A study of DDR-type zeolite crystals and membranes

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“In my beginning is my end.”

T.S. Elliot

Abstract

A zeolite membrane consists of a homogenous layer of intergrown zeolite crystals synthesized on the surface of a ceramic support. DDR zeolites consist of three types of window connected silica oxide cages that build up the rhombohedral DDR structure and have pore apertures of 0.36 x 0.44nm. Membranes (formed by a hydrothermal synthesis process) are gaining an important place in chemical technology as they are able to selectively control the permeation rate of chemical species that pass through it. The DDR membrane has been shown to separate CO_2 (g) from CH_4 (g).

The objective of this research was to acquire a better understanding of the properties of DDR zeolites in combination with ceramic membranes. Therefore investigations were initially carried out on the manufacture of ceramic membranes using Alcoa powder in conjunction with research on the DDR-type zeolite crystals, as the hydrothermal synthesis period of the DDR crystals is a lengthy 25 days. The aim of this investigation was to acquire a better understanding of DDR zeolites through optimization of the experimental procedure. This thesis investigated the coating of the DDR-type zeolite on to a ceramic membrane which has been accomplished only once before.

The manufacture of ceramic membranes was investigated using a cheaper source of α-alumina powder (Alcoa powder). The first treatment of pH flotation was optimized at a loading mass of 200g Alcoa powder suspended in a pH2 solution of HNO_3 with APMA as the dispersing agent. As a result of this acid treatment, SEM analysis showed that the fine particles remained in suspension and the heavier particles settled.

Secondly, a novel fractionation process using the heavy particles that had settled in the pH flotation showed optimum separation results at linear velocities of 5ml/min and 15ml/min using a 75g loading mass of Alcoa powder. Thereafter, centrifugal casting of the fractions was carried out to produce asymmetrical tubular green casts. Finally, a programme of

sintering allowed for strengthening and transformation of the green cast into a ceramic support.

To synthesize a DDR membrane, the crystals firstly had to be made and used as seeds to accelerate the growth of a DDR membrane. It was found that when the water concentration was decreased from 11240 moles to 7838 moles of water, homogenous crystals (1.4μm) of well defined morphology were obtained. During the hydrothermal synthesis of a DDR membrane various factors were investigated.

Results showed that a support refluxed in HNO_3 (aq) had improved zeolite attachment when compared to the pre-treatment of sonification. A seeding mass of 0.008g and a ten fold increase to 0.08g did not show a difference in the amount of coverage of the support with DDR crystals. When the seeding techniques of immersion and centrifugation were used, the same homogenous, but inadequate seed coverage was seen. Irrespective of the synthesis parameters investigated, a gel was consecutively produced on the support after hydrothermal synthesis. Only when the hydrothermal synthesis period was increased from 48 hours to 96 hours, some crystallization occurred.

This investigation on the manufacture of ceramic support was partly successful in that a cheaper Alcoa ceramic membrane was reached, although repeatability was poor. SEM and XRD analysis confirmed the size and purity of DDR crystals after using an optimized synthetic procedure. Information from this thesis lays the foundation for the successful synthesis of a DDR membrane, as it has provided valuable information to direct the future research on this topic.

Opsomming

‘n Zeolietmembraan bestaan uit ‘n homogene laag van zeolietkristalle wat op die oppervlakte van ‘n keramiek ondersteuningsmembraan gesintetiseer word. Die rombohedrale DDR-struktuur is opgebou uit DDR-zeoliete wat bestaan uit drie tipes venster gebonde silikondioksiedhokkies en ‘n poriegrootte van 0,36 x 0.44nm besit. Membrane (gevorm deur ‘n hidrotermiese sinteseproses) is besig om ‘n belangrike rol in chemiese tegnologie te speel aangesien hulle die permeasietempo van chemiese spesies wat deur die membraan beweeg selektief kan kontroleer . Dit is getoon dat die DDR-membraan CO_2 (g) van CH_4 (g) kan skei.

Die doel van hierdie ondersoek was om ‘n beter begrip oor die eienskappe van DDR-zeoliete in kombinasie met keramiekmembrane te verwerf. Om hierdie rede was ondesoeke aanvanklik uitgevoer op die vervaarding van keramiekmembrane deur gebruik te maak van Alcoa-poeier en terselfdertyd was navorsing op die DDR-tipe zeolietkristalle gedoen weens ‘n lang hidrotermiese sinteseperiode van 25 dae. Die doel van hierdie ondersoek was om ‘n beter begrip van DDR-zeoliete te ontwikkel deur optimalisering van die ekperimentele prosedure. Hierdie studie het die dekking van die DDR-tipe zeoliet op ‘n keramiekmembraan ondersoek wat slegs een maal vantevore verwesenlik is.

Die vervaardiging van keramiekmembrane is ondersoek deur van ‘n goedkoper bron van α-aluminapoeier (Alcoa-poeier) gebruik te maak. Die eerste behandeling van pH-flotasie was geoptimaliseer by ‘n laaimassa van 200g Alcoa-poeier gesuspendeer in ‘n pH2-oplossing van HNO_3 met APMA as die dispergeermiddel. Na die behandeling met suur het SEM-analise getoon dat die fyn deeltjes in suspensie bly en die swaarder deeltjes afsak.

Tweedens het ‘n unieke fraksioneringsproses met die swaarder deeltjies van die pH-flotasie getoon dat die beste resultate by lineêre snelhede van 5ml/min en 15ml/min met ‘n laaimassa van 75g Alcoa-poeier verkry word. Daarna was sentrifugering van die poeiers gebruik om asimmetriese tubulêre groenvorms te produseer. Ten slotte het ‘n program van sintering gesorg vir die versterking en omskakeling van die groenvorm na 'n keramiek membraanondersteuning.

Om 'n DDR-membraan te sintetiseer moes die kristalle eerstens gemaak word en dan as sade gebruik word om die groei van 'n DDR-membraan te versnel. Dit is gevind dat 'n verlaging in die waterkonsentrasie van 11240 mol na 7838 mol homogene kristalle (1.4μm) van goeie morfologie lewer. Verskeie faktore is tydens die hidrotermale sintese van 'n DDR-membraan ondersoek.

Die resultate het getoon dat ondersteuningsmateriaal wat onder terugvloei in HNO_3 (aq) gekook is beter zeolitiese binding as navoorbehandeling met sonifikasie lewer. 'n Saaimassa van 0.008g en 'n tienvoudige verhoging na 0.08g toon geen verskil in die hoeveelheid dekking van die ondersteuningsmateriaal met DDR-kristalle nie. Toe die saaitegnieke van onderdompeling en sentrifugering gebruik was, is dieselfde homogene, maar onvoldoende saaddekking gesien. Ongeag van die verskillende sinteseparameters wat ondersoek is, is 'n gel aanhoudend na hidrotermiese sintese op die ondersteuningsmateriaal geproduseer. Slegs toe die hidrotermiese sinteseperiode van 48 uur na 96 uur verhoog is, het 'n bietjie kristallisasie voorgekom.

Hierdie navorsing oor die vervaardiging van keramiek ondersteuningsmembrane was gedeeltelik suksesvol deurdat 'n goedkoper keramiekmembraan van Alcoa gemaak is, alhoewel die herhaalbaarheid laag was. SEM en XRD-analise het die grootte en die suiwerheid van die kristalle bevestig nadat 'n geoptimaliseerde sintetiese prosedure gebruik is. Inligting van hierdie studie lê die grondslag vir die suksesvolle sintese van 'n DDR-membraan, aangesien dit waardevolle inligting verskaf vir toekomstige navorsing oor hierdie onderwerp.

Chapter 1

A brief introduction

Content

1.1 Introduction

In this Chapter a brief description of the project will be presented. From this the reader will acquire an understanding of what experimental aspects were taken into consideration and evaluated during this research. Some basic concepts and definitions regarding zeolites and membranes, both of which are core entities in this thesis, will be introduced.

1.2 Zeolites

Zeolites are complex crystalline inorganic polymers consisting of indefinitely extending frameworks of AlO_4 and SiO_4 tetrahedra. The tetrahedra are linked to each other by the sharing of oxygen ions[1]. The framework structure consists of channels or interconnected voids that are occupied by cations and water molecules. Each zeolite type has a specific pore size which makes them suitable for processes requiring separations on a molecular level. In addition, zeolites can be used to separate mixtures based on their selective sorption properties due to their hydrophilic or hydrophobic nature[2]. In order to reduce the membrane thickness, a thin layer of zeolite is usually grown onto a ceramic membrane or support yielding a "zeolite composite membrane".

1.3 Membranes

Membranes have gained an important place in chemical technology and are used in a broad range of applications, most prominently in drug delivery and separation applications[3]. The key property that is exploited is the ability of a membrane to selectively control the permeation rate of a chemical species through the membrane. The membrane is a permselective barrier or interface between two homogenous phases[4].

1.4 Aims and objectives

The aim of this research is to intrinsically apply, as well as develop, my scientific research skills in the field of Membrane Science and Technology focusing on DDR type zeolite membranes. The objective is to obtain a better understanding of the properties of DDR zeolites in combination with ceramic membranes. The communication of this research will be first and foremost through literature reviews, secondly, experimental research and communiqué of my research in the form of a thesis and ultimately, the conveyance of my research through publications.

The research will be conducted in three basic areas:

1. Synthesis of Alcoa ceramic membranes
2. Hydrothermal synthesis of zeolite DDR crystals
3. Hydrothermal synthesis of a zeolite DDR membrane

1.5 Outline of thesis

1.5.1 Literature review

In chapter 2, an overview is given of literature pertaining to this study. Firstly, the history of zeolites is discussed in order to provide a better understanding into why and how zeolites were discovered and being used today. Next the classification of zeolites is discussed to provide a better understanding of the different zeolite frameworks that are found. In this section the dodecasil series DOH, MTN and DDR are introduced. The deca-dodecasil DDR is discussed in more detail. Subsequently, there is a short introduction to zeolite composite membranes. Susequently, composite membrane synthesis and zeolite synthesis are reviewed. This leads to a discussion on synthesis variables. The section is concluded with a look at zeolite applications emphasizing the local (South African) zeolitic industry.

1.5.2 Materials and methods

In Chapter 3, a description of the reagents used during the research, the methods applied and the techniques used for characterization is presented. Chapter 3 consists of three sub-sections:

- Synthesis of Alcoa ceramic supports
- Synthesis of DDR crystals
- Synthesis of DDR membranes

Synthesis variables and parameters are discussed in each sub-section.

1.5.3 Results and discussion

In Chapter 4 the results of the experiments are discussed in detail. This chapter will provide reasons or hypothesis for observations made during the research. Explanations and hypothesis are substantiated through literature and interpretation of characterization data.

1.5.4 Conclusion and recommendations

Finally, in chapter 5 the results and discussion are summarized. Important observations and their explanations are stressed. Proposals for further research conclude the thesis.

1.6 References

[1] **H. van Bekkum, E.M. Flanigen, P.A. Jacobs, J.C. Jansen**, *Introduction to Zeolite Science and Practice*, Elsevier, 2nd Edition, 137, 2001, Chapter 1, pp1.

[2] **A. Beranguer-Murcia, J. García-Martínez, D. Cazorla-Amorós, A. Linares-Solano, A.B. Fuertes**, Silicalite-1 membranes supported on porous carbon discs, *Microporous and Mesoporous Materials*, 70 (2004) pp173.

[3] **R. Baker**, *Membrane Technology and Applications*, Wiley and Sons, 2004, Chapter 1, pp1.

[4] **M. Mulder**, *Basic Principles of Membrane Technology*, 2nd Edition, Kluwer Academic Publishers, 1996, Chapter 1, pp7-13.

Chapter 2

Literature review

Content

2.1. History

The Swedish mineralogist Axel Cronstedt discovered zeolites in 1756[1]. He named the minerals zeolites since the crystals exhibited intumescences when heated in a blowpipe flame. The name zeolite is derived from the two Greek words, "zeo" and "lithos" meaning "to boil" and "stone". In 1840, Damour observed that zeolite crystals could be reversibly dehydrated, with no apparent change on their transparency or morphology[1] a property which made zeolites unique when compared to other minerals.

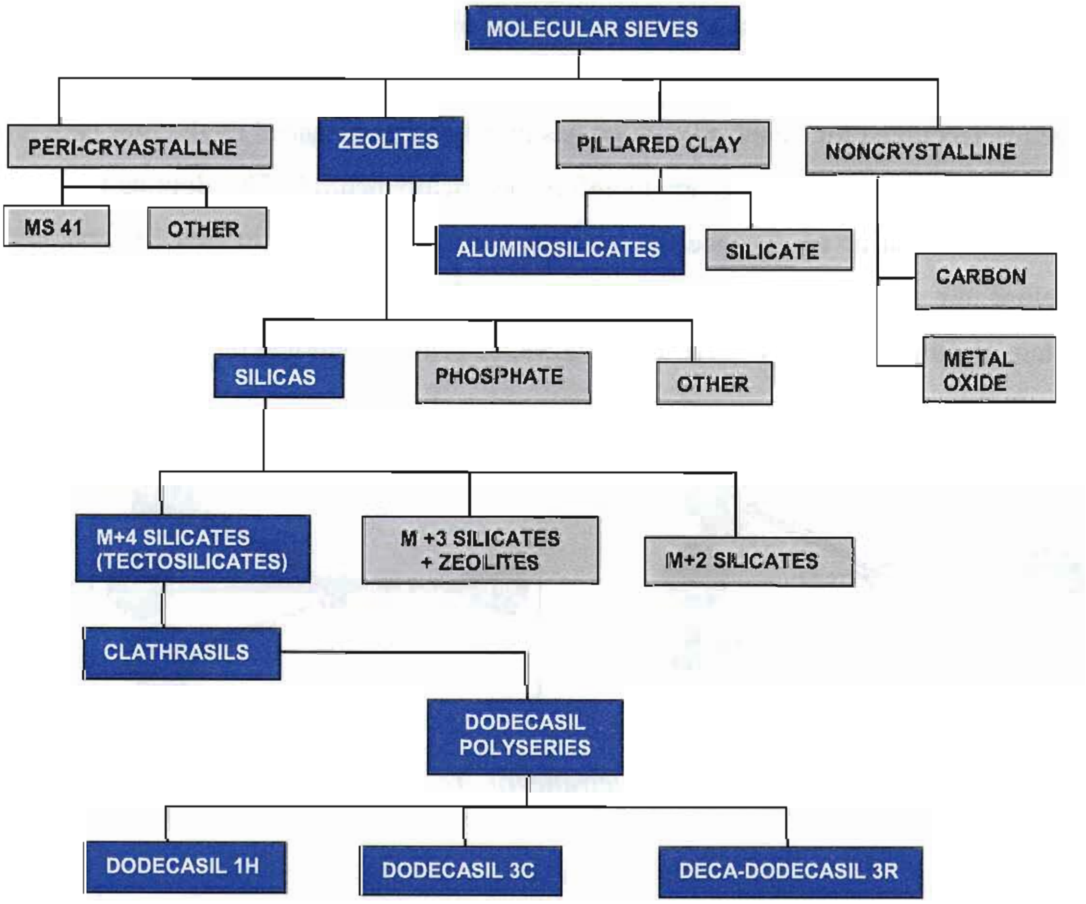
The concept that zeolites, when dehydrated, consist of open spongy frameworks was discovered by Friedel in 1896[1]. He observed that various liquids such as alcohol, benzene and chloroform were occluded by dehydrated zeolites. In the 19th century, Grandjeun demonstrated that dehydrated zeolite chabazite absorbed numerous molecules including ammonia, air and hydrogen. Neigel and Steinhoff introduced the use of zeolites as molecular sieves in 1925[1]. They demonstrated that chabazite excluded acetone, ether and benzene, but rapidly absorbed water, methyl alcohol, ethyl alcohol and formic acid.

Van Bekkum et al[1] noted that by the mid 1930s the literature discussing research on zeolites was paramount. Studies included ion exchange, adsorption, and structural properties of zeolites. Also at that time, a number of syntheses of zeolites were reported, however, these reports could not be substantiated due to the lack of characterization and experimental reproducibility.

This is where Richard Barrer's research on zeolites became significantly important to the industry. In 1948, he reported the first definitive synthesis of zeolites[1]. His work inspired the synthesis of the first major industrial zeolites A, X and Y by Milton and Breck[1]. These zeolites were the first industrial applicants for separation and purification within the petrochemical industry. Later, Mobil Oil expanded their use of zeolites and used zeolites X and Y as isomerization and cracking catalysts. Mobil reported the first synthesis of silica zeolites beta and ZSM-5, both of which are commercially significant today.

Since then the amount of patents and publications on zeolites have increased steadily. A reflection of this incline is seen by the increase in number of scientists affiliated with zeolite science. As a result, there has been a proliferation in the number of independent zeolite associations. Thus, we can safely assume that zeolites will play an ever-important role in our society's technology and development[2].

2.2 The classification of zeolites



Scheme 2.1: An overview of the subclasses of molecular sieves (M=cation)

2.2.1 Introduction

Zeolites are molecular sieves (any material that exhibits selective sorption properties[3]) because they can be used to separate components based on molecular size and shape[4]. In Scheme 2.1 an overview is given of the subclasses of molecular sieves. The highlighted sections will be elaborated on in this literature review.

2.2.2 Zeolite structure

The fundamental building blocks of zeolites are a tetrahedron of four oxygen anions surrounding a small silicon or aluminium ion[5]. These tetrahedra are arranged so that each of the four oxygen anions is shared in turn with another silica or alumina tetrahedron. The crystal lattice extends in three dimensions assuring that the -2 oxidation state of each oxygen is accounted for. Each silicon ion has its +4 charge balanced by the four tetrahedral oxygens and the silica tetrahedra are therefore electrically neutral. The alumina tetrahedron has a residual charge of -1 since the trivalent alumina is bonded to four oxygen anions. Therefore, the alumina tetrahedron requires a +1 charge from a cation in the structure to maintain electrical neutrality. Figure 2.1 shows the primary building blocks of zeolite.

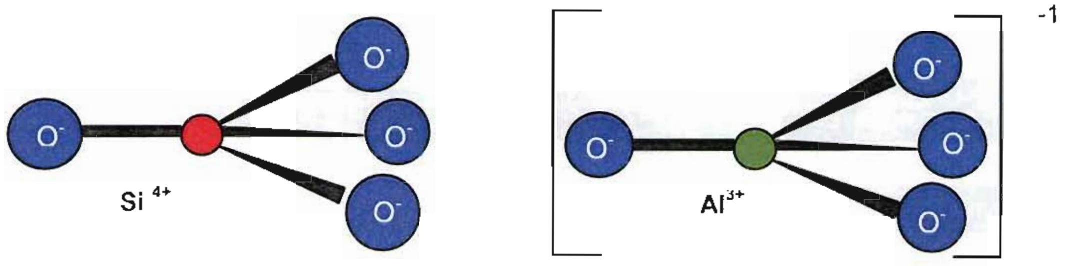


Figure 2.1: ***The silica and alumina tetrahedra are primary building blocks of zeolites*** [5]

2.2.3 Zeolite frameworks

Three-dimensional arrays are built when silica and alumina tetrahedra link to each other by the sharing of their corners as indicated with circles in Figure 2.2[6]. These assemblages of the primary tetrahedral units of structure are called secondary building units (SBUs). Complex aluminosilicate skeletons of zeolite structures are described by defining a series of these SBUs.

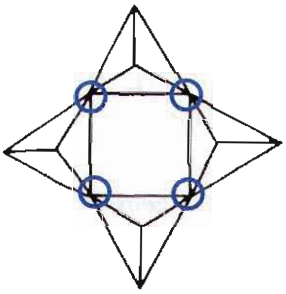


Figure 2.2: ***Linkages of tetrahedra to produce a zeolite structure*** [6]

An example of a simple SBU is the single four ring (S4R) structure circled in Figure 2.3. A simple illustration is depicted in Figure 2.3. This type of zeolite framework for example is built by the linking of four tetrahedra (Figure 2.2). In Figure 2.3 various SBUs that are used to categorize zeolitic frameworks, are presented.

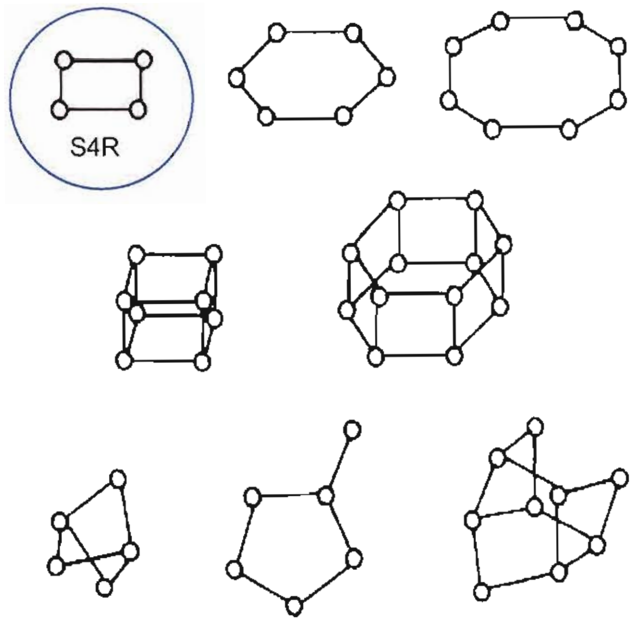


Figure 2.3: ***Secondary building units of zeolites*** [6]

SBUs are generally used to categorize zeolite frameworks[4]. For example, zeolite X, from the faujasitic group of zeolites, can be classified as the linking of SBUs called sodalite units (Figure 2.4). One-half of sodalite hexagonal faces are used to create a tetrahedral array in which each sodalite cage occupies a position in space. Thus, using the correct nomenclature, it can be said that sodalite is an easily recognized building cage present in the faujasitic group of zeolites.

