrystalline grains, the diffusion deviates from ordinary diffusion within single crystals due to the influence of intercrystalline boundaries and intercrystalline voids [2]. When the polycrystalline grains are large, intercrystalline mass transport effects at the internal boundaries between monocrystals that form the agglomerates can become significant and result in reduced catalytic activity. Polycrystalline grains contain second-order pores in addition to first-order pores in the ZSM-5 channels [2, 3]. Self-diffusion inside the second-order pores is faster than inside the first-order pores resulting in coke being mainly deposited within them resulting in decreased catalyst poisoning [10]. Diffusion of molecules in ZSM-5 depends on the degree of intergrowth of the crystals. The diffusion coefficients observed by Caro *et.al.* [11] for polycrystalline samples, were three orders of magnitude lower than for single crystals. Therefore, it can be concluded that intercrystalline boundaries represent transport barriers and in order to obtain optimal diffusion should be kept at a minimum. The lower diffusivities in intergrown samples may be caused by a slower rate of sorption through the (100) surface planes which only have pore openings that lead to ZSM-5's sinusoidal channels where as the (010) plane's pore openings lead to the straight channels. Diffusion through the straight channels is faster than through the sinusoidal channels. Another factor that may have an influence on diffusion through polycrystalline grains is a narrowed effective pore diameter of ZSM-5 by steric restrictions at the internal boundaries between the intergrown crystals [11]. Diffusion in polycrystalline grains deviate from ordinary diffusion [2] in single crystallites because of the the change in the migration modes as soon as the

Chapter 5

molecules pass from the intracrystalline space to the intercrystalline space. Molecular migration is enhanced by the existence of the free space between the individual crystallites and therefore more molecules should be able to participate in the faster motion outside the crystallites [2]. Therefore, larger polycrystals will have more intercrystalline voids and faster diffusion with less secondary reactions to convert primary olefin products to paraffins and aromatics. This is evident from Table 5.1 and Figures 5.11 and 5.12. The smaller than 75 μ m fraction had the lowest light olefin selectivity.

5.3. Catalyst A

5.3.1. *Smaller than 75 μ m*

5.3.1.1. SEM

SEM micrographs (Figure 5.1b) of Catalyst A showed crystals with different morphologies and sizes including crystals with a fairly large length/width aspect ratio which is a well known of ZSM-5 with a high Si/Al [2]. Catalyst A's crystals were also intergrown to form agglomerated polycrystalline grains as was observed for the as-synthesised ZSM-5.

5.3.1.2. XRD

The XRD spectra (Figure 5.13) of the Catalyst A showed the characteristic ZSM-5 peaks at at $2\theta = 7-9$ and $23-25$, and no other peaks, indicating ZSM-5 with high purity [3].

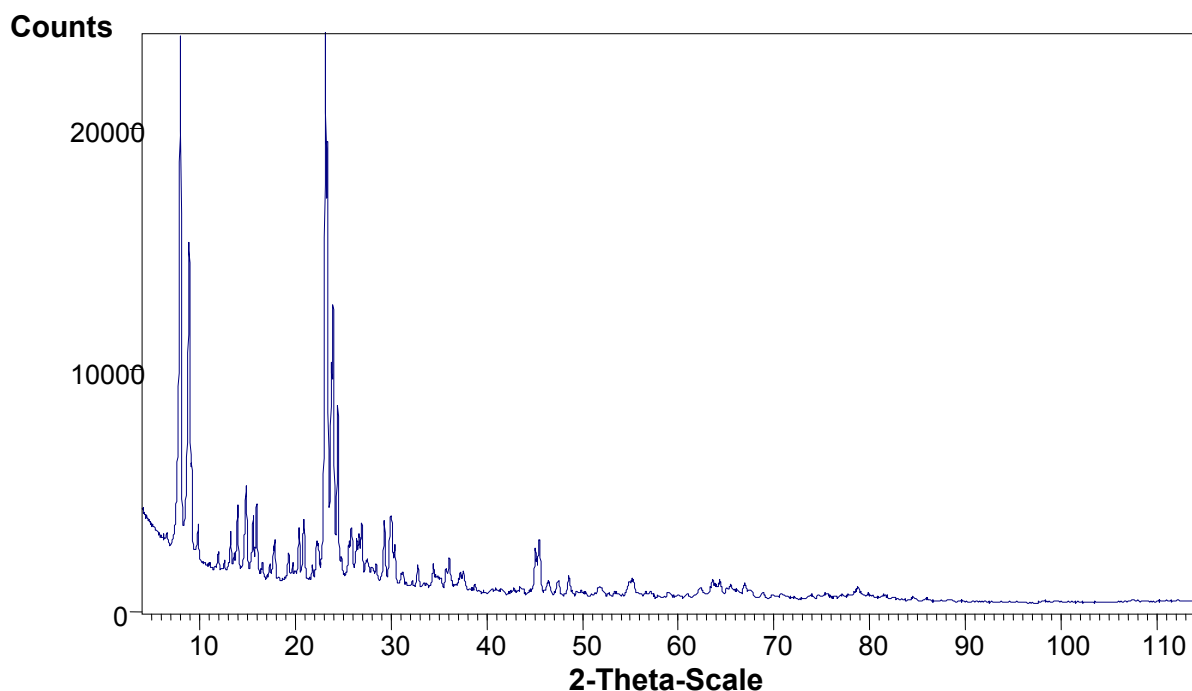


Figure 5.13: The XRD spectra of Catalyst A.

5.3.1.3. Light olefin selectivity

For the MTO reaction, 5.03g Catalyst A with polycrystalline grain sizes smaller than $75\mu\text{m}$ was loaded into the fixed bed reactor with a feed consisting of 20 wt% methanol in water and a flow rate of 0.5 ml/min, WHSV of 5.73 h^{-1} at atmospheric pressure and 450°C (Figure 5.14). Methanol conversion remained at 100% for 24 hours TOS. The $\text{C}_2\text{-C}_4$ selectivity reached a maximum of 87% at 0.87 hours TOS before showing a large decrease in selectivity from 86% at 1.77 hours to 35% at 2.87 hours where it then remained for more than 24 hours TOS. DME selectivity increased, suggesting that DME conversion to olefins decreased. This also suggests different active sites for methanol and DME conversion. The $\text{C}_2\text{-C}_4$ selectivity obtained was in accordance with results from previous studies [5].

Chapter 5

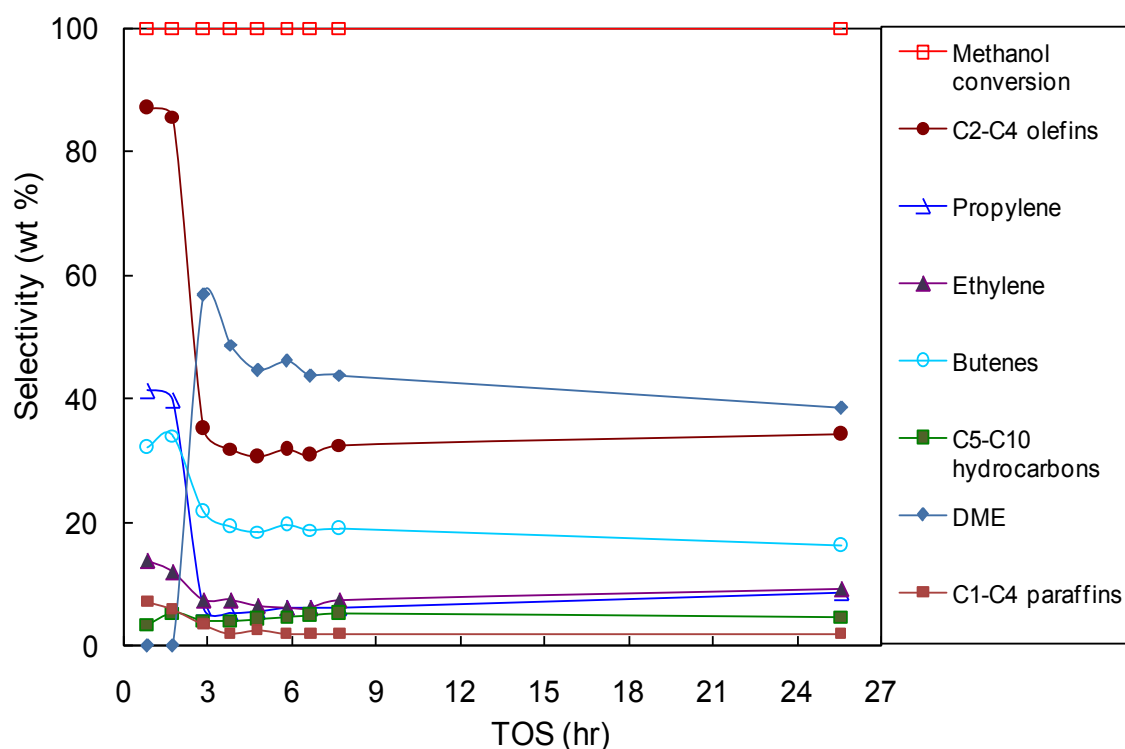


Figure 5.14: The product distribution of Catalyst A with agglomerated polycrystalline grain sizes smaller than $75\mu\text{m}$ used as catalyst during the MTO process.

