

**Zeolite Membranes:
Ozone Detemplation, Modeling,
and Performance Characterization**

Jelan Kuhn

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Zeolite Membranes: Ozone Detemplation, Modeling, and Performance Characterization

Zeolietmembranen: Ozon-detemplatie, Modelling
en Prestatiekarakterisering

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voor mijn vader

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Summary

This thesis addresses some of the current issues in the application, modeling and synthesis of zeolites and zeolite membranes. Aspects of membrane polarity, membrane stability, and low temperature calcination procedures for template removal are discussed. This work also presents a design and optimization of a novel hybrid membrane-crystallization process.

The polarity of a zeolite is an important parameter determining the transport and separation properties in zeolite packed beds and membranes. Chapter 2 is focused on the systematic variation of the zeolite polarity for membrane applications by varying the amount of silanol groups within the framework of the MFI zeolite by deboronation and consecutive heat treatment. The permeation of pure water through the modified silicalite 1 membranes is insensitive to the number of silanol groups. This is attributed to a decreased adsorption compensated by an increased diffusivity. The ethanol selectivity in water/ethanol mixture separation showed an increase with decreasing amount of silanol groups. The combination of deboronation and ozonation can further increase the number of silanol groups (Chapter 8).

The effect of ozonation for template removal on the membrane performance and the stability of high-silica MFI membranes were assessed by testing two multi-channel defect-free high-silica MFI membranes for the separation of ethanol from an aqueous solution under pervaporation conditions (Chapter 3). One membrane is detemplated by air calcination at 773 K, and one is ozonicated at 473 K. The flux and ethanol separation factor were measured at various temperatures and were used to characterize the membrane performance. The ethanol separation factors of both membranes were similar, but the calcined membrane showed a substantially higher flux than the ozonicated membrane, showing the presence of template residues. After

the ozonicated membrane was calcined at 723 K, the flux increased to a similar value as the initially calcined membrane, while the separation factor did not change. Both membranes showed an increase in flux by a factor of two after a subsequent calcination at 823 K, also without affecting the separation factor. The high calcination temperature required for complete detemplation indicates the presence of aluminum in the zeolite framework of the membrane. The membrane stability was monitored for 40 h and 177 h of operation for the initially calcined and ozonicated membrane, respectively. At 348 K the membranes showed stable performance, but the stability of the membranes at elevated temperatures is limited, showing a decrease in both flux and selectivity during operation at 373 K. The effect of the exposure to a water/ethanol mixture on the zeolite membrane is investigated by several analytical techniques using different MFI-type zeolite powders. The results reveal the most plausible mechanism causing the instability of the membrane is ethoxy formation of the ethanol with the silanol groups and Brønsted acid sites in the zeolite framework combined with formation of hydrophilic extra framework pathways by hydrolysis.

The use of hydrophilic membranes for de-watering, and hydrophobic membranes for ethanol enrichment has been quite extensively studied. But the use of a more thermo-chemically stable hydrophobic all-silica membrane for selective water separation based on molecular sieving, is a new concept. In Chapter 4, an all-silica dodecasil 3R (DD3R) membrane turns out to be well suited to separate water from organic solvents under pervaporation conditions, despite its hydrophobic character. Permeation of water, ethanol and methanol through an all-silica DDR membrane has been measured at temperatures ranging from 344 K to 398 K. The hydrophobic membrane shows high water fluxes and an excellent performance in dewatering ethanol and is also able to selectively remove water from methanol. This study reveals the small-pore all-silica zeolites as a new class of chemically stable membrane materials for selective water separation.

The mechanism of separation leading to these high selectivities was further elucidated in Chapter 5, which presents the first combined experimental and molecular modeling study on the adsorption and diffusion of water, ethanol and methanol on DD3R. The simulation data are compared with the permeation data presented in Chapter 4. The pure component isotherms are measured by vapor phase adsorption and are calculated by Grand-Canonical Monte Carlo (GCMC) simulations. The simulations are conducted using molecular models from literature without further adjustments; these models are already in fair agreement with the experimental ad-

sorption data. Mixture adsorption isotherms are calculated and show that both water and alcohol adsorption are increased at equal fugacity as compared to pure component adsorption and the shape of the water isotherm changes from type II to type I when alcohol is present. By calculating the transport diffusivities from the adsorption loading and the permeation data, it can be concluded that the mechanism of separation in the de-watering of alcohols using a DD3R membrane is based on the high diffusivity of water compared to that of the alcohols, where especially ethanol suffers from diffusion limitations due to its size.

In Chapters 2, 3, and 4 pervaporation was used as mode of separation to characterize the membrane performance. Pervaporation through zeolite membranes involves local heat effects and combined heat and mass transport. The current state-of-the-art Maxwell-Stefan models do not take these effects into account. In Chapter 6, transport equations for the coupled heat and mass transport through a zeolite membrane are derived from the framework of non-equilibrium thermodynamics (NET). Moreover, the assumption of equilibrium between the adjacent bulk phases at the feed and permeate sides of the zeolite layer is abandoned in favor of local equilibrium. The equations have been used to model pervaporation of water through a NaA type zeolite membrane, deposited on an asymmetric α -alumina support. This approach leads to discontinuities in the activity and temperature at the membrane interfaces. The calculated temperature drop (1.3 K) across the zeolite layer is significantly higher than when surface and coupling effects are not accounted for (0.4 K). The calculated decrease in temperature over the zeolite layer is dominated by that at the surfaces. This could indicate that temperature polarization is, to a large extent, a surface effect. The heat flux induces an extra driving force for mass transport, reducing the activity difference over the membrane. A positive jump in activity is observed at the interfaces, revealing the mass transport across the interfaces is governed by the coupling with the heat flux.

Ozonication is a technique which can be used to remove the template from zeolites at much lower temperatures than conventional calcination. The template removal by ozonation has been investigated for small pore zeolites of the DDR topology. The pore size of the DDR type zeolites ($4.4 \times 3.6 \text{ \AA}$) is smaller than the molecular diameter of ozone ($4.6 \text{ \AA}$). The detemplation of these zeolites confirms the assumption of ozone breaking down into radicals at the zeolite surface before diffusing through the pore system. All-silica DDR (DD3R), all-silica ZSM-58 and aluminum containing NaZSM-58 (Si/Al=170), all having the same zeolite topology, have been used in

this study. The differences observed in detemplation efficiency are expected to be due to the larger size of the structure directing agent for ZSM-58 compared to DD3R and to differences in the crystal sizes. The possibility of low temperature detemplation of this type of zeolites can have great benefits in zeolite membrane synthesis, reducing thermal stresses. It also allows synthesis on temperature-labile substrates.

The silanol groups not only enhance the polarity in the zeolite structure, but silanol nests within zeolites can be used as catalytic centers, or to facilitate *T*-atom insertion. As was shown in Chapter 2, deboronation can increase the number of silanol groups in the zeolite framework. However, at the high calcination temperatures required to remove the template, these silanol groups are condensed. Using ozone, the temperature required for calcination can be decreased drastically. In Chapter 8, boron containing MFI type zeolite powder ([B]MFI) has been successfully detemplated by means of ozonation, while 80% of the boron is retained in the framework. The boron can subsequently be leached out using an HCl solution, thereby leaving silanol nests. The ozonicated and deboronated [B]MFI sample exhibits 45-60% more silanol groups than conventionally deboronated [B]MFI and ozonicated silicalite-1. This method provides a faster and easier way of synthesizing MFI zeolite with a larger number of silanol groups, than previously developed methods, even without leaching of boron.

In Chapter 9, the ozonation technique has also been applied in the manufacturing of new selective gas sensors utilizing a *b*-oriented silicalite-1 layer-Metglas assembly. The sensors have been prepared by coating a magneto-elastic Metglas ribbon with an oriented, thin silicalite-1 zeolite layer. The thickness of the zeolite layer is that of a single crystal and the crystals are oriented in the *b*-direction, meaning the straight channels are perpendicular to the sensor surface, as confirmed by X-ray diffraction (XRD) analysis. Since the Curie temperature of the Metglas material is below the temperature required for conventional thermal calcination methods for silicalite-1, this method of detemplation can not be applied. The silicalite-1 coating was successfully detemplated by means of ozonation at 473 K, opening the possibility of applying templated zeolite coatings on sensor materials with limited thermal stability. This significantly increases the number of zeolite types that can be used for this application. The sensor showed an increase in resonance frequency when exposed to carbon dioxide and n-butane as compared to exposure to air, while it showed negligible response to the presence of iso-butane, indicating sensing selectivity.

In Chapter 10 the focus is on developing a methodology for optimizing hybrid

Membrane assisted Crystallization process using Reverse Osmosis (MaC-RO). In order to readily apply this methodology to experimental data and show the potential MaC-RO, a polymeric membrane-unit was considered. The proposed optimization approach, however, is generic and can also be applied with other membranes. The study reveals the high potential of the MaC-RO concept in decreasing energy conversion as compared to evaporative crystallization. A setup has been constructed for MaC-RO, using two separate loops for membrane separation and crystallization. In a dynamic optimization of a batch MaC-RO process, the energy conversion is minimized while maintaining a high, prior optimized product yield, defined as the volume based mean size. This results in a 6 times lower energy conversion as compared to evaporative crystallization with a final mean size that closely corresponds to the maximum mean size that can be achieved in a crystallizer with ideal control of super-saturation. This study demonstrates the potential of the concept of MaC-RO in terms of control over product quality and reduction of energy conversion.

Samenvatting

Dit proefschrift behandelt enkele huidige onderzoeksthema's en uitdagingen in de toepassing, modellering en synthese van zeolieten en zeolietmembranen. Membraanpolariteit, membraanstabiliteit, en de procedures voor templaatterwijdering (active-ring) bij lage temperatuur worden besproken. Tevens wordt een ontwerp en een optimalisatie van een nieuw hybride membraan-kristallisatie proces gepresenteerd.

De polariteit van een zeoliet is een belangrijke parameter die het transport in en de scheidingseigenschappen van zeolieten in een gepakt bed en in membranen bepaalt. Hoofdstuk 2 beschrijft de systematische variatie van de zeolietpolariteit voor membraantoepassingen door de concentratie silanolgroepen in een MFI zeolietstructuur te variëren door middel van boorextractie en opeenvolgende thermische behandelingen. De permeatie van zuiver water door deze gemodificeerde silicaliet-1 membranen is ongevoelig voor het aantal silanolgroepen. Dit wordt toegeschreven aan een zwakkere adsorptie die door een verhoogde diffusiviteit wordt gecompenseerd. De ethanolselectiviteit in water/ethanol scheiding vertoonde een toename bij een lagere silanolconcentratie. De combinatie van boorextractie en ozonisatie zorgt voor een verdere verhoging van de silanolconcentratie (Hoofdstuk 8).

Het effect van ozonisatie als templaatterwijdering op de membraanprestaties en de stabiliteit van *high-silica* MFI membranen zijn onderzocht door twee defectvrije *multi-channel* membranen te testen voor ethanolverrijking uit een waterige oplossing door middel van pervaporatie (Hoofdstuk 3). Eén membraan is geactiveerd door calcineren bij 773 K, en een is behandeld met ozon bij 473 K. De flux en ethanol-scheidingsfactor zijn bepaald bij diverse temperaturen en zijn gebruikt om de membraanprestaties te meten. De ethanol-scheidingsfactoren van beide membranen waren gelijkwaardig, maar het gecalcineerde membraan toonde een wezenlijk hogere flux

dan het geozoniseerde membraan. Dit toont de aanwezigheid van templaatesiduen in het zeoliet aan. Het met ozon behandelde membraan is vervolgens gecalcineerd bij 723 K, de flux nam daardoor toe tot een zelfde niveau als voor het aanvankelijk gecalcineerde membraan, terwijl de scheidingsfactor niet veranderde. De flux door beide membranen werd met een factor twee verhoogd na een extra calcinatiestap bij 823 K, eveneens zonder de scheidingsfactor te beïnvloeden. De hoge calcinatietemperatuur die voor volledige activering van de zeolietlaag vereist was wijst op de aanwezigheid van aluminium in de zeolietstructuur.

De membraanstabieliteit is onderzocht door de prestaties van de membranen gedurende een operatieduur van 40 h en 177 h te bepalen voor, respectievelijk, het gecalcineerde en het geozoniseerde membraan. Bij 348 K vertoonde de membranen een stabiele werking, maar de stabiliteit van de membranen bij hogere temperaturen blijkt beperkt, resulterend in een daling van zowel flux als selectiviteit tijdens gebruik bij 373 K. Het effect van de blootstelling aan een water/ethanolmengsel op het zeolietmembraan is onderzocht door verscheidene analytische technieken toe te passen op verschillende MFI-type zeolietpoeders. De resultaten laten zien dat de meest waarschijnlijke oorzaak voor de instabiliteit van het membraan een combinatie is van de reactie van ethanol met de silanolgroepen en met Brønsted-zure OH-groepen in het zeoliet en de vorming van hydrofiele defecten door hydrolyse.

Het gebruik van hydrofiele membranen voor het ontwateren, en hydrofobe membranen voor ethanolverrijking zijn vrij uitgebreid bestudeerd. Maar het gebruik van een de thermo-stabiele en chemisch stabielere hydrofobe *all-silica*-membranen voor selectieve waterscheiding, gebaseerd op moleculaire zeefwerking, is een nieuw concept. Hoofdstuk 4 laat zien dat een *all-silica* deca dodecasil3R (DD3R) membraan, ondanks zijn hydrofobe karakter, bijzonder geschikt blijkt om water van organische oplosmiddelen te scheiden door middel van pervaporatie. De permeatie van water, ethanol en methanol door een membraan van *all-silica* DDR is gemeten tussen 344 K en 398 K. Het hydrofobe membraan toont hoge waterfluxen en uitstekende prestaties in het ontwateren van ethanol. Het blijkt zelfs in staat water van methanol te kunnen scheiden. Deze studie laat zien dat *all-silica* zeolieten met kleine poriën een nieuwe klasse van chemisch stabiele membraanmaterialen vormen voor selectieve waterscheiding.

Het mechanisme dat tot deze hoge selectiviteit leidt is nader onderzocht in Hoofdstuk 5. Hierin wordt de eerste gecombineerde experimentele en moleculaire modeleringsstudie over de adsorptie en diffusie van water, ethanol en methanol in DD3R

gepresenteerd. De simulatiegegevens worden met de permeatiegegevens uit Hoofdstuk 4 gecombineerd om de diffusie-eigenschappen van de componenten te bepalen. De zuivere componentenisothermen zijn bepaald door dampadsorptiemetingen en door Grand-Canonical Monte Carlo (GCMC) simulaties berekend. Bij de simulaties is gebruik gemaakt van moleculaire modellen uit de literatuur zonder dat verdere aanpassingen zijn gedaan; deze modellen geven een redelijke overeenkomst met de experimentele adsorptiegegevens. De berekende mengadsorptieisothermen tonen aan dat zowel het water- als de alcoholadsorptie bij gelijke fugaciteit toeneemt in vergelijking met pure componentadsorptie. Ook verandert de vorm van de waterisotherm van type II in type I wanneer alcohol aanwezig is. De uit de adsorptielading en de permeatiegegevens berekende transportdiffusiviteiten laten zien dat het mechanisme van scheiding in het ontwateren van alcoholen met een DD3R membraan gebaseerd is op het verschil in diffusiviteit tussen de alcoholen en water, waarbij met name ethanol sterke diffusielimiteringen ondervindt.

In Hoofdstuk 2, 3 en 4 is pervaporatie gebruikt als scheidingsmethode om de membraanprestaties te bepalen. Pervaporatie door zeolietmembranen kan leiden tot lokale warmte-effecten en gecombineerd warmte- en massatransport. De huidige *state-of-the-art* Maxwell-Stefan transportmodellen houden geen rekening met deze effecten. In Hoofdstuk 6, worden de transportvergelijkingen voor het gekoppelde warmte- en massatransport door een zeolietmembraan afgeleid uitgaande van de *non-equilibrium* thermodynamica. Daarnaast wordt de aanname van evenwicht tussen de aangrenzende bulkfasen aan de voedings- en permeatzijde van de zeolietlaag losgelaten en vervangen door de aanname van lokaal evenwicht. De vergelijkingen zijn gebruikt om pervaporatie van water door een NaA membraan op een asymmetrisch α -alumina substraat te modelleren. Deze benadering leidt tot discontinuïteit in de activiteit en de temperatuur bij de grensvlakken van het membraan. De berekende temperatuurdaling (1.3 K) over de zeolietlaag is beduidend hoger dan wanneer oppervlakte- en koppelingseffecten niet worden meegenomen (0.4 K). De berekende temperatuursdaling over de zeolietlaag wordt voornamelijk bepaald door die aan de interfaces. Dit kan erop wijzen dat temperatuurpolarisatie voor een groot deel een oppervlakte-effect is. De warmteflux induceert een extra drijvende kracht voor massatransport wat resulteert in een vermindering van het activiteitenverschil over het membraan. Een positieve sprong in de activiteit is waargenomen bij de interfaces, wat laat zien dat het massatransport door de grensvlakken bepaald is door de koppeling met het warmtetransport.

Ozonisatie is een techniek die kan worden gebruikt om het templaar uit een zeolietstructuur te verwijderen bij veel lagere temperaturen dan bij conventionele calcineren. De templaarverwijdering door ozonisatie is onderzocht voor DDR type zeolieten. Deze topologie kenmerkt zich door de kleine poriegrootte ($4.4 \times 3.6 \text{ \AA}$), welke kleiner is dan de moleculaire diameter van ozon ($4.6 \text{ \AA}$). Detemplatie van dit type zeoliet bevestigt de veronderstelling dat ozon ontleedt buiten de zeolietporie alvorens door het poriesysteem te diffunderen. In deze studie zijn *all-silica* DD3R en ZSM-58 en het aluminiumhoudende NaZSM-58 (Si/Al=170) gebruikt, alle met dezelfde DDR topologie. De verschillen die in detemplatie-efficiëncy worden waargenomen zijn toe te schrijven aan de verschillen in grootte van de templaarmoleculen voor ZSM-58 in vergelijking met DD3R en de verschillen in de kristalgrootte. De mogelijkheid van detemplatie van dit type zeoliet bij lage temperatuur geeft een groot voordeel voor de synthese van zeolietmembranen doordat het ontstaan van thermische spanningen tijdens de calcineren worden vermeden. Verder geeft het ook de mogelijkheid voor zeoliet-synthese op temperatuurgevoelige substraten.