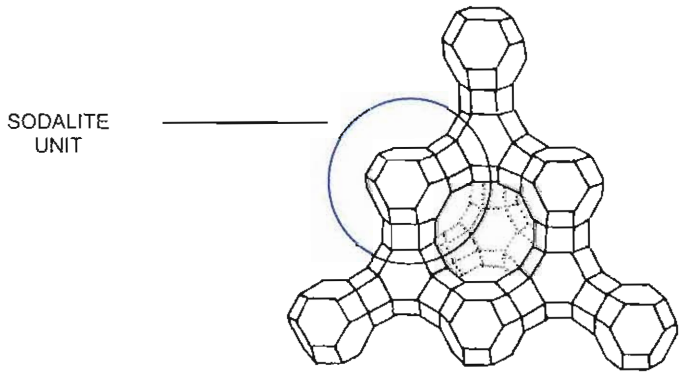


Figure 2.4: ***Sodalite units that complete the framework of Zeolite X*** [6]

Hauy introduced zeolite nomenclature in 1801[9]. He named the first zeolite -"stilbite" (STI) derived from the Greek word for "lustre". Nomenclature of synthetic zeolites followed the rules as proposed by Breck up to the 1970s[7]. However, by that time the research in zeolite synthesis had proliferated, more laboratories began exploratory synthesis efforts, and the proposed system of nomenclature became inadequate. In 1980, Barrer published a set of rules for naming both natural and synthetic zeolites[8]. Barrer's rules were directed toward writing zeolite formulas so that they provided as much information of the zeolite as possible. He proposed that topologies could be given a code *less* than three letters. Today, the structure commission of the International Zeolite Association[20] reviews new structures and suggests or accepts suggestions for three-letter code designations for each unique framework topology.

The law of priority is used in the nomenclature of natural zeolites[9]. This means that the merit of naming a zeolite is given to the discoverer of that mineral (e.g. the zeolite barrerite was named by Passagola and Pongilappi in 1975 to honour Richard Barrer). Szostak[9] further explains that zeolites that have the same framework topology can be referred to by using a genus name. Thus, barrerite *(STI)* and stellerite *(STI)* both have the same framework topologies as stilbite *(STI)* and thus both belong to the genus– stilbite (STI). Further identification by different names (*barrerite* and *stellerite*) is due to the differences in the location of the zeolite deposit, Si or Al ratio and cation content.

In general, zeolites that have high alumina content are categorized as aluminosilicates[9] (Scheme 1). The aluminosilicates, starting from a Si or Al ratio of 1 up to for example 10000, show the presence of Al in synthesis, characterization and application. Al-poor zeolites detect no Al-dependant behaviour and are thus denoted as Al-free materials. Al-poor zeolites are named silicates[9]. An example of silicates is seen in the category of tectosilicates (Scheme 2.1).

2.2.4 Tectosilicates

Mineralogists historically divided silicate minerals into categories, which were further divided into families[4]. For example, the category of tectosilicates is further divided into the families of (Scheme 2.1):

- M+4 silicates,
- M+3 silicates,
- M+2 silicates,

The families are minerals that contain three-dimensional frameworks of SiO_4 tetrahedra. Complex three-dimensional frameworks are obtained (Figure 2.5) when all four of the tetrahedral corners occupied by oxygen atoms are shared between two silica atoms.

Figure 2.5: Crystal structure of a tectosilicate[9]

2.2.5 Tectosilicates as clathrasils

Clathrasils are derived from the category of tectosilicates[9] (Scheme 2.1). They are different from zeolites since the windows formed by the connecting cages in their framework are too small to release stabilized guest species that are trapped there during synthesis.

Specific characteristics of a clathrasil are that they have an all silica composition and that they are able to trap or clathrate guest species. The recently synthesised decadodecasil-3R

(DD3R or DDR)[10] is one of the exceptions. DD3R is a clathrasil that contains windows of 8-rings of oxygen. Diffusion of small molecules through these windows is possible after calcination. Thus, DD3R can be considered to form an interface between the clathrasils and zeolites. Another exception is the Sigma-1 type zeolite, which is a modified form of DDR[9] Sigma-1 is seen as a link between clathrasils and zeolites because alumina isomorphously substitutes some of its silica-framework sites. Since the focus of this study is on DDR, a more in depth discussion of the dodecasil polyseries is appropriate.

2. 3 The dodecasil polyseries of zeolites

2.3.1 Dodecasil 1H

Dodecasil 1H is abbreviated as DOH and can be identified as D1H or DOH. It is hexagonal and has a structure type material consisting of $|C_5\ H_{11}\ N\ (N_2)_5|\ [Si_{34}\ O_{68}]$, where $C_5H_{11}N$ is the guest molecule piperidine[11].

In DOH frameworks, pentagondodecahedra cages or $[5^{12}]$ cages are formed by the corner sharing of tetrahedra of SiO_4. As a result, a 3-dimensional 4-connected net is built up from hexagonal layers of face sharing tetrahedra. The $[5^{12}]$ cages (Figure 2.6a) are regarded as the fundamental cages of the dodecasil series. From the $[5^{12}]$ cage, two types of cages-like voids arise: the $[4^3\ 5^6\ 6^3]$ cage (Figure 2.6b) and the icosahedron $[5^{12}\ 6^8]$ cage (Figure 2.6c). The $[5^{12}\ 6^8]$ cage can house guest molecules such as 1-adamantylamine while the $[4^3\ 5^6\ 6^3]$ cage can clathrate molecules of nitrogen.

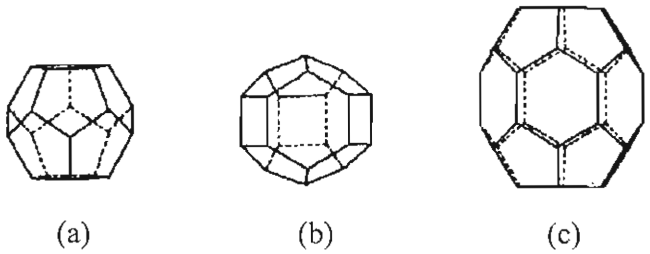


Figure 2.6: Cage structures of DOH dodecasil [11]

Literature on DOH is scarce. Gies et al[12] presented an interesting article where DOH is produced as a low temperature by-product during the synthesis of a clathrate compound of silica. It was concluded that as the guest molecule, 1-adamantylamine, stabilizes the framework at higher temperatures, while DOH can only be formed at lower temperatures (<165°C) during the synthesis. At higher temperatures, a different phase of zeolite is produced. The hydrothermal synthesis time was 4-6 weeks and the crystallographic properties of the product were analyzed and compared to those of other clathrasils.

Gies et al[12] noted that the produced clathrasil had the common characteristic of clathrasil frameworks since it had the ability to be stabilised by the same guest molecule at different synthesis temperatures. Further, it was shown that the product had a structural resemblance to the dodecasil DOH. The only difference between the product and DOH was that the guest molecule of the product was clathrated in a slightly smaller cage. The smaller cage seen in the product displayed no concurrence to the dodecasil polyseries of clathrasils.

Other investigations on DOH have studied the influence of synthesis conditions, the presence of DOH as a by-product in the synthesis of MCM-22 type zeolite[13,14], RUB-3 type zeolite[15] and DOH synthesis using metal complexes as structure directing/guest molecules[16].

2.3.2 Dodecasil 3C

Dodecasil 3C (D3C) is abbreviated as MTN. MTN belongs to the family of clathrasils as it is has a framework that consists of silica cages and are able to host or clathrate guest molecules[17]. MTN has a composition of | $(C_8H_{20}N^+)$ q $(OH)^-q$ | $[Si_{136} O_{272}]$, where $C_8H_{20}N^+$ is the guest molecule tetraethyl ammonium[18]. MTN has SiO_4 tetrahedra that are all corner connected, forming pentagon- dodecahedra cages, $[5^{12}]$. As in DOH, the cages are built in such a way that they form pseudohexagonal nets. Cubic close packing of the MTN results in a hexagonal $[5^{12} 6^4]$ cage (Figure 2.7)[17]. Guest molecules or structure directing agents such as trimethylamine or pyridine are located in the $[5^{12} 6^4]$ cages. Smaller molecules such as methane and atoms like Kr, Xe and Ar are usually enclathrated in the fundamental cage.

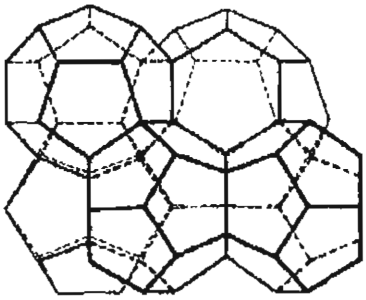


Figure 2.7: Projection parallel to the pentgondecahedra layer showing the $[5^{12}]$ cages and the $[5^{12} 6^4]$ cage structures of MTN dodecasil [17]

Most studies on MTN were carried out in the 90s[19, 20, 21, 22, 23]. In 1995, Konnecke and Fuess[19], used the guest molecules pyrrolidine and t-butlyamine to synthesise MTN. They used powder diffraction to analyse the phase transitions of the clathrated compound. In doing this, they found that at room and low temperatures, the structures of MTN were dependant on the symmetry of the enclathrated guest molecule. At high temperatures (180°C), the symmetry was cubic which means that the structure was no longer dependant on the guest molecules.

Dumont and Bougeard[20] used molecular dynamics to study the behaviour of methane clathrated in MTN cavities by molecular dynamics. Their studies showed that in the large cages, clathrated methane molecules are not located in the centre of the cages as in the case of smaller cages. Further, they described the motion of the methane molecules as a gliding movement of the molecules along the walls of the cages.

Balszunat et al[21] discussed the rotational excitations of the methane molecule in porous media. These studies concluded that MTN had the lowest potentials when compared to silica gels and MCM-41 type zeolites. The lower potentials were due to the smaller distance of the enclathrated molecule to the host structure.

Other articles have focused on the phase transition of MTN from cubic to tetragonal and the analysis thereof through powder diffraction (Knorr and Depmeier)[22]. It was observed by Grünewald et al [23] that MTN was a by–product, together with DOH, during the synthesis of the silicate RUB-type zeolite.

2.3.3 Deca-dodecasil 3R

Deca-dodecasil 3R can be abbreviated as DDR or DD3R. It consists of $|(C_{10}H_{17}N)_6(N_2)_9|$ $[Si_{120}O_{240}]$, where $C_{10}H_{17}N$ is the guest molecule 1-aminoadamantane[24]. DDR is built from corner sharing $[SiO_4]$ tetrahedra. The tetrahedra are connected to pseudohexagonal layers of face sharing pentagonal dodecahedra - the fundamental cage (Figure 2.8b) units of dodecasils. Two new types of cages (Figure 8)[24] can be obtained when the pseudohexagonal layers are stacked in a specific sequence and are interconnected by an additional $[SiO_4]$ tetrahedron. Six-membered rings are formed between the layers. A small decahedron $[4^3\ 5^{12}\ 6^1]$ cage (Figure 2.8a) and a large 19-hedron $[4^3\ 5^{12}\ 6^1\ 8^3]$ cage (Figure 2.8c) is formed[25] .

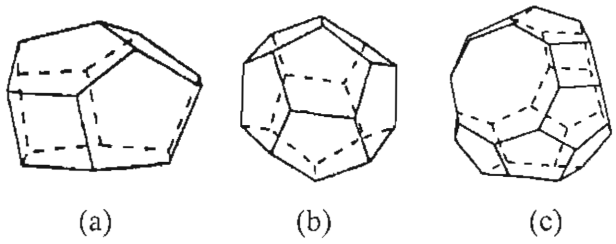

(a) (b) (c)

Figure 2.8: Cage structures of DDR dodecasil [24]

The 19-hedron cage is able to host the 1-aminoadamantyl (ADA). ADA is the guest molecule that is commonly used to synthesize DDR. When DDR has not been calcined, it is included in the clathrasil family. This is because the ADA is trapped in the 19-hedron cage during DDR synthesis. Calcination of DDR decomposes the clathrated ADA. The DDR is then transformed into a phase that possesses zeolitic properties. This explains why DDR is considered the link between clathrasils and zeolites[24].

Gies et al[24] used a synthetic molar ratio of {ethylenediamine (EDA) : Si O_2} = {1 : 0.5} for the synthesis of DDR. The guest molecule, ADA, was added to the solution at 35mg/ml aliquots and the synthesis took 6-8 weeks. Gies et al[24] went on to describe how DDR was co-synthesised with DOH, which can also be synthesized using ADA as a guest molecule. This polymorphism is dependant on the concentration of guest molecules present. High concentrations of ADA stabilize DDR whilst lower concentrations produce DOH. This however could not be confirmed when repeated by Den Exter et al[10].

Den Exter et al[10] used a synthesis ratio of 47ADA: 100SiO_2: 404EDA: 11240H_2O, to synthesize DDR. They reported that the formation of DOH is favoured at high temperatures and that DDR was only obtained when synthesis temperatures were less than 170°C. However, den Exter et al[10] reported that even at 160°C polymorphism occurred, whereby mixture products of DOH/DDR were obtained. They[10] further found that at higher water concentrations (11240 moles) within the synthetic molar ratio, pure DDR was produced. The synthesis was performed over a shorter period of 25 days. Crystal sizes obtained were between 5 and 10um.

To synthesize a DDR membrane[26], crystals or seeds of DDR are initially prepared prior to seeding and membrane synthesis. For their synthesis, Tomita et al[26] used the synthesis route suggested by den Exter et al[10]. After seed synthesis, a simple seeding process is used, followed by hydrothermal synthesis during which the membrane is grown[26]. The synthesis period for the membrane is considerably shorter (48hrs at 423K) when compared to the hydrothermal time used for seed synthesis. Further, the synthetic molar ratio for DDR membrane synthesis is notably more concentrated at 9ADA: 100 $Si0_2$: 150 EDA: $4000H_2O$.

As with other dodecasils, little research has been published on DDR. There are some articles that discuss gas separation characteristics of DDR crystals and membranes [26,27,28]. Tomita et al[26] achieved a separation factor of 220 for CO_2 and CH_4 molecules. Zhu et al[28] on the other hand demonstrated that absorbance through the DDR 8-ring cage is dependant on shape selectivity. In addition, den Exter et al[25] concluded that DDR membranes *"will be useful in the separation of small hydrocarbons"*. This is due to the three different cage structures within its framework where the fundamental cage clathrates the smaller atoms or molecules.

Thus, to summarize the dodecasil polyseries, it can be said that these all silica-type zeolites possess dual properties, as they are included in the clathrasil family of minerals. Dodecasils are able to clathrate or trap guest molecules and once clathrasils have undergone thermal treatment, the enclathrated guest molecule is cracked out and they transform to a phase that displays zeolitic properties.

A number of guest molecules can stabilize dodecasils and research studies have shown that even metal complexes can be used as structure directing agents during synthesis. The hydrothermal synthesis time is unusually long, when comparing the dodecasils to other more common zeolites. The DDR type zeolite is the only member of the polyseries that has been used to produce a membrane. According to the literature, DDR is extremely useful for the separation of CO_2 and CH_4. Finally, it should be emphasized that literature and hence confirmation on the repeatability of synthesis is scarce. However, since the literature on the dodecasil series is limited, in particular on the DDR-type zeolite, adding to the research on DDR has provided a suitable challenge.

2.4 Composite membrane manufacture

2.4.1 Introduction

Membranes are gaining an important place in chemical technology. The function of a membrane is to selectively control the permeation rate of a chemical species that passes through it. The membrane thus acts as a permselective barrier or boundary between two phases[29]. Membranes are used for a variety of biological and industrial separation processes. In controlled drug delivery, the goal is to control the permeation rate of the drug from a reservoir to the body. In industrial separation applications, the goal is to allow one component of a mixture to permeate the membrane freely, while hindering permeation of other compounds. A schematic representation of the fundamental process of membrane separation is given in Figure 2.9[30] .

Inorganic membranes have unique thermal, structural and chemical abilities and thus, have applications in high temperature and high-pressure separations, filtration and catalytic membrane reactors and processes[31]. Inorganic membranes can be divided into porous and dense membranes. Dense membranes such as palladium alloy have low permeances and high selectivities[31]. Alumina membranes on the other hand are porous, have high permeances and hence low separation selectivities.

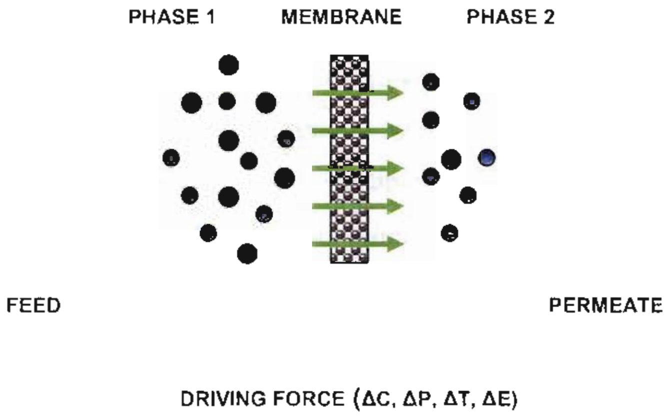


Figure 2.9: Schematic representation of a two-phase system separated by a membrane[30]

2.4.2 Ceramic membranes

2.4.2.1 Material

Research and development of alumina ceramic membranes has proved popular over the past few years, mainly because of their applications in filtration environments that are chemically aggressive and at high temperatures. Such environments require low fouling rates (applications requiring long life times), mechanical strength and cost effectiveness[32]. Alumina is frequently used for membrane synthesis, as it meets the above requirements.

Most industries use commercial α-alumina powders as the starting material for ceramic membrane synthesis. In this research, Alcoa CT3000 SG (Alcoa World Wide Chemicals, USA) is used as an alternative to the more expensive, AKP-powder range (Sumitomo Chemical Company Ltd, Japan).

Although the Alcoa is cheaper, its purity (99.8%)[36] is compatible with the purity of the AKP powder range (99.99%)[33]. The purity is important since impurities effect the surface chemistry of the powder and hence of the membrane, and the dispersion of the powder (e.g. zeta-potential). The composition of Alcoa powder is provided in Table 1[36]. In addition, since impurities have extensive buffering tendencies, more impurities imply more difficulty when stabilizing a dispersion electrostatically. Ceramic powders containing large amounts of impurities may also exhibit an unstable pH-region, which also affects the stability of the dispersed powder particles required for ceramic membrane synthesis.

Table 2.1: ***Composition of Alcoa powder*** [36]

Compound	**%**
Al_2O_3	99.8
Na_2O	0.08
Fe_2O_3	0.02
MgO	0.07
SiO_2	0.03
CaO	0.02

Materials used for ceramic membrane synthesis other than alumina are silica, titania or zirconia[34]powders. Ceramic material produce membranes that have lower thermal expansion coefficients, are brittle, and fracture with little deformation when compared to their metal counterparts[35]. For these reasons, synthetic methods for ceramic membranes can be difficult and costly.

Membrane synthesis requires that impure ceramic powder is treated prior to synthesis, to remove these impurities. In the next step during synthesis, the powder is dispersed in solution using dispersing agents and the material is shaped into tubular forms through centrifugal casting[36,37] or extrusion[32]. In this research, centrifugal casting was applied.

2.4.2.2 Centrifugal casting

Centrifugal casting is a technique used in the synthesis of tubular ceramic membranes[36, 37]. Once the ceramic powder has been dispersed in water and a dispersing polymer, it is transferred into tubular steel moulds. The mould is inserted into a horizontal or vertical centrifuge. Rotation occurs at speeds of approximately 17000rpm. Subsequent to centrifugal casting, the supernatant is discarded and the mould tube contains what is called a "green cast". The green cast is sedimented by the movement of suspended particles through the liquid due to the centrifugal forces acting on them. This means that particles are ordered into an asymmetrical configuration. The green cast now has a macroporous layer, an intermediate layer and a microporous layer[32]. The macroporous layer or outermost layer provides the mechanical strength to the system. The intermediate layer provides reduction in inherent defects and prevents infiltration of the top layer material into the pores of the support. The innermost layer is a microporous layer and is observed as a smooth surface. The green cast is air-dried, released from the mould and sintered[38].

2.4.2.3 Sintering

The effect of sintering has been widely studied but with little unanimity in results. Page et al[39] found that when sintering with increasing temperature, pore sizes of the green cast remain constant. Hillman et al[40] found that the pore size increases. Steenkamp et al[36] found that pore size transitions are dependant on the porosity of the green cast. This is again in agreement with work done by Wang et al[41].

In general, the sintering process is a strengthening process of the green cast into a ceramic support. The sintering requires that the green cast be treated under a controlled temperature program to:

1) Remove any organic impurities or polymers and
2) ensure adequate sintering.

Impurities that remain in the powder can cause irregularities in the pore shape while decreasing the surface area, resulting in an undesirable decrease in porosity. Furthermore, an increase in the neck area of the tubular support and grain growth is usually observed[42]. After sintering, the green cast is transformed into a ceramic composite or a ceramic support (Figure 2.10).

Figure 2.10: Tubular ceramic support made from Al_2O_3

2.4.3 Zeolite Synthesis

Zeolites are usually grown onto ceramic supports[35] as the permeability of the zeolite is proportional to membrane thickness, the zeolite layer grown onto the support should be as thin as possible. Zeolitic membranes are produced through hydrothermal synthesis.

2.4.3.1 Hydrothermal Synthesis

Van Bekkum et al[9] reported that the hydrothermal technique was developed from the understanding of mineral formation in nature, i.e. at elevated pressure and temperature in the presence of water. Schafthaul first adopted this technique to synthesise quartz crystals upon transformation of freshly precipitated salicylic acid (1845)[9]. The commercial importance of the hydrothermal technique for inorganic compounds was realized after Nacken (1946) synthesised large single crystals of quartz. The hydrothermal technique for zeolite synthesis as we know it today has its origins in the work of Richard Barrer (1948) whose significance in zeolite research has already been discussed.

Byrappa et al[43] pointed out that the term hydrothermal is of geological origin. Sir Roderick Murchison, a British geologist, used the term to describe the action of water at elevated temperatures and pressures resulting in noticeable changes in the earths crust leading to the formation of various rocks and minerals for example zeolites.