Propylene was the primary olefin product with the highest selectivity (41% at 0.87 hours TOS), followed by butenes (34% at 1.77 hours TOS). Ethylene had the lowest selectivity of the primary olefin products (14% at 0.87 hours TOS). As previously discussed, the methylation-cracking cycle that is present during methanol conversion leads to propylene being the primary olefin product with the highest selectivity [9].

DME showed a drastic increase from 0% at 1.77 hours TOS to 57% at 2.87 hours TOS. The increase in unconverted DME is expected because the decrease in active sites as well as coke formation on the catalyst with TOS leads to a lowered DME conversion. Lower temperatures causes DME to form and a temperature drop below 450°C in the reactor will also lead to DME formation [5].

The paraffin ($\text{C}_1\text{-C}_4$ paraffins) and aromatics (included in the $\text{C}_5\text{-C}_{10}$ hydrocarbons) selectivities increased slightly with TOS due to secondary reactions taking place at

strong acid sites which converts the primary olefin products as previously discussed [6].

The mass and carbon balance for this run is very low which can be attributed to problems with the GC-MS. However, the characteristic MTO process selectivity trend was still observed with selectivities in accordance with previous studies and literature [5].

The lifetime of Catalyst A was more stable than the as-synthesised catalyst. Factors such as acid strength and density affect deactivation and coking in ZSM-5 catalysts and have a profound influence on the catalyst's lifetime. High acid strength and density will lead to rapid deactivation [12]. ZSM-5 catalysts are often diluted with inert binder which might also limit coking, improve diffusion and extend the catalyst's lifetime. Pore size and morphology will also have an impact. This might explain the difference in Catalyst A and the as-synthesised ZSM-5's catalyst lifetime.

5.3.2. 75-150 μ m

5.3.2.1. Light olefin selectivity

For the MTO reaction, 5.05g Catalyst A with polycrystalline sizes of 75-150 μ m was loaded into the fixed bed reactor with a feed consisting of 20 wt% methanol in water and a flow rate of 0.5 ml/min, WHSV of 5.71 h⁻¹ at atmospheric pressure and 450°C (Figure 5.15). Methanol conversion remained at 100% for 24 hours TOS. The C₂-C₄ selectivity reached a maximum of 97% at 6.07 hours TOS and decreased slightly to 95% after 21.4 hours TOS. The 75-150 μ m fraction had a higher primary olefin yield than the smaller than 75 μ m fraction due to its larger external surface which leads to a smaller sensitivity towards coking and therefore higher catalyst activity [5]. Propylene had the highest selectivity of the light olefins, probably due to methylation of ethylene [3], with a 49% selectivity at 6.07 hours TOS that decreased to 30% at 21.40 hours TOS. While the propylene selectivity decrease the ethylene selectivity increased from 25% at 3.48 hours TOS to 44% at 21.4 hours TOS.

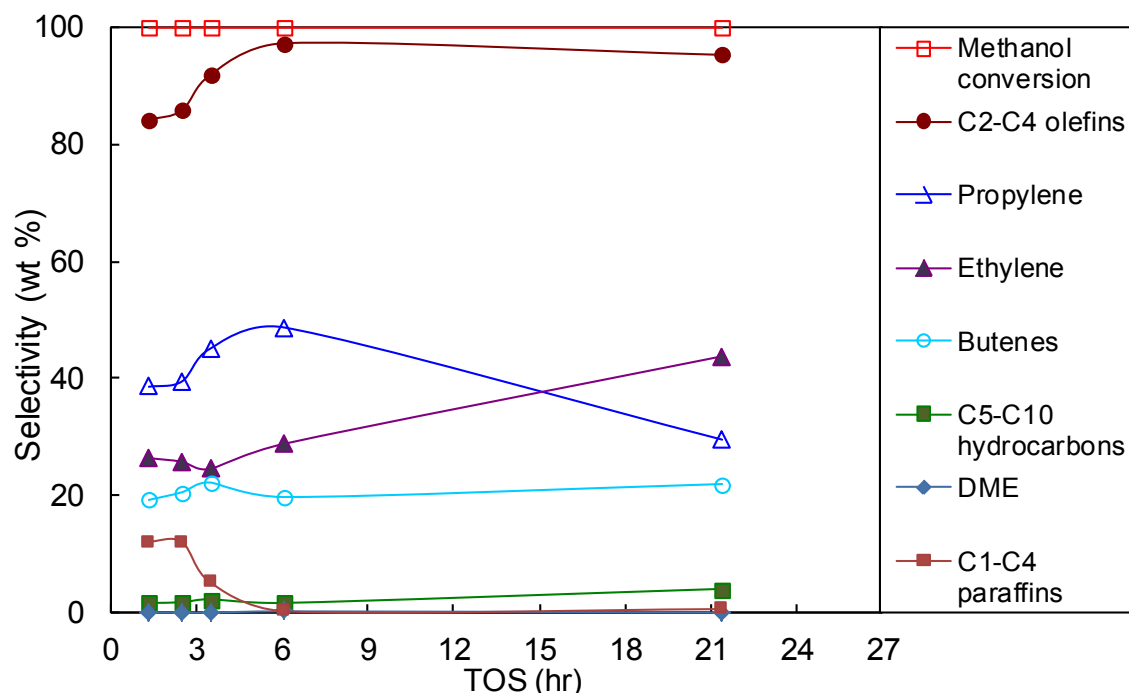


Figure 5.15: The product distribution of Catalyst A with polycrystalline grain sizes of 75-150 μ m used as catalyst during the MTO process.

Ethylene did not follow the characteristic intermediate trend of a short induction time with low selectivity, followed by an increase in selectivity to reach a maximum selectivity and then conversion of the olefin product via secondary reactions to paraffins and aromatics resulting in a decrease in selectivity with TOS. It seems that conversion of ethylene via secondary reactions as well as methylation to propylene took place to a lesser extent during this reaction. Polycrystalline grains have second-order, intercrystalline voids where diffusion takes place faster than in the intracrystalline voids and thus less olefin conversion takes place in the intercrystalline voids [12]. Butene selectivity followed the usual intermediate trend observed for primary olefin products with a maximum selectivity of 22% at 3.48 hours TOS. The C₁-C₄ paraffins followed an unusual trend with high selectivity during the induction period at the beginning of the reaction which decreased with TOS. Aromatic species usually not present in the product stream were detected by the GC-MS and a probable explanation for this could be that some of the organic species that form the active reaction centers escaped through the intracrystalline

pores [6]. The effect of the grain size on the product distribution will be discussed in Section 5.3.4.

5.3.3. 150-300 μm

5.3.3.1. Light olefin selectivity

For the MTO reaction, 5.00g Catalyst A with polycrystalline grain sizes of 150-300 μm was loaded into the fixed bed reactor with a feed consisting of 20 wt% methanol in water and a flow rate of 0.5 ml/min, WHSV of 5.77 h⁻¹ at atmospheric pressure and 450°C (Figure 5.16).