De silanolgroepen vergroten niet alleen de polariteit van de zeolietstructuur, maar de zogenoemde 'silanolnesten' binnen de zeolietstructuur kunnen eveneens als katalytische centra worden gebruikt of *T*-aatom substitutie vergemakkelijken. Zoals in Hoofdstuk 2 is aangetoond, kan boorextractie de silanolconcentratie in de zeolietstructuur verhogen. Echter, bij de hoge calcinatiemperaturen die nodig zijn voor het verwijderen van het templaar, verdwijnen deze silanolgroepen via condensatiereacties. Door ozon te gebruiken, kan de benodigde temperatuur voor templaarverwijdering drastisch worden verminderd. Hoofdstuk 8 beschrijft de detemplatie van boorhoudend MFI zeolietpoeder ([B]MFI) door middel van ozonisatie, waarbij 80% van het boor in de zeolietstructuur blijft behouden. Het boor kan vervolgens worden geëxtraheerd met behulp van een HCl oplossing, daardoor silanolnesten achterblijven. Geozoniseerd en gedeboroneerde [B] MFI bevat 45-60% meer silanolgroepen dan conventioneel gecalcineerd en gedeboroneerd [B]MFI en geozoniseerd silicaliet-1. Ozonisatie geeft de mogelijkheid tot een snellere en eenvoudiger manier om de silanolconcentratie in een MFI type zeoliet te verhogen dan eerder ontwikkelde methodes, zelfs zonder het extraheren van boor.

In Hoofdstuk 9 is de ozonisatietechniek toegepast in de productie van nieuwe selectieve gassensoren bestaande uit een *b*-georiënteerde silicaliet-1 laag gecoat op een Metglas strip. De dikte van de zeolietlaag is dat van een enkel kristal en de kristallen zijn georiënteerd in de *b*-richting, wat betekent dat de rechte kanalen loodrecht

staan op het sensoroppervlak. Dit is bevestigd door middel van Röntgen diffractie (XRD) analyse. Aangezien de Curie-temperatuur van het Metglas-materiaal lager is dan de temperatuur vereist voor conventionele thermische calcineren, kan deze detemplatiemethode niet worden toegepast. De detemplatie van de silicaliet-1-laag door middel van ozonisatie bij 473 K was mogelijk. Dit opent de mogelijkheid om zeolietlagen op sensormaterialen met beperkte thermische stabiliteit te synthetiseren. Dit verhoogt het aantal zeoliettypes dat voor deze toepassing kan worden gebruikt beduidend. De sensor toonde een verhoging van de gemeten resonantiefrequentie bij blootstelling aan kooldioxide en n-butaan ten opzichte van blootstelling aan de lucht, terwijl het een te verwaarlozen respons op de aanwezigheid van isobutaan gaf. Dit gedrag bevestigt de selectiviteit van de gassensor.

In Hoofdstuk 10 is een methodologie ontwikkeld voor het optimaliseren van een hybride, membraan geassisteerd proces waarbij omgekeerde osmose wordt gebruikt bij het creëren van oververzadiging in een kristallisator (MaC-RO). Om deze methodologie direct toepasbaar te maken op experimentele data, is een polymeer membraan gebruikt. De voorgestelde benadering is generiek en kan dan ook voor andere membranen worden toegepast. De studie laat de hoge potentie van het MaC-RO-concept zien voor het verminderen van de energieconsumptie ten opzichte van verdampingskristallisatie. Een MaC-RO-opstelling is ontworpen en gebouwd waarin twee afzonderlijke circulatiestromen worden gebruikt, één voor membraanscheiding en één voor kristallisatie. In een dynamische optimalisatie van een *batch* MaC-RO-proces wordt de energieconsumptie geminimaliseerd terwijl een hoge, eerder geoptimaliseerde productopbrengst, gedefinieerd als de volumegebaseerde gemiddelde grootte, wordt gehandhaafd. Dit resulteert in een 6 keer lagere energieconsumptie in vergelijking tot verdampingskristallisatie met een uiteindelijke kristalgrootte die de waarde benadert van een kristallisator met een ideaal oververzadigingsprofiel. Deze studie toont het potentieel van het MaC-RO-concept in het verbeteren van de controle over de productkwaliteit en de vermindering van de energieconsumptie.

Introduction

1.1 Introduction

The chemical industry has played a major role in the development of our industrial society. As a society, we now all have the obligation to address environmental issues such as air and water pollution, global warming and depletion of raw materials. This now calls for a different approach to process and product design. The use of renewable energy sources is becoming a necessity and sustainability is the key feature in novel process and product design. The general opinion that more sustainable processes are a necessity is now shared by many nations, which is reflected in the signing of the Kyoto protocol by 129 countries and the Nobel Peace Prize for Al Gore and the intergovernmental panel on climate change (IPCC) in 2007. But, although climate change and sustainability are now on the political agenda in many developed countries, the global emissions of greenhouse gases are still increasing [1]. The most obvious future challenge and immediate obligation for chemical engineers is to provide society with the requisites to keep a high standard of living, while at the same time reducing the negative environmental impact of this proceeding. In recent years the energy efficiency in the chemical process industry has increased through optimization of unit operations. To further significantly increase the efficiency of the industrial processes innovative and alternative technologies must be incorporated in the design. This is covered nowadays by the concept of process intensification [2].

1.2 Membrane technology

A major part of the energy consumption within the (bio)chemical industry is used for separation processes [3], mostly distillation. The yearly energy consumption of the Dutch petrochemical process industry was recently estimated at 480 PJ, of which 200 PJ could be allocated to separation processes [4]. Membrane technology provides a more energy efficient way to perform thermally driven separations [5, 6]. Using membranes can reduce the energy consumption by a factor 6 to 10 as compared to thermally driven processes [6]. In the Dutch Innovation Roadmap Separation Technology, membrane technology has been identified as a key technology to achieve the goals of reduced energy consumption [4]. The field of membrane technology is a growing market in the (petro)chemical industry; waste water treatment and food and beverage industry being the largest markets [7]. The largest application field of membranes is ultrafiltration, but reverse osmosis and pervaporation show a rapidly grow-

ing market share [7, 8]. One can make a distinction between membrane separations (i.e. osmosis, dialysis, pervaporation) and filtration (i.e. micro- and ultrafiltration). The latter one is not a thermal separation process, but purely pressure driven. In this thesis we focus on the chemical potential-driven membrane separations.

Since the desired product flow is directly proportional to the required membrane surface area, membrane technology has a poor economy of scale. The application of membrane processes as replacement of conventional separation processes in highly heat-integrated bulk chemical plants, which often have a surplus of low-pressure steam, is not always economically viable. However, in stand-alone processes, such as bio-ethanol de-watering and waste water treatment, membranes are already applied with great success. Combining membranes with conventional separation techniques, such as distillation [9] or crystallization [10–12] can also lead to substantial energetic and financial benefits.

Hybrid distillation/vapor permeation systems can decrease the energy demand for azeotropic or close boiling mixtures significantly. Membrane assisted processes can strongly reduce energy demands of gas separation which conventionally require cryogenic distillation. In ethanol dehydration, a hybrid distillation/vapor permeation process reduces the energy consumption by 50% as compared to a conventional process [13]. Combining pervaporation with distillation can reduce the operating costs with 40% in the purification of dimethyl carbonate [14]. In the production of MTBE, using a hybrid distillation/vapor permeation process can reduce the operating costs by 22% [15], while hybrid processes show a total cost reduction between 25% and 60% in comparison with conventional processes in the separation of acetonitrile/water mixtures [16]. The energy consumption in oxygen production from air can be reduced by an estimated 21%, by applying perovskite membranes [17].

Membranes also offer an interesting opportunity to generate supersaturation as alternative to conventional evaporative crystallization, which is an energy demanding process [6]. Membranes can be used to increase the surface area available for evaporation per unit crystallizer volume and there is no restriction related to entrainment. Furthermore, local gradients in supersaturation can be anticipated in the design phase as a designer can decide at which places solvent removal takes place. This can lead to smaller and more efficient equipment. Finally, membranes can be used for thermal labile compounds as they can be applied at low temperatures, far from boiling conditions [18, 19].

Using membranes to *in situ* remove products from reactors also shows high po-

tential in increased process efficiency and energy savings [20–22]. Applying zeolite SOD membranes for *in situ* water removal from a Fischer-Tropsch reactor can potentially increase the revenues by 28% [23, 24]. Recently Tokyo Gas developed a commercial scale Pd-based membrane reformer producing $40 \text{ m}^3 \cdot \text{h}^{-1}$ hydrogen and showing an increased energy efficiency by $\sim 20\%$ as compared to conventional processes [25].

These new processes and fields of application have increased the demands on membrane materials, such as thermal and chemical stability. Although most applications of membrane technology use polymeric membranes, these materials can hardly fulfill the structural and functional requirements of many potential fields of application in the process industry [8, 26]. The limited thermal and chemical stability and the swelling of polymeric membranes are the major limitations. Therefore, increasing research effort is put in the development and improvement of inorganic and mixed matrix membranes. The latter consist of zeolite crystals incorporated in a polymer matrix [5]. The inorganic membranes can be classified in two groups, the porous and dense membranes. The dense membranes include palladium and doped zirconia and perovskite based membranes [27, 28]. The porous membranes include carbon, silica, alumina, titania, zirconia, and zeolite materials and can be classified according to the pore size. Macroporous membranes ($d_{\text{pore}} > 50 \text{ nm}$) find their application in ultrafiltration and are mainly alumina, zirconia and porous glass membranes. The mesoporous membranes ($2 \text{ nm} < d_{\text{pore}} < 50 \text{ nm}$), i.e. γ -alumina and titania, can be used for nano filtration. Microporous membranes ($d_{\text{pore}} < 2 \text{ nm}$) are capable of separating molecules based on size exclusion and/or preferential adsorption. These membranes include silica, titania and zeolitic membranes [29].

Amorphous silica showed increased fluxes and selectivities compared to polymeric membranes for de-watering and separations of organic mixtures [30–32]. These membranes exhibited limited stability, but this can be drastically improved by methylation [33, 34], Ni-doping, or CVD [22]. Methylated amorphous silica membranes have been tested for the separation of methanol from MTBE [35, 36]. Ni-doped and CVD membranes have shown high potential for gas separations and showed to be stable under steam reforming condition [22]. Hybrid organic-inorganic nanoporous materials have shown stable performance in the dehydration of butanol for over 1.5 years of operation at 423 K [37].

This thesis focuses on zeolite membranes, but comprises work ranging from zeolite synthesis and detemplation to transport modeling and process optimization. The

applications and performance of zeolite membranes in various processes is elaborated on in the next sections. The synthesis of zeolites and zeolite membranes is discussed, emphasizing on detemplation, and important factors controlling the membrane performance are outlined. Finally, several methods for transport modeling are discussed ranging from phenomenological methods to molecular simulations.

1.2.1 Zeolite membranes

Zeolites are microporous crystalline aluminosilicates which have uniform, molecular-sized pores. They are capable of separating molecules based on difference in molecular size and in adsorption and diffusion properties (Figure 1.1). Zeolitic membranes are therefore well applicable as separators for gas and liquid phase mixtures. Although the first zeolite was already described in 1756, the zeolites were not commercially utilized until the discovery of synthetic zeolites in the early 1950's [38]. Currently over 150 zeolite framework topologies are synthetically available [39] and new ones are discovered frequently. Apart from aluminosilicates, also other metasilicates, all-silica, and aluminophosphate (AlPO) materials are referred to as zeolites, or zeotypes. Several types are widely used in the (petro)chemical industry as catalysts, adsorbents and ion-exchangers [40]. Zeolitic membranes were first synthesized in the late 80's [41] and, after which, the number of publications on zeolite membranes increased significantly until 2002, since then the number has remained fairly constant (Figure 1.2). Most of the research effort on zeolite membranes has focused on a few topologies, i.e. LTA [42–48], containing 8 and 6 membered ring openings (MR), the 10 MR MFI [49–55], the 12 and the 8 MR MOR [56, 57], the 12 and 6 MR pores containing FAU [42, 58] and BEA [59–61], and 8 MR DDR [62–64]. But many more framework topologies show good potential for membrane synthesis.

Zeolite membranes are thin polycrystalline zeolite layers deposited on porous inorganic supports. Due to their crystallinity zeolites have a well-defined pore size, and are chemically and thermally stable. This makes them suitable for gas separation [49, 63, 65] and membrane reactors [21, 66]. Zeolite membranes offer several advantages over polymeric membranes and other inorganic membranes [67]. Zeolites show an increased chemical stability compared to polymers and amorphous silica and don't swell. Zeolites are more thermally stable, allowing significantly higher driving forces (temperatures and pressures) and potential *in situ* separations from chemical reactors. Because of the well defined pore size, true molecular sieving can be achieved resulting in high selectivities.

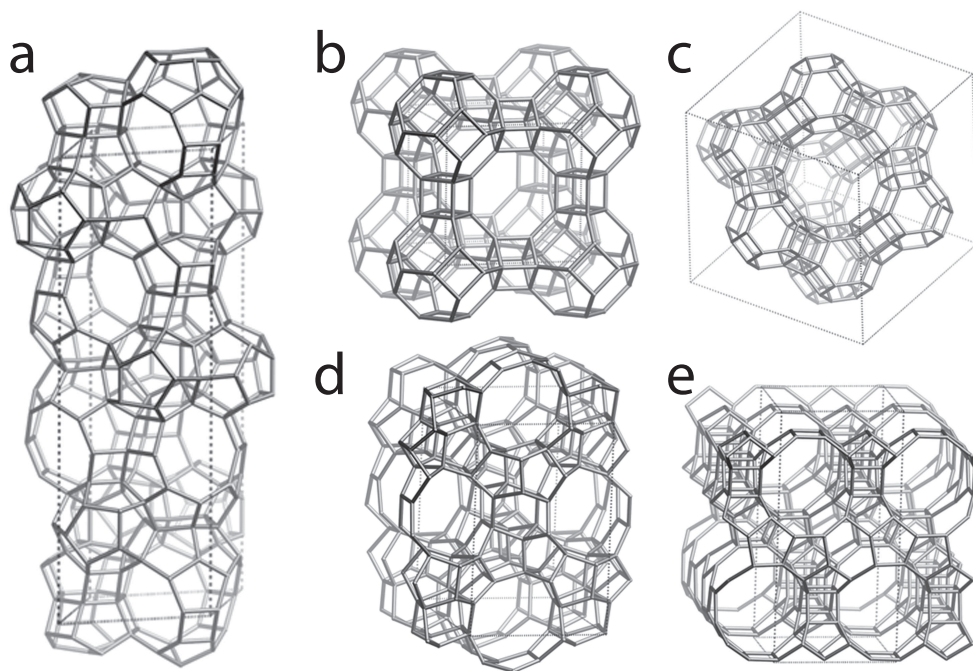


Figure 1.1: Unit cells of the clathrasils (a): DDR, (b): LTA, and (c): FAU, and the pentasils (d): MFI and (e): BEA zeolite framework types, taken from Reference [39].

1.2.2 Pervaporation and vapor permeation

Pervaporation (PV) is a mode of operation in membrane separation processes (Figure 1.3), where a liquid mixture is fed to a membrane while a vacuum or gas purge is applied to the permeate side. One or more components from the mixture selectively permeate through the membrane, and evaporate into the vapor phase (hence the word 'pervaporation'). Vapor permeation (VP) of a saturated vapor is essentially the same as pervaporation [68]. In VP the membrane is fed with a vapor, so no pre-heating to provide the heat of vaporization is required. Unless the feed in VP is super-heated, the driving forces are lower than in PV. This makes the high thermal stability of zeolites particularly attractive for this application.

Pervaporation is a relatively new technique for liquid separations and the industrial development has so far been limited in the number of commercial applications [69]. The main industrial application of pervaporation is dehydration of ethanol using polymeric membranes, which became commercially available in the 1980's from, the

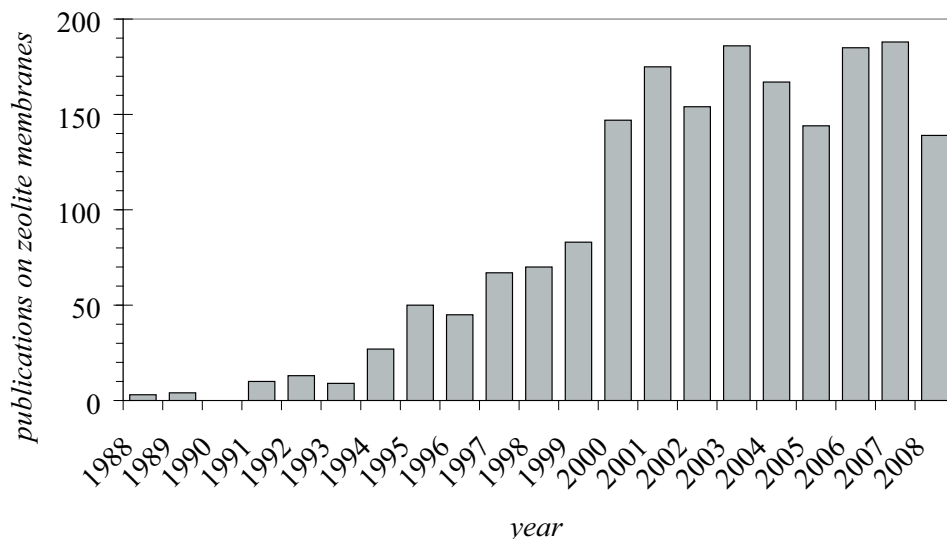


Figure 1.2: Number of publications on zeolite membranes (CAS database) from 1988 until 2008.