The term hydrothermal synthesis has been defined by many, but with no unanimity. Byrappa[43] summarises that Mond and Niggli defined hydrothermal synthesis as *a method where components are subjected to the action of water, at temperatures above the critical temperatures of water, in closed bombs and therefore under the corresponding high pressures developed by the solutions.* Further, they include that Yoshimira, proposed the following definition: *reactions occurring under the conditions of high temperature and high pressure (> 100°C, >1 atm.) in an aqueous solution, in a closed system.* Most definitions, however, include no lower limit for the pressure and temperature conditions. Thus, Byrappa et al[43] propose a more rounded definition, which I would like to include: "Any *heterogeneous chemical reaction in the presence of a solvent (whether aqueous or non-aqueous) above room temperature and pressure greater than 1 atm in a closed system.*"

For the hydrothermal synthesis of specific zeolites, the reagents within the chemical reactions are present in specific molar oxide ratios. For example, the DDR-type zeolite[10] can be hydrothermally synthesised from a molar ratio of 47 ADA: 100 TMOS: 404 EDA: 11240 H_2O. From the molar oxide ratio, the different volumes of reagent required for the synthesis can be calculated. To reiterate (Section 2.1.2), Al-rich zeolites (aluminosilicates) would show the presence of Al in the synthesis, characterization and application. Subsequently, aluminosilicates contain a $n\mathrm{Al_2O_3}$ component within their synthetic molar ratio. Silicates such as DDR show no Al-detection, thus they do not have a $n\mathrm{Al_2O_3}$ component within their synthetic molar ratio. The successful synthesis of both aluminosilicate and silicate zeolites is largely due to the rapid advances in the apparatus involved. The vessel used during hydrothermal synthesis is generally dependant on the hydrothermal temperature (Table 2.2)[9]

To maintain a liquid phase during hydrothermal synthesis, the autoclave is filled 30-70% with the reaction mixture. Memory effects caused by zeolitic nuclei of preceding synthesis in cavities of the reaction vessels' Teflon inserts, may take effect. It is thus important that inserts be cleaned with a hydrofluoric solution at room temperature or a saturated sodium hydroxide solution at the reaction temperature after each synthesis[9]

Table 2.2: Common lab-scale reaction vessels, impurities and temperature ranges [9]

Reaction Vessel	**Volume (ml)**	**Impurity**	**Temperature (°C)**
Plastic bottle	< 11	Zn	< 100
Stainless steel	< 51	Fe, Cr	< 200
Stainless steel & Teflon lining	< 21	Nuclei of preceding synthesis	< 200
Quartz autoclave	< 5	Si	< 200

Most common reaction vessels are stainless steel autoclaves with Teflon inserts (Figure 2.11).

Figure 2.11: An example of a stainless steel autoclave with a Teflon insert

2.4.3.2 Seeding-assisted synthesis

In some instances, before hydrothermal synthesis, zeolite seed crystals, that are sub-micron in size are deposited onto the support to encourage the nucleation and growth of the zeolite. Noack et al[44] describe four methods of seed assisted synthesis:

a) Seeding in two-step crystallization

Vroon et al[45] provided a good literary example of this type of synthesis. They initially prepared seed crystals through hydrothermal synthesis on the surface of a support. In the second step, the support was hydrothermally treated for a second time using a fresh precursor solution. A subsequent continuous zeolite layer was formed.

b) Synthesis of seeds externally and attachment using zeta potential differences

In making MFI–type zeolites, Tsapatsis et al[46] demonstrates this technique clearly. Pure SiO_2 seeds are attached to the α-alumina supports at pH 8. Due to the opposite zeta potentials on the surface of the alumina and silica, the seeds crystals are electrostatically attached. After hydrothermal treatment, a closed MFI membrane was obtained.

c) Synthesis of seeds externally and attachment using cationic polymers

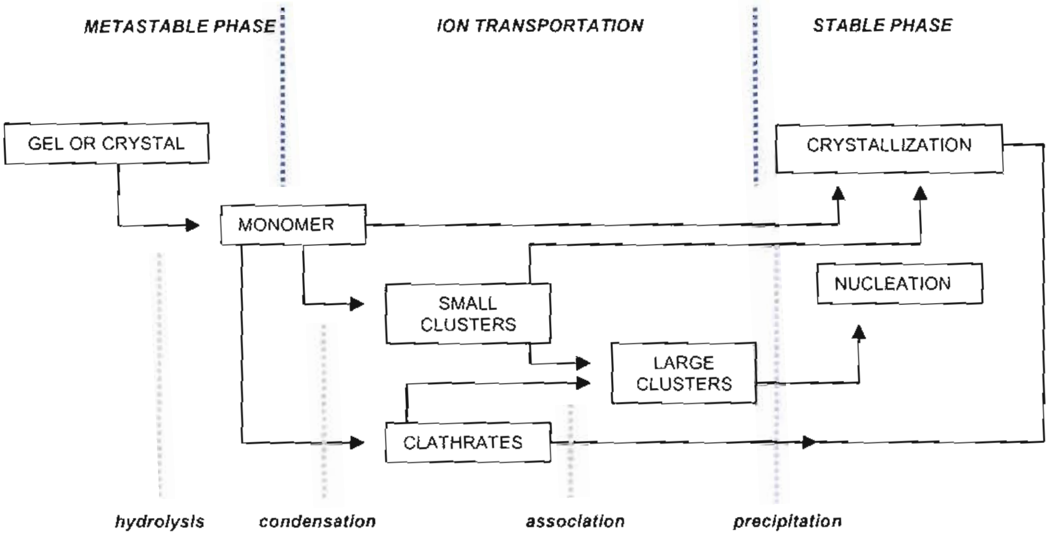
This is a 2-step seeding method. Hedlund et al[47] absorbed a monolayer of colloidal seeds onto the support using a cationic polymer. The polymer was then thermally decomposed to allow its removal from the support. A second layer of zeolite was subsequently synthesized using a diluted precursor mixture. A closed MFI zeolite layer was formed.

d) Synthesis of seed externally and reattachment using physical coating

Kusakabe et al[48] rubbed commercial X or A–type zeolite onto a α-alumina support surface. A closed zeolite membrane was produced after one or more hydrothermal synthesis steps.

2.4.3.3 Crystallization

Crystallization occurs step-wise (Scheme 2.2) during hydrothermal synthesis. With the onset of hydrothermal synthesis, the solution is in a meta stable phase. During this stage, a hydrogel is formed due to the aqueous phase present between the dissolution of the precursor gel and the growth phase of the already forming crystals. Next, ion transport begins an induction period where, the hydrogel rearranges through hydrolysis forming monomers. These monomers are the primary building blocks of the zeolite. It is through condensation on the surface and between the monomers that small clusters (clusters of monomers and secondary building units) and clathrates are formed. Continuous hydrolysis and condensation leads to the formation of more monomers at the expense of the clusters. Also during ion transport, water and inorganic cations play a role in structure direction[9]



Scheme 2.2: Schematic representation of zeolite crystallization processes[9]

During this process of ion transport, small clusters and clathrates associate to form larger clusters. Next, nucleation and crystal growth occurs due to the precipitation of monomers and small and large clusters[9] Two nucleation processes can occur: crystal formation in solution (homogeneous nucleation) or crystal growth on the support (heterogeneous nucleation)[49]. There is spontaneous deposition of material onto the nuclei and larger crystallites form. It can be assumed that both nucleation and crystal growth exhaust the same precursor species and nucleation will reach a maximum before it declines. As a result, crystal growth will limit the availability of the precursor solution for further nuclei formation.

2.4.3.4 Washing and Drying

After the required period of hydrothermal synthesis has been completed, the zeolite membrane is repeatedly sonified with distilled water until pH neutrality has been reached.

Sonification speeds up the neutralization process. Zeolites can then be dried at room temperature or calcined to remove the template that may be clathrated.

2.5 Synthesis Variables

2.5.1 Effect of silica

The dissolution of the hydrogel may occur through a S_N2-type neucleophilic mechanism as proposed in Figure 2.12. At some stage after the initiation of the hydrolysis and condensation phases of the hydrothermal synthesis, the monomers and SBUs in solution are in equilibrium with the gel phase. During this stage, monomeric silica species are released, via hydrolysis and condensation reactions from the gel.

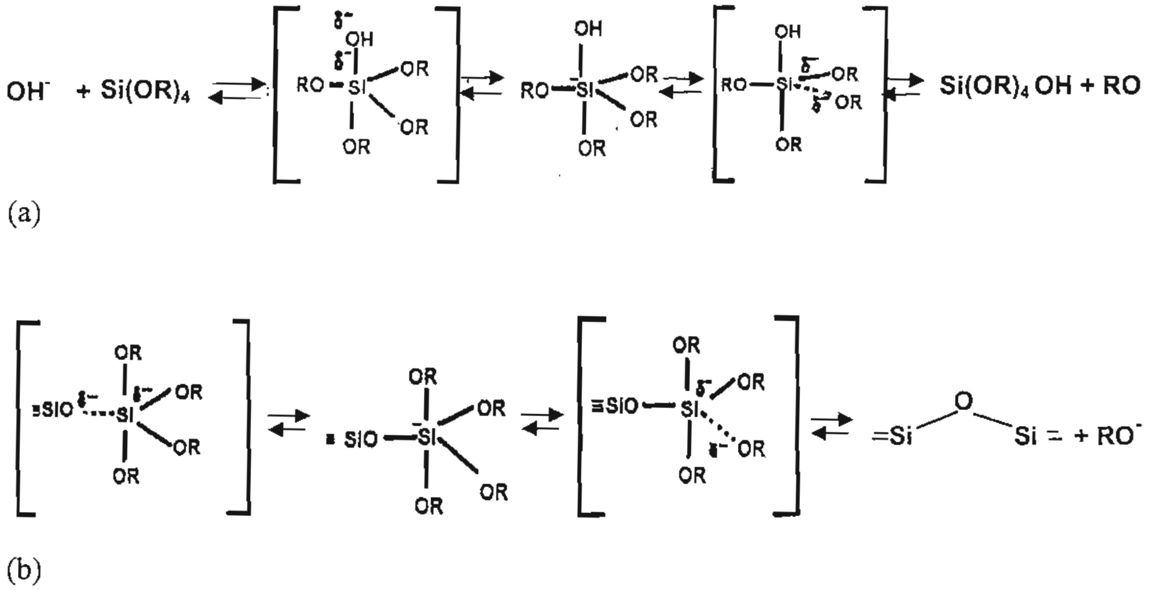


Figure 2.12: (a) hydrolysis and (b) condensation mechanism of silicate species [9]

This causes an increase in the pH of the system due to the presence of OH^- ions. However, if the silica species is present in low concentrations, the pH decreases after the hydrolysis and condensation reactions. Secondly, if less silica is present, neutral monomeric silica-species can be formed. Various types of silicate clusters can be produced through condensation reactions, for example monomers can form dimers, trimers, tetramers, cyclic tetramers and higher order rings[9].

2.5.2 Guest molecules

In general, the guest molecules or templates are mainly alkaline or ammonium ions. They can be charged or neutral molecules containing functional atoms or groups. The guest molecule influences the structure directing process during crystal growth.

Wang et al[41] studied the effect of the concentration of the structure–directing agent TPAOH during the synthesis of MFI-type zeolites. They observed that by increasing the amount of the guest molecule, the pH of the system increased, favouring crystal growth but altering crystal morphology.

Gies et al[24] describe the use of ADA in the structure direction of DDR-type zeolites. The ADA occupies the larger $[4^3\ 5^{12}\ 6^1\ 8^3]$ cage within the DDR framework since ADA is too large to occupy the fundamental cage. Further, in the case of DDR, the structure-directing role of the template is dominated by the stereo specific space filling and stoichiometery between the template and the framework. Structure directing is hence less influenced by framework charge compensations.

2.5.3 Water concentration

Den Exter et al[10] demonstrated that increasing the water concentration from 5600 moles to 11240 moles at a hydrothermal temperature of 160°C, resulted in the production of pure DDR crystals. In systems where the dilution was increased (160°C), the DDR crystals decreased in size from 150μm to 5-10μm. Wang et al[41] confirmed this observation, when synthesising all-silica MFI zeolites. These results also correlate with the results obtained by Kalipcilar et al[50]. This has been related to the affect of the water concentration on the rate of nucleation.

2.5.4 Ageing

During zeolite ageing the system equilibrates[51]. Seed nuclei are generated during ageing which is either done at room temperature or at elevated temperatures, but still below the crystallization temperatures of the zeolite phase of interest. When ageing is done at elevated temperatures, the rate of crystallization will increase. Lin et al[52] proposed that increasing the ageing period results in the increase of nucleation and or depression of crystal growth. Further, Stozak[51] reported that if shaking or stirring is incorporated to achieve conditions that are more homogeneous, this could affect the course of the crystallization process to the extent that a different type of crystal is obtained. Thus, it is important to document whether a system has been stirred, static, rolled or vibrated.

2.5.5 Temperature

Van Bekkum et al[9] showed that the main event occurring at the reaction temperature is the formation of zeolites from the hydrogel. The chemical reactions that are accelerated due to the high temperatures are:

a) Further reorganization of the precursor solution

b) Heterogeneous and homogeneous nucleation and secondary crystal nucleation

c) Precipitation is in the form of crystallization.

Singh et al[53] observed that as the temperature increases, the rate of crystallization increases and the length of the induction decreases.

2.6 Zeolite applications

Zeolites are being used in progressively more diverse applications from housing construction to advanced 21st century electronics. They are specifically used as sorbents and catalysts in a variety of processes within the chemical, petroleum, petrochemical and food industries. More importantly, zeolite applications within South Africa are progressing positively.

Süd Chemie (Germany)[54], a technological partner for the petrochemical industry Süd Chemie Zeolites, produces zeolite catalysts for use in refineries and petrochemical plants to improve the performance of petrol, diesel and lubricants within South Africa. Süd Chemie has two plants, one in Natal and the other at the PetroSA refinery in Mossel Bay. In South Africa, Süd Chemie controls Süd Chemie SA (Pty) Ltd ("SCSA") which in turn controls Süd Chemie Zeolites (Pty) Ltd, as to 70% and Süd Chemie Sasol, as to 80%, Süd Chemie Adsorbents SA (Pty) Ltd as to 100%, Süd Chemie Water and Process Technologies (Pty) Ltd as to 100% and Nedhigh Investments (Pty) Ltd as to 100% [54]. It can thus safely be assumed that Süd Chemie plays an important role in zeolitic applications in South Africa.

NGK Insulators Ltd. (Nagoya, Japan) has commenced the production of HONEYCERAM®, ceramic substrates for automotive exhaust catalytic converters in South Africa (2001). The South African government decided to extend its Motor Industry Development Programme (MIDP) up to the year 2007. This is an incentive programme to support the South African car industry in areas where it can be globally competitive. Local automotive manufacturers, that export components, generate export credits which enable them to claim back duty on imports. As a result, automotive manufacturers are purchasing more zeolitic catalytic converters made in South Africa. Responding to this growing market, NGK established NGK Ceramics South Africa (Pty) Ltd. in February 2000, and began plant construction with a 2 billion yen investment in May 2000. NGK group companies are currently manufacturing HONEYCERAM in Japan, Belgium, the US, Indonesia. NGK Ceramics South Africa (Pty) Ltd. becomes the fourth overseas production base of NGK Insulators Ltd. (Nagoya, Japan)[55].

Sasol (South Africa) has established their European Research Centre for Homogeneous Catalysis at the School of Chemistry, University of St Andrews[56]. Zeolite catalysis and materials is an important area of research at this centre. Sasol uses zeolites for a number of diverse applications in South Africa (Table 2.3)[57]. In Table 2.3 an extensive list is presented of most of the uses of zeolites in South Africa. Sasol Olefins & Surfactants (a division of Sasol) concentrates solely on zeolitic applications, which have also been included in Table 3[57].

Table2.3: ***Uses of zeolites in South Africa*** [57]

Application	**Zeolite Type**	**Sasol Brand Name**	**Use**
Building and construction industry	Lightweight aggregates, pozzolans and building stone	-	Fillers
Paper industry	clinoptilolite	-	Paper filler and coating

Agriculture industry	various	-	Soil conditioners
Animal feed	clinoptilolite	-	Additives
Water treatment	clinoptilolite	-	Molecular sieves
Detergents	A, P, X	VEGOBOND® AF VEGOBOND®ADS VEGOBOND®AX VEGOBOND®SC VEGOBOND®GS VEGOBOND®GP VEGOPOUND®HD VEGOPOUND®SP	Builder in detergent formulation replacing STPP, enhancing capacity of powder, washing powder of the surfactant
Adsorbents/ Desiccants (molecular sieves)	3A, 4A, 5A, 13X	VEGOBOND®3A VEGOBOND®4A VEGOBOND®5A VEGOBOND®13X	Pressure swing absorption gas separators desiccants ether in cooperation or competition with silica gel and activated alumina, for the removal of water, hydrocarbons and other liquids, removal of water and hydrocarbons indouble glazing and brake system and the drying of industrial gases
Catalyst	Y, USY, ZSM-5	Y, USY	Fluid Catalytic Cracking
PVC industry	A	PH54A PH55A PH54ALW	PVC Heat Stabilizing

Cosmetic industry	A, AX	COSMABOND®4A LW COSMABOND®3A LW COSMABOND®AX	Make-up, non-aqueous personal care product
Leather industry	A	KORABOND®A KORABOND®AX	In wet-white processes as auxiliaries for greater Cr+3 float exhaustion and a better leather hydrothermal stabilization
Animal feed	A	MYCOBOND®4A	Within prevention of some of the toxic effects of mycotoxins in animal growth

2.6.1 Uses of DDR Zeolites

The separation of carbon dioxide (CO_2) from natural gas, consisting predominantly of methane (CH_4), is an important practical challenge[58]. A method for separation of CO_2 from CH_4 is to exploit the subtle differences in the molecular dimensions of the two molecules (Figure 2.13)[58] by allowing these molecules to adsorb and diffuse through zeolites. DDR-type zeolite has specially been tested for this purpose.

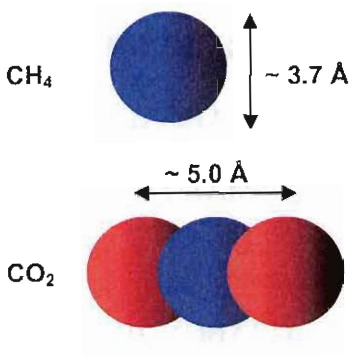


Figure 2.13: The approximate molecular dimensions of CH_4 and CO_2[58]

DDR-type zeolite membranes offer the potential to selectively remove carbon dioxide and increase the purity of methane from a mixture of these gases [10, 25, 26, 58]. Thus, these zeolites will potentially be used in natural gas refining plants and biogas plants. Past research on the development of membranes for carbon dioxide, selective sieving using organic polymer membranes ran up against difficulties in the industrialization of the membranes, due to inadequate resistance to pressure, heat, and harsh chemical environments[58]. As research on DDR zeolites has only begun recently, there are numerous novel applications of this zeolite yet to be investigated.

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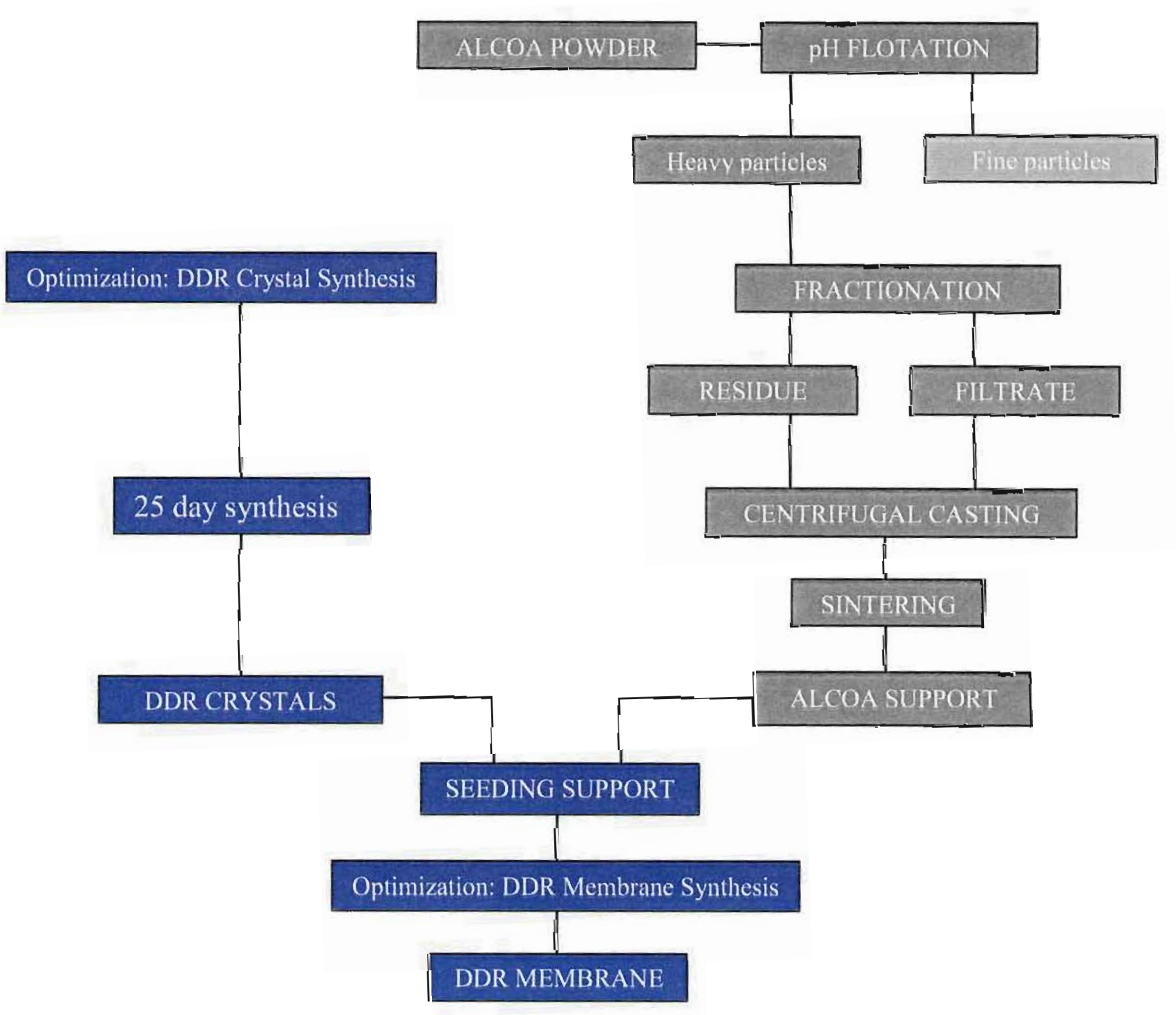
Chapter 3

Materials and methods

Content

3.1 Introduction

A schematic diagram of the experimental procedures for this research is presented in Scheme 3.1. Accordingly, experiments were conducted in the areas of ceramic membrane support synthesis; DDR crystal synthesis and DDR coated ceramic membrane synthesis.