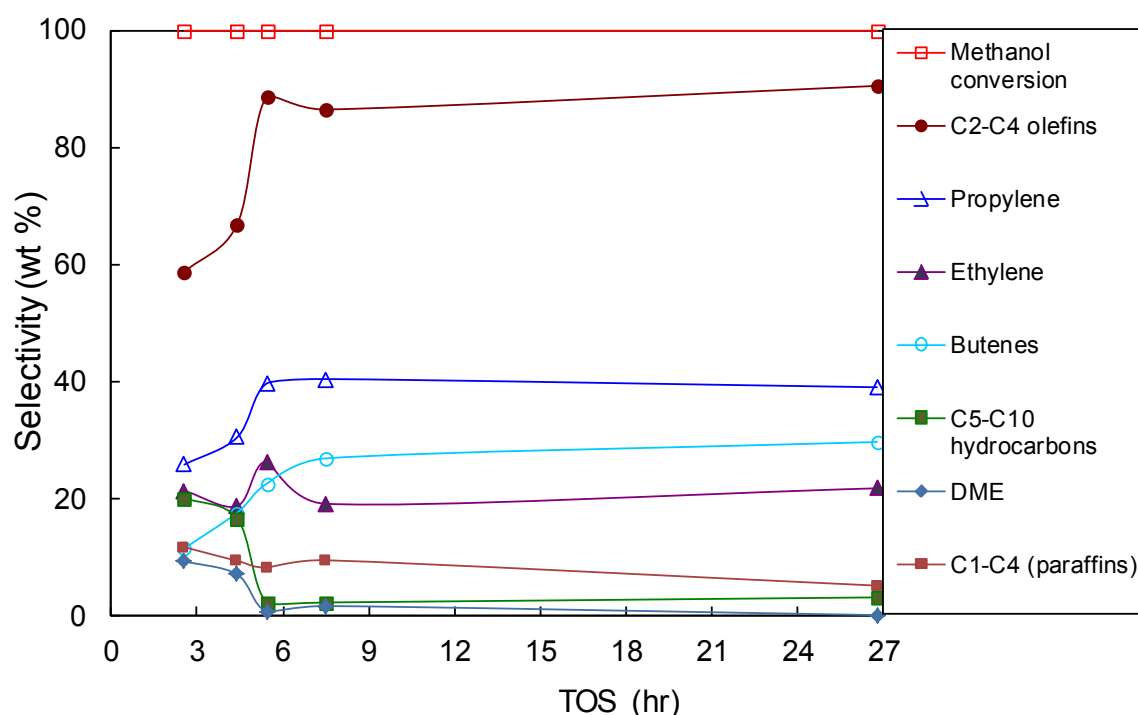


Figure 5.16: The product distribution of Catalyst A with polycrystalline grain sizes of 150-300 μm used as catalyst during the MTO process.

Methanol conversion remained at 100% for 24 hours TOS. The C₂-C₄ selectivity reached a maximum of 89% at 5.43 hours TOS and decreased slightly to 88% after 24 hours TOS following the characteristic intermediate trend. The 150-300 μm fraction had a higher primary olefin product selectivity than the smaller than 75 μm

Chapter 5

fraction but not as high as the 75-150 μ m fraction's selectivity (Figures 5.14 and 5.15). Propylene had the highest selectivity of the olefins (40% at 5.43 hours TOS) followed by butene (30% at 27 hours TOS) and ethylene (26% at 27 hours TOS). Ethylene followed the intermediate trend and all of the primary olefin products had selectivities that were comparable to the results of previous studies conducted [5]. However, propylene and the butenes' selectivity did not decrease with TOS as the usual intermediate trend would suggest. The C₁-C₄ paraffins and C₅-C₁₀ hydrocarbons also deviated from their unusual increasing trend. From this result we can conclude that secondary reactions were not as significant in converting propylene and butenes to paraffins and aromatics during this reaction. This can be caused by reduced Brönsted acid strength or rapid diffusion of the primary olefin product molecules through the polycrystalline grains [6, 12].

5.3.4. Effect of fraction size on the MTO product distribution

In Figure 5.17, the methanol conversion and C₂-C₄ selectivities of the three size fractions of Catalyst A are presented while Figure 5.18 shows the propylene and ethylene selectivity of the commercial catalyst. The primary olefin product selectivities of Catalyst A at 3.5 hours TOS are presented in Table 5.2.

From Table 5.2 and Figures 5.17 and 5.18 it is clear that the 75-150 μ m fraction gave the highest C₂-C₄ selectivity followed by 150-300 μ m and the smaller than 75 μ m fraction produced the lowest C₂-C₄ selectivity. The 75-150 μ m fraction produced the highest selectivity of propylene as well as ethylene, followed by the 150-300 μ m fraction and the smaller than 75 μ m fraction producing the lowest propylene and ethylene selectivities. This may have been caused by more rapid diffusion within the intercrystalline voids leading to less secondary reactions [2]. For larger polycrystallites the number of intercrystalline voids increases resulting in faster diffusion rates. However, an increase in size will also increase the non-shape selective outersurface of the ZSM-5 catalyst which will reduce light olefin selectivity. From the results obtained during this study it seems that the intermediate 75-150 μ m fraction has the best balance between activity and selectivity for light olefin selectivity. Similar results have been obtained from previous studies on single

ZSM-5 as catalyst for the MTO process

crystals where an intermediate crystallite size provides the optimum balance between activity and selectivity for a certain product selectivity [3, 13] as well as the as-synthesised ZSM-5. Diffusion through polycrystalline grains is the sum of diffusion through the monocrystal (intracrystalline diffusion which follows Einstein's relation for ordinary diffusion) diffusion through the internal monocrystallite boundaries and diffusion through the intercrystalline voids [2].

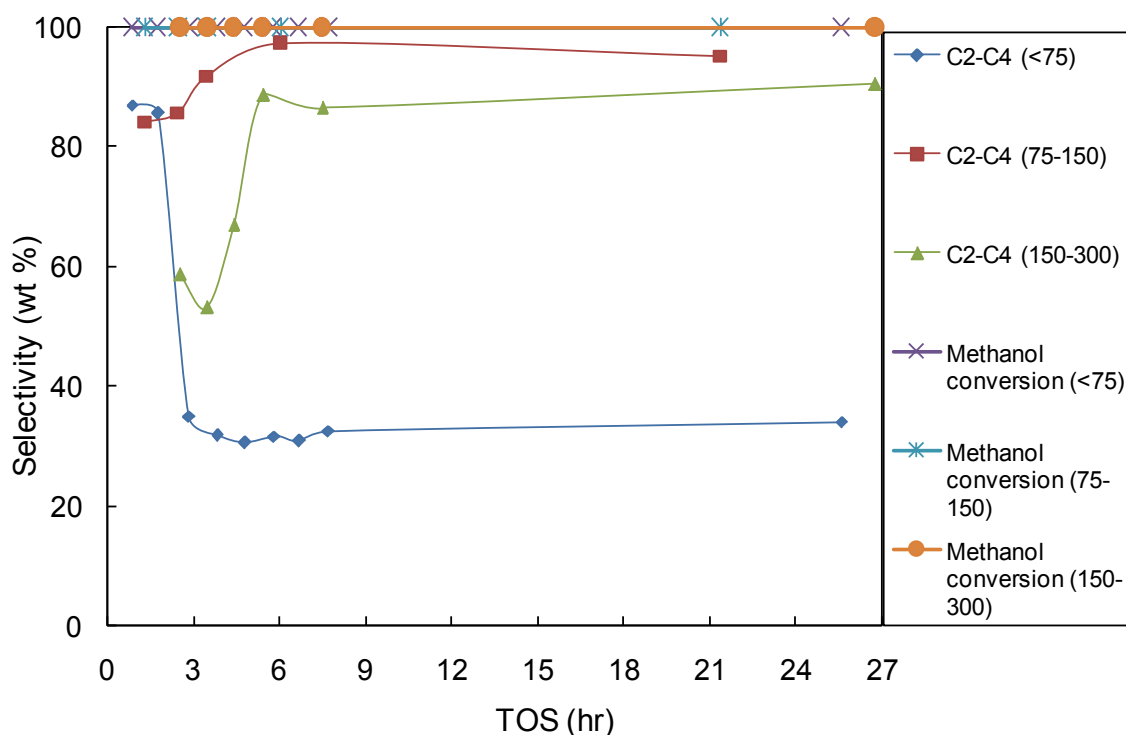


Figure 5.17: Methanol conversion and C₂-C₄ selectivity of MTO reactions with Catalyst A with different agglomerated polycrystalline grain sizes as catalyst.

Chapter 5

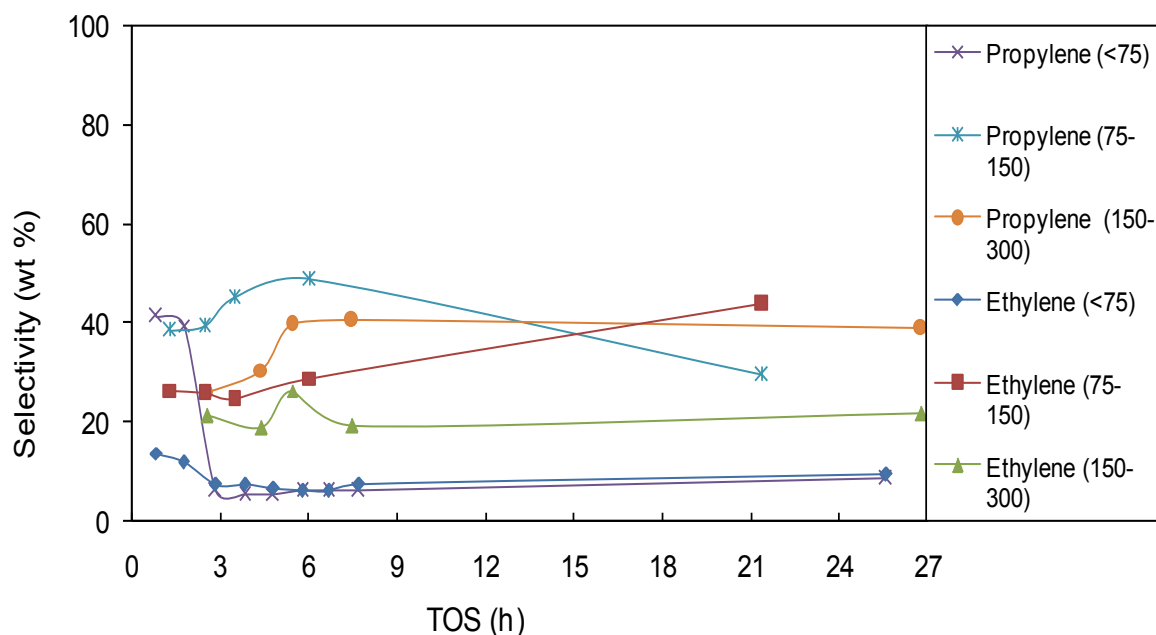


Figure 5.18: The propylene and ethylene selectivity of Catalyst A with various polycrystalline grain sizes.