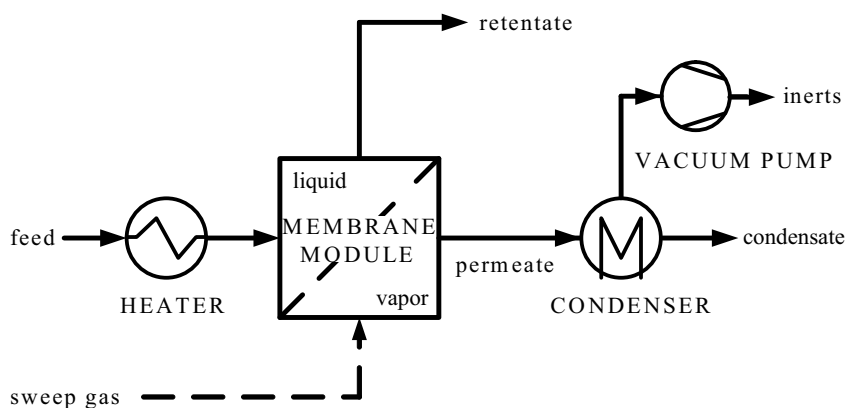


Figure 1.3: Schematic representation of a pervaporation process

in 1997 by Sulzer Chemtech acquired company, GFT [70, 71]. More recently, also removal of organics from water, and organic-organic separations are feasible with commercially available membranes [14, 70]. Vapor permeation is finding new industrial application rapidly, mainly focused on recovery of organics from gaseous effluents [69]. Vapor permeation is also highly attractive as a hybrid separation pro-

cess combined with distillation, as the vapor top product can be directly fed to the membrane. Moreover, it has been observed that zeolite membranes exhibit longer life-times in vapor permeation as compared to pervaporation [72, 73].

1.2.3 Zeolite membranes in pervaporation

Although most industrial applications use polymeric membranes, zeolite membranes have also been used for pervaporation both industrially and in laboratory studies. In 2002, the first large scale plant using zeolite membranes was taken into operation by Mitsui & Co. Ltd. Japan [5, 74]. Since then, several commercial scale dehydration plants went into production [5, 13, 74] (Figure 1.4).

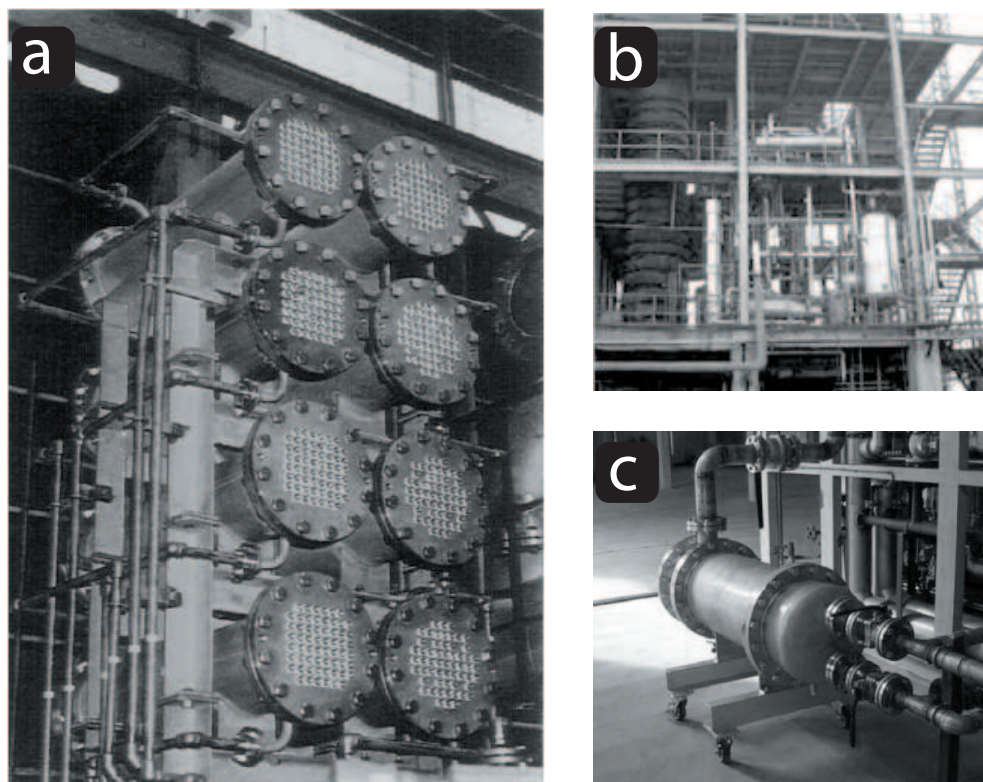


Figure 1.4: Zeolite membranes used on a commercial scale in (a): the first large scale plant using zeolite membranes with a capacity of $10 \text{ t} \cdot \text{d}^{-1}$ dehydrated solvent (Mitsui & Co., Japan) [74] and (b): $24 \text{ t} \cdot \text{d}^{-1}$ ethanol dehydration plant (Daurala Sugar Works, India), using four (c): zeolite NaA modules with a membrane surface area of 7.5 m^2 [5, 13].

Much research effort has been focused on the separation of water from organics

by pervaporation and vapor permeation [75, 76]. Most of the zeolitic de-watering membranes are hydrophilic, but recently a hydrophobic DD3R zeolite has been successfully applied for water removal from alcohols [64]. Table 1.1 gives an overview of fluxes and water separation factors measured for water/ethanol separation using zeolite membranes.

Table 1.1: Fluxes and water separation factors in ethanol dehydration by different types of zeolite and composite membranes. $\alpha_{i,j} = \frac{y_i x_j}{x_i y_j}$

Zeolite membrane	T_{feed} / K	feed water conc. / wt%	$\alpha_{w,e}$	flux / $\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$	ref.
NaA	298	0.6	77000	0.660	[77]
NaA	348	5	5900	1.10	[78]
NaA	318	5	54000	0.86	[79]
NaA	318	5	8000	0.25	[80]
NaA	348	10	10000	2.2	[81]
NaA	348	10	10000	5.6	[82]
NaA	348	10	10000	8.5	[48]
NaA	343	10	18000	1.12	[83]
NaA	348	10	42000	2.1	[84]
NaA	373	10	>5000	12.5	[85]
NaA	413	10	10000	38	[48]
NaA	333	30	2140	2.1	[86]
PVA/NaA	333	24	710	0.936	[87]
PVA/NaA	353	24	383	2.140	[87]
MOR	293	10	3000	n.a.	[57]
MOR	423	10	310	0.33	[88]
NaY	298	0.6	135	1.32	[77]
NaY	348	10	130	n.a.	[89]
NaX	348	10	360	n.a.	[89]
NaX	348	10	410	n.a.	[90]
[B-Al]ZSM-5	313	5	472	0.33	[91]
[Al]ZSM-5	348	10	24	n.a.	[90]
Zeolite T	343	10	1000	0.91	[83]
Zeolite T	348	10	4400	n.a.	[89]
DDR	373	10	1320	1.30	[64]
DDR	348	12	1100	0.85	[92]
SOD	473	5	> 10 ⁶	0.10	[93]

Also, selective removal of alcohols from aqueous solutions using hydrophobic membranes is possible [50, 55, 76, 94–98]. For zeolite membranes, most research is focused on the MFI topology. Silicalite-1 (all-silica MFI) membranes have also been applied for selective removal of ketones from aqueous solutions [99, 100]. These type of organo-selective separations are particularly interesting for selective removal of bio-alcohols from fermentors [101, 102]. Applying these membranes in fermen-

tation processes could increase the alcohol production, and can be used to design a continuous process [98]. Table 1.2 gives an overview of zeolite membranes which have been used for ethanol enrichment from an aqueous solution. Silicalite-1 shows the best performance for this separation with typical separation factors of 10-60 and fluxes around $0.5 \text{ kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$. As there is no molecular sieving effect involved, the separation factors are lower than for the water selective membranes. As the separation is based on adsorption, low temperatures enhance the separation, however, this reduces the flux. Nevertheless, separation factors up to 100 have been reported at reasonable fluxes.

Table 1.2: Fluxes and ethanol separation factors in ethanol enrichment by different types of zeolite membranes.
 $\alpha_{i,j} = \frac{y_i x_j}{x_i y_j}$

Zeolite membrane	T_{feed} / K	feed ethanol conc. / wt%	$\alpha_{e,w}$	flux / $\text{kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$	ref.
Silicalite-1	298	5	10	0.07	[103]
Silicalite-1	303	5	41	0.1 - 0.5	[94]
Silicalite-1	303	5	58	0.76	[96]
Silicalite-1	343	9.4	1.3	2.1	[52]
Silicalite-1	305	9.7	11.5	0.10	[99]
Silicalite-1	303	10	100	0.56	[104]
Silicalite-1	303	11.8	63	0.60	[105]
[Al]ZSM-5	298	5	9.4	0.06	[103]
[Fe]ZSM-5	298	5	3.4	0.06	[103]
[B]ZSM-5	298	5	2.1	0.05	[103]
[Ge]ZSM-5	298	5	29	0.11	[103]
[Ge]ZSM-5	303	5	47	0.223	[106]

1.2.4 Stability of zeolite membranes

Natural (alumina containing) zeolites are stable at $\text{pH} > 6$, at lower pH the framework disintegrates due to the leaching of aluminum. High and all-silica zeolites exhibit higher acid stability but lack the ion exchange capacity [38]. Cui *et al.* have shown high silica zeolite T exhibits good acid stability in acetic acid, but showed signs of decomposition after 1 h in 0.5 M hydrochloric acid [107]. High and all-silica MFI have successfully been tested as a corrosion resistant and thermally stable coating [108]. Exposure to high pH solutions, however, also leads to dissolution of all-silica zeolites. To a certain extent, even quartz is soluble in water [109]. Exposure of thin silicalite-1 membranes to pure water has shown to eventually degrade the zeolite structure [110]. The limited hydrothermal stability of LTA type zeolite membranes in

pervaporation is attributed to dissolution of the amorphous-like material in the grain boundaries [111].

Although zeolites are crystalline materials, it has been shown that, for several zeolite topologies, the framework exhibits some flexibility, making it possible for molecules that seem to be too large for the pores, to still enter the framework [112]. This has been shown by van Koningsveld *et al.* for the case of adsorption of naphthalene (molecular diameter of 5.8 Å) in MFI (pore window of 5.4 Å) [113], and is also the basis of the permeation of water through SOD membranes [93, 114]. SOD has window openings which are, at room temperature, similar as the molecular diameter of water. Due to the flexibility, permeation of small molecules is possible at elevated temperatures. Noack *et al.* investigated the changes of the unit cell dimension for zeolites LTA, FAU, MOR and MFI as a function of temperature and water content [115]. A strong change was found for all Al-rich zeolite types as a result of the de-watering. Increasing aluminum content also reduces the chemical stability of the zeolite and reduces zeolite membrane quality [115, 116]. The flexibility of some zeolite structures can also cause swelling of crystals due to adsorption of certain compounds, which in the case of membrane materials, can alter the separation properties [116, 117].

Nevertheless, zeolites can be considered chemically and thermally robust membrane materials, and show good prospectives in applications in chemically and thermally harsh conditions.

1.2.5 Synthesis of zeolite membranes

Zeolite membranes are most often prepared by a hydrothermal reaction of a gel in alkaline media [118]. The gel is composed of a silica source, a source for tetrahedral framework atoms other than Si, and -in most cases- a structure directing organic agent (SDA) or template in an alkaline solution usually in aqueous [67, 119–122] or sometimes in fluoride media [123–125]. During hydrothermal synthesis, a zeolite layer is crystallized onto a porous support, usually in a Teflon lined reactor at temperatures between 353 K and 473 K [126]. During synthesis, the system can be heated using conventional [119, 121] or microwave heating techniques [44, 126–130]. Crystal seeds can be added to the support material prior to the crystallization step to reduce primary nucleation, thereby improving the controllability of the crystal growth. Seeds can be attached to the support by dipcoating [39], slipcasting [39] or electrophoretic deposition [131]. Vapor deposition [119, 132], electrophoretic depo-

sition [133, 134] and laser ablation techniques [135] can be used to deposit grown zeolite crystals on a substrate, usually followed by hydrothermal treatment to create a zeolite film. Other routes for preparing zeolite membranes, such as dry gel methods [136], have also been used. Recently McLeary *et al.* presented a novel route for the synthesis of silicalite-1 membranes, starting from a continuous amorphous silica layer on an α -alumina support [137]. This method seems to yield an oriented layer on the substrate due to the high local concentration of silicon nutrients [138].

The scale-up of the zeolite membrane synthesis from lab scale to commercial scale is non-trivial, and not many zeolite types have been commercialized so far. The LTA membranes that are currently used on a commercial scale are developed and produced by a subsidiary of Mitsubishi Chemical Company, Japan: BNRI (Bussan Nanotech Research Institute). BNRI also produces smaller ZeoSepA membranes and FAU membranes, which are mainly applied for dewatering iso propyl alcohol (IPA) [5], and recently presented a method for the commercial production of NaY zeolite membranes [139]. NGK Insulators have developed DD3R [140] and high-silica MFI membranes [141]. The DD3R show good results for liquid [64, 92] and gas separations [62, 63], but are not used on a commercial scale yet. Inocermic GmbH, a subsidiary of HITK Hermsdorf, Germany, also produces LTA membranes for dewatering [142] and have also developed silicalite-1 membranes [143].

These manufacturers all use shell and tube type of membrane modules. Another method for the scale-up of zeolite membranes using micro membranes or zeolite micro reactors. Zeolite micro membranes have the advantage of being manufactured using traditional semiconductor fabrication methods, which is a mature technology [144]. Micro membranes have been tested in gas separation [145] and in micro fuel cell applications [146]. Zeolite micro channels [147] and micro reactors [148] have also been manufactured and show to be promising techniques for scale-up.

1.2.6 Detemplation

Most zeolites require an organic SDA for a successful synthesis. To make the porous structure of the zeolite accessible, this organic molecule needs to be removed from the zeolite structure after the synthesis. Conventionally, this is done by calcination at temperatures between 623 K and 973 K. High detemplation temperatures are very undesired in fragile materials with unusual framework compositions, or in applications such as membranes or coating of sensors, or other materials with a low dielectric constant. In the case of coatings and membranes, heating can lead to crack formation.

Even when applying low heating rates the chance of creating defects is profound. Moreover, many sensor materials are not capable of withstanding the high temperatures required for template removal.

Chemical or photochemical detemplation at mild thermal conditions allows the removal of the template, while preserving the silanol groups. Several non-thermal detemplation techniques have been developed. Masuda *et al.* have used nitric acid and hydrogen peroxide in detemplating a silicalite-1 membrane [149]. Heng *et al.* used a mixture of oxygen and 50 to 100 g·Nm⁻³ ozone at elevated temperatures (473 K) to remove the template from silicalite-1 and ZSM-5 membranes [150]. Melian Cabrera *et al.* have successfully detemplated zeolite beta crystals under mild conditions by means of Fenton chemistry, using hydrogen peroxide and an iron salt [151]. Fenton chemistry [152] is the reaction of OH radicals with an organic molecule. The radicals are formed by a reaction between hydrogen peroxide and a Fenton reagent (Fe²⁺/Fe³⁺). Parikh *et al.* have detemplated a thin silicalite film (<500 nm) using short-wavelength UV-light (184-257 nm) [153] and Maesen *et al.* have investigated the detemplation of [B]MFI using oxygen plasma [154]

It has been shown that ozone/oxygen mixtures can be used to remove coke deposition in MFI and FAU type zeolites at mild thermal conditions [155–157]. Under similar conditions also thin MFI zeolite membranes have been detemplated [150]. In this thesis we apply this technique successfully to the detemplation of DDR type zeolites [158], [B]MFI zeolite powder [159] and sensors coated with silicalite-1, [B]MFI and FAU films [160] and a high-silica MFI membrane [161].

The detemplation process is a complicated series of degradation reactions and oxidation of the organic molecules in the structure. Although the thermal calcination is normally done in air, most studies on the detemplation mechanism focus on the removal of the organic template under inert atmosphere, such as nitrogen, helium, or argon [162–164]. The thermal detemplation of TPA from MFI type zeolites can be described by several consecutive reactions. The first involves the Hofmann degradation of TPA to tripropylamine or ammonium, tripropylamine (Pr3N) and propene. Secondly, the consecutive fragmentation of tripropylamine and the dimerization of propene, followed by alkylamination of alkenes, produce secondary amines [165, 166]. The presence of crystalline imperfections, such as OH⁻ or SiO⁻ are believed to initiate the TPA degradation at relatively low temperatures [167]. In the presence of trivalent T-atoms, TPA is more stable, resulting in more difficult detemplation [162], this is also observed for template removal by ozonation [150].

Karwacki *et al.* monitored the thermal degradation of the template in MFI zeolite and AFI type AlPO crystals by means of fluorescence microscopy [168]. The larger fluorescent species showed to accumulate at internal crystal grain boundaries, revealing the intergrowth and channel structure of these zeolite types.