Scheme 3.1: Schematic representation of the experimental procedures

Since the hydrothermal synthesis period of DDR crystals was 25 days, research of centrifugally casted tubular supports using Alcoa powder could be investigated. Since DDR membranes seem to require a seeding process before hydrothermal synthesis[1], a seeding step was included. The experimental processes in Scheme 3.1 are discussed in more detail in this chapter.

3.2 Synthesis of Alcoa ceramic support

3.2.1 Materials

The following materials were used: Alcoa CT3000 powder (Alcoa World Chemicals, USA), nitric acid (55%, Labchem), APMA (Darvan C, R.T. Vanderbilt Company, Inc. Norway, USA), wash ethanol (99%) and deionized water.

Ultrasonification was applied using a Model 250 Sonifier (Branson Ultrasonics Corporation, Danbury, USA) with an ultrasonic tip. Peristaltic pumps (Watson Marlow 502S) were used to provide the necessary flow-rates. Characterization techniques included scanning electron microscopy (SEM) (FEI ESEM Quanta 200) and particle size analysis (Malvern Mastersizer).

3.2.2 Methods

The synthesis of the ceramic membrane support can be divided into 4 processes (Scheme 3.1) namely flotation, fractionation, centrifugal casting and sintering.

3.2.2.1 pH flotation

600 ml of distilled water and a magnetic stirrer was placed in a 1L Pyrex beaker. The pH of the water was adjusted to pH2 using 55% nitric acid[2]. Two hundred grams of the Alcoa powder was added to the acidified water with stirring. The resulting suspension was stirred for 1 hour. Thereafter, the stirrers were turned off and the suspension was left for 2 days.

Subsequently, the top layer of the suspension was removed by pipetting 550ml of the solution into another 1L Pyrex beaker. This beaker was labelled as "fine particles". The remaining suspension was considered to be the "heavy particles". Both fine and heavy suspensions were air-dried for 72 hours.

3.2.2.2 Fractionation

The heavy particle powder from the acid treatment in 3.1.2.1 (Scheme 3.1) was then prepared for the next steps. 250ml of 99% wash ethanol was placed into a 600ml Pyrex beaker equipped with a large magnetic stirrer. The required mass (loading mass) of fine powder was pulverized using a pestle and mortar and added to the 250ml of wash ethanol while stirring. Loading masses of 65g, 75g, and 85g powder were used in this study.

After the powder had been added, the resulting suspension was stirred vigorously for 1 hour. Thereafter, the suspension was ultrasonificated at a frequency of 20 kHz and a transducer output of 100W. This treatment was continued for 2 sessions of 15 minutes with 1 minute of no sonification between each session. The suspension was then loaded into funnel 2 (F2) of the fractionation apparatus (Figure 3.1) and left to settle for 24hours.

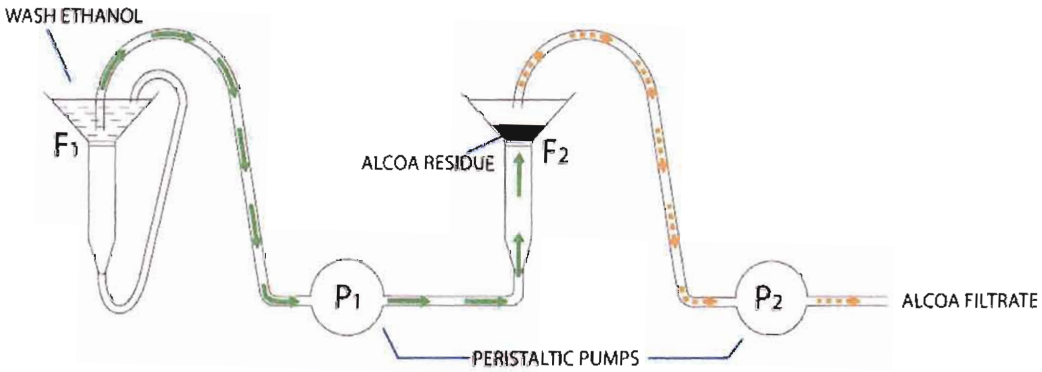


Figure 3.1: Fractionation apparatus

After settling (24 hours), the peristaltic-pump 1 (P1) was started with the required flow rate. Flow rates of 5ml/min, 7ml/min, 10ml/min and 15ml/min were used in this research

After the flow-rate was set, the wash ethanol from funnel 1 (F1) was pumped up through F2. As the wash ethanol flowed up F2, it carried with it the suspended powder. When the wash ethanol was near to flowing over the edge of F2, the topmost layer (Alcoa filtrate) was carefully removed using a second peristaltic-pump (P2) and collected in a 2L Pyrex beaker. This process was continued until the wash ethanol flowing though F2 was transparent. The remaining powder in F2 (Alcoa residue) was transferred in to a 600ml Pyrex beaker. Both fractions of Alcoa, residue and filtrate, were then air-dried in a fume-cupboard.

3.2.2.3 Centrifugal casting

To produce a tubular support, the treated Alcoa powder had to subsequently undergo centrifugal casting[2,3]. Both powder fractions were used for centrifugal casting. To achieve this, 16 ml of distilled water was firstly added to a 50ml Pyrex beaker equipped with a small magnetic stirrer. Darvan C (3.423ml) was added to the distilled water. The pH of the water was adjusted to 9.5 using 25% ammonium hydroxide. 17g of the powder fraction was added while stirring. The suspension was stirred for 5 minutes. Thereafter, the suspension sonified for 10 minutes, at a frequency of 20 kHz and a transducer output of 100W. After that, the suspension was poured through a 10μm-seive and the filtrate collected. The filtrate was then poured into a steel mould of which the inner surface had been coated with a thin layer of Vaseline. The mould containing the filtrate was then sealed and spun in a custom-made small centrifuge (Figure 3.2) at 16000rpm for 10 minutes. The resulting green cast of Alcoa powder in the mould was then left to air-dry for 3 days.

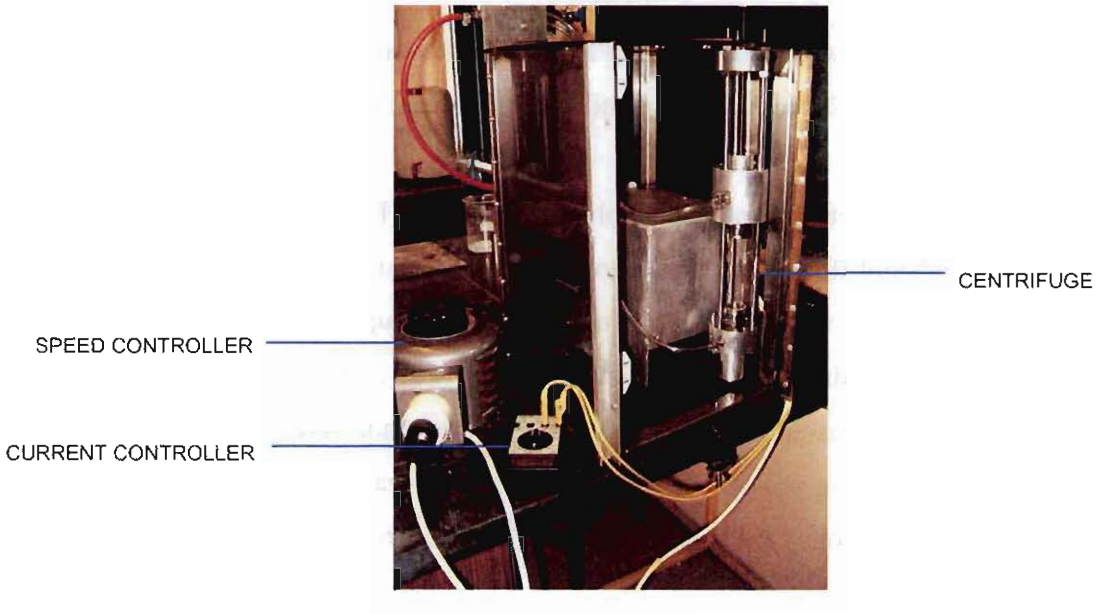


Figure 3.2: A custom-made small centrifuge

3.2.2.4 Sintering

After 3 days, the green cast was removed from the mould for sintering. The following sintering programme was adopted from Bisset et al[2]:

- ramp-up from 25°C to 400°C at a rate of 0.3°C/min
- maintain temperature at 400°C for 15 minutes
- ramp-up from 400°C to maximum sintering temperature of 1150°C at 0.3°C/min
- maintain temperature at 1150°C for 1 hour
- ramp-down from 1150°C to 25°C at a rate of 1°C/min

The resulting tubular ceramic membrane was then characterized.

3.2.3 Characterisation

A Malvern Mastersizer was used to analyse the particle size of the powders produced after fractionation (3.2.2.2). For analysis the powder was prepared as follows: 2.391g of distilled water was placed into a 5ml Pyrex beaker. The beaker was equipped with a small magnetic stirrer. 0.525g of Darvan C, the dispersing agent, was added to the distilled water. Then, 2.041g of the powder was added to the solution of Darvan C and distilled water. The solution was stirred for 5 minutes before particle analysis.

The particles were also investigated visually using scanning electron microscopy, SEM (FEI ESEM Quanta 200). For Sample preparation a small amount of powder be pulverized and placed on adhesive carbon paper. The powder was then coated with a gold/palladium layer using an ion-coater (EMScope). After this, the powder was analyzed.

3.3 Synthesis of DDR crystals

3.3.1 Materials

DDR crystal synthesis required the in-house production of 1-adamantanamine (ADA) from 1-adamantanamine hydrochloride (99+%, Acros Organics), sodium hydroxide (Rochelle Chemicals) and diethylether (Merck). Industrial reagent ADA (97%) was acquired from Fluka. Other reagents used were ethylenediamine (EDA) (99%, Aldrich) and tetramethoxysilicate (TMOS) (99%, Fluka).

A conventional oven was modified to accommodate four stainless steel autoclaves (Figure 3.3). An electrical stirrer (IKA, LABORTECHNIK RW20.*n*, Germany) was used to rotate the autoclaves during hydrothermal synthesis.

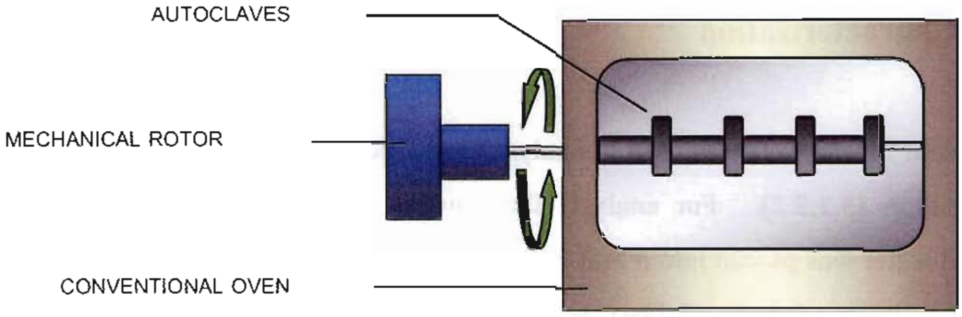


Figure 3.3: Modified oven to host four autoclaves

3.3.2 Methods

3.3.2.1 Synthesis of ADA

The synthetic procedure for ADA was taken from Den Exter et al[4]. A 2.66mol/dm^3 of aqueous sodium hydroxide was added to a 2.66mol/dm^3 solution of 1-adamantanamine hydrochloride. The resulting mixture was extracted three times using diethylether. The solvent was removed by rotor evaporation at 80°C with cooling in ice. This was continued until all the diethylether had been removed. The ADA product was dried in a dessicator.

3.3.2.2 Synthesis of DDR crystals

In this study the crystals were prepared according to the method described by Den Exter et al[4], which is regarded as the "standard procedure". For the optimisation all parameters investigated were varied starting from the standard procedure. In all cases the hydrothermal synthesis was for 25 days at 433K[4]. Preparation of the crystals according to the standard recipe was as follows:

According to the standard crystal recipe a molar ratio of 47 ADA: 100TMOS: 404EDA: 11240H_2O is used[4]- (1.58g ADA, 2,73g TMOS, 4.35g EDA and 36.33g H_2O). For the synthesis, the required amount of deionised water was weighed (Table 3.1). Next, the required amount of EDA was added to a 100ml autoclavable bottle equipped with a mechanical stirrer. The required quantity of ADA was added to the EDA and the pre-weighed distilled water added rapidly. Variation of the water concentrations is presented in Table 3.1.

3.3.2.2.1 Water concentration

Table 3.1: Synthesis conditions with varying water concentrations

Exp.	**Variation (%)***	**Molar oxide ratio (ADA: TMOS: EDA: H_2O)**	**Figure**
1	-30	47 : 100 : 404 : ***7868***	4.8(a)
2	-25	47 : 100 : 404 : ***8429***	
3	-20	47 : 100 : 404 : ***8990***	
4	*den Exter et al[4].*	47 : 100 : 404 : ***11240***	
5	-15	47 : 100 : 404 : ***9555***	
6	+60	47 : 100 : 404 : ***17983***	
7	+30	47 : 100 : 404 : ***14612***	4.8(b)

**Percentage deviation from literature[4]*

The mixture was shaken for 1 hr at 25°C before being placed in a water-bath at 368K. The temperature of the water bath was kept constant using a thermostat. Ageing of the solution was carried out in a water bath at various temperatures and times (Table 3.2). When temperatures above 368K were required, an oil-bath was used. The temperature of the oil-bath was also kept constant using a thermostat. Ageing was done with stirring.

3.3.2.2.2 Ageing time and temperature

Table 3.2: Variations in ageing time and temperature

Exp	Ageing Time (h)	Ageing Temp (K)	Figure
8	2.5	368	4.10(a)
9	2.0	368	
10	1.5	368	
11	0.5	368	4.10(b)
12	1.0	388	4.12 (a)
13	1.0	383	
14	1.0	373	
15	*Den Exter et al*[4]	368	4.12(b)
16	2.5	388	
17	2.5	373	

After the ageing, the solution was cooled in ice-water for 20min, after which ice-cooled TMOS was added drop-wise over a 1 minute period with vigorous stirring using a magnetic stirrer. The affect of different concentrations of TMOS was investigated (Table 3.3). After the TMOS had been added, the mixture was again placed in a temperature-controlled water bath or oil bath and stirred a clear solution was obtained. After cooling the mixture for 30 minutes, 45ml of the solution was pipetted into autoclaves equipped with Teflon inserts.

The autoclaves were tightly sealed and inserted into the pre-heated conventional oven. Hydrothermal synthesis took place at 433K for a period of 25days.

3.3.2.2.3 Silica source

Table 3.3: Synthesis conditions using various TMOS concentrations

Exp.	Variation (%)*	Molar oxide ratio (ADA: TMOS: EDA: H_2O)	Figure
18	- 10	47 : ***90*** : 404 : 11 240	4.13(a)
19	*den Exter et al*[4]	47 : ***100*** : 404 : 11 240	
20	+10	47 : ***110*** : 404 : 11 240	4.13(b)
21	+20	47 : ***120*** : 404 : 11 240	

* *Percentage deviation from the literature*[4]

3.3.2.2.4 Post-treatment

After the hydrothermal synthesis the crystals were neutralized by centrifuging in distilled water at 5000rpm for 6x15 minutes. The neutralized crystals were rinsed using washed ethanol and dried overnight at 323K in a conventional oven.

3.3.3 Characterisation

In-house ADA and reagent ADA was analysed using GC-MS (AutoSpec ETOF). The spectra produced were compared to reference data[5]. DDR crystal size and composition were characterized using scanning electron microscopy, SEM (FEI ESEM Quanta 200).

The Authenticity of the DDR crystal production was confirmed by X-ray diffraction, XRD (D-501, Siemens, Cu Kα radiation).

3.4 Synthesis of DDR Membrane

3.4.1 Materials

DDR membrane synthesis required the in-house production of 1-adamantanamine, ADA (refer to section 3.3.2.1) from 1- adamantanamine hydrochloride (99+%, Acros Organics), ethylenediamine, EDA (99%, Aldrich) and tetramethoxysilicate, TMOS (99%, Fluka).

3.4.2 Methods

3.3.2.1 Support pre-treatment

In order to optimize zeolite adhesion, the effects of refluxing, refluxing with hydrothermal treatment[6] and sonification[7] were investigated in terms of their suitability as support pre-treatments (Table 3.4). After each of the pre-treatments, the supports were neutralized by sonification in distilled water using an ultrasonic bath (Integral Systems) for 6 x 10 minutes. The various times and temperatures, at which they were dried, are included in Table 3.4.

Table 3.4: Support pre-treatments

Refluxing		**Hyrodrothermal treatment**			**Sonification**		**Drying**		**Figure**
Solution	**Time (h)**	**Solution**	**T° (K)**	**Time (h)**	**Solution**	**Time (h)**	**T° (K)**	**Time (h)**	
HNO_3	3						373	0.5	
HNO_3	3						373	2	
HNO_3	3						623	4	4.18
HNO_3	3	NaOH	433	1			393	12	
					$C_4H_{10}O$/ ADA	1	323	0.5	4.17(a)
					$C_4H_{10}O$	1	323	0.5	4.17(b)

3.4.2.2 Seeding

The seeding process was carried out as reported by Tomita et al[1]. The tubular ceramic support was wrapped in Teflon tape and immersed in a mass of crystals (Table 3.5) that had been dispersed in distilled water. The support was immersed overnight then dried at 323K for 30 minutes.

Seeding by centrifugation was also investigated. In this method a mass of crystals (Table 3.5) was dispersed in distilled water, and stirred vigorously for 20 minutes in order to ensure dispersion. Thereafter a tubular ceramic support was placed in a steel mould and the dispersion of crystals was pipetted into the inner-area of the tubular support. The mould was tightly sealed and placed in a custom-made large centrifuge (Figure 3.5). Centrifugation took place at a speed of 16000rpm for 20 minutes. After this, the supernatant was pipetted out; the seeded support was removed form the mould and dried in a conventional oven at 323K for 30 minutes. The effect of no seeding was also investigated (Table 3.5).

Table 3.5: The various seeding techniques investigated

Exp.	**Seeding mass (g)**	**Centrifugation (16000rpm)**	**Immersion (12hrs)**	**Figure**
1	0	-	-	
2	0.08	√		4.19(b)
3	0.0088	√		4.19(a)
4	0.08		√	
5	0.0088		√	

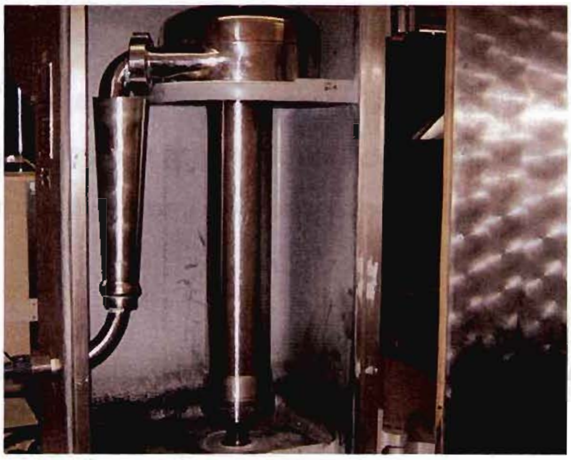


Figure 3.4: A custom-made large centrifuge

3.4.2.3 Zeolite synthesis

A seeded (control: non-seeded) support was then used for DDR membrane synthesis. For membrane synthesis a molar ratio of 9ADA: $100SiO_2$: 150EDA: $4000H_2O$ was used. This molar ratio and synthesis procedure was adopted from Tomita et al[1]. They describe a process where the gel is prepared and directly used for hydrothermal synthesis. In order to optimize the synthesis, the effects of water concentration (3.4.2.3.1), ageing (3.4.2.3.2) and hydrothermal synthesis time (3.4.2.3.3) were investigated in this study. During optimization, the hydrothermal synthesis was kept constant at 423K for 48 hours, except where the hydrothermal synthesis time was varied (3.4.2.3.3).

3.4.2.3.1 Gel preparation

Firstly, the required amount of deionised water was weighed (Table 3.6). The EDA was then placed in a 100ml autoclavable bottle. The required amount of ADA was added to the EDA and the pre-weighed distilled water was added rapidly. Finally, the solution was shaken for 10 minutes.

Table 3.6: Variations of water concentration

Exp.	Variation (%)*	Molar oxide ratio (ADA: TMOS: EDA: H_2O)	Figure
6	-30	9 : 100 : 150 : ***2800***	4.21(a)
7	+100	9 : 100 : 150 : ***8000***	4.21(b)
8	+30	9 : 100 : 150 : ***5200***	
9	+150	9 : 100 : 150 : ***10000***	

3.4.2.3.2 Gel aging

TMOS was added drop-wise (to the solution) and with vigorous stirring, over a 4 minute period. The gel that was produced was aged with stirring at room temperature (301K). The various ageing times that were used are shown in Table 3.7.

Table 3.7: Ageing periods for DDR gel

Exp	Ageing Time (h)	Figure
10	0	
11	¼	
12	½	4.22(a)
13	0	
14	60	
15	73	4.22(b)

3.4.2.3.3 Hydrothermal synthesis

After the ageing period, 45 ml aliquots of the gel were pipetted into a stainless steel autoclave equipped with a Teflon insert and a seeded ceramic support. The autoclave was tightly sealed and placed in the conventional oven. Hydrothermal synthesis took place for 48 hours at 423K. The hydrothermal synthesis was varied for the periods of 96, 72 and 60 hours. (Expts. 16, 17 and 18 respectively).

3.4.2.3.4 Post treatment

After the hydrothermal synthesis, the autoclave was allowed to cool whist rotating for 3 hours. Subsequently, the membrane was removed and neutralized by sonification in deionised water for 6x10min. After neutralization, the membrane was dried overnight at 323K.

3.4.3 Characterisation

The membrane surface was investigated by SEM, and the membrane composition was analyzed by EDS. Sample preparation for characterization is as described in Section 3.3.3.

3.5 References

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Chapter 4

Results and Discussion

Content

4.1 Introduction

The research consisted of three sections. Firstly, the manufacture of a ceramic supports from a cheap α-alumina source in the form of Alcoa powder. Secondly, the optimization of DDR zeolite crystals and thirdly the coating of the ceramic support with a DDR zeolite layer.