Table 5.2: Primary olefin product selectivities (at 3.5 hours TOS) obtained from various polycrystalline grain fractions of Catalyst A.

Olefin products	Selectivity(wt%)		
	<75μm	75-150μm	150-300μm
C ₂ -C ₄ olefins	32	92	53
Ethylene	7	25	15
Propylene	5	45	24
Butenes	19	22	14

5.4. Deactivation and coking

Deactivation of zeolite catalysts can be caused by coking. Coke formation takes place at strong acid sites and decreases the catalysts activity and shape selectivity by covering some of the acid sites or by blocking the channels of the zeolite and preventing access to the acid sites inside the zeolite channels and cages [23, 26]. TPO/R-MS (temperature-programmed oxidation/reduction mass spectrometry) studies are employed in the analysis of the decomposition of compounds in an

ZSM-5 as catalyst for the MTO process

oxygen/hydrogen atmosphere, and can be used to analyse carbon-containing compounds like coke on zeolite catalysts [27]. The location and nature of the coke on spent catalyst has an effect on coke-oxidation kinetics, which is a factor when considering catalyst regeneration [28]. One of the major advantages of ZSM-5 compared to other zeolites is its low tendency towards coke formation [29]. Intracrystalline coke formation is a shape-selective reaction and therefore the pore structure influences coke formation. SAPO-34 has large cages where large aromatic molecules can form and too small channels for the aromatic molecules to diffuse through. This leads to extensive coking in SAPO-34 where as ZSM-5's cages are too small for larger aromatic molecules to form and the medium-pore channels are big enough for the majority of molecules that form inside the zeolite cages to leave the zeolite. Coking on ZSM-5 therefore occurs mainly on the external surface of the zeolite and the active sites are not covered by coke, [29, 30, 31 and 32]. The coke precursors form inside ZSM-5 and then diffuse out of the catalyst to form coke on the external surface of the zeolite. TPO-MS analysis was performed on a sample of the spent Catalyst A (150-300 μ m) in order to determine the type and amount of coke produced during the MTO reaction on ZSM-5. The results are presents in Figures 5.21 and 5.22.

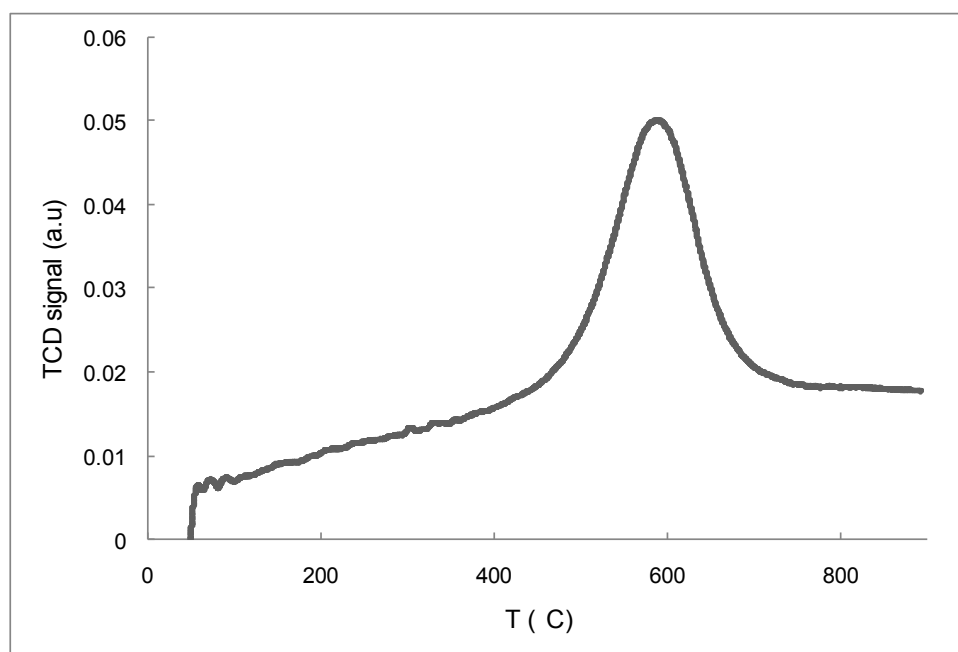


Figure 5.21: TPO-MS of the oxidation peak for spent Catalyst A (150-300 μ m).

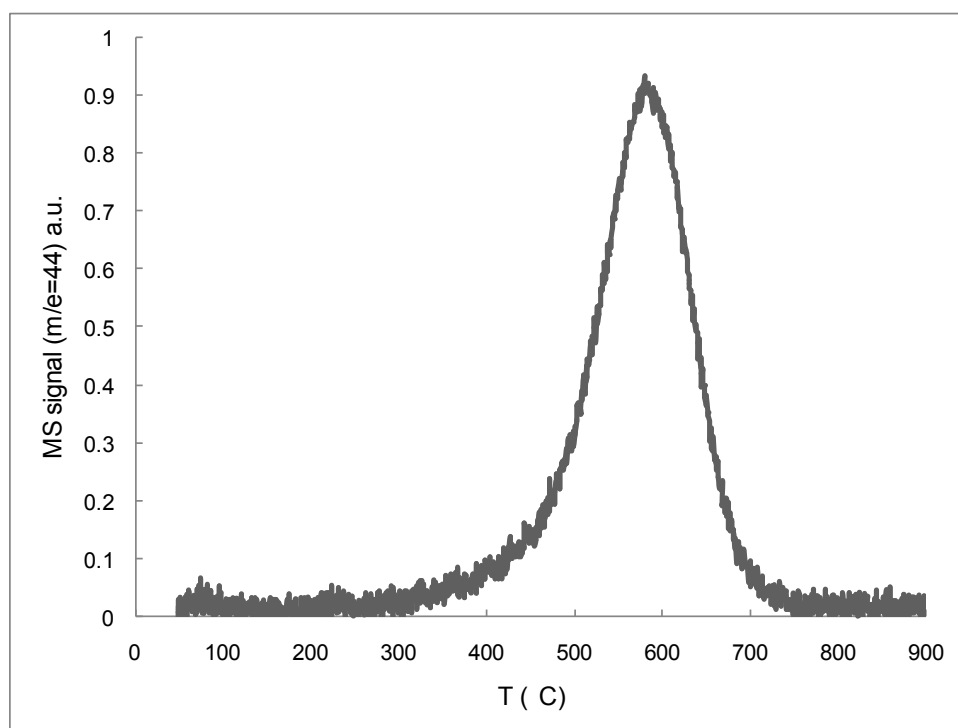


Figure 5.22: CO₂ formed during TPO of spent Catalyst A (150-300 μ m).

A single peak with a maximum at 588°C was obtained during oxidation of the spent Catalyst A (Figure 5.21) and a single peak at 593°C was observed for CO₂ formation during TPO. The single peak near 600°C is an indication of polymeric coke that formed on the catalyst. The TPO peak is proportional to the amount of coke on the catalyst and it was found that Catalyst A (150-300 μ m) formed 2.5% polymeric coke. Schulz [33] obtained values of 2.6% for ZSM-5 coking during the MTO process and therefore the TPO results obtained from this study compares well to the results from previous studies.

5.5. Conclusion

Since time spent in the catalyst is dependent on the zeolite's crystal size, it has been shown for single ZSM-5 crystals that a decrease in crystallite size increases the light olefin selectivity. The increase in light olefin selectivity is a consequence of the shortened diffusional pathways in smaller crystals and therefore reduced conversion of light olefins via secondary reactions. However, ZSM-5 tends to form agglomerated polycrystalline grains within which deviations from ordinary diffusion occur. Diffusion

ZSM-5 as catalyst for the MTO process

of molecules through the intercrystalline voids between the monocrystals that form a polycrystal is much faster and less restricted than through the channels and cages of the monocrystals. Secondary reactions occur to a lesser extent inside the intercrystalline voids. Larger polycrystalline grains will contain more monocrystals and therefore more intercrystalline voids. This will lead to more rapid diffusion and less secondary reactions.