1.3 Zeolite coatings in sensor applications

Chemical and biochemical sensors are becoming of great importance in industrial applications. Many sensors are based on selective adsorption or absorption of certain analytes from gas or liquid environment. The significant parameters determining the performance of these sensors are selectivity, sensitivity, reversibility and response time. The mechanism of sensing can be based on the selective alteration of various sensor properties, such as: electrochemical, electronic, optical, acoustic or other properties. Applying a selective coating on an appropriately chosen material can enable or improve the selective detection and quantification of gaseous or solvated species. Porous materials, especially those exhibiting order and uniform pore channel networks, such as mesoporous silica [169] or zeolites [170], have shown great potential for sensing applications. Some applications of microporous materials in gas sensors are taking advantage of the high surface area of the mesoporous material, functionalized by an assembly with a probe that aids in selective detection of specific chemicals. Varieties of fluorescent probes were assembled in porous materials for sensing purposes. Encapsulating ruthenium (II) complexes inside the supercages of a FAU-type zeolite was successfully applied as a fluorescent oxygen probe. Particularly zeolites with pore sizes comparable to many industrially important molecules are interesting candidates for sensor materials. A zeolite layer can act as a barrier which selectively limits gas exposure on the sensing surface or enriches specific analytes, enhancing the selective detection of small molecules. One of the major advantages of using zeolites, is the possibility to functionalize continuous coatings. Coating of oxygen selective sensors with a zeolite film has shown to improve the detection of oxygen due to molecular sieving and adsorption selectivity of the zeolite layer. An magnetoelastic ribbon coated with a FAU type zeolite layer has been successfully applied as a carbon dioxide sensor [171, 172]. Silicalite-1 has been used to introduce chemical selectivity into surface acoustic wave (SAW) devices [173]. Mintova *et al.* reported the development of a humidity micro-sensor, based on LTA-type zeolite film grown on a quartz crystal microbalance [174]. Introducing chromium cations

into zeolites, by means of ion exchange has shown to improve the selectivity of metal oxide gas sensors [175]. The limited thermal stability of many sensor materials poses a challenge in applying zeolites which need to be detemplated before they can be effective. Ozonation has shown to enable successful detemplation of silicalite-1 coated magneto-elastic ribbons at mild thermal conditions [160].

1.4 Membrane selectivity and polarity

The polarity of permeating components and of the host framework, strongly determines the host-guest interaction and thus the transport through polymeric [70] and inorganic membranes [176]. In inorganic membranes the strong interaction results in strong adsorption; however, this also decreases the mobility of permeating molecules. Figure 1.5 shows the self-diffusivity and the saturation adsorption of water for several zeolites versus the silica to aluminum ratio. A lower Si/Al ratio corresponds to a more polar zeolite framework. Water is a highly polar molecule, and the hydrophilicity of a zeolite thus increases with polarity. Different zeolite types with a similar Si/Al ratio have also shown to exhibit different polarity [177]. Tuning the zeolite polarity would enable the optimization of the trade-off between adsorption and diffusion. The zeolite polarity is determined by the silica to alumina ratio, the cation type, the pore configuration and the amount of silanol groups [178]. At low Si/Al ratio, however, the intercrystalline transport becomes increasingly important because the membrane quality decreases [51] and a larger portion of the flow will pass through non-zeolitic pores [74, 75, 86]. Changing the cation type or the pore configuration also changes the pore diameter [179] and therefore the membrane transport. It is therefore difficult to do a systematic investigation of the zeolite polarity by changing the Si/Al ratio or the cation type.

1.4.1 Hydrophobic and hydrophilic zeolite membranes in de-watering

Conventionally hydrophilic membranes are used for dehydration of solvents. For zeolite membranes this usually implies a low silicon to aluminum ratio. High fluxes and selectivities have been measured in pervaporation and vapor permeation experiments using zeolite membranes with a high aluminum content [48, 74, 75]. Sodium LTA (NaA) type of membranes are already being used in industry [74]. FAU type membranes, with a Si/Al ratio of 1.5 - 1.6, have also been used to dehydrate alco-

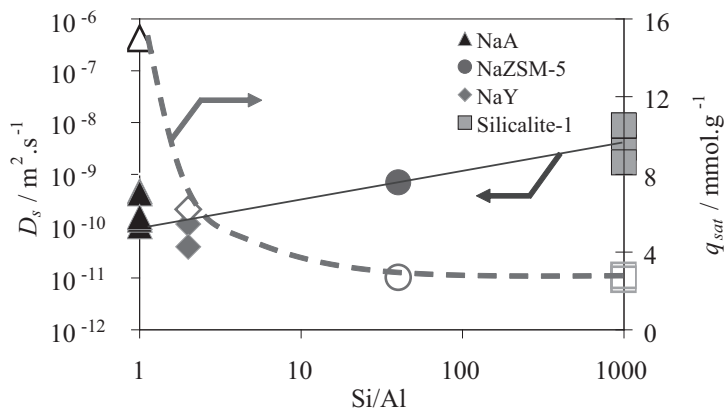


Figure 1.5: Self-diffusivity (D_s , closed symbols), and saturation loading (q_{sat} , open symbols) of water in zeolites as a function of Si/Al ratio (compiled from literature, both experimental and computational data [180–189]). The lines only indicate the trend.

hols, albeit with a lower selectivity and flux than the LTA type membranes [42, 58]. Well inter-grown LTA membranes have shown ideal selectivities higher than Knudsen selectivities for He/N_2 and H_2/N_2 [47, 190], however, in LTA membranes a large portion of the flow is through the non-zeolite pores [74, 75, 86]. This type of membrane is capable of separating water from gases [190], but fail in separating inert gases. The mechanism of separation is thus based on preferential adsorption and diffusion through both zeolitic and non-zeolite pores. The high selectivity for water/alcohol mixtures is mainly caused by the preferential adsorption of water. Small defects can even enhance the membrane performance in dehydration because the flux is increased, while the selectivity is maintained due to the strong adsorption in the NaA zeolite [191]. Dehydration of alcohols is already done on industrial scale using zeolite LTA type membranes [5, 74]. Also sodalite (SOD) membranes have been successfully synthesized and tested for absolute water separation [114]. However, the high aluminum content of these hydrophilic membranes results in reduced chemical and hydrothermal stability [38, 107] and reduced membrane quality, due to inter-crystalline transport [51]. All-silica membranes can be manufactured without these defects, but, they are hydrophobic. Silicalite-1 membranes have been used to selectively separate ethanol from an aqueous solutions, based on preferential adsorption [55, 94, 104]. If water is to be removed selectively by hydrophobic membranes, separation based on size exclusion is required, and one has to reside to small pore

(8-ring or smaller) all-silica membranes. Many 8-ring zeolites exist (i.e. LTA, CHA, DDR, MER, ANA) and some have been synthesized in the all-silica form. However, only very few have successfully been synthesized as all-silica membranes. Tiscornia *et al.* have recently synthesized aluminum-free LTA membranes (ITQ-29), which have been tested for N_2/CH_4 and N_2 /propane separation [192]. These membranes are however, not all-silica, since germanium was also present in the synthesis mixture [192, 193]. Recently, scientists at AIST, Japan, have developed a CDS-1 membrane [194] that is water selective for a water-ethanol mixture when calcined at 673 K ($\alpha_{w,e} = 30$, flux = $0.2 \text{ kg}\cdot\text{m}^{-2}\text{h}^{-1}$), whereas the selectivity inverts after calcination at 873 K and the membrane selectively permeates alcohol ($\alpha_{e,w} = 53$, total flux = $0.5 \text{ kg}\cdot\text{m}^{-2}\text{h}^{-1}$). This effect is attributed to the condensation of silanol groups at temperatures above 823 K [195]. All-silica DDR (DD3R) membranes have been developed by NGK Insulators, Japan [62], and have been successfully applied for CO_2/CH_4 separation [63, 196, 197] and de-watering of alcohols and other organic solvents [64, 92].

1.5 Transport modeling

Besides the diffusion through the zeolite layer itself, the transport from feed to permeate side of a zeolite membrane also involves the diffusion from the bulk feed fluid to the membrane surface as well as the transport through the porous support material. These can both have a profound effect on the separation performance of the system.

A variety of models and techniques have been used to describe the diffusion in zeolites, ranging from phenomenological models [198], irreversible thermodynamics [199] and the Maxwell-Stefan formulation [200, 201] to Monte Carlo simulations [202–204] and molecular dynamics [205–207]. Quantum mechanical (QM) and molecular dynamic (MD) calculations can provide detailed insight in the diffusion process at molecular level. However, the computational work involved in these calculations is profound. The current computational power does not yet allow the modeling of multi body diffusion through a zeolite pore at a quantum mechanical level. There are many studies describing the diffusion of molecules through a zeolite lattice using Dynamic Monte Carlo simulations (DMC) [202–204, 208].

The transport through a zeolite membrane is generally described following an adsorption-diffusion mechanism, in which five steps are distinguished: [67].

1. diffusion from the bulk to the zeolite surface

2. adsorption on the zeolite membrane surface and in the pores
3. diffusion through the membrane
4. desorption at the permeate side of the membrane
5. diffusion into the bulk permeate through the support pores

1.5.1 Mass transport resistance in support and film

The major transport resistance is generally in the membrane layer (step 3), although the bulk diffusion (step 1) and the transport resistance in the support (step 5) can contribute significantly to the total mass transport resistance in the membrane separation process. The porous support, on which zeolite membranes are deposited, can have a profound influence on the overall transport resistance of the membrane [36, 94]. Most modeling on transport in membranes is based on the dusty gas model (DGM) [36, 143, 201]. Although the model neglects the Maxwell slip term [209, 210], it has shown to model the transport in porous media with relative high accuracy. In the DGM, the membrane is considered as a pseudo species in the mixture which is motionless and of infinite molar mass. The flux through the support is described by a combination of Knudsen diffusion and viscous flow

$$J_i = -c_{i,pore} D_{isup}^{Kn,eff} \frac{\nabla \mu_{i,T}}{RT} - \frac{d_p^2}{32\eta} \nabla P \quad (1.1)$$

Also the transport resistance on the liquid feed side of the membrane can have an influence on the membrane performance. Concentration polarization is a common problem in many membrane processes, and can also be of importance in pervaporation and vapor permeation [211]. Also temperature polarization can have a detrimental effect on membrane performance and has been observed in pervaporation processes [212]. The heat and mass transport in the liquid, or vapor, boundary layer are generally modeled using dimensionless parameters: the Nusselt and the Sherwood numbers are thereby expressed as functions of the Reynolds, the Prandtl and the Schmidt numbers [213, 214].

1.5.2 Adsorption and diffusion in the zeolite layer

Adsorption in a zeolite from the vapor phase is generally physisorption and is therefore an exothermic, non-activated process [67]. When a component adsorbs from the

liquid phase, the net enthalpy change depends on the heat of adsorption (defined from the vapor phase) and the heat of evaporation. In current modeling it is generally assumed that the membrane has a uniform temperature [215] and the heat of adsorption (step 2) and desorption (step 4) cancel out, leaving a net enthalpy change equal to the enthalpy difference of the feed and permeate.

To predict the flux through a zeolite membrane, the flux has to be correlated to a certain driving force. The easiest way of describing the relation between flux and driving force is by Fick's law [213].

$$(J) = -[D](\nabla c) \quad (1.2)$$

Although the formulation developed by Fick is conceptually simple, it breaks down in qualitatively simple cases [201, 216, 217]. Fick's law can be generalized to treat some simple multi-component systems [213]. Despite these shortcomings, Fick's law remains the most natural formulation for transport diffusion. The Maxwell-Stefan Theory (M-S) can be used to describe the (multi-component) diffusion through zeolites. The advantage of the M-S theory is that the non-ideality of the mixture is not incorporated in the diffusivities (like in Fick's law), therefore the M-S diffusivities are far more constant compared to the concentration and composition dependent Fick diffusivity [201]. The M-S method relates the driving forces to the friction forces acting on the species in a system.

In current modeling, the use of the Maxwell-Stefan (M-S) equations are widely accepted to model mass transport in zeolites and zeolite membranes [201, 218], and have been successfully applied to several systems [205, 219–221]. The M-S equations have also been successfully used to model permeation through zeolite membranes [222–224]. Bakker *et al.* and van den Broeke *et al.* have investigated permeation of several gases and binary gas mixtures through a silicalite-1 membrane [49, 225–227]. They were able to describe the transport behavior at various conditions, using equations for surface diffusion, and gas translational diffusion. The adsorption behavior is a key parameter in correctly modeling the permeation through a zeolite membrane, as was also shown by Zhu *et al.* [228, 229]. Combining the M-S equations with the ideal adsorbed solution theory (IAST), has shown to be suitable for predicting permeation behavior of several gases through silicalite membranes [200]. In some cases, however, it was seen that this method is not sufficient to capture the complex adsorption and diffusion behavior [230]

The M-S equations balance the driving forces with the friction exerted on molecules

and are consistent with the theory of irreversible thermodynamics [231]. The M-S equation can be written as

$$-\frac{\nabla\mu_{i,T}}{RT} = \sum_{\substack{j=1 \\ j \neq i}}^n \frac{x_j}{D_{ij}} (v_i - v_j) \quad (1.3)$$

Where $\nabla\mu_{i,T}$ denotes the chemical potential gradient at constant temperature as the driving force for mass transport. The Maxwell-Stefan (M-S) equations, in the form given in equation 1.3, do not account for the coupling between heat and mass transport. These equations thus only hold at isothermal conditions. A thermodynamic coupling of heat- and mass transport is currently omitted in the relevant literature on zeolites. Whenever a simultaneous transport of heat and mass is modeled, the consideration is limited to effect of temperature polarization on the liquid side, which reduced the driving force, and to the temperature dependency of adsorption equilibria and diffusivities [35, 232].

The theory of non-equilibrium thermodynamics (NET) is based on the assumptions of local equilibrium and linear flux-force relations. NET allows for a consistent description of coupling between fluxes, in particular between heat and mass transport. In current modeling of zeolite transport, equilibrium between any two adjacent phases is assumed, i.e. the adsorbed phase in the zeolite is assumed to be in equilibrium with the bulk fluid at the zeolite surface. Only recently, Kjelstrup and Bedeaux [233, 234] abandoned the assumption of equilibrium across the interfaces and defined the interface properties using local equilibrium instead.

Determining the transport parameters is of key importance for any model. The main parameters required for modeling transport through zeolites are adsorption parameters and diffusivities. Adsorption isotherms are generally measured by uptake or breakthrough experiments [218, 231]. Several experimental methods for determining diffusivities in zeolites are: uptake experiments [235, 236], transient permeation measurements [237], interference microscopy [238], the zero-length-column (ZLC) method [239, 240], pulse field gradient (PFG)-NMR [182, 241] and quasi elastic neutron scattering (QENS) [186]. Thermal diffusivities can also be measured experimentally [242]. The properties of the surfaces are generally determined from molecular simulations [243]. These transport and adsorption parameters can also be determined from molecular simulations [244].

1.5.3 Molecular modeling

To elucidate the permeation behavior of membranes, molecular modeling can be applied. Molecular modeling is a powerful tool to determine adsorption and diffusion behavior of components in a zeolite [245]. Molecular modeling can be used to elucidate complex mechanisms of transport in shape, size and affinity selective zeolite systems [216]. Many modeling techniques are available and have already been applied to study zeolite systems. These techniques include Monte Carlo (MC) simulations, also including kinetic MC, molecular dynamics (MD) and non-equilibrium MD (NEMD), *ab-initio* MD and hybrid QM/MM approaches. Recently, Smit *et al.* gave an extensive overview of molecular modeling techniques applied to zeolites [244]. Most of the earlier studies were focused on adsorption of hydrocarbons in silicalite-1 [244], but om recent time many other systems were investigated, including adsorption and diffusion of water in silicalite-1 [246–248] and systems considering extra framework cations, e.g. water [187, 249] and water/ethanol in NaA and [180]. For both MD and MC simulations the interaction parameters are either determined by *ab-initio* calculations or fitted from experimental data.

The equilibrium adsorption on zeolites is usually determined by Grand-Canonical MC simulations. In GCMC simulations statistical averages are calculated over a large number of configurations, the zeolite host is equilibrated with a resevoir of guest molecules at constant chemical potential and temperature. The method has been successfully applied to many zeolite-host systems [203]. Diffusion properties can be determined by molecular dynamics (MD) [244, 250, 251] or Kinetic Monte Carlo (KMC) [203, 216] simulations. In KMC simulations, the diffusion is treated as a series of jumps from one adsorption site to the next, while in MD simulations, the trajectory of molecules is calculated by integrating Newton's second law ($F = ma$). Dubbeldam *et al.* recently provided a review on molecular modeling of diffusion in zeolites [252]. Diffusivities can be obtained from equilibrium simulations, but dynamic processes can also be simulated in molecular modeling using NEMD [244]. Sanborn *et al.* used this technique to study CH₄, CF₄ and alkanenes in a FAU zeolite [253, 254]. Newsome *et al.* have used NEMD to investigate the influence of internal grain boundaries of MFI crystals on diffusion [255, 256]. Although there is often a discrepancy between experimental measurements and simulations, MD has shown to be able to predict diffusion behavior in zeolites well [205, 257]. The difference between the various experimental techniques and simulations is often ascribed to the imperfections in zeolite samples used in macroscopic measurements. When the load-

ing dependency of the diffusivity is considered, the differences between the different techniques is already significantly reduced [251].

1.6 Outline of the thesis

The work described in this thesis covers a wide range of different aspects, spanning from fundamental research on tuning the zeolite polarity, applying molecular simulations and modeling transport using the framework of NET to applications of zeolite membranes in alcohol dehydration and ethanol enrichment and from applying ozone detemplation for sensor applications to characterizing the membrane assisted crystallization process. This chapter has given an introduction to the field of zeolites, zeolite membranes, and transport modeling. Some of the current challenges in the field of zeolite membranes, such as detemplation, membrane stability, and transport modeling are addressed. The contents of the other chapters is briefly outlined below and is graphically presented in Figure 1.6, showing how the different topics are related.

Most of the work covered in this thesis is related to zeolites and zeolite membranes with the emphasis on framework polarity, which is an important property determining transport through zeolite membranes. The second chapter analyzes the influence of framework polarity on the transport through an MFI zeolite membrane. The objective is thereby to eliminate the influence of possibly varying membrane quality and thus single out the effect of polarity. The polarity is altered by incorporating silanol groups within the zeolite framework by deboronation and subsequently condensing them in cycles of heat treatment. Non-thermal detemplation, such as ozonation, can also increase the number of silanol groups in a zeolite.