4.2 Synthesis of an Alcoa ceramic support

While the Alcoa powder is substantially cheaper than the AKP powder (Sumitomo Chemical Co. Ltd., Japan), it does contain more impurities and has a wider particle size distribution (Figure 4.1). The particle size distribution was confirmed by Bissett[1] who investigated the fractionation of the Alcoa powder. According to the particle size analysis (Malvern Mastersizer), the Alcoa powder has a bimodal particle size distribution. Due to these two reasons it was not possible to manufacture a ceramic membrane from the Alcoa powder when using the established centrifugal casting method[2]. To reduce these impurities and the particle size distribution, two pre-treatments were investigated, i.e. pH flotation and fractionation.

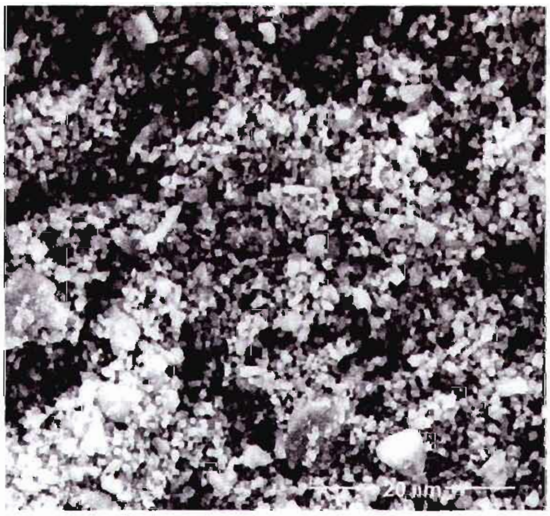
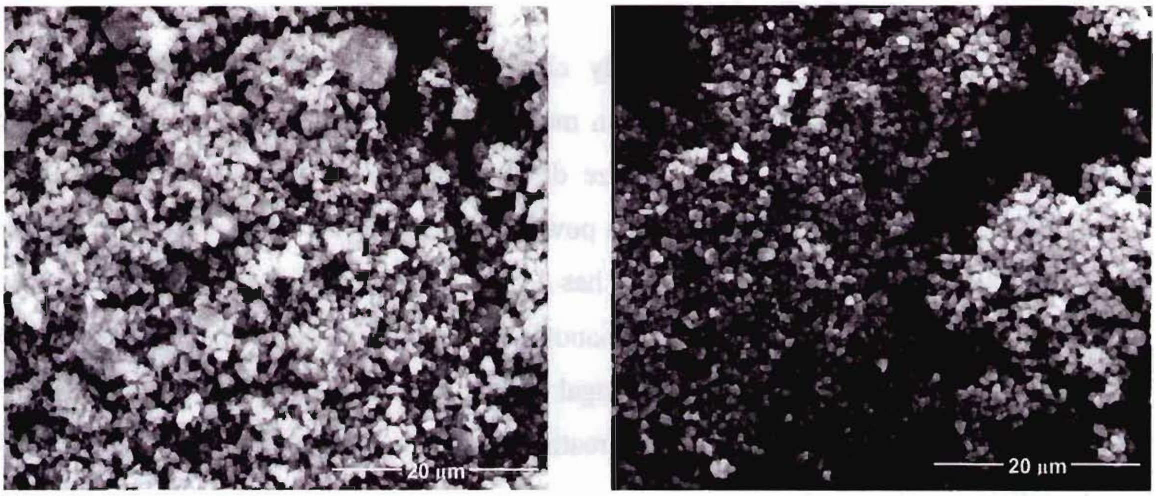


Figure 4.1: SEM of untreated Alcoa powder

4.2.1 pH flotation

It was previously shown that by treating the Alcoa powder in an acidic solution some of the fine particle fraction can be removed from the solution[1]. It seems that after the fine particles are removed the particle size distribution of the powder is within the correct range for ceramic support synthesis. In Figure 4.2 SEM images are shown of the two dried fractions after acid treatment, i.e. the settled fraction (Figure 4.2a) and the fraction removed with the suspension (Figure 4.2b).



(a) (b)

Figure 4.2:* *SEM images of Alcoa powder after pH treatment: (a) heavy particles, (b) fine particles

The dispersion and settling of the alumina particles in acidic conditions can be explained using Scheme 4.1. According to Hofman-Züter et al[3], when α-alumina powder is exposed to an acidic solution, the following reactions take place on the surface of the particles (Scheme 4.1).

A. *Hydration*

1. $Al_2O_3 + 3\ H_20 \longrightarrow 2\ Al(OH)_3^+$

2. $Al_2O_3 + H_20 \longrightarrow 2\ AlOOH$

B. *Hydrogen ion absorption*

1. $2\ Al(OH)_3^+ + H^+ \longrightarrow 2\ Al(OH)_2^+ + H_2O$

2. $AlOOH + H^+ \longrightarrow Al(OH)_2^+$

C. *Acid reaction*

1. $Al(OH)_2^+ + 2H^+ \longrightarrow Al^{3+} + 2\ H_2O$

3. $Al(OH)_2^+ \longrightarrow AlOOH + H^+$

Scheme 4.1: Reactions of alumina in an acidic environment[3]

It is seen that positive species are formed during the reactions of the alumina with the acid. The positive species on the surface of the particles exert repulsive forces on each other, allowing them to be kept in dispersion[4]. For the larger particles, the opposing force of gravitation is larger than the repulsive forces between the particles and as a result the larger particles settle.

A pH2 was used for pH flotation since it was shown that above pH2 negligible amounts of small particles remained in suspension[1]. It was clearly seen that the pH treatment effectively removed the finest particles from the Alcoa powder resulting in decreased particle size distribution. To optimize this process further, Bissett[1] investigated the effect of pH and solid loading on the amount of fine particles in suspension. The results of this investigation are summarized in Table 4.1. The author found that at pH 1.2-2.0, the highest amount of fine particles remained in dispersion. He further showed that the effect of loading mass was negligible on the amount of dispersion.

Table 4.1: ***Concentration of fine particles in suspension (%m/m) as a function of pH and solid loading.*** [1]

pH	Solid loading (g/ml)		
	100	**150**	**200**
1.3	10	14	13
1.5	30	27	30
2.0	16	21	20
3.0	0	0	0
4.5	0	0	0

4.2.2 Fractionation

In a second step, to further reduce the pore size distribution, the powder was fractionated as described in Section 3.2.2.2. Stokes' law (Eq.1) can be used to estimate the size of particles that are in a specific fraction during this process. This information can be used to elucidate the effect of the flow rate of the ethanol solvent and loading on fractionation i.e. on the maximum particle size that will be carried over with the solvent at a specific flow rate. According to Stokes' law, a frictional force (F) acts on spherical particles of radius (r) in a fluid that has a viscosity, η. The spherical particles will be falling in the fluid at a falling velocity, v. Stokes' law relates these parameters using Equation 4.1[5]:

$$F = 6\pi r\eta v \tag{4.1}$$

The frictional force that is exerted on the particle is proportional to the falling velocity of the particle. The falling particle reaches a terminal velocity or settling velocity. At this point, depending on the size, a particle will stop falling and remain in dispersion. An opposite force that is exerted on the spherical particle at a certain linear velocity will cause the particle to move upward. Since the density of the Alcoa (Al_2O_3) particles is known, the size of the particle can be estimated using a derivation of Stokes' Law (Eq. 4.2)[5]:

$$Vs = \frac{2r^2}{9} \frac{g\,(\rho_p - \rho_f)}{\eta} \tag{4.2}$$

where Vs is the linear velocity ($L.m^{-2}.s^{-1}$), r is the particle radius (μm), g is the gravitational force ($m.s^{-1}$), ρ_p is the density of the particle ($kg.m^{-3}$), ρ_f is the density of the fluid ($kg.m^{-3}$) and η is the viscosity of the fluid ($kg.\ m^{-2}.\ s^{-1}$).

Using the flow rate (obtained from the peristaltic pump), the linear velocity (Vs) of the solvent was obtained using Equation 4.3.

$$Vs = \frac{V}{\Pi R^2} \tag{4.3}$$

where, V is the flow rate (L/min) and R is the surface area at the top of the funnel (m^2). Thus, the maximum particle size being transported by the solvent at a specific linear velocity can be calculated. In Table 4.2 these radii are presented as a function of the flow rate i.e. the linear velocity.

Table 4.2: Estimation of the maximum theoretical particle size removed during fractionation

Flow rate (ml/min)	**Linear velocity x 10^{-4}($L.m^{-2}.\ s^{-1}$)**	**Radius of particle (μm)**
5	6.88	0.11
7	9.61	0.13
10	13.80	0.16
15	20.70	0.19

It is clear from these calculations, that the increase in particle size with increasing flow rate is minimal. Particle size distribution (after fractionation) was determined using a Malvern Mastersizer. The effect of loading was investigated by determining the fractionation at 65g, 75g and 85g loading mass. According to the Malvern results, no separation between fine and heavy particles was attained for loading masses of 65g and 85g, irrespective of the flow rates used. (Figure 4.3). (The filtrate fraction using a 75g loading mass is depicted in Figure 4.4.)

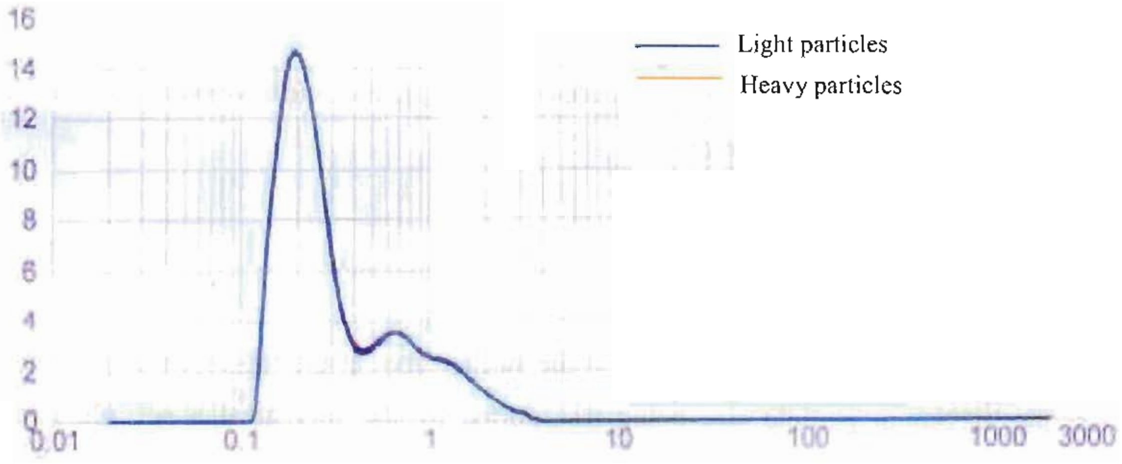


Figure 4.3: Particle size analysis after fractionation using a 65g loading mass

To obtain the percentage separation, the untreated Alcoa powder was taken as a control, of which the average particle size of the fine and heavy fractions was determined using the Malvern Mastersizer. The amounts of fine and heavy particles that are in the untreated powder were calculated by integration of the bimodal peaks that were obtained from each spectrum. This was done for each of the filtrate fractions that were produced from the various flow rates of the process. These heavy and light fractions were then expressed as the ratio of the untreated powder to determine the percentage separation as a function of the flow rate.

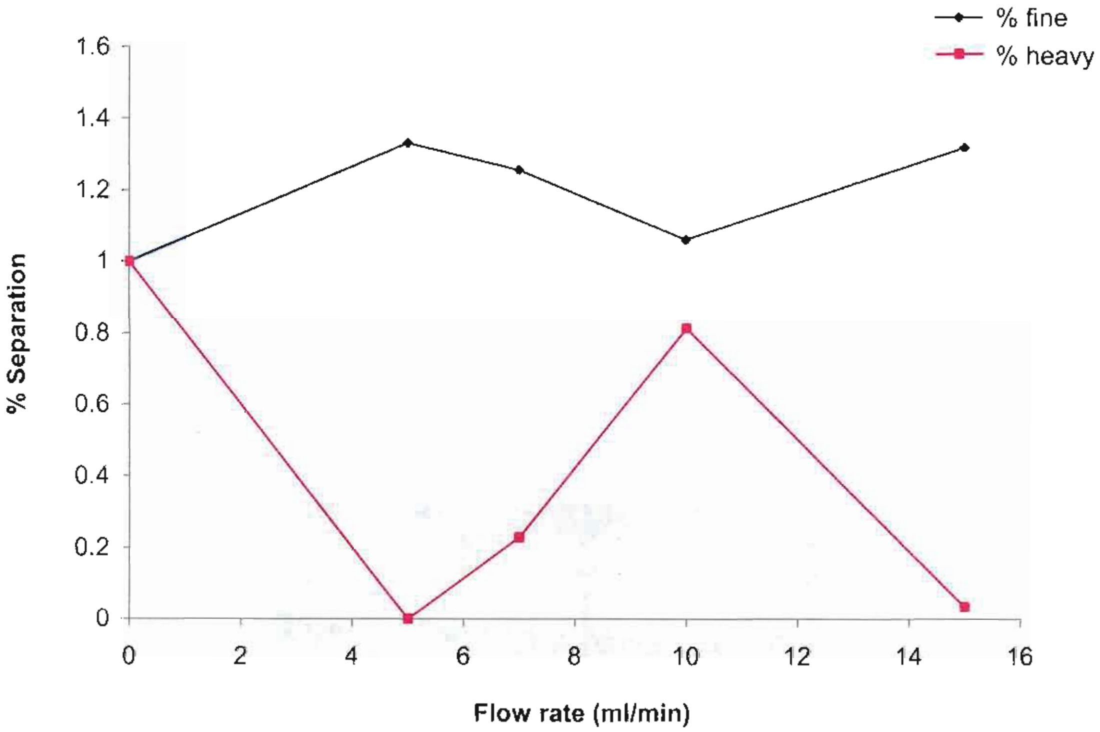


Figure 4.4: ***Fractionation as a function of flow rate with a 75g loading mass***

It is clear from Figure 4.4 that separation of the fine and heavy particles was achieved. In fact, at 5ml/min and at 15ml/min hardly any heavy particles were found in the filtrate. This means that at these flow rates there was maximum separation of particles. Subsequently, the powder fractions obtained at 5ml/min and 15ml/min were used for centrifugal casting.

4.1.3 Centrifugal casting

For centrifugal casting, the Alcoa particles in suspension were poured into a tubular mould and subjected to centrifugal forces to produce a green cast[6]. Centrifugal forces at (16000rpm) were applied to overcome the yield stress of the particles in suspension. Once the yield stress has been overcome, there is a structured flow within the suspension with irreversible deformation[7]. The green cast that is formed is the result of this deformation. It can therefore be said that the primary difference between the suspension and the green cast is the yield stress; i.e. the green cast by definition has the higher yield stress[8]. The green casts that were obtained from centrifugal casting had a 21mm outer diameter, 18mm inner diameter and a length of 60mm.

4.1.4 Sintering

After sintering the casts to a maximum temperature of 1150°C, the resulting supports of the 10ml/min filtrate and residue, and the 5ml/min residue showed similar warping and cracking as shown in Figure 4.5.

Figure 4.5: Warping and cracking of Alcoa casts after sintering

Warping of the cast may have resulted from a difference in the direction of shrinkage during the sintering process. Shui et al[9] describes this phenomenon as shrinkage anisotropy. It basically means that shrinkage begins in areas of the cast where the particles have less contact points accelerating the shrinkage in these areas. Bissett[1] suggested that the difference in the direction of shrinkage may be due to the differences in the density gradients of the cast due to centrifugal casting.

Cracking of the casts may have been due to the fact that the particle size distribution was too wide. This would cause a significant difference in sintering rates between the large particles on the outside areas of the cast and the smaller particles on the inner surface of the cast resulting in significant shrinkage anisotropy and hence cracking.

The only fraction that was intact after sintering was the Alcoa 5ml/min filtrate. It had an outer diameter (OD) of 20.33mm. The percentage shrinkage of the Alcoa 5ml/min support is compared to results in Table 4.3 attained from previous studies, using Alcoa[1], AKP 30 and AKP 15/30 mixtures[10], that had also been sintered at 1150°C.

Table 4.3: Comparison of the percentage shrinkage of centrifugally casted ceramic membranes

Support type	*OD after sintering (mm)*	*% Shrinkage*	*Reference*
Alcoa 5ml/min	20.33	3.19	-
Alcoa 4	20.58	3.02	1
Alcoa 5	20.70	2.99	1
Alcoa 6	20.74	2.78	1
AKP 30	20.45	3.00	10
AKP 15/30	20.70	2.00	10

According to Table 4.3, the percentage shrinkage of the Alcoa 5ml/min is similar to those obtained in previous studies. This would imply that the Alcoa 5ml/min consisted of a near monomodal distribution of fine particles that are packed equivalently. During sintering, the shrinkage of the smaller particles in this fraction is uniform and occurs in a short period as there are more contact points per volume and a larger driving force than for larger particles[10]. This confirms that the warping and cracking is due to uneven shrinkage of the heavy and fine particles, since the Alcoa 5ml/min filtrate fraction was the only sample where a membrane was obtained and it was also the only fraction that did not contain any heavy particles (Figure 4.4).

However, the repeatability of the Alcoa 5ml/min membrane manufacture was poor. In fact only one successful Alcoa membrane was manufactured without any defects. After numerous attempts to manufacture an Alcoa support under varying conditions it was decided to alternatively use the in-house produced ceramic supports made from AKP-15 powder (Sumitomo Chemical Co. Ltd., Japan). The AKP-15 supports that were produced had the following dimensions: 21mm outer diameter, 18mm inner diameter and had a thickness of 1.5mm. The successful repeatability of the AKP-15 ceramic support manufacture allowed for its use in the attempted synthesis of a DDR membrane.

4.2 DDR Crystal Synthesis

DDR crystal synthesis has so far only been described by one research group: den Exter et al[17] who investigated the 25 day hydrothermal synthesis of DDR-type crystals in studying the separation of small gaseous molecules. The synthesis of DDR crystals is described in Section 3.3, the recipe consisted of a molar ratio of 47 ADA: 100TMOS: 404EDA: 11240 H_2O. In order to optimize the synthesis, the influence of the water concentration was investigated since it is initially used to solubilize ADA and EDA. The next step in the experimental procedure involves ageing, where both the period and temperature was investigated. Finally the effect of the amount of TMOS (silica source) which is added after ageing was investigated.

4.2.1 Synthesis of ADA

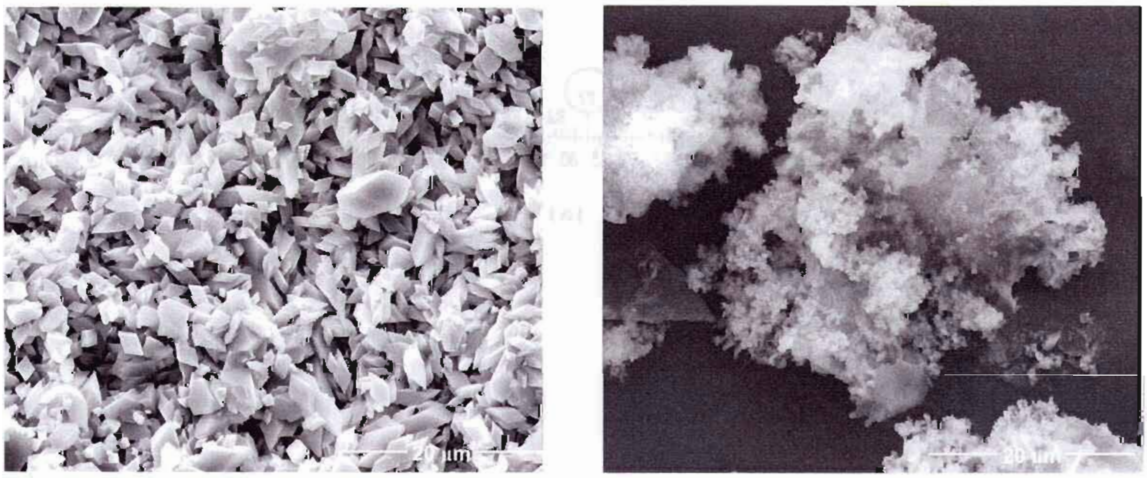
A pre-experimental step (Section 3.3.2.1) had to be included which entailed the synthesis of the guest molecule, 1-adamantanamine (ADA), from 1-adamantanamine chloride according to:

$$C_6H_5\,NH_3Cl + NaOH \longrightarrow C_6\,H_5\,NH_2 + NaCl + H_2O \qquad (4.1)$$

Preliminary investigations included the effect of in-house manufactured ADA and commercial reagent ADA on DDR crystal morphology after the 25 day hydrothermal synthesis.

The guest molecule (ADA) influences the structural direction of the zeolite during synthesis[11]. To synthesize ADA, an equimolar amount of 1-adamantanamine hydrochloride was reacted with a solution of NaOH (aq). The white product was extracted with diethylether. After shaking the diethyl ether and water during extraction, two colourless immiscible layers were observed. Since diethylether is less dense than water, the top layer contained the ADA. To ensure the maximum removal of the ADA, the extraction was performed four times, each time removing and combining the top layers. After extraction, the diethylether was evaporated and ADA was produced in the form of a white crystalline product. The ADA was dried in a desiccator (as it is hygroscopic) and the percentage yield of the ADA was calculated. The synthesis was done in triplicate and the average percentage yield was 50%.