From the results of the as-synthesised ZSM-5, it is evident that the 75-150 μm fraction produced the highest propylene selectivity although not the highest ethylene selectivity. The smaller than 75 μm produced the lowest propylene and ethylene selectivities which may be caused by a smaller amount of intercrystalline voids which will cause diffusion to proceed mainly via intracrystalline and internal boundary diffusion. The slower diffusion rate within the smaller polycrystallites will lead to enhanced primary olefin product conversion via secondary reactions.

From the results of Catalyst A, it can be observed that the 75-150 μm fraction produced the highest ethylene and propylene selectivity for the MTO reaction. As mentioned previously, larger polycrystals contain more monocrystals and therefore intercrystalline voids. When only considering diffusional transport limitations, it would be expected that the largest polycrystalline grain fraction (150-300 μm) will give the best light olefin selectivities but it is apparent that the 75-150 μm gave the best light olefin selectivity. With an increase in polycrystalline grain size the non-shape selective external surface also increased which had a negative influence on the light olefin selectivity [3, 13]. From the results it can be concluded that the 75-150 μm fraction had the most favorable compromise between activity and selectivity towards light olefin formation.

5.6. References

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Chapter 6

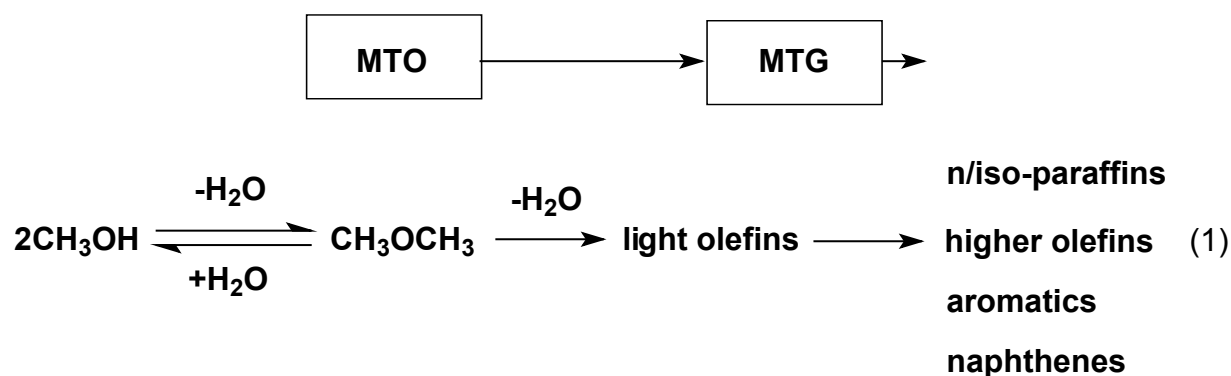
Evaluation and recommendations

6.1. Introduction	81
6.2. Zeolite synthesis	83
6.3. MTO process	84
6.4. Evaluation	88
6.5. Recommendations	90
6.6. References	90

6.1. Introduction

Ethylene and propylene are probably the two most important olefins in the petrochemical industry [1]. These olefins are used for the production of polymers used for example in plastics (i.e. polyethylene and polypropylene) as well as various chemical precursors including paraffins and aromatics as shown in Scheme 1.

Light olefins such as ethylene and propylene can be obtained from the MTO process where methanol is converted to hydrocarbons using ZSM-5 as catalyst. The main steps of the methanol conversion reaction can be presented by Scheme 1.



ZSM-5 is a versatile crystalline *aluminosilicate* zeolite catalyst belonging to the pentasil family of zeolites that consist of a three dimensional structure built from tetrahedral units linked by oxygen atoms. The substitution of an aluminum ion (charge 3+) for a silicon ion (charge 4+) requires the additional presence of a cation [2]. When the ion-exchangeable cations are replaced by protons, the zeolite becomes a solid acid [3]. The compensating protons are electrostatically bonded to aluminium and located in the zeolite's channels or channel intersections to form strong Brönsted acid sites where methanol conversion to primary olefin products occurs, as well as the conversion of the intermediate olefin products to paraffins and aromatics via secondary reactions [3]. ZSM-5's pores are wide enough to allow cyclization and intermolecular hydride transfer reactions which convert the primary olefin products to paraffins and aromatics [4].

Evaluation and recommendations

It is widely accepted that methanol conversion over a ZSM-5 catalyst proceeds via the hydrocarbon pool mechanism [4]. Studies conducted by Haw and co-workers [4] and Cui and co-workers [5], found that the MTO process could only take place in zeolites that have transition-state shape selectivity in order for the hydrocarbon pool mechanism to occur. The hydrocarbon pool mechanism proposes that methanol and DME react on cyclic organic species inside the cages and channels of ZSM-5. These organic species form during the induction period and act as scaffolds to which methanol and DME add while ethylene is split off. The cyclic organic species will however eventually become polycyclic aromatic hydrocarbons (coke) which deactivate the ZSM-5 catalyst [4]. Svelle and Bjorgen [6, 7] proposed that the MTO process proceeds through a dual cyclic reaction. Ethylene forms through the hydrocarbon pool mechanism and propylene, butenes and higher olefins form via an olefin methylation-cracking cycle [8].

ZSM-5 has two dimensional channels- a straight channel running parallel to (010) and an intersecting sinusoidal channel running perpendicular to (100). The straight channel has an ellipsoidal form with ten ring openings and a free dimension of $5.4 \times 5.6 \text{ \AA}$. The sinusoidal channels also have ten ring openings with a free dimension of $5.1 \times 5.4 \text{ \AA}$. This ordered pore structure leads to ZSM-5's shape selective properties but also causes diffusion limitations within the zeolites. Diffusion along the straight channels is more rapid than through the sinusoidal channels [8]. Shorter diffusional paths, for example due to smaller crystal sizes, provide less opportunity for secondary reactions to convert primary olefin products to paraffins and aromatics at the strong Brönsted acid sites and also enhances the reaction rate [7, 9].

The ratio of non-selective acid sites on the external surface to shape-selective intracrystalline acid sites largely determines the selectivities towards certain MTO products. Smaller crystallites (i.e. higher ratio) and hence higher acid site concentrations on the non-selective external surface will lead to the increased formation of unwanted aromatics and branched isomers [3]. Therefore by varying crystallite size, the optimal balance between activity and selectivity can be sought leading to the best ethylene and propylene yield [10].

Chapter 6

During zeolite synthesis various soluble species, amorphous phases and polymerization reactions are present and therefore the zeolite's crystallite size is dependent on physical effects such as stirring, aging, synthesis time, synthesis temperature and order of reactant addition [10, 11].

The purpose of this study was to modify ZSM-5 used as catalyst for the MTO process in such a way as to obtain the optimal ethylene and propylene yield. Due to the primary olefin products' dependence on the crystallite/polycrystalline grain size, variables that have a significant influence on the ZSM-5 zeolite's size such as synthesis temperature, synthesis time and aging time were investigated while various ZSM-5 size fractions were used as catalyst for the MTO process.

6.2. Zeolite synthesis

ZSM-5 was synthesized by a hydrothermal crystallization method in an autoclave system as developed by Vorster [12]. TPA-Br and TPA-OH were used as templating agents while TEOS was added as silica source, and sodium aluminate as the source of aluminium. The synthesis was done to obtain ZSM-5 with a Si/Al ratio of 45 and a molar composition of $100 \text{ SiO}_2 : 123 \text{ TPA}^+ : 63.7 \text{ OH}^- : 14200 \text{ H}_2\text{O} : 2.22 \text{ Al}_2\text{O}_3$. The standard synthesis parameters used were 72 hours synthesis time, 170°C synthesis temperature and 60 minutes of aging. The results obtained by this synthesis method were presented in Section 4.2 showing intergrown ZSM-5 crystallites forming bigger agglomerated polycrystalline grains irrespective of the conditions that were varied, which is a well known phenomenon for ZSM-5 [11].

In order to control the crystallite size, the synthesis temperature was varied from 12-72 hours at constant temperature and aging time. The results, as discussed in Section 4.3 showed intergrown polycrystalline grains with the characteristic ZSM-5 morphology observed for ZSM-5 synthesized using TPA derivatives as templating agents [13] as confirmed by XRD. The crystal sizes forming the polycrystalline grain were measured using the SEM micrographs and it was shown that the crystallite size decreased slightly from 12 -72 hours. It became clear that synthesis time only had a

small influence on the crystallite size since a standard deviation of $0.4\mu\text{m}$ was obtained with an average crystal size of $5.7\mu\text{m}$.