The third chapter compares the performance of ozonicated and thermally detemplated multi-channel MFI type zeolite membranes in ethanol enrichment from an aqueous solution under pervaporation conditions. The membrane stability is investigated for over 177 h of operation revealing possible mechanisms for a decreasing performance with the membrane life-time.

In the fourth chapter the performance of a hydrophobic DDR membrane in dehydration of alcohols is investigated. Water is selectively removed from ethanol and methanol under pervaporation conditions using this highly stable all-silica membrane. Despite the hydrophobic character of the zeolite, high selectivities are observed for water removal from ethanol, which are even comparable to hydrophilic LTA type zeolites. Even dehydration of methanol can be performed with high fluxes

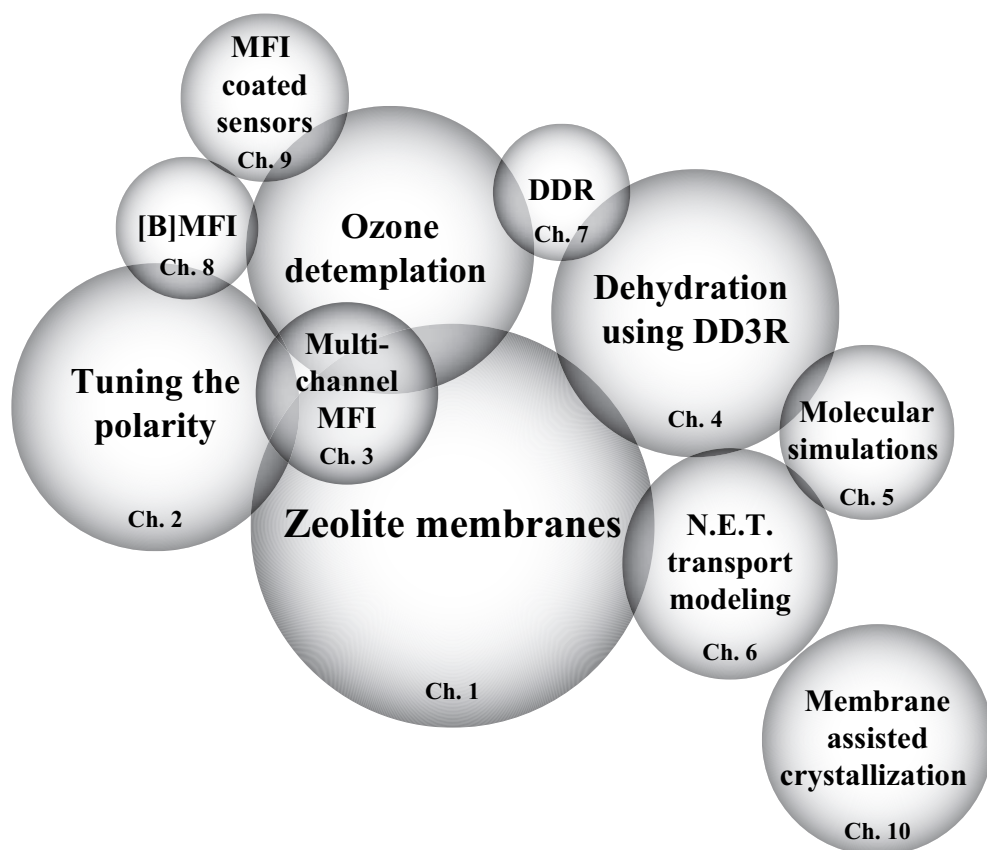


Figure 1.6: Graphical representation of the outline of the thesis showing the connection of the main topics and the corresponding chapter numbers.

and reasonable selectivity. This study shows that these membranes are powerful candidates for water separation under high temperature or acidic conditions, where polymeric or hydrophilic zeolite membranes fail.

Chapter 5 presents the first study, combining measurement and molecular modeling, on the adsorption and diffusion of water, ethanol and methanol on DD3R. Mixture adsorption isotherms are modeled using GCMC, based on single component experiments using force fields from literature without further adjustment. The single component adsorption and simulations show the alcohol loading is an order of magnitude higher than the water loading. Mixture adsorption simulations, however, show that the water adsorption increases significantly in the presence of alcohol, but there is still an adsorption selectivity for the alcohols. The diffusivities of the components

are calculated from permeation measurements and the mixture adsorption simulations and reveal the water diffusivity to be substantially higher than that of the alcohols, which explains the high selectivities measured under pervaporation conditions.

Although zeolite membranes are already commercially available, elucidating the mechanism of transport through this type of membranes still is a major scientific topic. Chapter 6 is a modeling study on the transport under pervaporation conditions, based on the framework of non-equilibrium thermodynamics. The enthalpies of adsorption, desorption and evaporation impose strong temperature effects at the membrane/fluid interfaces in pervaporation processes. For the first time, transport equations are set up incorporating coupling between heat and mass transfer in a pervaporation process, thereby abandoning the assumption of equilibrium between adjacent phases in favor of local equilibrium. Distinct differences are observed compared to the conventional model approach, showing discontinuous temperature and fugacity profiles across the membrane.

Ozonication is a novel technique for detemplation of zeolites at mild thermal conditions. Chapters 7 and 8 describe successful application of this technique to DDR and boron containing MFI zeolites, respectively. The DDR topology is a small pore clathrasil. Showing that these type of zeolites can successfully be detemplated using ozone, proves that the radicals produced from ozone are the species that diffuse into the zeolite pores, since the pore aperture does not allow ozone to enter. The ozonication of boron containing MFI allows for a faster and easier method of synthesizing an MFI type zeolite with an enhanced number of silanol nests.

In Chapter 9 the same ozonication technique is used to detemplate a thin zeolite membrane coated on magnetoelastic Metglas ribbons, which can be used for sensor applications. The material on which the zeolite is coated loses its magnetic properties when it is heated above 573 K. Conventional, thermal calcination procedures for the activation of silicalite-1 are, therefore, not possible. Ozonication allows template removal at much lower temperatures, allowing successful activation of these zeolite-Metglas assemblies.

Chapter 10 presents the characterization and dynamic optimization of a hybrid membrane assisted crystallization process, which uses a membrane to generate supersaturation in a crystallizer. The focus in this chapter is on developing a methodology for optimizing hybrid membrane-separation processes. A setup is presented, capable of performing experiments at high feed pressures, and high flow rates, simulating commercial scale operating conditions. The membrane performance in mem-

brane assisted crystallization of adipic acid is characterized, and a model describing the complete process is developed. This model is used to show the potential of membrane assisted crystallization through a dynamic optimization of the process. In order to readily apply this methodology to experimental data, a polymeric membrane-unit was considered. The proposed optimization approach, however, is generic and can also be applied to hybrid separation processes using zeolite membranes.

The chapters have been written as individual papers and can therefore be read individually without having to read the complete thesis. Because of this, some information is duplicated.

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Tuning the framework polarity in MFI membranes by deboronation: Effect on mass transport

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Abstract The polarity of a zeolite is an important parameter determining the transport and separation properties in zeolite packed beds and membranes. This study focuses on the systematic variation of the zeolite polarity for membrane applications by varying the amount of silanol groups within the framework of the MFI zeolite by de-boronation and consecutive heat treatment from 9 to 4 silanol groups per unit cell. The decrease in the number of silanol groups after heat treatment is confirmed by diffuse reflection infrared Fourier transform (DRIFT) and ^{29}Si Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR). The permeation of pure water through the modified silicalite membranes is insensitive to the number of silanol groups, attributed to a decreased adsorption compensated by an increased diffusivity. The ethanol selectivity in water/ethanol mixtures shows an increase with decreasing amount of silanol groups. Residual boron in the zeolite may react with ethanol and decrease its adsorption capacity. A reduction in flux through the debronated MFI membranes was not observed after ethanol/water permeation.

2.1 Introduction

The polarity of permeating components and of the host framework, strongly determine the host-guest interaction and thus the transport through inorganic membranes [1]. Strong interactions result in strong adsorption; however, this also decreases the mobility of permeating molecules. Figure 2.1 shows the self-diffusivity and the saturation adsorption of water for several zeolites versus the silica to aluminum ratio. Tuning the zeolite polarity would enable the optimization of the trade-off between adsorption and diffusion.

A lower Si/Al ratio corresponds to a more polar zeolite framework, and these types of zeolites are conventionally used for water separation, although recently an apolar DD3R membrane has also been successfully applied to dehydrate solvents based on molecular sieving [2]. The polarity of a zeolite is not only determined by the Si/Al ratio, but also by the cation type, the pore configuration and the amount of silanol groups [3]. Different zeolite types with a similar Si/Al ratio have also been shown to exhibit differences in polarity [4].

At low Si/Al ratio, the intercrystalline transport becomes dominant because the membrane quality decreases [5] and a large portion of the transport will take place through non zeolitic pores [6–8]. It is therefore difficult to conduct a systematic investigation of polarity by changing the Si/Al ratio. Changing the cation type or the pore configuration also changes the pore diameter [9] and therefore the membrane transport. In this chapter we focus on tuning the amount of silanol groups within a zeolite membrane, in order to understand the influence of the zeolite polarity on the permeation properties of the membrane. A systematic variation of silanol groups is feasible since the silanol groups are removed through condensation reactions when exposed to high temperatures (673–873 K) [10, 11]. A stepwise reduction of silanol groups can be accomplished by performing cycles of thermal calcination at increasing temperatures as shown by Masuda *et al.* [11]. Recently, scientists at AIST, Japan, have developed a CDS-1 membrane [12] that is water selective for a water-ethanol mixture when calcined at 673 K ($\alpha_{w,e} = 30$, flux = $0.2 \text{ kg} \cdot \text{m}^{-2} \text{h}^{-1}$), whereas the selectivity inverts after calcination at 873 K and the membrane selectively permeates alcohol ($\alpha_{e,w} = 53$, total flux = $0.5 \text{ kg} \cdot \text{m}^{-2} \text{h}^{-1}$). This effect is attributed to the condensation of silanol groups at temperatures above 823 K [13].

Chemical or photochemical detemplation at mild thermal conditions allows the removal of the template, while preserving the silanol groups present in the zeolite.

Several non-thermal detemplation techniques have been developed using nitric acid and hydrogen peroxide [11], ozone [14], Fenton chemistry [15] or short-wavelength UV-light [16]. These methods are, however, limited to the amount of defects which form during synthesis. A method for introducing significant numbers of silanol groups is by synthesizing boron-containing zeolites, where silanol nests are introduced upon subsequent deboronation, as was done by Hölderich *et al.* for the preparation of MFI catalysts for the Beckmann rearrangement [17, 18]. The silanol nests provide polarity, while not significantly influencing the pore diameter of the zeolite [9]. De Ruiter *et al.* have shown that boron containing MFI crystals can be detemplated without removing the boron from the zeolite framework. Subsequently the boron can easily be removed from the [B]MFI zeolite, leaving silanol nests of four silanol groups around any position where boron had been present [19]. This is illustrated in Figure 2.2. The deboronated MFI zeolite will be indicated by [de-B]MFI. The silanol nests in deboronated zeolites can also be used to incorporate transition metals in the zeolite framework [9, 20]. Up to four boron molecules per unit cell can be isomorphically substituted in an MFI zeolite synthesized in alkaline media [10]. A higher boron content can be obtained when other cations or fluoride media are used [21–23].

In this study, the influence of the polarity of MFI zeolite membranes on mass transport is investigated. This is done by first synthesizing a [B]MFI membrane in alkaline media, which, after deboronation contains an increased number of silanol groups. By cycles of heat treatment, the number of silanol groups will be reduced, and the effect of this treatment on pure water permeation and water/ethanol separation for these membranes is analyzed.

2.2 Experimental

2.2.1 Membrane synthesis and characterization

Boron containing MFI membranes were synthesized on α -alumina supports (Pervatech AKP30, 25 mm diameter, 2 mm thickness). The supports are ultrasonically cleaned and put vertically in a Teflon holder inside a Teflon lined autoclave. The synthesis mixture for the preparation of [B]MFI has the molar composition of 4.44 TPAOH (1.0 M solution, Aldrich), 19.46 SiO_2 (Ludox AS40, Aldrich), 1.55 B(OH)_3 (Aldrich) and 500 H_2O . The mixture is aged for 5 h at room temperature and then put

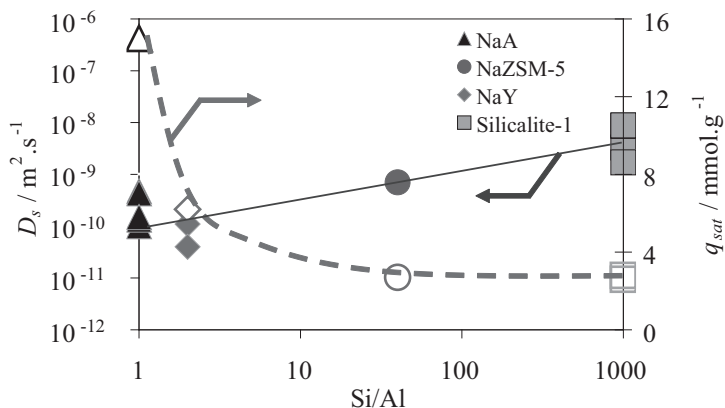


Figure 2.1: Self diffusivity (D_s , closed symbols), and saturation loading (q_{sat} , open symbols) of water in zeolites as a function of Si/Al ratio (compiled from literature, both experimental and computational data [24–33]). The lines only indicate the trend.

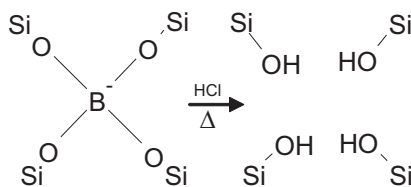


Figure 2.2: Deboronation, leaving a silanol nest consisting of four silanol groups.

into the autoclave. The synthesis is carried out at 443 K for 16 - 24 h [34]. After the synthesis the membrane is rinsed with water and dried over night at 373 K. Because of the instability of boron during calcination in the presence of water and/or oxygen, the calcination is performed under a dry ammonia atmosphere. The membranes are placed in a quartz tube and heated to 723 K for 0.5 h at a heating rate of $1\text{ K}\cdot\text{min}^{-1}$. A flow of $15\text{ ml}\cdot\text{min}^{-1}$ anhydrous ammonia is continuously fed to the quartz tube. During this calcination step the organic template is degraded, resulting in a brown color of the zeolite membrane. The presence of sodium ions during calcination has shown to stabilize the framework boron [35], therefore the membranes are subsequently ion exchanged using 1.0 M aqueous sodium bromide solution during 24 h. After ion exchange, the membranes are calcined in air at 823 K, removing the organic residues. By applying this calcination procedure, the loss of framework boron is minimized

[19]. Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis (PerkinElmer Optima 5300 DV) was used to analyse the chemical composition of the residual zeolite powder collected from the autoclave after membrane synthesis. The ICP-OES analysis shows the synthesized [B]MFI zeolite contains ~ 2 boron atoms per unit-cell.

After removing the template from the zeolite membrane, the framework boron can be removed by treating the zeolite with a HCl solution ($\text{pH} = 1.1$) at 373 K under reflux for 24 h. Subsequently the membranes are rinsed with a diluted aqueous NaOH solution ($\text{pH} = 11$) to remove the extra framework boron. X-ray diffraction (XRD) analysis (Bruker-AXS D5005) confirms the MFI topology before and after calcination and deboronation. Only membranes with no nitrogen permeation before calcination were used for further processing. Two membranes have been successfully synthesized, and have undergone the same treatment and testing. The results of both membranes are presented in this study. Apart from the membranes, also zeolite powder is synthesized using the same recipe and treatment. Figure 2.3 shows scanning electron microscope (SEM) (Philips XL20) micrographs of the [de-B]MFI membrane and the zeolite powder used for the analysis.

To stepwise remove part of the introduced silanol groups, the zeolite is exposed to high temperatures. This is done for a period of 2 h isothermally, using a heating/cooling rate of $1 \text{ K} \cdot \text{min}^{-1}$ to prevent crack formation in the membrane during calcination. ^{29}Si Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) (Bruker Avance 400) is used to quantify the amount of silanol groups. The NMR measurements were conducted using a 4 mm zirconium holder at 298 K with a frequency of 79.449 MHz, a relaxation delay of 15 s and a spinning frequency of 11 kHz. The chemical shifts were referenced with respect to tetramethylsilane (TMS). For the ^{11}B MAS NMR measurements, the chemical shift was referenced with respect to a 1% solution of boric acid (H_3BO_3) at 298 K. A frequency of 128 MHz, a spectral window of 25062.65 Hz and an acquisition time of 0.05 s was used with a delay of 1 s and a spinning frequency of 11 kHz. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) (Thermo Nicolet, Nexus) using KBr as background was used to analyze the framework composition. The DRIFT measurements were conducted in ambient air without purge gas or heat treatment. Water adsorption tests were conducted (Quantachrome Autosorb-6B) to characterize the hydrophilicity of the zeolite. Also ethanol and nitrogen adsorption were measured to characterize the zeolite. Prior to the gas-adsorption measurements, the samples were dried in vacuum at 573 K in

order to remove present moisture and other volatile components (the weight of the sample after drying is used in the calculations). For the NMR and DRIFT analysis and the nitrogen adsorption measurements, the zeolite powder was used.