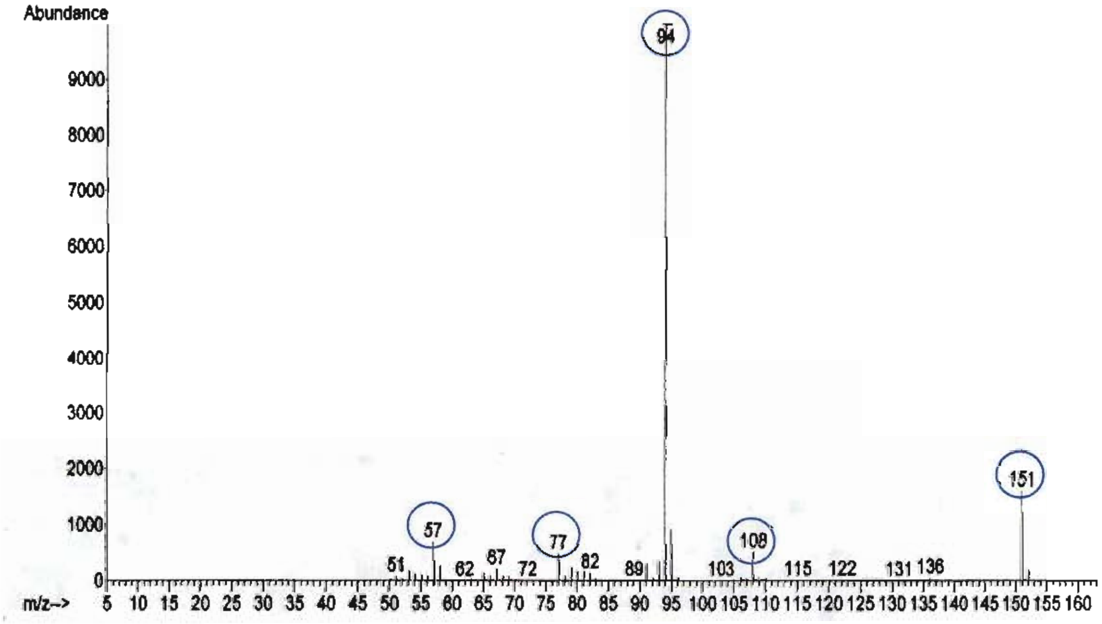
According to the SEM analysis of the DDR crystals produced after a 25 day hydrothermal synthesis poor growth and morphology was obtained when using the reagent, i.e. commercial ADA, compared to the morphology and growth obtained when using the in-house synthesized ADA (Figure 4.6).



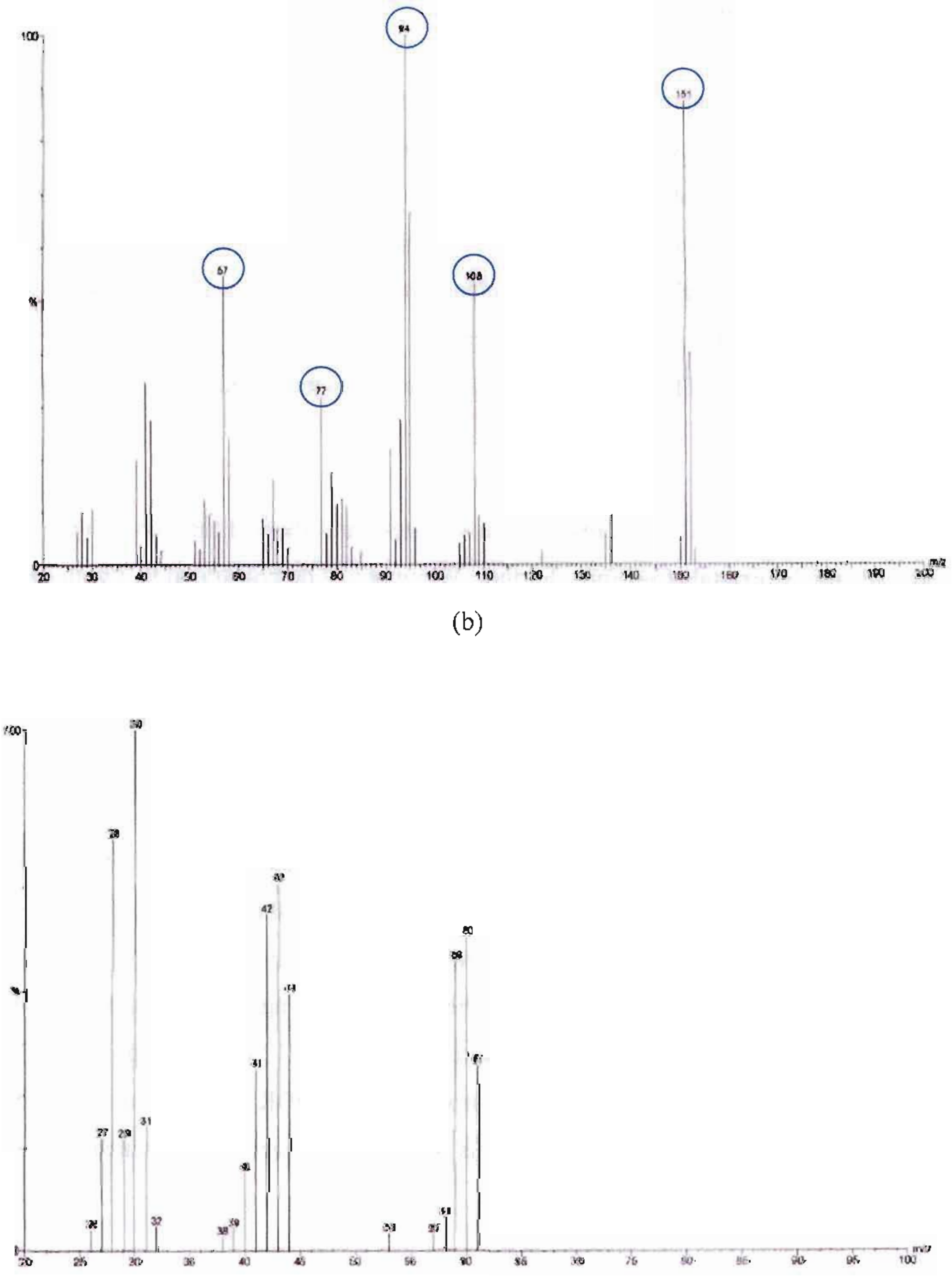
(a) (b)

Figure 4.6: ***DDR crystals produced using (a) in-house manufactured ADA and (b) commercially obtained ADA***

In an attempt to understand this difference in performance, mass spectra (Autospec ETOF) of each of the ADA sources (Figure 4.7b and c), were compared to standard spectra of ADA obtained from literature[12] (Figure 4.7a). It is clearly visible that the spectra of the in-house synthesized ADA exhibits the 5 main peaks as seen in the standard reference[12] (m/z 55, 77, 94, 108, 151). However, the spectra of the reagent ADA showed no fragmentation into these peaks. This means that it is likely that the commercial product did not contain ADA. To elucidate the molecular identity of this substance, however, was beyond the scope of this study.



(a)



(b)

(c)

Figure 4.7: Mass Spectra of ADA (a) standard reference (b) in-house synthesized and (c) commercially obtained ADA

4.2.2 Water concentration

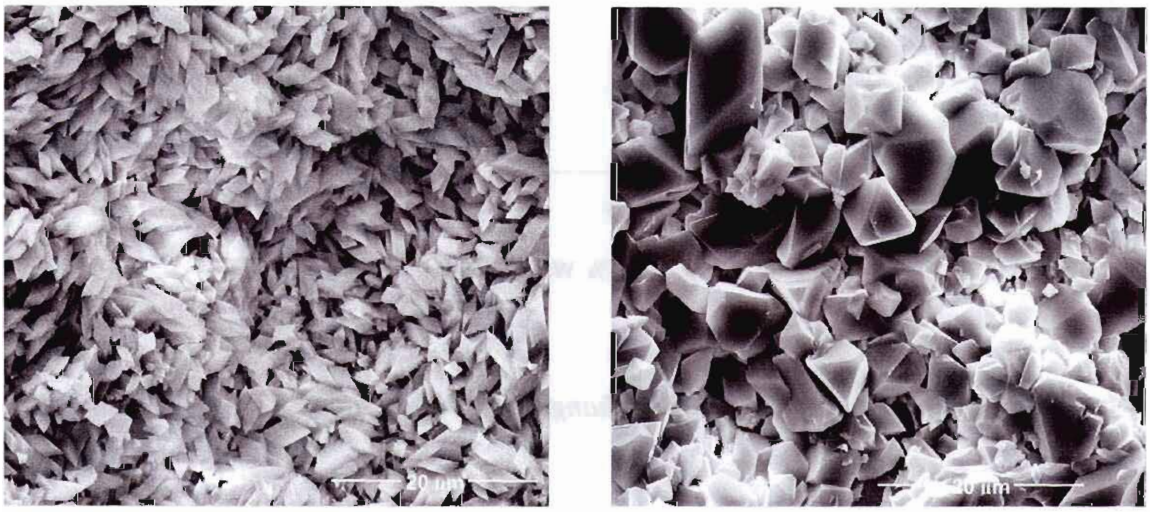
Having optimized the ageing process, the next step was to determine the influence of the water on DDR crystal synthesis. Water not only acts as a solvent during the 25 day hydrothermal synthesis of DDR crystals[13], but has a significant effect on the intergrowth between the crystals and on the crystal size[14]. Van Niekerk[15], in her research on the MFI-type zeolite, found that when the water content within the system was increased, the growth rate decreased and the crystal sizes increased. Similarly, when decreasing the water concentration in the MFI system, the growth rate was increased and crystal sizes were smaller.

However, Kalipcilar et al[16] did research on silicate-1 and showed that more dilute systems produced smaller crystals (6-9μm). Further, Wong et al[14] demonstrated that with increased water concentrations, sil-1 zeolite growth was negligible and etching of the seed layer occurred. Thus, no unanimity is seen in the effect of water concentration on crystal size and morphology. Hence, the importance of studying the effect of water for each novel zeolite synthesis.

Den Exter et al[17] are the only researchers that provide information on the influence of water on DDR. In their research 11240 moles of H_20 were used in the synthesis of DDR crystals. They varied the water concentration to optimize DDR production. Initially, 5600 moles of H_20 were employed without rotation of the mixture during hydrothermal synthesis at 160°C. Polymorphs of DDR and DOH with crystal sizes of 125μm were produced. When increasing the water concentration, a shift from DOH to DDR is observed. Den Exter et al[17] were able to produce pure DDR crystals of 5-10μm in size. They stated further, that the nucleation rate is faster with rotation.

To investigate the effect of water concentration on the size and morphology of DDR crystals, a 25 day hydrothermal synthesis with rotation was carried out according to literature[17]. Synthesis conditions were kept the same except for the water concentration in the molar ratio, which was deviated by percentages more or less than those from den Exter et al[17] (see Section 3.3.2.2.1). Crystal sizes were deduced by SEM analysis which yielded an average experimental error of 12%.

Smaller and sharply defined crystals of DDR were produced with decreased moles of water. In Figure 4.8, the influence of the change in crystal size as a function of the change in percentage of water content is presented. Since the initial water concentration was 11240 moles, +30% means 14612 moles and -30% means 7868 moles. For seeding it is generally better to have the smallest seed crystals possible as this will ultimately affect the crystal sizes and the membrane thickness of the membrane. Hence according to Figure 4.8(b) 30% less water produced the most suitable DDR crystals for membrane synthesis with an average crystal size of 1.4μm.



(a) (b)

Figure 4.8: ***DDR crystals produced with varying water concentrations deviating (a) -30%, (b) +30 from literature***[17]

From Figure 4.9 it can be seen that there is a linear increase in particle size with increasing water content. These results are in agreement with Basaldella et al[18] who found that in systems with decreased water, there is an increase in heterogeneous nucleation thus resulting in smaller crystals. This observation is due to the high solute concentrations which result in lower inter-nuclei spacing and faster nucleation[15]. Thus, at lower water content, more and smaller crystals are formed while with increasing water content, less and larger crystals are formed.

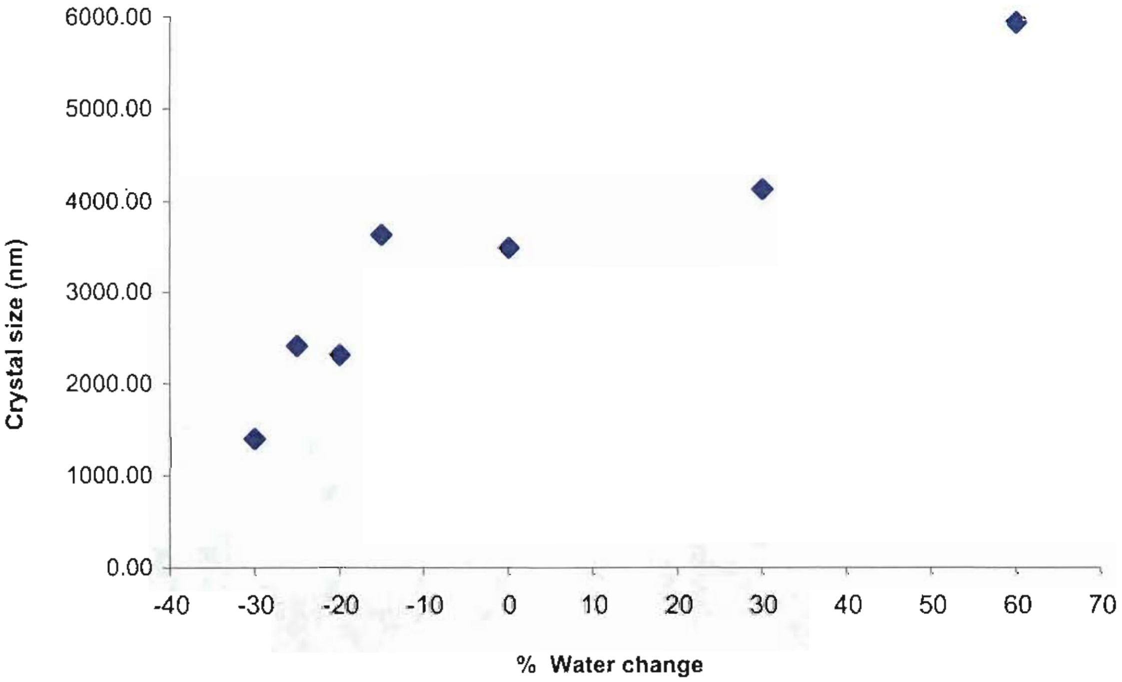


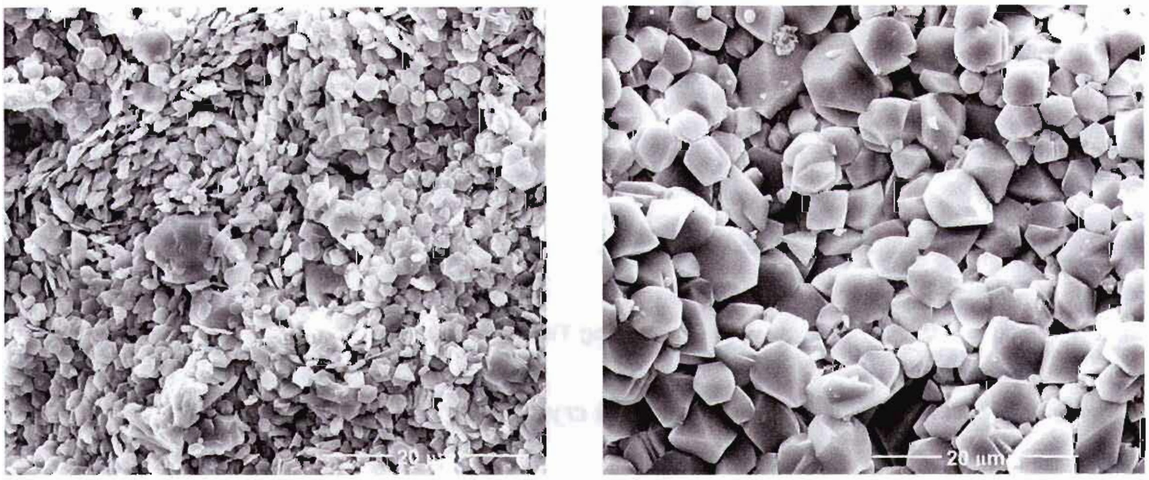
Figure 4.9: Influence of the % water change on DDR crystal size

4.2.3 Ageing time and temperature

Ageing was done (see Section 3.3.2.2.2) in a water bath or oil bath (depending on the temperature required) with stirring of the solution. Szostak[19] refers to the ageing process as a generation of ***in situ*** seeds. She elaborates further by stating that ageing occurs when a zeolite precursor gel is allowed to stand at room temperature or elevated temperatures below the normal crystallization temperature for the zeolite phase of interest. The system is allowed to equilibrate while generating seed nuclei.

Lin et al[20] demonstrated, whilst synthesising silicate 1 – type zeolite, that the induction period during the crystallization process is gradually reduced as the ageing time is increased. Thus, an increase in the ageing time will result in an increase in nucleation and depression of crystal growth.

After the 25 day hydrothermal synthesis, SEM analysis confirmed that variations in ageing time agreed with literature[20] :- Figure 4.10(a) indicates that with larger synthesis ageing times, more favourable, smaller crystals were obtained.



(a) (b)

Figure 4.10: Influence on ageing time of (a) 2.5 hours and (b) 30 minutes on crystal size and morphology

In Figure 4.11 a graph is presented of crystal size plotted as a function of ageing time. SEM analysis was again used to deduce the crystal sizes and for this section the error was 25%. It can be clearly seen, that long ageing periods resulted in smaller crystal sizes. The largest crystals (+/-5µm) were produced at an ageing period of 30 minutes. After having optimized the ageing time, the effect of ageing temperature was investigated.

It has previously been stated that when the temperature is increased during the ageing process, the rate of crystallization will increase[19]. However, studies provided on the crystal growth rates of zeolites A and X have shown that kinetic and chemical factors regarding the growth of zeolite crystals from their precursor solutions do not depend on the ageing time nor on the temperature of aging and that the effects observed in the crystal growth are caused by the development of nucleation during ageing[21].

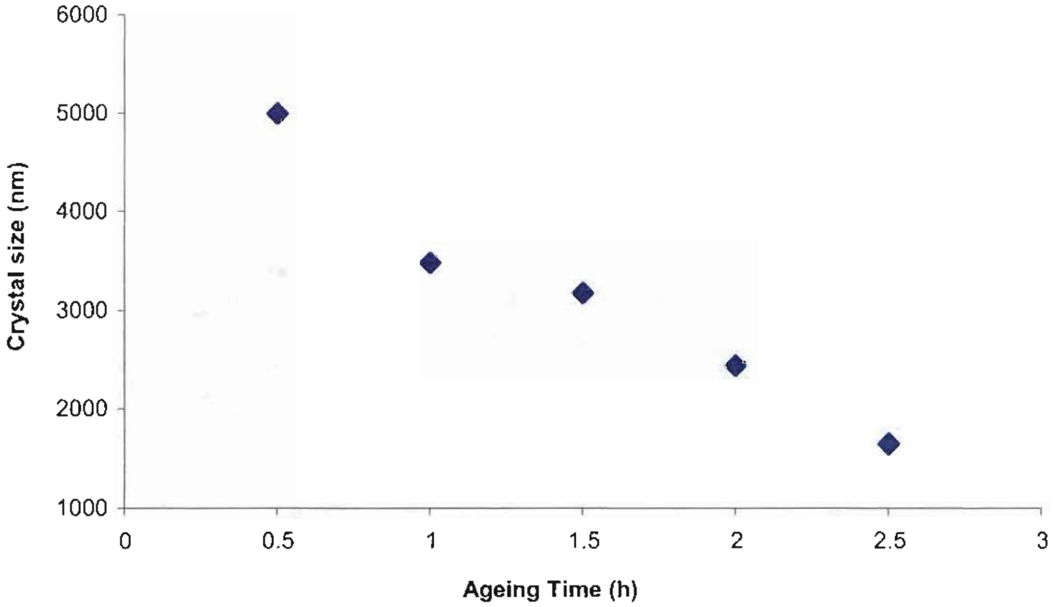
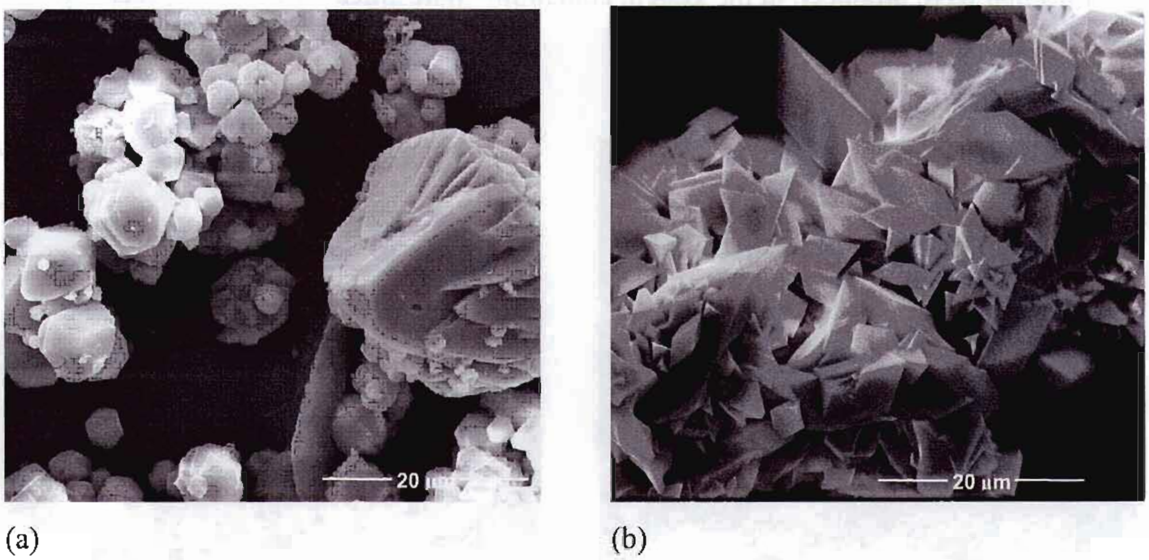


Figure 4.11: The effect of ageing time on crystal size

In Figure 4.12 SEM images of DDR crystals aged at temperatures of (a) 388K and (b) 363K (standard ageing temperature) are presented. The micrograph in Figure 4.12(a) shows that larger crystals are produced at increased ageing temperatures. The results agree with the statement made by Stozak[19], (that the rate of crystallization will increase with ageing temperature) assuming that crystal sizes increase with the rate of crystallization.

The micrograph in Figure 4.12(a) also shows that the crystal morphology is altered at higher ageing temperatures and that the morphology has changed from the typical rhombohedral shape of DDR crystals (Figure 4.12b). This observation of increased crystal growth is sustained by the statement made by Subotić and Bronić[21], i.e. that there is increased nucleation during ageing at elevated temperature.