Subsequently, ZSM-5 was synthesised at temperatures of 130°C , 150°C and 170°C with synthesis time and aging time constant at 72 hours and 60 minutes respectively. According to Section 4.4, intergrown polycrystalline grains with characteristic ZSM-5 morphology was obtained. It was shown that crystallite size increased with increasing temperature and that temperature variation had a larger influence on crystallite size than synthesis time. An average crystallite size of $13.1\mu\text{m}$ was obtained with a standard deviation of $4.9\mu\text{m}$.

When aging time was varied during zeolite synthesis for 30, 60 and 90 minutes, crystals were again intergrown to varying degrees. An average degree of intergrowth was obtained at 30 minutes, least intergrown at 60 minutes and most intergrown after 90 minutes of aging. While crystallite size increased with aging time, aging time had had the largest influence on the crystallite size of the three parameters investigated during this study. An average crystallite size of $21.6\mu\text{m}$ was obtained with a standard deviation of $10.8\mu\text{m}$. With varying aging time and constant synthesis time and temperature, the largest crystallites with the biggest crystal size distribution were obtained.

6.3. MTO process

Due to the intergrown nature of the as-synthesized ZSM-5, diffusion of reactants and products through the catalyst did not occur via ordinary diffusion as would have been the case with single crystallites [11]. When ZSM-5, used as a catalyst for the MTO process, consists of intergrown agglomerated polycrystalline grains, diffusion deviates from ordinary diffusion due to the influence of intercrystalline boundaries and intercrystalline voids [2]. ZSM-5 used as catalysts for the MTO process such as Catalyst A, are often diluted with an inert binder to form polycrystalline grains as was shown in Figure 5.2. Due to the intergrown nature of the as-synthesized ZSM-5, the ZSM-5 for the MTP process was synthesized with the previously mentioned method

Chapter 6

at 72 hours, 170°C and 60 minutes aging time. The obtained polycrystalline grains were then divided into three fractions using sieves: smaller than 75µm, 75-150µm and 150-300µm. The ethylene and propylene selectivity of the different agglomerated polycrystalline grain size ranges for the as-synthesized catalysts were investigated and presented in Chapter 5, and summarized in Figure 6.1.

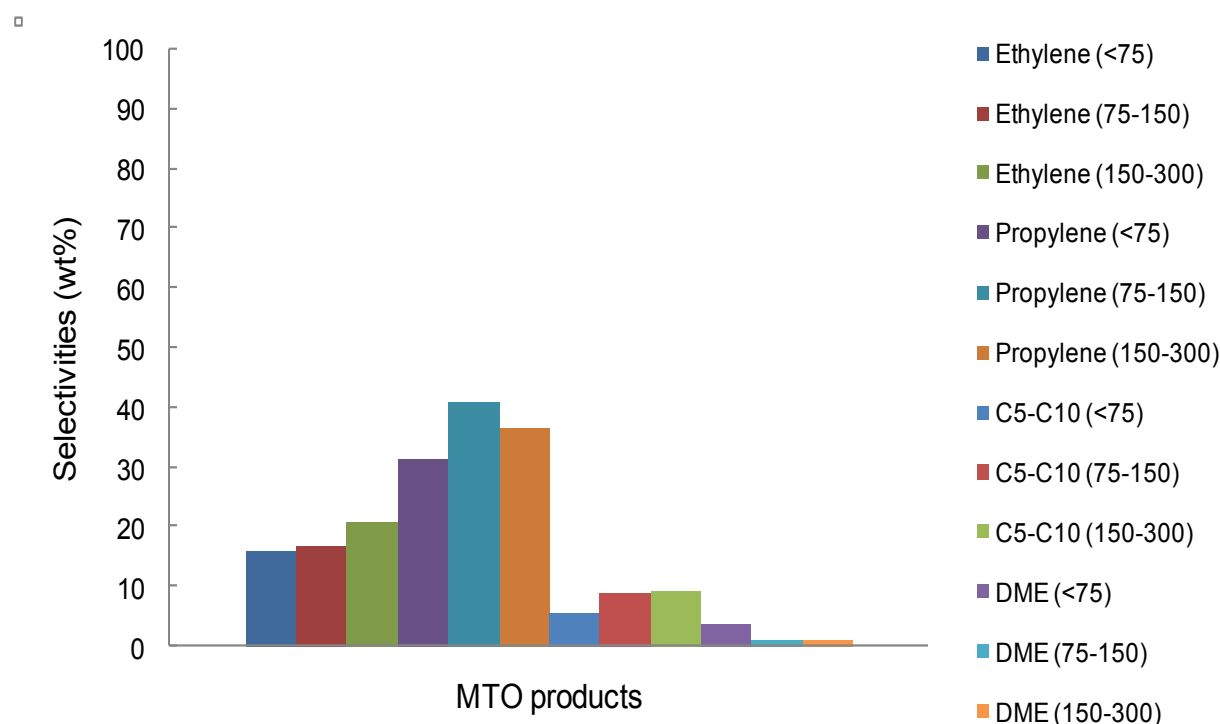


Figure 6.1: MTO product selectivities of as-synthesized ZSM-5 at TOS=3.5 hours.

From Figure 6.1 it is clear that the MTO reaction at 400°C, atmospheric pressure a 20wt% methanol to water feed, produced higher propylene selectivity than ethylene selectivity. The selectivities obtained for propylene and ethylene compared well to results from literature studies with similar reaction conditions [14]. The smaller than 75µm fraction produced the lowest light olefin selectivity of the three fractions. In contrast, DME selectivity of the smaller than 75µm fraction was higher than the other fractions, indicating that less DME was converted to products by the smaller than 75µm fraction which was also reflected by the lower paraffins and aromatics (C₅-C₁₀ hydrocarbon) selectivity. Coking in ZSM-5 mainly occurs on the zeolite's external surface and the influence of the *external surface* of zeolites with smaller crystal size is especially significant [15]. The 75-150µm fraction had the highest propylene and

Evaluation and recommendations

the second highest ethylene yield and a low DME and C₅-C₁₀ hydrocarbon selectivity which indicates good activity and selectivity from the catalyst. The 150-300 μ m fraction had the highest ethylene and second highest propylene yield with low DME and reasonably low C₅-C₁₀ hydrocarbon selectivities which indicates that most of the DME was converted to olefinic products and some of the olefinic products to paraffins and aromatics. When taking into account that all three fractions were synthesized at the same conditions, then it can be assumed that the monocrystals forming the polycrystalline grains have the same size and that the polycrystalline grain's size is a function of the amount of monocrystals that form the polycrystalline grain. Larger polycrystalline grains will therefore have more intracrystalline and intercrystalline boundary diffusion restrictions which will lead to slower diffusion and more secondary reactions taking place. The paraffins and aromatics converted from the primary olefin products were produced with much lower selectivity than the olefins' which is an indication that secondary reactions were inhibited. Low DME selectivity shows that after 3.5 hours TOS catalyst deactivation and coking did not have a profound influence on the MTO reaction.

Catalyst A was also sieved into similar fractions and used as catalyst for the MTO process in a fixed bed reactor. The ethylene and propylene selectivity of the different agglomerated polycrystalline grain size ranges for Catalyst A were investigated and presented in Chapter 5 and summarized in Figure 6.2.

The selectivities obtained for propylene and ethylene with Catalyst A at 400°C, atmospheric pressure and a 20wt% methanol to water feed, compared well to results from literature studies with similar reaction conditions [14]. From Figure 6.2, it is clear that the smaller than 75 μ m fraction produced the least ethylene of the three fractions and substantially less propylene than the other fractions. The smaller than 75 μ m fraction had a much higher DME selectivity than the other fractions and a low C₅-C₁₀ selectivity which means that secondary reactions didn't have such a profound influence on the product distribution. These results may be attributed to the fact that conversion of DME at the Brönsted acid sites could have been inhibited by coking on Catalyst A's external surface [15].