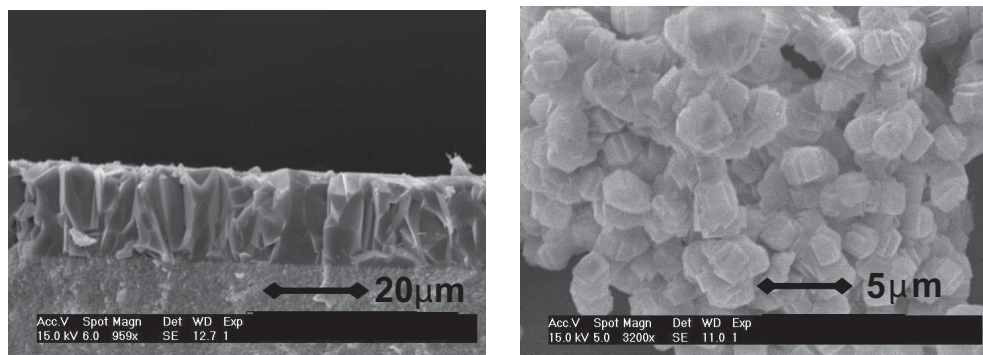


Figure 2.3: SEM micrograph of the cross section of a [de-B]MFI membrane and of [B]MFI zeolite powder synthesized using 4.44 TPAOH: 19.46 SiO₂: 1.55 B(OH)₃: 500 H₂O at 443 K for 16 h.

2.2.2 Equipment

Water permeation is measured in a setup as depicted in Figure 2.4. The flux through the membrane is measured using the rate-of-rise technique [36]. The valve V2 is thereby temporarily closed and from monitoring the pressure increase at PI2 along with temperature at TR1 one gets the permeating flux. Because of the low pressure at the permeate side, the ideal gas law is used to correlate the pressure increase to the molar flow rate. The membrane module and the control volume for the flux measurement are placed inside an oven. The feed pressure can be increased up to 20 bar using the back pressure regulator BPR1. The permeating water flow is condensed in cold trap CT1 using liquid nitrogen. The permeate tubing outside the oven is electrically traced to prevent condensation before the cold traps. The permeate pressure during experiments can be controlled using needle valve V7, and is kept at 10 to 30 mbar.

2.3 Experimental Results and Discussion

2.3.1 Tuning the polarity

The deboronation step leaves silanol nests, consisting of four Si-OH groups, at the location of the framework boron, resulting in an increase in framework polarity. Ap-

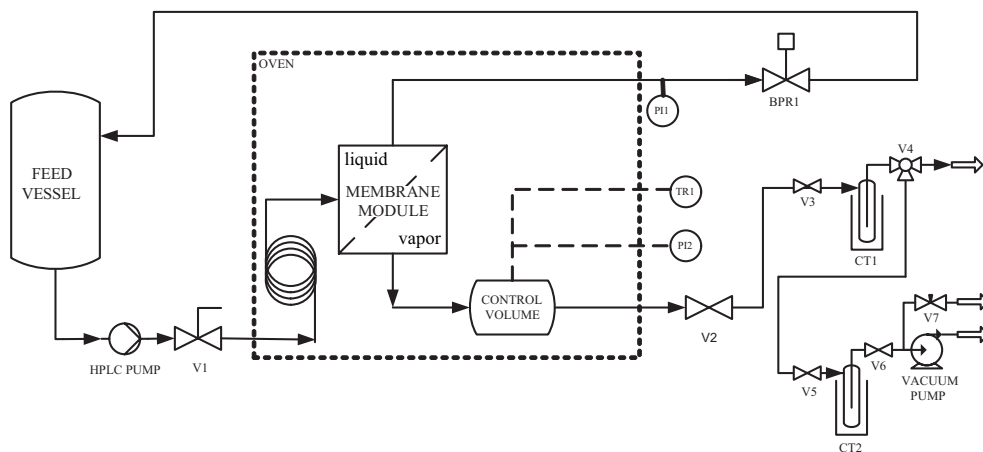


Figure 2.4: Schematic representation of the pervaporation setup

proximately 8 silanol groups are initially present per unit-cell. ^{29}Si -NMR and DRIFT analysis, depicted in Figures 2.5 and 2.6, show the presence of the Si-OH bonds. The DRIFT spectra indicate the decrease of silanol groups after heat treatment at 673 K and 873 K. The IR-bands indicating OH groups ($3200 - 3700 \text{ cm}^{-1}$), also including water, as well as the IR-band associated with silanol nests (950 cm^{-1} [19]) clearly show a decreased absorbance after the heat treatment.

To determine the influence of the framework polarity, i.e. the decreased silanol concentration, on the transport of water through the membrane, water permeation is measured under pervaporation conditions. The deboronated membranes are subsequently calcined in several steps with increasing temperature cycles in order to progressively remove an increasing part of the silanol groups. The permeation of water is determined after each step. This protocol of reducing the amount of silanol groups in steps ensures a truly systematic way of characterizing the influence of framework polarity, because the effect of decreasing numbers of silanol groups is singled out, while the membrane thickness, amount of defects and pore size remain constant [9]. The Q^3 peak in the ^{29}Si -NMR plot ($\delta = -103 \text{ ppm}$) is ascribed to the $(\text{Si-OH})(\text{Si-O})_3$ groups, while the Q^4 signal ($\delta = -113 \text{ ppm}$) is ascribed to the $\text{Si}(\text{Si-O})_4$ units [37]. The Q^3/Q^4 ratio of the ^{29}Si -NMR plot equals the ratio of $(\text{Si-O})/(\text{Si-OH})$ units. The right shoulder of the Q^4 peak increases with increasing Q^3 intensity. The Q^4/Q^3 ratio of a sample calcined at 1073 K which was exposed to water at 363 K for 24 h did not change after this treatment, confirming that the structure and the silanol

groups are stable under the experimental pervaporation conditions. The MFI structure contains 96 T-atoms per unit cell [38], so the number of (Si-OH) groups equals $96/(Q^4/Q^3 + 1)$. Because of the small error, we neglect the effect of the reduction in T-atoms by deboronation. The Q^4/Q^3 ratios and the number of silanol groups per unit cell, calculated from that number are shown in Table 2.1.

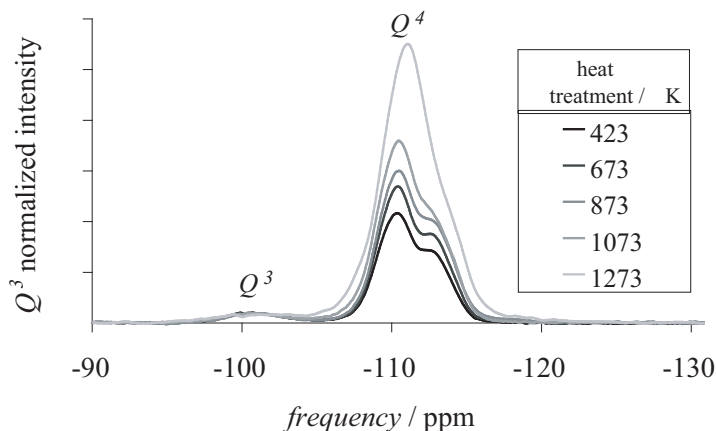


Figure 2.5: ^{29}Si -NMR spectra of [de-B]MFI zeolite powder, after heat treatment at 423 K to 1273 K. The Q^3 peaks indicate the silanol groups, while the Q^4 is assigned to the $\text{Si}(\text{Si-O})_4$ units. The spectra are normalized by Q^3 , so that a lower Q^4 peak reflects a higher number of silanol groups.

Table 2.1: Q^4/Q^3 ratios and the number of silanol groups per unit cell for [de-B]MFI zeolite powder after heat treatment at various temperatures.

Heat treatment /K	Q^4/Q^3	Si-OH /u.c.
423	9.8	8.9
673	12.7	7.0
873	16.3	5.5
1073	15.8	5.7
1273	21.9	4.2

The water adsorption isotherms on the powder samples that have undergone heat treatment is measured at 273 K, 303 K and 323 K show a weak dependency on the temperature of the heat treatment (Figure 2.7). Figure 2.8 shows a stepwise decrease of the water loading of 16% after calcination at 700 K, which is the temperature at which silanol groups start to condense. Hunger *et al.* found that the water adsorption capacity decreased proportionally with the number of silanol groups [37]. The

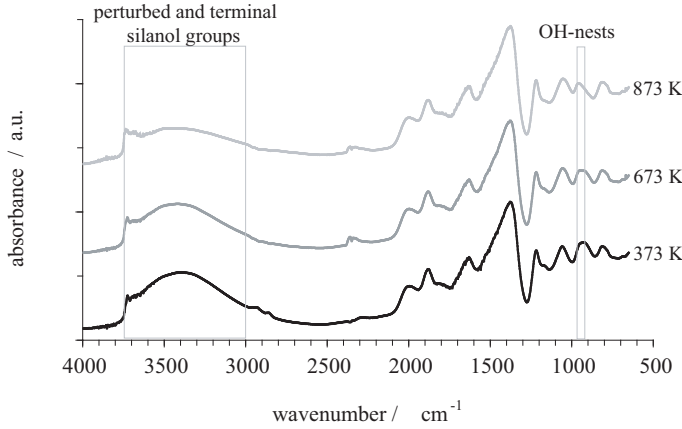


Figure 2.6: DRIFT spectra of [de-B]MFI zeolite powder after in-situ heat treatment at 373 K, 673 K and 873K

measured isotherms can be described by a single site Langmuir model

$$q_w = q_{w,sat} \frac{K_w f_w}{1 + K_w f_w} \quad (2.1)$$

where q_w is the water loading in the zeolite, q_w^{sat} is the saturation loading, and f_w denotes the water fugacity. The temperature dependency of the Langmuir adsorption parameter, K_w , can be expressed using the adsorption enthalpy by

$$K_w = K_{0,w} \exp\left(\frac{-\Delta_{ads} H_w}{RT}\right) \quad (2.2)$$

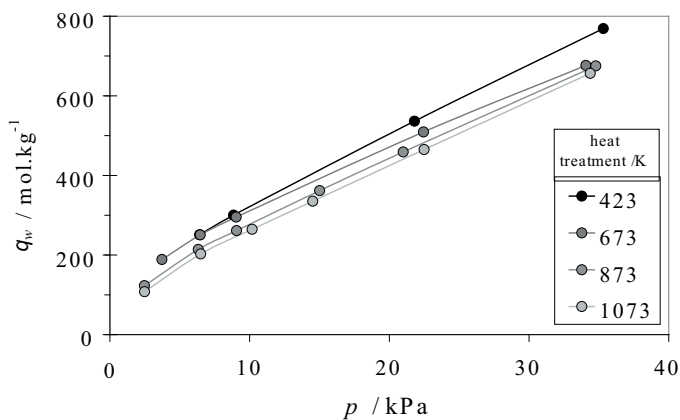
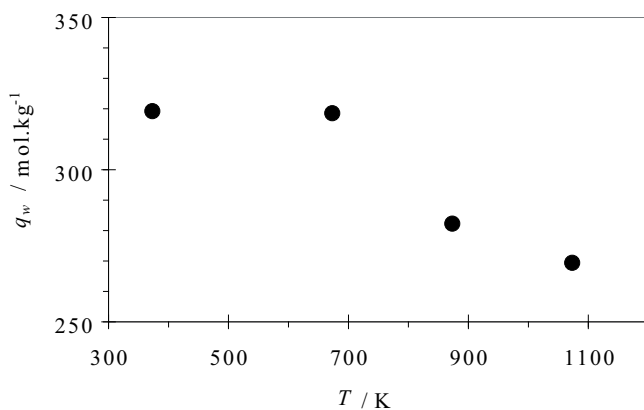
The fitted adsorption parameters for the sample treated at 423 K and 1073 K are listed in Table 2.2. The lower values of the adsorption parameter and saturation loading confirm the regressed decrease in adsorption at increasing temperature of heat treatment, whereas the heat of adsorption stays fairly constant. The capacity has decreased by 40%, which is reasonably in-line with the $\sim 50\%$ decrease in silanol groups determined from the NMR results, and confirms the conclusion of Hunger et al. [37]

2.3.2 Pure water permeation

To show reproducibility, the permeation of pure water through two [de-B]MFI membranes were measured at 363 K. The membranes were synthesized according to the

Table 2.2: Langmuir adsorption parameters of water adsorbed on [de-B]MFI powder after heat treatment at 423 K and 1073 K.

T_c/K	$K_{Qw}/10^{-11}\text{Pa}^{-1}$	$q_w^{sat}/\text{mol}\cdot\text{kg}^{-1}$	$\Delta_{ads}H_w/\text{kJ}\cdot\text{mol}^{-1}$
423	3.3	3.1	-34
1073	2.1	1.9	-36

**Figure 2.7:** Water adsorption isotherms on [de-B]MFI measured at 323 K. The [de-B]MFI material has undergone heat treatment at different maximum temperatures**Figure 2.8:** Water loading (q_w) measured at 10 kPa and 323 K versus calcination temperature

same recipe and been exposed to the same heat treatment. The water flux through both membranes revealed to be essentially insensitive to the feed pressure (up to 6 bar), indicating a low contribution of viscous flow through macroscopic defects [39, 40]. The treatment with the diluted NaOH solution does not seem to decrease the membrane quality. The amount of silanol groups is stepwise decreased by subjecting the [de-B]MFI membranes to a heat treatment of respectively 423 K, 673 K, 873 K, 1073 K and 1273 K. After each heat treatment the water permeation is measured. The dependency of the flux on absolute pressure is also measured after each calcination step to ensure that no macroscopic defects have been formed during the heat treatment. The permeation of water is found to be insensitive to the heat treatment (Figures 2.9 and 2.10).

A simple model for single component permeation, assuming low adsorption, is [41]

$$N_w = -\rho_w q_w^{sat} K_w \frac{\bar{D}_w}{\delta} \Delta f_w \quad (2.3)$$

where N_w is the water flux and $\bar{D}_w$ is the Maxwell-Stefan diffusivity. From this equation it is evident that the Henry adsorption parameter, $q_w^{sat} K_w$, and the diffusivity both have a proportional impact on the flux. Since the water adsorption decreased with heat treatment (Figures 2.7 and 2.8) and the flux has shown to remain constant (Figure 2.9 and 2.10), the diffusivity must compensate for the decrease in adsorption and thus must have increased with heat treatment.

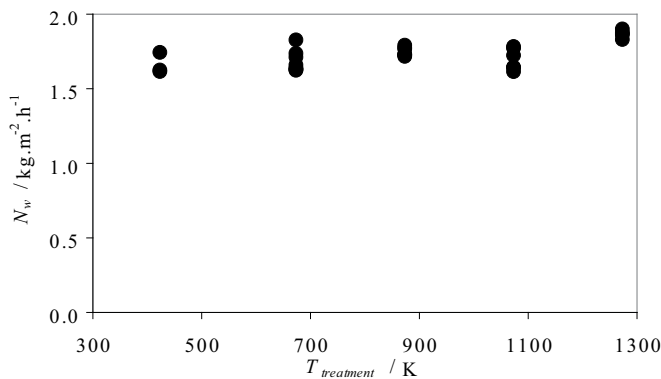


Figure 2.9: Pure water flux through membrane 1 measured at 363 K and atmospheric pressure for a [de-B]MFI membrane that has undergone heat treatment at various temperatures.

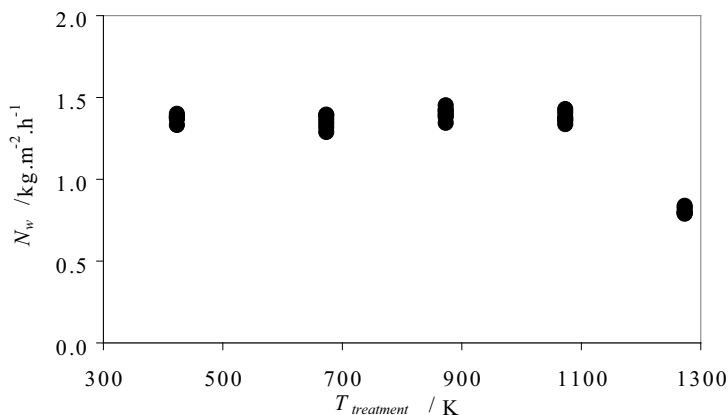


Figure 2.10: Pure water flux through membrane 2 measured at 363 K and atmospheric pressure for a [de-B]MFI membrane that has undergone heat treatment at various temperatures thereby varying the number of silanol groups.

2.3.3 Water/ethanol permeation

The flux and separation factor of water/ethanol mixtures (water molar fraction in the feed, $x_w = 0.5$) has been measured as a function of the calcination temperature. The low ethanol selectivity and total flux both increase with calcination temperature, confirming the membrane becomes more hydrophobic (Figure 2.11). The mixture flux is an order of magnitude lower than that of pure water. Using normal silicalite-1 membranes, separation factors of 5 and fluxes of $0.05 \text{ kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ have been measured at this feed composition, while in this work the measured flux increases from 0.045 to $0.185 \text{ kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$.

Ethanol adsorption experiments have been conducted using the samples treated at 423 K and at 873 K. The adsorption showed a type 1 behavior with high uptake at low pressures. Before each adsorption measurement, the sample was degassed at 573 K under vacuum. After each ethanol adsorption/desorption cycle on the sample calcined at 423 K, the adsorption capacity appeared to decrease (Figure 2.12). The sample calcined at 873 K showed similar behavior. The decreased adsorption capacity was also observed for nitrogen adsorption experiments at 77 K. At moderate and high relative pressures, hardly any nitrogen uptake is observed suggesting the absence of a significant contribution of both meso- and small macropores. A capacity decrease was also observed when the sample was not heated during degassing, but kept under vacuum at room temperature for 48 h.

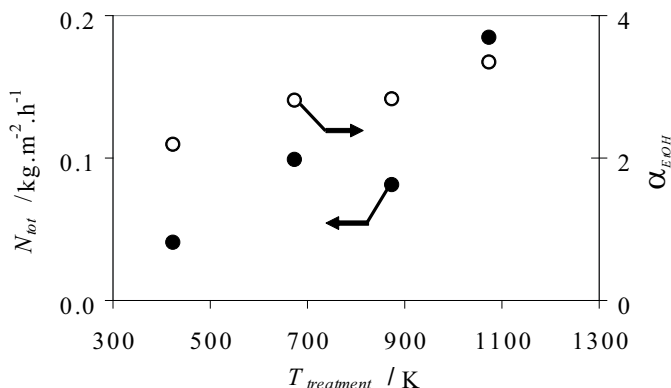


Figure 2.11: Total flux and ethanol separation factor of a water/ethanol mixture ($x_w=0.5$) measured under pervaporation conditions at 348 K and atmospheric pressure for a [de-B]MFI membrane that has undergone heat treatment at various temperatures thereby varying the number of silanol groups.