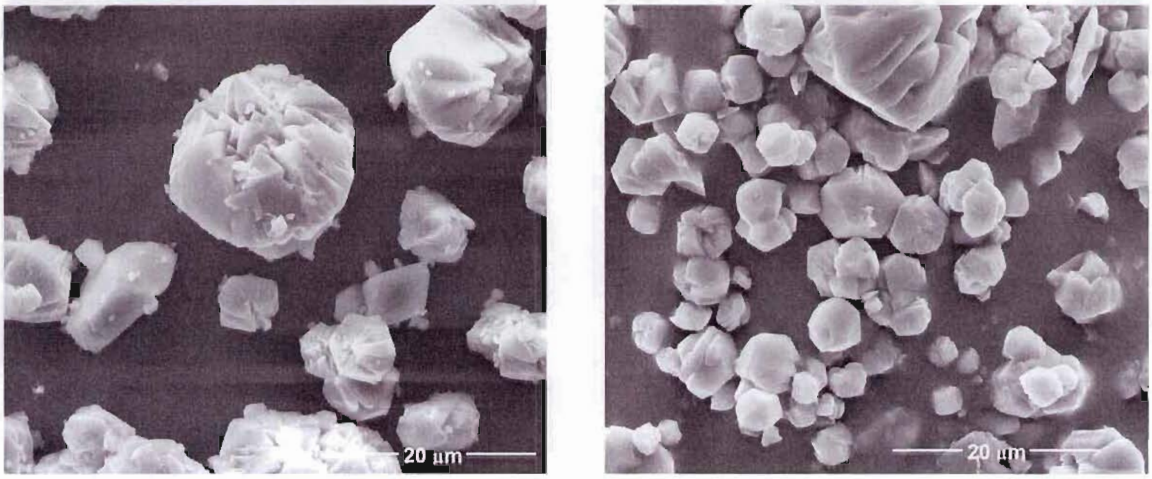
(a) (b)

Figure 4.12:* *Influence of aging temperature at (a) 388K, and (b) 368K on crystal size and morphology

4.2.4 Silica source

Wong et al[14] investigated the effect of increasing the silica source (TEOS) in the synthesis of sil-1. They concluded that increasing the concentration of the silica source results in an enhancement of crystallization. Further, Subotić and Bronić[21] found during investigations on the silicate-1 zeolite, that in systems where there is increased content of the silica source, crystal morphology was altered and elongated crystals with high length to width ratios had been formed.

According to the standard DDR synthetic ratio Den Exter et al[17] use 100 moles of TMOS are used[17]. In this research the silica was varied by e.g. -10% (90 moles) and by +10% (110 moles). The results shown in Figure 4.13(a) differ to what was observed by Subotić and Bronić[21] since both higher and lower TMOS concentrations have led to altered DDR morphologies. DDR crystals are 5.2μm in size at +10% TMOS. Figure 4.13(b) shows that there is an enhancement of crystallization as there are a larger amount of small crystals (4.1μm) that were produced in the system containing more silica. This is in agreement with Wong et al[14].



(a) (b)

Figure 4.13: Influence of (a) -10% and (b) +10% TMOS on crystal growth and morphology

4.2.5 Conclusion

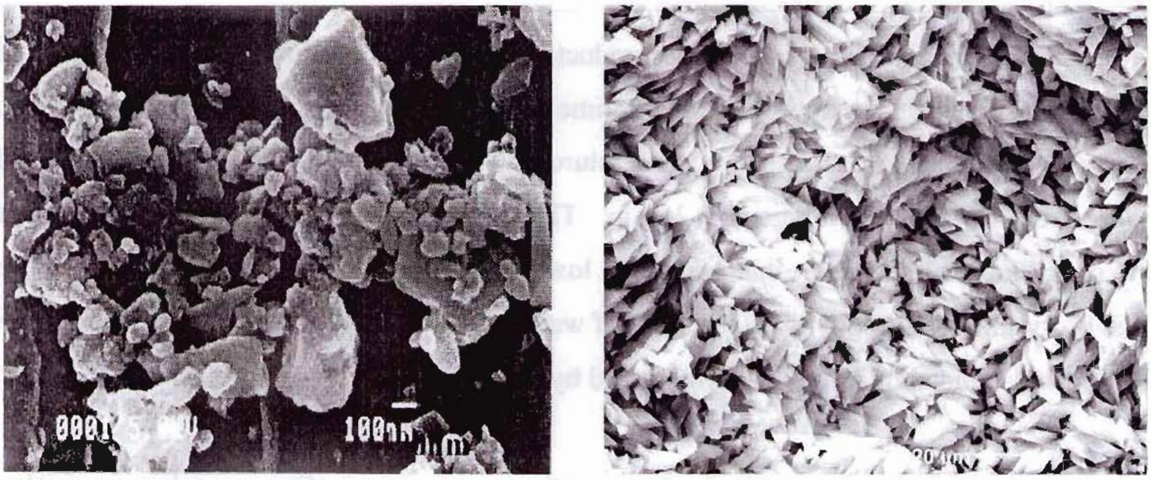
To optimize the experimental procedure obtained from literature [17], the source of the guest molecule- ADA was initially investigated. Next, the crystal size and morphology was optimised by varying the TMOS concentration, water concentration and ageing time and temperature.

It can be concluded that the in-house production of ADA is required for the synthesis of pure DDR crystals. An optimized ageing time of 2.5 hours produced DDR crystals with an average size of 1.7μm. An ageing temperature of 368K (as from den Exter et al) produced pure DDR crystals of average size 3.1μm. The smaller and pure DDR crystals of 1.4μm were produced in a system that contained low water concentrations of 7868 moles. The DDR crystals produced with 7838 moles of water, are smaller than the crystal sizes of den Exter et al[17] and similar to those synthesised by Tomita et al[22] (Table 4.4).

Table 4.4: Comparison of molar oxide ratios and corresponding crystal sizes of DDR crystals

Manufacturer	**Molar oxide ratio** **(ADA: TMOS: EDA: H_2O)**	**Crystal size**
Den Exter et al[17]	47 : 100 : 404 : ***11240***	5-10μm
Tomita et al[22]	47 : 100 : 404 : ***11240***	Larger than 1μm
Alves	47 : 100 : 404 : ***7868***	1.4μm

In terms of the purity of these DDR crystals, it seems that our results were as good as those obtained by Tomita et al. In Figure 4.14 a comparison of the SEM photos is presented. It seems that our synthesis (Figure 4.14b) had yielded crystals that are more regular in shape.

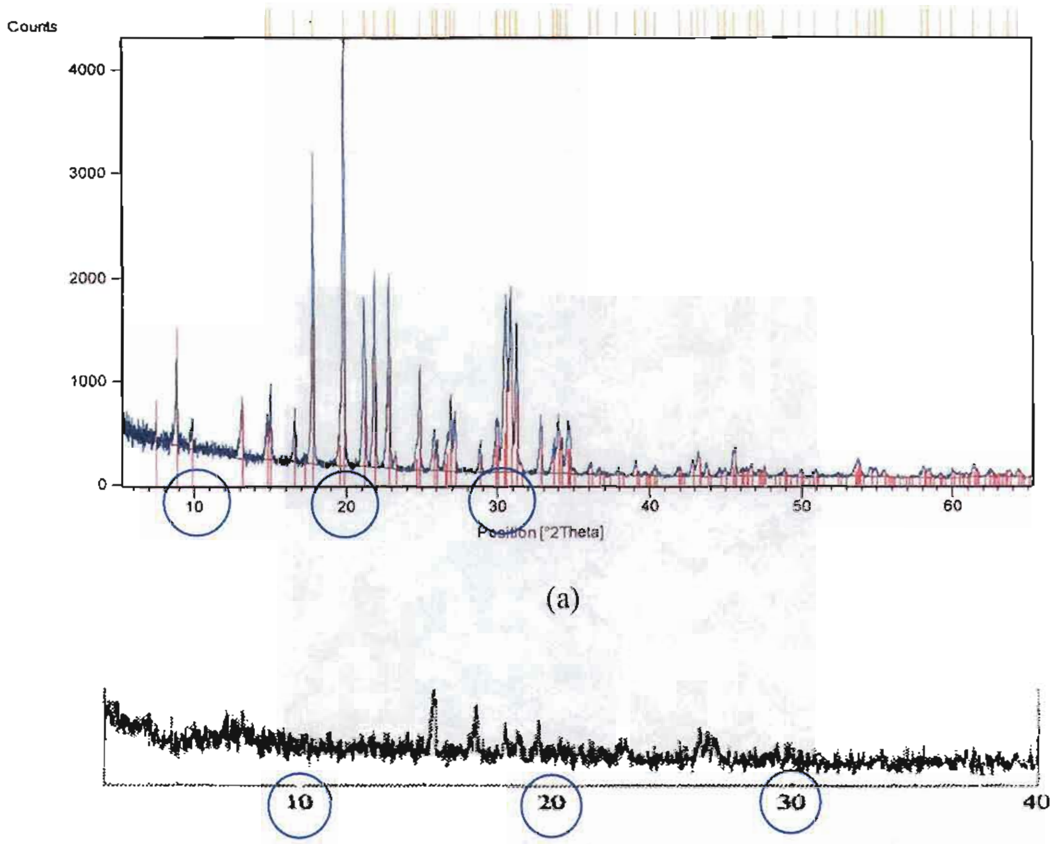


(a) (b)

Figure 4.14:* *Comparison of SEM images from (a) literature[22] and (b) this research

This is further confirmed when the XRD spectra (Figure 4.15) of the DDR crystals produced in this research are compared to those in literature[22]. XRD Spectra of DDR crystals produced from this research (Figure 4.15a) correlate with standard spectra[23]. Figure 4.15a shows 3 clear peaks at approximately 10°, 20° and 30°, indicating that the crystals are of decent morphology. XRD spectra given by Tomita et al[22] however show diffuse scattering (Figure 4.15b) giving the idea that there are defects and disorders in crystal morphology.

It is clear that by optimising the operating conditions of the 25 day hydrothermal synthesis, a pure and well defined DDR crystal was obtained with an average size ideally suited for DDR membrane synthesis.



(a)

(b)

Figure 4.15: Comparisons of XRD from (a) this research and (b) literature[22]

4.3 DDR Membranes

Tomita et al[22] are the only research group that have published the synthesis of a DDR membrane. In their experimental technique, they use a seeding technique of immersion before hydrothermal synthesis. DDR crystals are seeded to the ceramic support and immersed in a precursor solution of 9ADA: 100$Si0_2$: 150EDA: 4000H_2O. Hydrothermal synthesis is at 423K for 48hours. To optimize this experimental procedure (see Section 3.4.2) the parameters of gel ageing, water concentration and hydrothermal time were varied. Preliminary studies included investigations on seeding and pre-support treatments.

4.3.1 Support pre-treatment

Initially the effect of zeolite adhesion on an untreated AKP-15 support, with no seeding, was investigated. A bulky gel and little zeolite attachment were obtained after hydrothermal treatment (Figure 4.16).

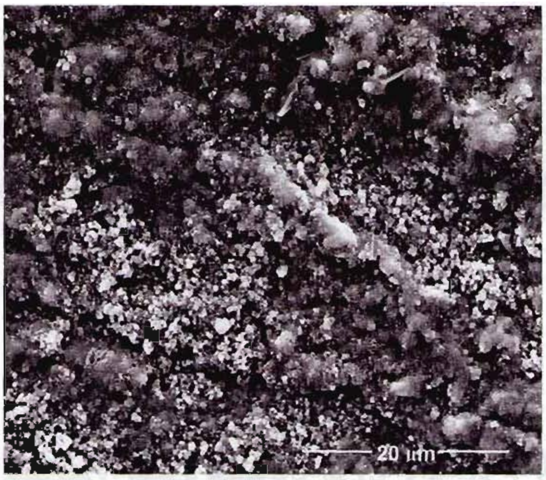
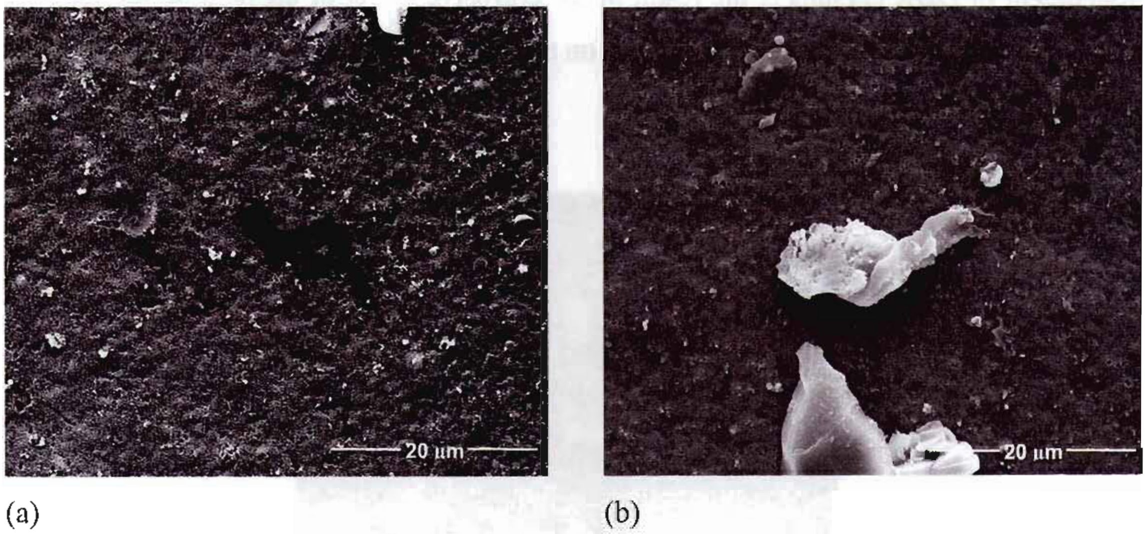


Figure 4.16: SEM showing the effect of zeolite adhesion after hydrothermal synthesis on an untreated ceramic support

In order to improve zeolite attachment and in turn zeolite growth, the support was pre-treated with sonification (a) in an amorphous mixture of $C_4H_{10}O$/ ADA and (b) sonification in $C_4H_{10}O$ (Section 3.3.2.1). According to literature, this pre-treatment allows for a coating on the support, which provides a low catalytic effect in the growth of zeolite crystals[24].

After the individual pre-treatments, a hydrothermal synthesis in a precursor solution of 9ADA: $100SiO_2$: 150EDA: $4000H_2O$ was carried out for 48 hours. SEM analysis showed in both cases the presence of a gel layer with little growth of pure DDR zeolites (Figure 4.17).



(a) (b)

Figure 4.17: ***SEMs showing the results after hydrothermal synthesis, support pre-treatments of (a) sonification in a mixture solution of $C_4H_{10}O$/ ADA (b) sonification in $C_4H_{10}O$***

The gel-like formation is attributed to the zeolite coating that is formed from the sonification pre-treatment. Van der Puil et al[24] found, while optimizing the synthesis of ZSM-5, that in some instances the zeolite coating remained amorphous after hydrothermal synthesis. Thus, in Figure 4.17a and Figure 4.17b it is assumed that the gel-like layer is amorphous material from the zeolite coating, i.e. precursor solution.

Further, Van der Puil et al[24] showed that sonification of the support in a template or a solvent/template mixture, (as was done in this investigation) resulted in poor zeolite attachment. This is seen in both SEMs of Figure 4.17. However, in this research, when the support had been pre-treated with sonification in $C_4H_{10}O$ (after hydrothermal synthesis), there was some additional crystallization (Figure 4.17b).

In a third attempt to improve the attachment, the supports were refluxed in HNO_3 (aq). After hydrothermal synthesis, using the support that had been refluxed in HNO_3 (aq), SEM analysis showed gel formation and some attachment of pure DDR crystals. The improved attachment of DDR crystals is the result of the corrosive effect of the acid on the top layer of the ceramic support, etching the support on a molecular level[25]. However, there was still a gel layer coating the support.

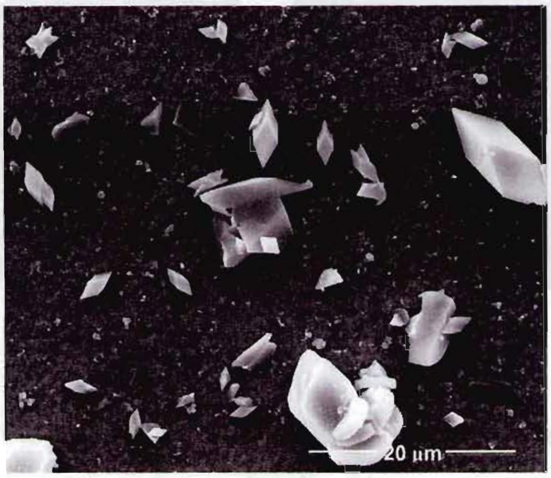


Figure 4.18: SEM after hydrothermal synthesis with support pre-treated by refluxing in HNO_3 (aq)

The production of the gel layer that is seen after each hydrothermal synthesis, irrespective of the pre-treatment, is possibly due to the reaction of the silica source (TMOS) with the nitric acid refluxed support. TMOS undergoes a sol-gel process whereby it is hydrolyzed and condenses, where nitric acid acts as a catalyst for these reactions. Murata and Schaech[26] summarized the action on various sources of silica by stating that silicates of continuous oxygen frameworks, incorporating a sufficient number of iron or alumina atoms (which are removed by acids), yield gelatinous silica.

Thus, to eliminate the production of the gel during the hydrothermal synthesis and produce growth of a DDR membrane, the support was dried at elevated temperatures for different periods of time (See Table 3.4) to ensure that there was no presence of nitric acid. However, the result that was produced after hydrothermal synthesis was similar to that of Figure 4.18.

In summary, the pre-treatment of refluxing of the support in HNO_3 (aq) showed better zeolite adhesion when compared to the zeolite adhesion obtained after the sonification pre-treatments (Figure 4.17). It is clear that other parameters have to be investigated to resolve the gel formation.

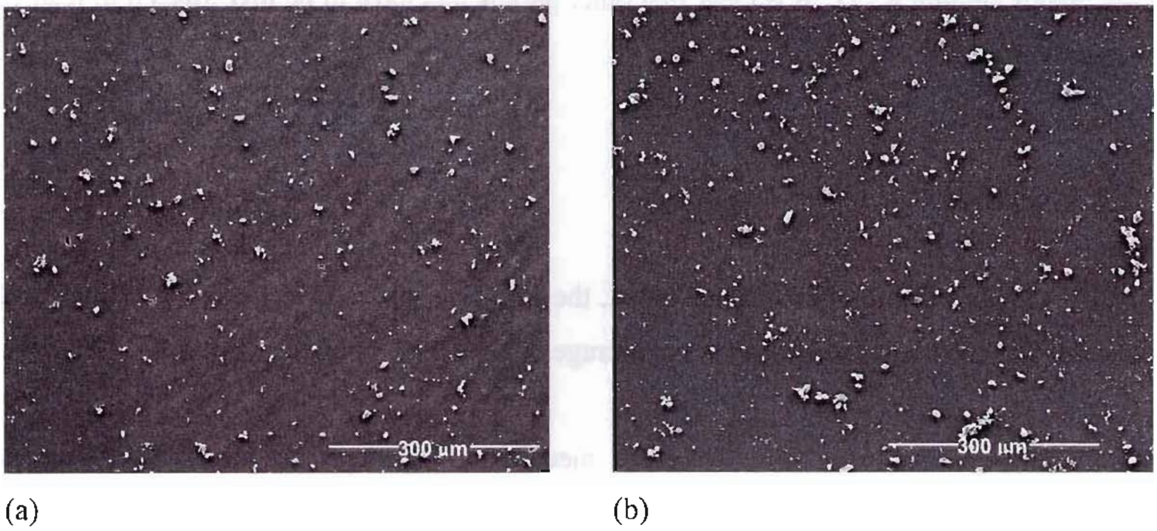
4.3.2 Seeding

After the optimization of the pre-treatment, the next step was to investigate the effect of the amount and method of seeding on the coverage of DDR on a ceramic support.

In the hydrothermal synthesis of a DDR membrane, Tomita et al[22] described a seeding technique whereby the ceramic support is immersed in a solution of crystals that are dispersed in deionised water. While they did not disclose the seeding mass that they used, the seeding mass is important as it could affect the ultimate membrane thickness[27].

To investigate the mass of crystals that should be used for seeding, the theoretical mass required for total theoretical support cover was calculated. Firstly the density of a DDR crystal, (produced from the standard synthetic procedure) was calculated using mercury intrusion (Micromeretics Auto pore III). Using the density of a DDR particle (0.414g/ml), the surface area of a single crystal of average length of 6.84μm could be calculated ($(6.84 \times 10^{-6})^2$ m^2). Since the surface area of the inner surface of the support is known ($3.11 \times 10^{-3} m^2$); the mass of the seeds that should cover the entire inner surface of the support was calculated to be 0.0088g.

When the immersion technique was evaluated using two different seeding masses (0.08g and 0.0088g), the same homogenous coverage however, was obtained (Figure 4.19a and b). While, a theoretical mass of seeds (0.0088g) was calculated to cover the whole inner surface of the support, it is seen that even when this mass is increased (0,08g), the inner surface of the support remains not completely covered. Therefore, since the seed mass had little affect on surface coverage, the theoretical amount of 0.0088g of seed was used for DDR membrane synthesis by immersion.



(a) (b)

Figure 4.19: Seeding techniques using (a) 0.0088g and (b) 0,08g seeds

Another technique of interest was seeding by centrifugal depositioning. Tiscareño-Lechuga et al[28] describe a system for the synthesis of NaA membranes on the inner surface of tubular ceramic supports. The support is placed inside a device that rotates around its longitudinal axis during the synthesis. Centrifugal forces that are produced by high rotational speeds drive the crystals and crystal nuclei formed in the homogeneous phase towards the support surface, facilitating the formation of a more continuous and dense layer. Further, Pera-Titus et al[29] applied a centrifugal field (100rpm) for the hydrothermal syntheses of NaA. The formation of the membrane was accelerated when the synthesis was carried out under a centrifugal field, because of a faster supply of nutrients to the growing crystal layer.

It is therefore possible that a centrifugal field could provide a possible centrifugal seeding technique which should yield instant homogenous coverage of the inner surface of the tubular support with DDR crystals. While, SEM analysis after centrifugal seeding with a mass of 0.0088g, using a centrifugal force of 16000rpm showed that homogenous coverage of the support was achieved, the surface coverage was quantitatively poor. In an attempt to improve the quantitative surface coverage, the seeding mass was increased to 0.08g. This however, again resulted in homogenous surface coverage that was quantitatively poor. In fact, the results were very similar to those obtained by the immersion technique.

To further elucidate the coverage during centrifugation, the crystals in dispersion were weighed before and after centrifugation. The difference in mass correlated with the mass used for seeding i.e. the difference in mass resulted in a mass close to 0.0088g.