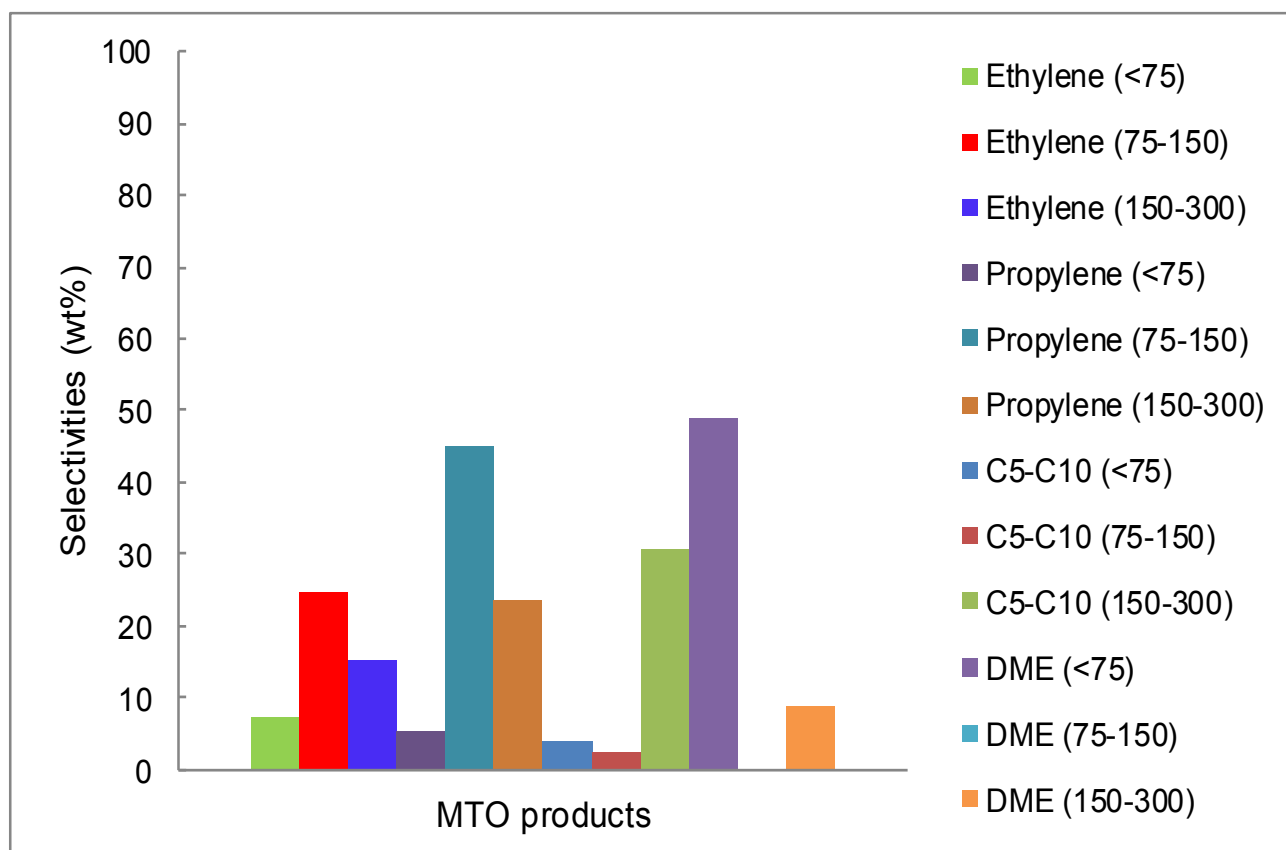


Figure 6.2: MTO product selectivities of Catalyst A at TOS=3.5 hours.

The 75-150 μ m fraction produced the highest ethylene as well as propylene yield with a very low DME as well as C₅-C₁₀ hydrocarbon selectivity. The low C₅-C₁₀ selectivity obtained shows that secondary reactions were inhibited and the low DME selectivity implies that coking on the ZSM-5 zeolite's external surface hasn't affected DME conversion significantly after 3.5 hours TOS. The 150-300 μ m fraction had a higher ethylene and propylene yield than the smaller than 75 μ m fraction but lower than the intermediate fraction. A rather high C₅-C₁₀ selectivity was observed for the 150-300 μ m fraction which is an indication of secondary reactions caused by the slower diffusion rate through the larger polycrystalline grains with more diffusional restrictions. This may explain the high C₅-C₁₀ hydrocarbon yield for the 150-300 μ m fraction.

At 3.5 hours TOS, the paraffins and aromatics converted from the primary olefin products were produced with much lower selectivities than that of the primary olefins which is an indication that secondary reactions were inhibited to a reasonable

degree. The low DME selectivity shows that at 3.5 hours TOS catalyst deactivation and coking did not have a profound influence on the MTO reaction.

6.4. Evaluation

As previously mentioned all three polycrystalline grain sizes were synthesized under the same conditions and synthesis parameters and therefore an assumption can be made that the monocrystallites forming the polycrystalline grains have the same size and that the polycrystalline grain size is a function of the amount of monocrystallites forming the particle.

The overall diffusion in polycrystallites is controlled by three different types of diffusion as presented in Figure 6.3. Intracrystalline diffusion (D_1) through the zeolite pores and cages, which is governed by Einstein's relation for ordinary self-diffusion [11, 16]. Diffusion through the intercrystalline voids (D_2), which form second order pores in the polycrystalline grains and in which self-diffusion is enhanced and coke is preferentially deposited [17] and intercrystalline boundary diffusion (D_3), where diffusion coefficients can be two to three orders smaller than for ordinary self-diffusion. Therefore, it can be concluded that intercrystalline boundaries represent transport barriers and in order to obtain optimal diffusion these should be kept at a minimum.

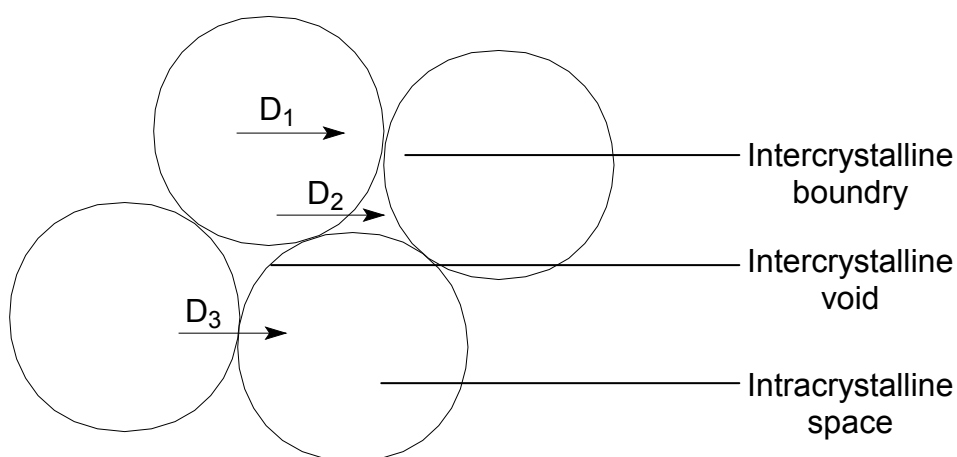


Figure 6.3: Schematic representation of possible diffusion pathways in agglomerated polycrystalline grains.

Chapter 6

The different ZSM-5 particle size fractions can be presented as spherical monocrystals that form the polycrystalline grains as presented in Figure 6.4.

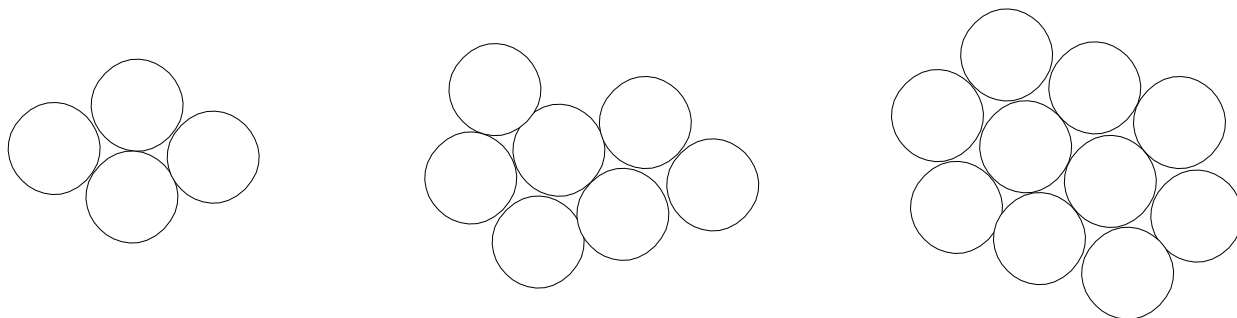


Figure 6.4: Schematic representation of different agglomerated particle sizes.

Diffusion in polycrystalline grains deviate from ordinary diffusion at the intercrystalline boundries (slower self-diffusion) and at the intercrystalline voids (enhanced self-diffusion). When considering the influence of the different possible diffusion pathways in polycrystalline grains with different particle sizes, it is clear that with increasing size the molecular migration seems to be promoted by the existence of more free space between the monocrystallites [11]. However, an increase in size also increases the number of intercrystalline boundries as well as the non-shape selective outer surface which will lead to reduced light olefin selectivity. A decrease in polycrystalline grain size will reduce the amount of intercrystalline boundries as well as the amount of intercrystalline voids but coke, which forms mainly on ZSM-5's outer surface, has a greater influence on product selectivity when the particle's outer surface is smaller.