DRIFT analysis of the powder sample after the ethanol adsorption shows an increased absorbance at the wavenumbers assigned to the CH-stretching vibrations ($2800\text{--}3000\text{ cm}^{-1}$). By increasing the temperature these absorbances diminish and, at 723 K, the absorbances have disappeared (Figure 2.13). After heating the sample to 723 K, also the adsorption capacity is restored.

^{11}B MAS NMR of the sample after ethanol adsorption revealed a peak at -22.9 ppm , indicating that some tetragonally coordinated boron was still present in the framework.

2.4 Discussion

The ^{29}Si MAS NMR data (Figure 2.5) and the DRIFT spectra (Figure 2.6) show that the number of silanol groups within the zeolite framework is increased by deboronation and are tunable by heat treatment (Table 2.1). The adsorption measurements show a slight decrease in the water uptake after heat treatment (Figure 2.7 and 2.8).

From Figure 2.13 it is obvious that increasing the temperature decreases the absorbance at 950 cm^{-1} , corresponding to silanol nests. Comparing the absorbance before heat treatment (Figure 2.13a) with the one after heat treatment (Figure 2.13f), a clear decrease in silanol nests is observed, as well as the absorbance decrease in the $3200\text{--}3700\text{ cm}^{-1}$. The isolated silanol vibrations ($\sim 3740\text{ cm}^{-1}$ [42]) are much

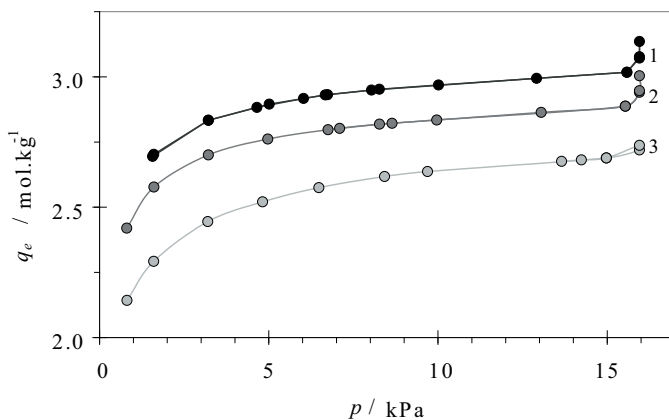


Figure 2.12: Ethanol adsorption on [de-B]MFI treated at 423 K after 3 adsorption/desorption cycles measured at 273 K.

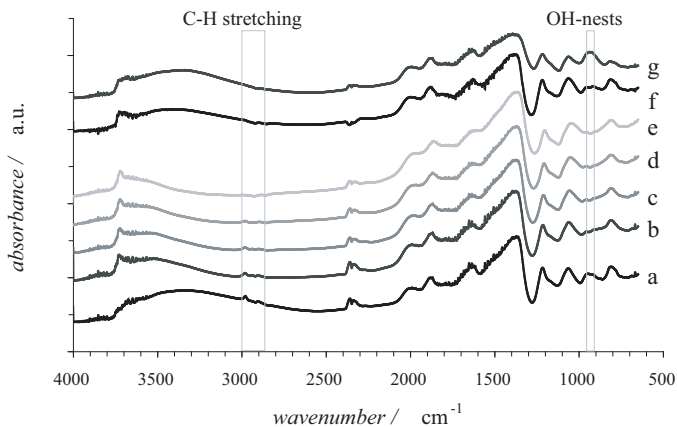


Figure 2.13: DRIFT spectra of [de-B]MFI after ethanol adsorption measured at 298 K (a), 423 K (b), 523 K (c), 623 K (d), 723 K (e), and again at 298 K after cooling down from 723 K (f) and a sample before ethanol adsorption, measured at 298 K (g)

better visible after heat treatment. The decrease in silanol groups due to condensation is irreversible, as is concluded from the unchanged Q^4/Q^3 ratio in the NMR measurements after water exposure at 363 K.

Despite the decreased number of silanol groups, the pure water permeation is independent on the post synthesis heat treatment. The two synthesized membranes yield similar results, showing the reproducibility of the applied method. The insensitivity of pure water permeation to heat treatment also holds for normal silicalite-1 membranes [43]. The measured fluxes are, however, a factor two up to four times higher than for normal silicalite-1 membranes [43, 44]. The insensitivity could be explained by the trade-off between adsorption and diffusion, as the decreased water adsorption is compensated by an increase in water diffusivity (Equation 2.3). Since the presence of silanol nests does not significantly alter the pore diameter [9], steric hindrance due to silanol groups is not expected to affect mass transport.

The decrease in the water saturation loading (fitted from the isotherms in Figure 2.7) by 40%, is reasonably in-line with the $\sim 50\%$ decrease in silanol groups determined from the ^{29}Si MAS NMR results (Figure 2.5), and confirms the conclusion of Hunger et al. [37]

The water/ethanol selectivity confirms the increased hydrophobicity with heat treatment (Figure 2.11). Despite the increased number of silanol nests, the membrane is still selective for ethanol. So an inversed selectivity, as was observed for CDS-1 [13], is not obtained for [de-B]MFI. The ethanol separation factor increases with 50% from 2.2 to 3.3 after heat treatment up to 1273 K, but does not fully reach the levels of pure silicalite-1 membranes. The initial boron content of the zeolite can further be increased up to six boron per unit cell, using a synthesis in fluoride media [22, 23]. Combining the deboronation with a non-thermal calcination procedure can further increase the number of silanol groups to a level where the membrane is selective for water [11, 45].

Ethanol appears to bind strongly to the [de-B]MFI zeolite. Although the sample is degassed at 573 K under vacuum before measuring, the ethanol uptake decreases after each adsorption experiment (Figure 2.12). From the DRIFT spectra of the [de-B]MFI samples after ethanol adsorption, hydrocarbon vibrations are observed, indicating residual carbonaceous material (Figure 2.13a). A similar capacity decrease was observed without heating and no hysteresis was observed during the uptake experiments, indicating that no reaction or pore blockage occurs during the ethanol adsorption experiments. It appears a reaction takes place after the adsorp-

tion measurement or during degassing. Since the loading of ethanol is low after the experiment, this could explain the consecutive decrease in capacity. Ether formation of ethanol with terminal silanol groups in zeolites has been observed [46], but seems unlikely at this temperature [47]. Moreover, the reaction of ethanol with the surface silanol groups in a NaY type zeolite, showed to be irreversible [46], while here, the material is regenerated after heat treatment at 723 K. More probable, the ethanol could have formed an ethyl borate with residual boron in the framework [48]. The tetragonal coordination of the boron, revealed by NMR, excludes the reaction of ethanol with boric acid yielding triethyl borate, which is trigonally coordinated. This could result in blockage of the pores and explain the reduced adsorption capacity after each consecutive adsorption/desorption cycle. These observations emphasize that care must be taken to completely remove the boron from the sample. During the water/ethanol permeation experiments, however, no systematic decrease in flux was observed. This could indicate a more complete deboronation of the membranes compared to the zeolite powder.

2.5 Conclusions

The influence of variable numbers of silanol groups introduced by deboronation within an MFI zeolite membrane on the permeance of water has been investigated. Tuning the polarity by means of the silanol groups allows for a systematic investigation of the polarity, since the amount of silanol groups can stepwise be changed for a single membrane. [B]MFI membranes containing 2 B/u.c. have been synthesized and deboronated, leaving two silanol nests of four silanol groups per unit cell. ^{29}Si -NMR and DRIFT analysis confirm the amount of silanol groups is tunable by heat treatment between 423 K and 1273 K. However, after heat treatment at 1273 K there are still 4 silanol groups present per unit cell, which could be non-condensable, surface silanol groups. Although ICP analysis confirms the deboronation, ^{11}B MAS NMR analysis shows there is still boron present in the framework of the powder sample. The measured pure water fluxes of the [de-B]MFI membranes are higher than through normal silicalite-1. However, no effect of the variation in the amount of silanol groups on the pure water permeation flux is observed. The water adsorption decreases with increasing calcination temperature, meaning the diffusivity increases accordingly, keeping the flux constant.

The selectivity shows more sensitivity for changes in the number of silanol groups.

The total water/ethanol flux and ethanol separation factor increases with decreasing number of silanol groups. The total flux and ethanol separation factor after treatment at 1273 K are comparable to values measured for silicalite-1 membranes. An inverse in water/ethanol selectivity could not be obtained.

Residual boron in the framework may react with the ethanol and reduce the adsorption capacity of the zeolite. The membrane samples were well deboronated, since no irreversible reduction in flux was observed after ethanol permeation through the [de-B]MFI membranes.

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Performance and stability of multi-channel MFI zeolite membranes detemplated by calcination and ozonation in ethanol/water pervaporation

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Abstract Two multi-channel defect-free high-silica MFI membranes have been tested for the removal of ethanol from a 7 and 3 mol% aqueous solution under pervaporation conditions. One membrane is detemplated by calcination at 773 K, and one is ozonicated at 473 K. The flux and ethanol separation factor were determined at 348 K, 360 K, and 373 K. The ethanol separation factors of both membranes were similar and ranged from ~ 20 at 373 K to ~ 40 at 348 K. The ethanol and water fluxes through both membranes in this temperature range are proportional to the component fugacity difference over the membranes. The calcined membrane showed an 80% higher flux than the ozonicated membrane, showing the ozonation could not completely remove the template. After the ozonicated membrane was calcined at 723 K, the flux increased to a similar value as the initially calcined membrane, while the separation factor did not change. Both membranes showed an increase in flux by a factor of two after a subsequent calcination at 823 K, also without affecting the separation factor. The high calcination temperature required for complete detemplation indicates the presence of aluminum in the zeolite framework of the membrane. The membrane stability was monitored for 40 h and 177 h of operation for the initially calcined and ozonicated membrane, respectively. At 348 K the membranes showed stable performance, but the stability of the membranes at elevated temperatures is limited, showing a decrease in both flux and selectivity during operation at 373 K. The effect of the exposure to a water/ethanol mixture on the zeolite membrane is investigated by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, magic angle spinning nuclear magnetic resonance (MAS NMR), Thermogravimetric analysis (TGA), and nitrogen adsorption experiments using several MFI-type zeolite powders. The most plausible mechanism causing the instability of the membrane is ethoxy formation of the ethanol with the silanol groups and Brønsted acid sites in the zeolite framework combined with formation of hydrophilic extra framework pathways by hydrolysis.

3.1 Introduction

The use of renewable energy sources is becoming a necessity and sustainability is the key feature in novel process and product design. The depletion of raw materials gives rise to the utilization of alternative, renewable fuels. Bio-alcohols are one the most used non-fossil alternative transport fuel in the world. Brazil's decision to produce fuel alcohol from sugar cane, and the use of bio-ethyl-tert-butylether (bio-ETBE) in the U.S. as an octane enhancer of gasoline, replacing the more environmentally unfriendly methyl-tert-butylether (MTBE), have made transportation bio-alcohol a relatively well-developed industry [1]. Bio-alcohols can be produced by fermenting bio-mass, such as sugar cane and beets, corn and wheat. Although several alcohols can be produced by fermentation, most of the produced bio-alcohol is ethanol. Since the required water content for ethanol as bio-fuel or fuel additive is below 1.0 mass% in the U.S. and below 0.24 mass% in the E.U. [2], ethanol enrichment after the fermentation process is required. This can be done by means of distillation, but also NaA (LTA) membranes are already being used on a commercial scale for dehydration of bio-alcohols [3]. The production of ethanol by fermentation is usually operated in a batch system, and the inhibition by ethanol on the fermentation process limits the maximum attainable concentration in the fermentor [4]. Selective removal of the ethanol from the fermentor would increase the alcohol production, and can be used to design a continuous process. Organo-selective membranes can be used to selectively remove ethanol from the fermentation broth. Polymeric, ceramic and liquid membranes are being investigated for this purpose [5, 6]. Silicalite-1 zeolite membranes show good fluxes and selectivities for ethanol separation from aqueous solutions [4, 7]. Table 3.1 shows an overview of fluxes and ethanol separation factors, $\alpha_{e,w}$, for ethanol enrichment from aqueous solutions.

Using ozone allows the detemplation of zeolites to be carried out at temperatures far below conventional calcination temperatures [15]. This method reduces the change of crack formation due to thermal stresses. Because the zeolite is not heated above 473 K, the silanol groups in the zeolite framework are preserved. ^{29}Si MAS NMR shows a higher number of silanol groups of ozonicated silicalite-1 compared to calcined silicalite-1, meaning ozonation yields a more polar zeolite framework [16].

Zeolites are generally more chemically and thermally robust than polymers [17] and all-silica zeolites are more chemically and thermally stable than aluminum con-

Table 3.1: Fluxes and ethanol separation factors in ethanol enrichment by different types of zeolite membranes.

Zeolite membrane	T_{feed} / K	feed ethanol conc. / wt%	$\alpha_{e,w}$	flux / $\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$	ref.
Silicalite-1	303	5	41	0.1 - 0.5	[4]
Silicalite-1	303	5	58	0.76	[8]
Silicalite-1	343	9.4	1.3	2.1	[9]
Silicalite-1	303	11.8	63	0.60	[10]
Silicalite-1	303	10	100	0.56	[11]
Silicalite-1	305	9.7	11.5	0.10	[12]
Silicalite-1	298	5	10	0.07	[13]
[Al]ZSM-5	298	5	9.4	0.06	[13]
[Fe]ZSM-5	298	5	3.4	0.06	[13]
[B]ZSM-5	298	5	2.1	0.05	[13]
[Ge]ZSM-5	298	5	29	0.11	[13]
[Ge]ZSM-5	303	5	47	0.223	[14]

taining zeolites [18]. Nevertheless, it is shown that aqueous solutions can eventually deteriorate zeolite membranes [19, 20]. To determine the stability of this silicalite-1 membrane at elevated temperatures in aqueous ethanol solutions, the flux and separation factor are examined for over 177 h of operation.

3.2 Experimental methods

The membrane used is an all-silica multi-channel MFI zeolite membrane (NGK Insulators, Japan), consisting of a zeolite layer of 10 to 15 μm coated on the inside of the channel walls of an α -alumina asymmetric monolithic support (length of 80 mm and 30 mm outer diameter) with 37 channels of 3 mm in diameter giving a total membrane surface area of $2.79 \times 10^{-4} \text{ m}^2$ (Figure 3.1). The outer ends of the membrane are glazed and the membrane is mounted in a module and sealed with Kalrez o-rings.

In this work we investigate the ethanol enrichment from an aqueous solution by a multi-channel MFI zeolite membrane (NGK Insulators, Japan) under pervaporation conditions. Two membranes have been tested of which one is detemplated by means of calcination (M1), while the other membrane has been initially detemplated by means of ozonation (M2).



Figure 3.1: Multi-channel monolithic high-silica MFI type zeolite membrane and module.

3.2.1 Template removal

3.2.1.1 Calcination

The calcination of membrane M1 was done by NGK Insulators in air at 773 K for 4 h and a heating and cooling rate below $100 \text{ K} \cdot \text{h}^{-1}$. The ozonicated membrane, M2, was calcined in a static air programmable furnace (Carbolite CSF1100) at 723 K for 4 h with a heating and cooling rate of $30 \text{ K} \cdot \text{h}^{-1}$ after the separation performance was determined.

3.2.1.2 Ozonation

The detemplation of the zeolite membrane by ozonation is carried out in a stainless steel membrane module, sealed with Kalrez o-rings (Figure 3.1). The module is placed in a programmable oven (Binder FP53) which was heated to 473 K using a heating/cooling rate of $60 \text{ K} \cdot \text{h}^{-1}$. Dry oxygen from a gas cylinder is passed through a Corona discharge ozone generator (A2Z Ozone Systems, SOZ-16GLAB) (Figure 3.2). The inlet pressure of oxygen at the ozone generator is set at 2 bar using a pressure reducer (RV). The needle valve before the ozone detector (NV) can be used to increase the system pressure. Using a mass flow controller (MFC1) (Bronkhorst Hi-Tech B.V.), the zeolite sample is exposed to a flow of $12 \times 10^{-3} \text{ m}^3 \cdot \text{h}^{-1}$ (STP) dry oxygen containing $80 \text{ g} \cdot \text{m}^{-3}$ (STP) of ozone, where standard conditions are 298 K and 1.01 bar. The second mass flow controller (MFC2) can be used to dilute the ozone stream with pure oxygen. The checkvalves (CV1 and CV2) ensure no back flow of ozone to the mass flow controllers. The ozone concentration at the outlet of

the oven is monitored using an ozone detector (Lenntech, BMT 964) after which it is sent through a manganese dioxide/copper oxide catalytic ozone destructor. The setup can be shut down by closing a solenoid valve (SV) and the ozone generator. Before ozonation, the system is flushed with pure oxygen at 473 K to ensure a water-free atmosphere.

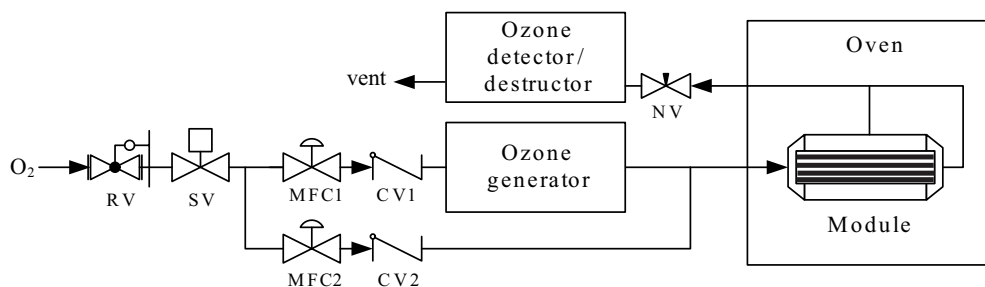


Figure 3.2: Schematic illustration of ozonation setup. RV: pressure reducer, SV: solenoid valve, MFC: mass flow controller, CV: check valve, NV: needle valve.