Although it cannot explain the poor coverage, an additional factor for the poor coverage could be the result of crystals joining together or fusing during centrifugation as has been reported by Tiscareño-Lechuga et al[28] and Xu et al[30] . Tiscareño-Lechuga et al[28] used centrifugal forces to facilitate fusing of crystals during synthesis of a NaA membrane. Some crystal fusing was observed during SEM analysis (Figure 4.20).

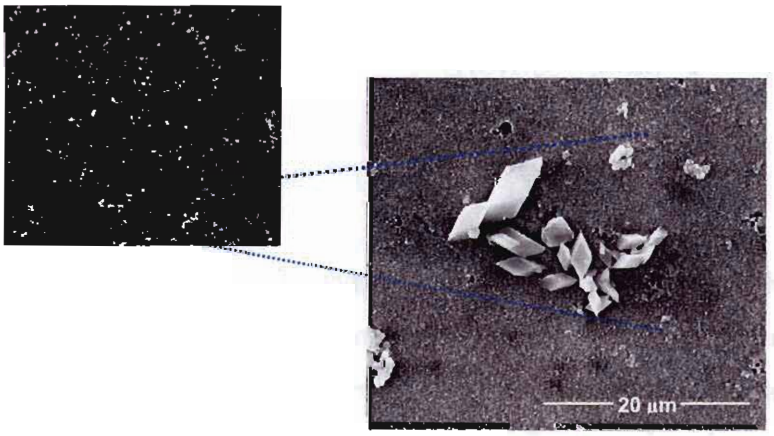


Figure 4.20: Crystal fusing during centrifugal seeding of DDR crystals

4.3.3 Water concentration

In the production of a zeolitic membrane, water can act as a guest molecule or as a solvent or as both as has been stated previously[31]. During the formation of the gel, this is the result of a sol-gel process that occurs in the presence of silica (TMOS), the water acts as a solvent for complex condensation and hydrolysis reactions. This has already been discussed in a general manner in Chapter 2 (2.5.1), but will be discussed here specifically analysing the sol-gel reactions that occur due to TMOS.

Lee et al[32] describes the hydrolysis reaction, which starts immediately after the TMOS sol is prepared by the reaction between TMOS and water:

$$Si\,(OCH_3)_4 + n\,H_2O \longrightarrow Si\,(OCH_3)_{4-n}(OH)_n + n\,CH_3OH_2 \qquad (4.4)$$

Additional linkage of the hydrated silica tetrahedra occurs by the condensation reactions as shown in reactions (4.5) and (4.6), which eventually results in a solid network after condensed silica species link together,

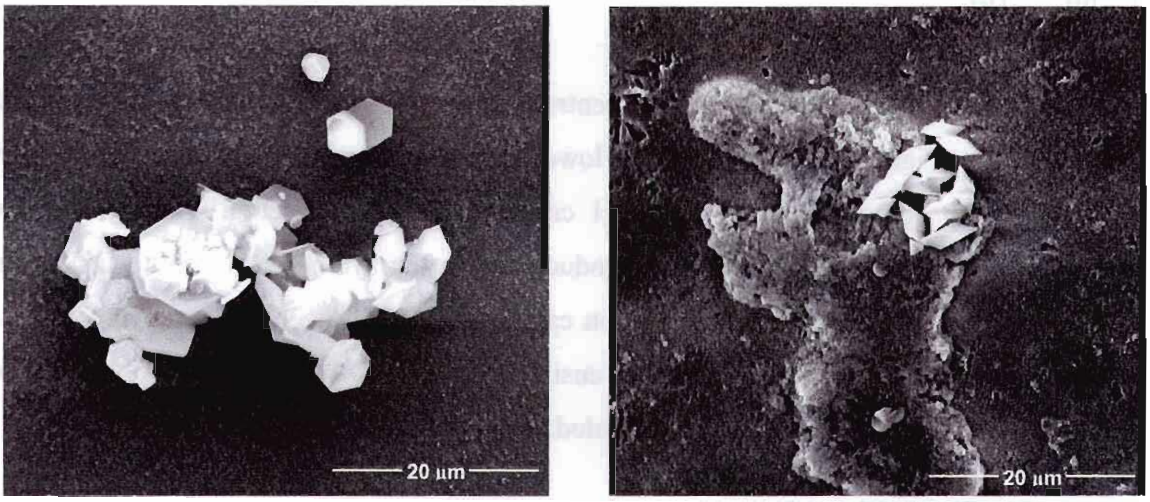
$$SiOH + CH_3OSi \longrightarrow SiOSi + CH_3OH_2 \qquad (4.5)$$

or

$$SiOH + HOSi \longrightarrow SiOSi + H_2O \qquad (4.6)$$

Thus, the sol-gel process that occurs in the presence of TMOS results in a gel that consists of silica oxygen linkages (*SiOSi*). The formation of the gel through the sol-gel process of TMOS is a possible explanation as to why a gel has been formed after the hydrothermal synthesis in our previous investigations.

Matsuyama et al[33], who undertook Raman and GC-MS study of the initial stage of the hydrolysis of tetramethoxysilane (TMOS) in acid and base catalyzed sol-gel processes, suggested that the rate of hydrolysis depends on the amount of water. Thus increasing and decreasing the water within the zeolite recipe (see Section 3.4.2.3.1) could show an increase or decrease on gel production. To investigate the effect of the water concentration on gel growth, the concentration was decreased by 30% and increased by 100% with respect to the synthesis suggested by literature[22].



(a) (b)

Figure 4.21: Variation in water content of gel at (a) -30% and (b) + 100% deviations from literature [22]

After hydrothermal synthesis, SEM analysis was used to investigate the effect that the water content in the system had on gel growth. It is seen in Figure 4.21(a) that at low water concentrations, there is some crystal formation (large white cluster) on a flecked-white gel (on black background). At high water contents (Figure 4.21b), there is some formation of crystals (white cluster on SEM) growing on continuous layers of gel (bulky mass next to crystals). The gel is formed by the complete hydrolysis of TMOS; as a result, dense silicate clusters (bulky gel in Figure 4.21b) are formed.

These results are in agreement with literature Wonorahardjo et al[34] confirmed that the gel structure is strongly influenced by the water content of the reaction mixture. At low water concentration, predominantly linear silicate chains with only weak cross-linking occurs.

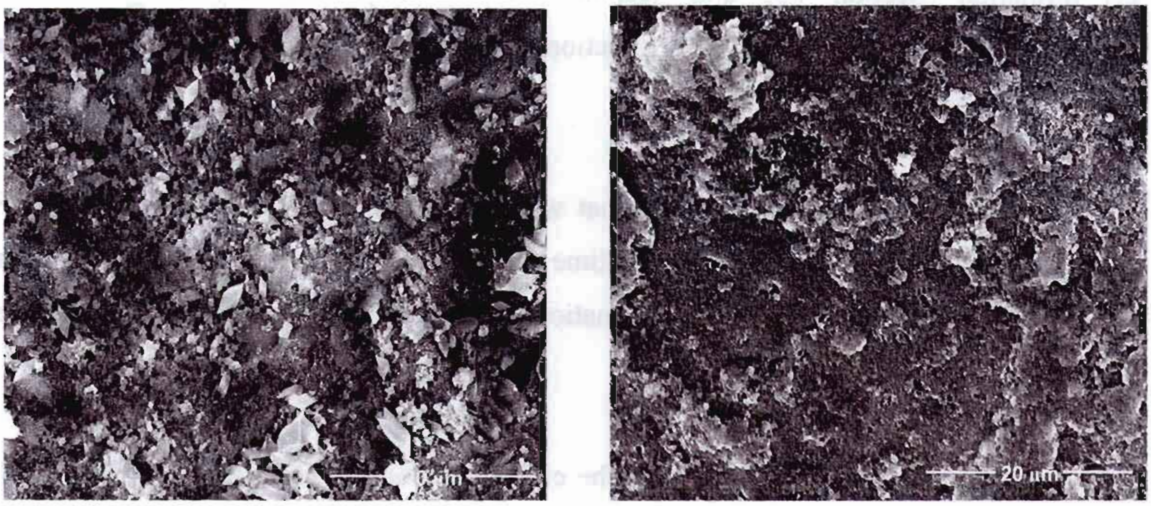
(This can be seen in form of the fletched gel in the background of Figure 4.21a). Further, they found that during gelation, aggregation of initially formed sol particles or clusters occurs. The clusters diffuse together and eventually aggregate to form a network, which spans the system. (This is clearly seen by the continuous gel layers that have formed in Figure 4.21b).

Moreover, it is seen that with higher concentrations of water there is some growth of pure DDR crystals (Figure 4.21b). Whilst at lower concentrations of water, there is less gel formation with some formation of DOH crystals. Den Exter et al[17] stated that the polymorph DOH forms easily as a co-product during the synthesis of zeolite DDR. In addition, they found that this co-production can be avoided if the ADA is prevented from separating from the synthesis. Thus to ensure that the ADA remains dissolved in the synthesis solution, gel ageing was investigated.

4.3.4 Gel ageing

Khoabane et al[35] investigated the effect of synthesis conditions involved in the sol-gel process of silica in an alkaline system. They used TEOS as the silica source and researched the variations of a number of parameters during the sol-gel process of TEOS. For their ageing studies, they varied the period from 1min to 24hrs. Analysis of the gels that were produced revealed that when ageing was carried out for longer than 3 h (even at 25 °C) fragmented silica structures (tubes and hollow spheres) were produced. After 24hrs ageing, the structures were still present with the amount of amorphous material increasing substantially, while prolonged ageing periods showed that the silica structures dissolved in the alkaline system.

The ageing period of the DDR synthesis mixture in this study was varied from 15 minutes to 72hrs. SEM analysis of the gels that were produced after hydrothermal synthesis showed that, in agreement with literature[35], at shorter ageing periods amorphous silica structures are obtained in which the DDR crystals are embedded (Figure 4.22a). When ageing of the DDR synthesis mixture is lengthened, no signs of crystallization were visible (Figure 4.22b). It can be assumed that the crystals dissolve on prolonged contact with the basic medium[35]. This implies however, that irrespective of the ageing time, it was not possible to obtain an inter-grown DDR zeolite membrane.



(a) (b)

Figure 4.22: Variations in gel ageing times of (a) 30 minutes and (b) 73 hours

4.3.5 Hydrothermal synthesis

Since we obtained a continuous gel layer irrespective of the water concentration (Section 4.3.3) and ageing (Section 4.3.4), it can be assumed that irrespective of the conditions, there is hydrolysis and condensation of the silica that leads to the formation of the gel.

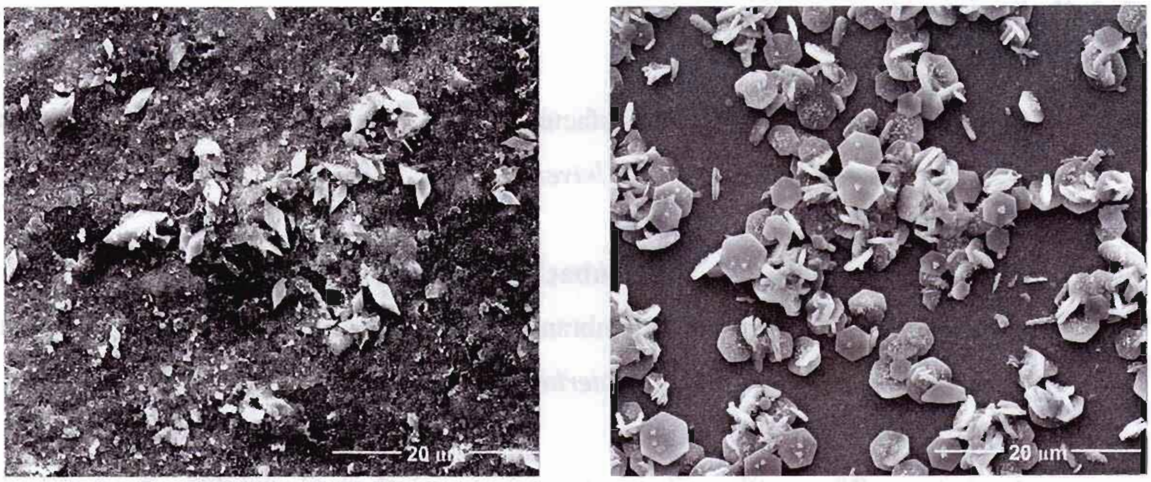
An explanation of gel formation can be presented by reiterating Section 2.4.3.3 (Chapter 2) where crystallization during hydrothermal synthesis is discussed. Once the precursor solution has reached a meta-stable phase, ion transport takes place to form a stable-phase

(Scheme 2.2). During ion transport, gel formation (formation of small and large clusters of silicate material) through hydrolysis and condensation reactions takes. Ion transport is complete when the gel precipitates, causing nucleation and ultimately the formation of crystals.

Thus, hydrothermal synthesis has not reached a complete process of ion transport, if there is gel formation (Section 4.33 and Section 4.3.4). To promote crystal growth, the hydrothermal period was increased (Section 3.4.2.3.3) so that ion transport can be completed and crystallization achieved.

SEMs were taken of DDR membranes that were synthesized for the literary time of 48 hours (Figure 4.23a) and an investigation time of 96 hours (Figure 4.23 b). It can be seen from Figure 4.23(a) that there is gel formation after 48hrs, which completely disappears after 96hrs (Figure 4.23 b).

However, it is seen in Figure 4.23b that the crystal structure is typical for the polymorph DOH crystals[17]. Den Exter et al[17] had previously stated that the co-synthesis of DOH can be avoided when the poorly soluble guest molecule ADA is prevented from separation from the aqueous synthesis mixture. This can be achieved by assuring that ADA has properly dissolved in EDA by increasing the time of the shaking process in the experimental procedure (Section 3.4.2.3.1).



(a) (b)

Figure 4.23: Crystal growth after (a) 48hr and (b) 96 hr hydrothermal synthesis

4.3.6 Conclusion

From the results it can be concluded that, to increase adhesion of DDR crystals onto a ceramic support, the support has to be refluxed in HNO_3 (aq) and dried at 623K. Seeding techniques of immersion and centrifugation allow for inadequate yet homogenously dispersed coverage. Further, the mass of crystals used for seeding does not affect the amount of coverage during seeding. Ageing periods longer than 30 minutes may result in DDR crystals dissolving due to prolonged contact with the alkaline system. Decreasing the water concentration by 30% during hydrothermal synthesis led to a decrease in the amount of gel that was produced. Finally, a longer hydrothermal synthesis period of 96 hours produced a stable phase as seen by the transformation of the gel phase into crystals of DOH which co-synthesise easily with the DDR-type zeolite.

While growth of a DDR membrane has not been achieved using the experimental procedure as described by Tomita et al[22] and variation thereof, this research has laid the foundation needed for further studies on the development of DDR composite membranes.

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Chapter 5

Conclusions and recommendations

Content

5.1 Conclusions

5.1.1 General conclusions

The most important objective of this thesis has been achieved, which was to obtain a better understanding of the properties of DDR zeolites in combination with ceramic membranes. In the production of an Alcoa ceramic support, successful separation of fine and heavy particles was obtained using a novel fractionation process. However, the in-house production of a support using AKP-15 powder had better reproducibility when compared to the manufacture of a support using the Alcoa powder.

In general two research groups have published research on the DDR-type zeolite: Den Exter et al[1,2] and Tomita et al[3]. It can therefore be said that the information from this thesis will add to the knowledge base that is currently available on the DDR-type zeolite and its properties. The experimental procedure of the crystal synthesis was adapted from Den Exter et al[1]. The 25 day hydrothermal synthesis as described from their publication was initially tested and then modified to produce pure DDR crystals.

Tomita et al[3] are the only authors to describe the synthesis of a DDR membrane. In carrying out a 48 hour hydrothermal synthesis as described from their publication, without variation in parameters, resulted in the growth of a gel but no zeolite layer, on the ceramic support. The attempt to optimise the experimental procedure for the manufacture of a DDR-membrane proved to be challenging. This is confirmed by the scarcity of publications on the hydrothermal synthesis of DDR-type membranes. However, the work done in this study of DDR membranes certainly does contribute to the lacking knowledge base and does take our research a step closer to the manufacture of a DDR membrane using a cheaper Alcoa ceramic support.

5.1.2 Synthesis of an Alcoa ceramic support

- pH flotation was used to remove the majority of fine particles from commercial Alcoa (Alcoa World Chemicals, USA) powder. This process is best suited at a pH 2 with a loading mass of 200g of Alcoa powder. APMA is chosen as the dispersing agent for centrifugal casting of the filtrate and residue from the fractionation process resulted in the asymmetric distribution of particles to form default-free green casts. Centrifugal casting was operated at a current of 20 kHz, a rotational speed of 16000rpm for 10 minutes.

- Fractionation of the Alcoa heavy particles, that are sedimented after pH treatment, was achieved using a novel fractionation process. The fractionation was achieved using peristaltic pumps with specific flow rates through two identical funnels. The process can be explained using Stokes' Law: the flow rate of the solvent exerts an upward linear velocity on the particles that have reached a terminal falling velocity. As a result, particles of certain sizes are transported up the funnel depending on the linear velocity that is exerted.

- Optimisation of the fractionation process is with a 75g loading mass of Alcoa powder. Results showed that at flow rates of 5ml/min and 15ml/min the best percentage separation (100%) between heavy and fine particles is achieved.

- To produce an Alcoa ceramic support, sintering of the green casts was successful with the 5ml/min filtrate (loading=75g) produced from the fractionation process.

- The green casts were sintered to a maximum temperature of 1150°C. Shrinkage of the Alcoa green casts was 3.2 % which could be ascribed to boundary diffusion. As the reproducibility of the Alcoa supports was however not reliable, in-house produced AKP-15 supports were used for DDR-membrane synthesis.

5.1.3 Synthesis of DDR crystals

- For the synthesis of DDR crystals, the experimental procedure required that 1-adamantanamine had to be synthesised from 1-adamantyl chloride. It was shown that when comparing commercial ADA to in-house manufactured ADA, only the in-house manufactured ADA produced pure DDR crystals of acceptable morphology.

- For the optimization of the experimental procedure[1], it was found that ageing time of 2.5 hrs with a subsequent 25 day hydrothermal synthesis, where all other parameters were kept constant, resulted in small DDR crystals of 1.4μm in size. Crystal sizes increased to 4.9μm when the ageing time decreased to 30 minutes. When the ageing time was increased the DDR morphology exhibited secondary growth in the x, y and z directions due to the increased rate of crystallization.

- An optimised recipe molar ratio, containing 110moles of TMOS (10% higher than the standard) subsequent to a 25-day synthesis with all other parameters kept constant, resulted in crystals of 4.1μm in size. When 90 moles of TMOS is used, DDR crystals of 6.0μm were produced.

- After a 25-day hydrothermal synthesis with the water concentration decreased to 7838moles from 11240moles and all other parameters kept constant, pure DDR crystals of 1.4μm in size were produced. The molar ratio of 40:100:404:7838 is the optimised molar ratio of DDR crystals according to this study.

- SEM analysis showed that DDR crystals produced from 7838moles of water produced crystals of superior morphology and smaller in size when compared to crystals produced from 11240moles (literature) of water in the system. Thus, high solute concentrations resulted in lower inter-nuclei spacing and faster nucleation during DDR crystal growth.

5.1.4 Synthesis of a DDR-membrane

- SEM analysis confirmed that a pre-support treatment of refluxing in HNO_3 resulted in improved seed attachment when compared to sonification in a $C_4H_{10}O$/ ADA mixture or sonification in $C_4H_{10}O$.

- SEM analysis also confirmed that there was no difference in the quantitative seed coverage of a support when the theoretically calculated mass of 0.008g or 0.08g mass of DDR crystals was used.

- Homogenous coverage of the support with DDR crystals was achieved when a centrifugal field was used as a seeding technique. However, when a centrifugal field is used as a seeding technique there is fusing of the DDR crystals, which resulted in a decrease in quantitative seed coverage.

- When immersion is used as a seeding technique (as described by Tomita et al[3]) there was no observed improvement in seed coverage. Moreover, when following the experimental procedure, in the synthesis of a DDR membrane, as described by Tomita et al[3], poor zeolite growth was observed.

- Variation in the parameters of gel ageing, water concentration and hydrothermal time were investigated in an attempt to optimise the experimental procedure as described by Tomita et al[3]. The growth of a gel onto the support was observed with each variation. The growth of the gel was explained by analysis of the sol-gel process of TMOS. According to the process, silica gel forms as the result of the condensation and hydrolysis reactions of TMOS which eventually results in a solid network once condensed tetrahedral silica species have linked together.

5.2 Recommendations

5.2.1 Synthesis of an Alcoa ceramic support

Literature[4,5,6] on the synthesis of ceramic supports shows that the use of polymer binders other than APMA can act as sufficient dispersing agents for successful ceramic support manufacture. Further, these polymer binders can act in combination with the additives and solvents to enhance the stability of the ceramic particles in dispersion and thus allow for increased particle distribution during the manufacturing process[7]. Therefore, it is recommended that other polymers, for example PVC, be investigated in the manufacture of an Alcoa ceramic support.

To investigate large-scale production of the fractionation process, the use of funnels with a larger surface area and the use of tubing of a larger diameter are suggested. This allows for an increase in the loading mass of the Alcoa powder that is used, which inevitably will lead to more fractionation into filtrate and residue fractions. In turn, this might allow for a more efficient fractionation process due to improved control.

5.2.2 Synthesis of DDR crystals

Literature[8,9] shows that dodecasils DOH and MTN can be stabilized by various guest molecules. Thus research in the synthesis of DDR crystals using a different guest molecule is suggested for a more economical experimental procedure which could possibly further reduce the ease with which the polymorph DOH co-synthesises with the DDR-type zeolite.

5.2.3 Synthesis of a DDR membrane

As in the synthesis of DDR crystals, it is recommended that investigations into substitution of ADA as the guest molecule will result in a cheaper and possible more effective experimental procedure. In this research, support pre-treatments, seeding mass and techniques, as well as parameters of ageing, water concentration and hydrothermal time have been investigated. It is recommended that a combination of variations be investigated e.g. an increased ageing period with an increased hydrothermal synthesis time. A combination of variations may avoid the production of a gel layer and encourage the attachment and growth of DDR crystals. Through the above mentioned process, the successful manufacture of a DDR membrane could be achieved.

5.3 References

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“In my end is my beginning.”

T.S. Elliot