From the results in Chapter 5 and Figures 6.1 and 6.2 it is seems that the intermediate 75-150 μm fraction yielded the highest ethylene and propylene selectivities for both as-synthesized and Catalyst A's agglomerated polycrystalline grains. The smaller than 75 μm fraction had lower activity than the other fractions probably due to coking on the zeolite's external surface. Although Catalyst A is more resistant towards coking than the as-synthesized ZSM-5, particle sizes used commercially are usually much larger (150-500 μm) and the same amount of coking will have a more profound influence on the smaller than 75 μm particle's activity than on the 150-500 μm particles. Reactant and product molecules have to diffuse through more intercrystalline boundries in the 150-300 μm fraction than the smaller fractions

which leads to slower diffusion and more secondary reactions taking place as apparent from the high C₅-C₁₀ hydrocarbon selectivity (Figures 6.1 and 6.2). The intermediate 75-150µm fraction had the highest light olefin selectivities for both the as-synthesized as well as Catalyst A. The 75-150µm particle sizes had a large enough external surface to reduce the effects of coking and not as much intercrystalline boundaries to slow down diffusion rates for secondary reactions to have a profound effect on the ethylene and propylene selectivity.

6.5. Recommendations

- In order to investigate the influence of certain synthesis parameters on ZSM-5 crystallite's size, it would be more convenient to use a synthesis method that produces single crystalstallites such as the novel hydrothermal synthesis method developed by Kadono and co-workers [19].
- It would be interesting to investigate the influence of other synthesis parameters such as alkalinity, water content, template/silica molar ratio, aluminum content, and the presence of alkaline cations on crystallite size, in order to relate this to the observed MTO product distribution.
- In order to study methanol and primary olefin product conversion reactions at the strong Brönsted acid sites, n-propylamine temperature-programmed desorption (TPD) as well as infrared (IR) spectroscopy would prove useful.

6.6. References

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Chapter 6

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Appendix

7.1: Compounds detected by GC-MS	93
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Appendix

Table 7.1: Compounds detected by GC-MS.

Gases	Oils	Organic components in the liquid phase
CO	1-Propene	DME
CO ₂	Isobutane	Acetone
methane	1-Butene	MeAcetate
ethylene	Butane	MeOH
ethane	t-2-Butene	MEK
propene	c-2-Butene	2-propanol
dimethyl ether	2-me-1-butene	EtOH
propane	Isopentane	1-propanol
isobutene	1-Pentene	Acetaldehyde
1-butene	3-me-1-butene	butanol
t-2-butene	Pentane	Water
c-2-butene	1,2-pentadiene	
butane	trans-2-pentene	
1-pentene	cis-2-pentene	
3-me-2-butene	2-methyl-2-butene	
2-me-1-butene	trans-1,3-pentadiene	
n-pentane	1,3-cyclopentadiene	
trans-2-pentene	C ₅	
cis-2-pentene	Cyclopentene	
2-Me-2-Butene	4-me-1-pentene	
Cyclopentene	3-me-1-pentene	
4-me-1-pentene	Cyclopentane	
2-me-pentane	2,3-dimethylbutane	
3-me-pentane	2-me-pentane	
2-me-1-pentene	4-me-pentane	
1-hexene	3-me-pentane	
trans-2-hexene	2-me-1-pentene	
2-Me-2-pentene-t	1-hexene	
3-Me-2-pentene-c	n-hexane	
cis-2-hexene	trans-3-hexene	

3-Me-2-pentene-t	cis-3-hexene
me-cyclopentane	trans-2-hexene
2,3-dimethyl-2-butene	2-me-2-pentene
Mecyclopentene	cis-3-me-2-pentene
Benzene	Me-cyclopentene
2-me-hexane	cis-2-hexene
C6 diene	3-me-cyclopentene
2,4-dimethyl-1-pentene	trans-3-me-2-pentene
2,4-dimethyl-2-pentene	C6 diene-1
2,3-dimethyl-1pentene	Me-cyclopentane
3-me-hexane	2,3-dimethyl-2-butene
1,3-dime-cyclopentane-c	C6 diene-2
1,3-dime-cyclopentane-t	3-methylenecyclopentene
1,2-dime-cyclopentane-t	cyclohexadiene
3-Me-3-hexene-c	1-Methyl-2-cyclopentene
2-Me-2-hexene	2,4-dimethylpentane
3-Me-3-hexene-t	Methylene-cyclopentane
trans-3-heptene	1methyl-3,3-dimethyl-cyclopropene
n-heptane	Unknown C6-1
3-et-2-pentene	3-me-2-hexene
2,3-dime-2-pentene	benzene
3-et-cyclopentene	Cyclohexane
1,2-dime-cyclopentane-c	Unknown C6-2
Me-cyclohexane	Unknown C6-3
Et-cyclopentane	Unknown C6-4
4-Me-Cyclohexene	trans-4-methyl-1-hexene
1,2,3-trime-	2-me-hexane

Appendix

cyclopentene	
1,2,4-trime-	5-me-1-hexene
cyclopentene	
1-Et-cyclopentane	4-me-1-hexene
unknownC7-1	Cyclohexene
unknownC7-2	3-me-hexane
unknownC7-3	1,1-dimethylcyclopentane
unknownC7-4	3-me-1-hexene
unknownC7-5	cis-1,2-dimethylcyclopentane
unknownC7-6	Unknown C6-5
unknownC7-7	Unknown C6-6
unknownC7-8	2-me-1-hexene
Toluene	1-heptene
1-octene	5-methyl-2-hexene
n-octane	cis-1,3-dimethylcyclopentane
trans-2-octene	trans-1,3-dimethylcyclopentane
2-me-heptane	trans-1,2-dimethylcyclopentane
4-me-heptane	n-heptane
cis-2-octene	3-me-3-hexene
unknownC8-1	C7 Diene
3-me-heptane	3-methyl-trans-2-hexene
unknownC8-2	Unknown C7-1
unknownC8-3	cis-2-heptene
unknownC8-4	3-methyl-cis-2-hexene
unknownC8-5	3-methyl-1-hexene
unknownC8-6	methylcyclohexane
unknownC8-7	Unknown C7-2
unknownC8-8	Unknown C7-3
1-nonene	unknownC7-4
n-nonane	ethylcyclopentane
MP-xylene	Unknown C7-5
cis-2-nonene	2,4-dimethylhexane
O-xylene	unknownC7-6

4-me-octane	2,5-dimethylhexane
2-me-octane	Unknown C7-7
3-me-octane	1-trans-2-cis-4-trimethylcyclopentane
2-me-1-octene	3,3-dimethylhexane
Trime-benzene	Unknown C7-8
n-decane	Toluene
1-decene	1,2-dimethyl-cis-cyclopentane
5-me-nonane	2,3,4-trimethylpentane
	2,3-dimethylhexane
	Unkonwn C8-1
	Unknown C8-2
	4-me-heptane
	Unknown C8-3
	Unknown C8-4
	Unknown C8-5
	cis-1,3-dimethylcyclohexane
	3-ethyl-3-methylpentane
	3-me-heptane
	Unknown C8-6
	2-me-heptane
	C8
	cis-1,3-ethylmethylcyclopentane
	1-octene
	2-me-1-heptene
	Unknown C8-7
	Unknown C8-8
	trans-4-octene
	trans-3-octene
	cis-2-octene
	2,2,4-trimethylhexane
	trans-1,2-dimethylcyclohexane
	Unknown C8-9

Appendix

Unknown C8-10
Unknown C8-11
cis-3-octene
2,3-dimethyl-2-hexene
Unknown C8-12
2,3,5-trimethylhexane
Unknown C8-13
Unknown C8-14
Unknown C8-15
Unknown C8-16
Unknown C8-17
2,6-dimethylheptane
Unknown C8-18
1,1,3-trimethylcyclohexane
Unknown C8-19
2,5-dimethylheptane
Ethylbenzene
n-octane
m-xylene
p-xylene
ethylcyclohexane
4-ethylheptane
trans-2-octene
3-ethylhexane
c,t,c-1,2,4-trimethylcyclohexane
3,4-dimethylhexane
Unknown C8-20
Unknown C8-21
Unknown C8-22
o-xylene
3-me-octane
1,1,2-trimethylcyclohexane
4-me-octane

2-me-octane
Unknown C9-1
1-nonene
2-me-1-octene
trans-3-nonene
cis-3-nonene
trans-4-nonene
n-nonane
trans-2-nonene
Unknown C9-2
Unknown C9-3
cis-2-nonene
Unknown C9-4
Unknown C9-5
Unknown C9-6
Unknown C9-7
Unknown C9-8
unknownC9-9
Unknown C9-10
Unknown C9-11
Propylbenzene
Ethylmethylbenzene-1
Ethylmethylbenzene-2
Ethylmethylbenzene-3
isopropylbenzene
1,2-dimethyl-1-pentyl-cyclopropane
2-octene
unknown C9-12
TrimethylBenzene
2,6-dimethylheptene
1-decene
n-decane
trans-5-decene

Appendix

cis-3-decene
cis-2-decene
trans-5-decene
trans-2-decene
trans-4-decene
cis-4-decene
trans-3-decene
cis-3-decene
4-decene