3.2.2 Pervaporation experiments

Permeation measurements have been conducted under pervaporation conditions using aqueous ethanol mixtures consisting of demineralized water and 100% technical grade ethanol. The permeation experiments were conducted using the setup shown in Figure 3.3. The setup consists of a feed vessel, heated by a thermostatic bath, which controls the temperature at the membrane outlet (TIC1). The liquid feed is pumped around between the feed vessel and the membrane module and the pressure in the module (PI1) can be adjusted using a valve (V1). The permeate is condensed using a cold trap, which is cooled using liquid nitrogen. The tubing on the permeate side is electrically traced to prevent condensation before the cold trap. The inerts are removed using a vacuum pump. The setup can be heated to temperatures up to 423 K and can be pressurized up to 16 bar using nitrogen as a pressurizing gas. Due to the heat generated by the pump, the minimum temperature at which experiments can be conducted is 348 K.

The flux is measured by determining the weight increase in time of the cold trap. The weight is measured every 10-30 min, depending on the flux. When the flux is stabilized the data is collected. To prevent the depletion of the permeating component a dosage pump is used to add the preferentially permeating component back into the

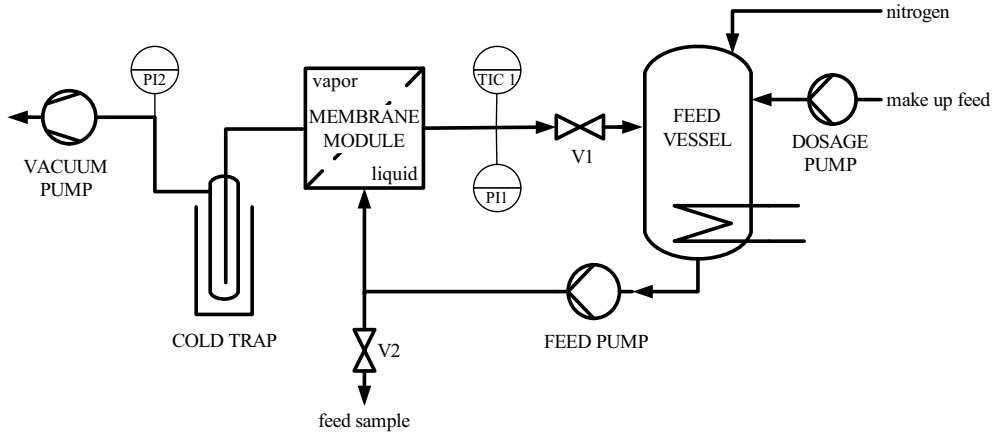


Figure 3.3: Schematic illustration of the pervaporation setup

feed vessel.

In pervaporation processes the membrane performance is often characterized using the permeance, Π_i , comprising from both adsorption and diffusion effects and relating the flux, N_i , to the fugacity difference over the membrane, Δf_i [21, 22]. Under pervaporation conditions, the Poynting factor can be neglected and the fugacity coefficients are assumed to be unity. This results in [22]

$$N_i = \Pi_i \Delta f_i = \Pi_i (x_i \gamma_i P_i^0 - y_i P_{perm}) \quad (3.1)$$

The temperature dependence of the permeance can be characterized by an apparent activation energy, E_{app} , and a pre-exponential factor, $\Pi_{i,0}$. The apparent activation energy comprises a contribution of both the activation energy for diffusion as well as the enthalpy of adsorption [23].

$$\Pi_i = \Pi_{i,0} \exp \left(\frac{-E_{app}}{RT} \right) \quad (3.2)$$

The selectivity of the membrane is characterized by the separation factor, which is defined as

$$\alpha_{i,j} = \frac{y_i x_j}{x_i y_j} \quad (3.3)$$

As the driving force is insensitive to the absolute pressure (Poynting factor is negligible), the flux dependency on the absolute pressure can be used to assess the membrane integrity. When macroscopic defects are present, a part of the flux across

the membrane will be transported by non-selective viscous flow, which correlates linearly with the pressure [24]. To ensure there is no contribution of macroscopic defects, the pressure dependency of the flux and separation factor is measured. This is done by increasing the pressure in two steps from ~ 100 to ~ 1000 kPa using nitrogen as pressurizing gas, after which the pressure is again reduced to the ~ 100 kPa to verify the membrane stability during the pressure test.

The composition of the feed and permeate is determined by means of densimetry (Anton Paar DMA5000). The organic impurities in the feed are analyzed by gas chromatographic (GC) analysis (Chrompack CP9001, with an FID detector and a CP-Sil-SCB 25 m, 0.53 mm column with a 5 μm film thickness, using N_2 as sweep gas), using a temperature program heating the column from 323 K to 523 K with a heating rate of $20 \text{ K}\cdot\text{min}^{-1}$.

The asymmetric support of the membrane with its complex topology imposes a mass transport resistance, especially for the inner channels. Support resistance can have a profound effect on the membrane performance [25]. However, DD3R type membranes have shown similar permeances for multi-channeled [26] and single tube supports [18]. Also, because the porosity characteristics of the support layers were not available, the permeate pressure is not corrected for the support resistance in this study. Thereby we assume that most of the mass transport resistance is in the zeolite layer [17].

3.2.3 Analysis of zeolite powders

To determine the effect of exposure to the feed mixture on the zeolite membrane several analytical techniques have been applied. Since the membrane can not be non-destructively analyzed directly, calcined and ozonicated silicalite-1 powder and calcined ZSM-5 powder (HZSM-5 with a silica to alumina ratio, $\text{Si}/\text{Al}=50$), which were synthesized according to recipes from literature [27, 28], were used in the analysis. The crystal morphology of the silicalite-1 crystals was examined by Scanning Electron Microscopy (SEM) (Philips XL20). The aluminum content of the ZSM-5 powder was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) analysis (PerkinElmer Optima 5300 DV). The ZSM-5 powder serves to investigate the possible influence of incorporated aluminum from the support material into the zeolite framework.

To simulate the experimental conditions the powder samples were put in a Teflon lined autoclave, containing a water/ethanol mixture with the same composition as

the feed of the pervaporation experiments (7 mol% ethanol), and put in a convection oven at 373 K for 24 h. The samples were subsequently filtered and dried in air for 24 h at 373 K. To determine the effect of heat treatment after the exposure to the water/ethanol mixture, the samples were again treated at 648 K to 723 K and analyzed.

DRIFT spectroscopy was conducted to determine the presence of hydrocarbons after the ethanol exposure. The DRIFT analysis (Bruker IFS66) were conducted at room temperature using KBr as background. Prior to the analysis, the samples were heated, *in situ*, to 393 K to remove any moisture and volatile components. Both the analysis and pre-treatment were carried out under helium atmosphere. After the analysis, the samples which had been exposed to the water/ethanol mixture are subsequently heated *in situ* to 648 K (maximum attainable temperature of the apparatus), and again analyzed at room temperature to study the reversibility by heat treatment.

The TG analysis (Mettler Toledo, TGA/SDTA 851e) was conducted in an air atmosphere using a heating rate of $10\text{ K}\cdot\text{min}^{-1}$. The analysis serves to verify the removal of the template as well as to determine the presence of any adsorbed or reacted organic material in the framework due to the exposure to the water/ethanol mixture.

Nitrogen adsorption characterization was conducted (Quantachrome Autosorb-6B) to investigate the possibility of pore blockage or reduction in pore volume by irreversible adsorption or chemisorption of ethanol or hydrolysis of the framework by water. Prior to the nitrogen gas-adsorption measurements, the samples were dried in vacuum at 573 K in order to remove present moisture and other volatile components (the weight of the sample after drying is used in the calculations). The nitrogen adsorption and desorption isotherms were measured at 77 K. The BET method was used to calculate the specific surface area of the samples and the *t*-plot method was applied to determine the micropore volume.

^{29}Si , ^{27}Al , and ^{13}C magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy and cross polarization (CP) MAS NMR spectroscopy were used to investigate the structure of the organic material in the zeolite pores and to determine the presence of extra framework aluminum. The NMR measurements were conducted using a 4 mm zirconium holder with a spinning frequency of 11 kHz at 298 K. The ^{29}Si MAS NMR were measured with a frequency of 79.449 MHz, a relaxation delay of 15 s. The ^{27}Al MAS NMR spectrum was obtained at 104.201 MHz, a relaxation delay of 1 s. For the ^{13}C CP MAS NMR measurements, a frequency of

100.555 MHz and a delay of 5 s was used. The chemical shifts of the ^{29}Si and ^{13}C NMR measurements were referenced with respect to tetramethylsilane (TMS) with an acquisition time of 0.05 s. The ^{27}Al NMR measurements were referenced with respect to $\text{Al}(\text{NO}_3)_3$ with an acquisition time of 0.08 s.

3.3 Experimental Results

The ozonation of M2 was done for 60 h, treatment for an additional 30 h did neither increase flux nor alter the membrane selectivity. After ~ 40 h of operation, membrane M2 was calcined at 723 K, this membrane is referred to as M2c. The membrane performance was monitored for 40 and 177 h of operation for M1 and M2, respectively, during which the the membrane integrity was tested regularly by performing a pressure test.

3.3.1 Pressure test

The total flux and ethanol separation factor were measured as a function of the feed pressure and both are not affected by an increase in absolute pressure of the feed, indicating the membranes do not contain any defects giving rise to unselective viscous flow. Figure 3.4 gives a typical profile during a pressure test of M1 measured at 348 K after 28 h of operation. The flux and selectivity are both insensitive to changes in absolute pressure in the range of 120 kPa to 1010 kPa, indicating no contribution of non-selective viscous flow, and confirming the absence of macroscopic defects. This observation was consistent throughout the complete experimental series.

3.3.2 Comparison of ozonicated and calcined membrane in ethanol/water pervaporation

Membrane M1 and M2 are compared under the same conditions in the enrichment of a 7 mol% aqueous ethanol solution at temperatures of 348 K, 361 K, and 373 K. The measured total flux and ethanol separation factor are shown in Figures 3.5A and B. The separation factor decreases with temperature, while the flux increases. Figures 3.6A and B give the ethanol and water component flux, respectively, as a function of the species fugacity difference over the membrane. The linear trend shows equation 3.1 gives a fair description of both the ethanol as well as the water flux. Figure 3.7

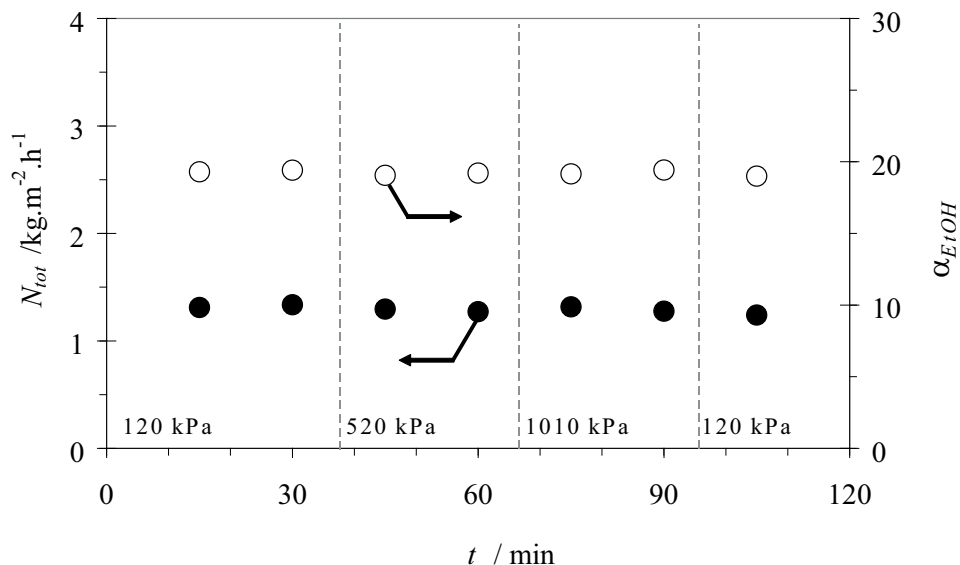


Figure 3.4: The total flux (●) and ethanol separation factor (○) as a function of time during a pressure test at 348 K of membrane M1 after 28 h of operation, showing no pressure dependency of flux and separation factor.

gives an Arrhenius plot of the permeance data, showing the temperature dependencies of both the ethanol and the water permeance are well described by equation 3.2.

The apparent activation energies and the pre-exponential factors for water and ethanol are listed in Table 3.2. Extrapolating the membrane performance to 303 K, using the values from Table 3.2, yields a total flux of 0.36, 0.19, and 0.57 $\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ with an ethanol separation factor of 145, 204, and 107 for membrane M1, M2, and M2c, respectively.

Table 3.2: Apparent activation energies, E_{app} and pre-exponential factors, Π_0 , for ethanol and water permeation through membranes M1, M2 and M2c at $T = 348, 360$, and 373 K and $x_e = 0.07$.

Membrane	$E_{app,e}$ $\text{kJ}\cdot\text{mol}^{-1}$	$\Pi_{0,e}$ $\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$	$E_{app,w}$ $\text{kJ}\cdot\text{mol}^{-1}$	$\Pi_{0,w}$ $\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$
M1	-10.3	2.2×10^{-8}	13.7	1.1×10^{-5}
M2	-9.6	1.5×10^{-8}	20.6	6.4×10^{-5}
M2c	-17.8	0.2×10^{-8}	9.3	0.4×10^{-5}

There is no observable difference in the selectivity of the ozonicated and the cal-

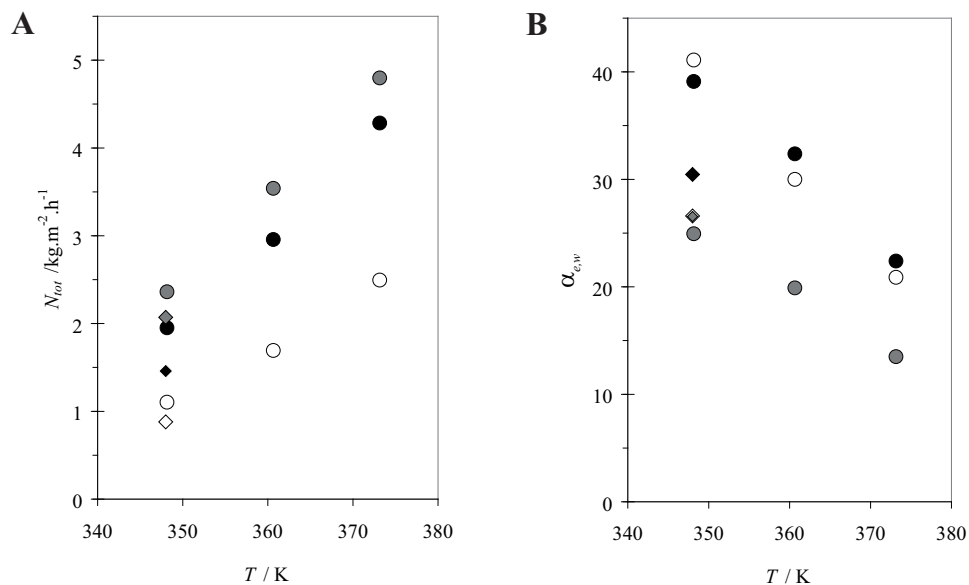


Figure 3.5: (A): Total mass flux and (B): ethanol separation factor versus temperature for membrane M1 ($\bullet$), M2 ($\circ$), and M2c ($\bullet$) at the feed ethanol concentration $x = 0.07$. The measurements at $x = 0.03$ are also given for M1 ($\blacklozenge$), M2 ($\diamond$), and M2c ($\blacklozenge$).

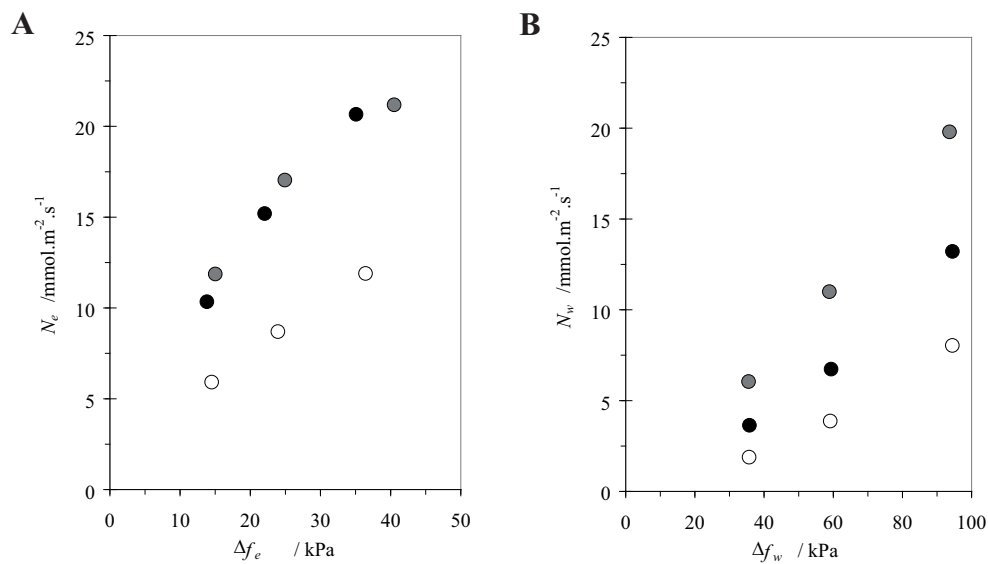


Figure 3.6: The molar fluxes of (A): ethanol and (B): water as a function of the fugacity difference over the membrane and support layers, for M1 ($\bullet$), M2 ($\circ$), and M2c ($\bullet$).

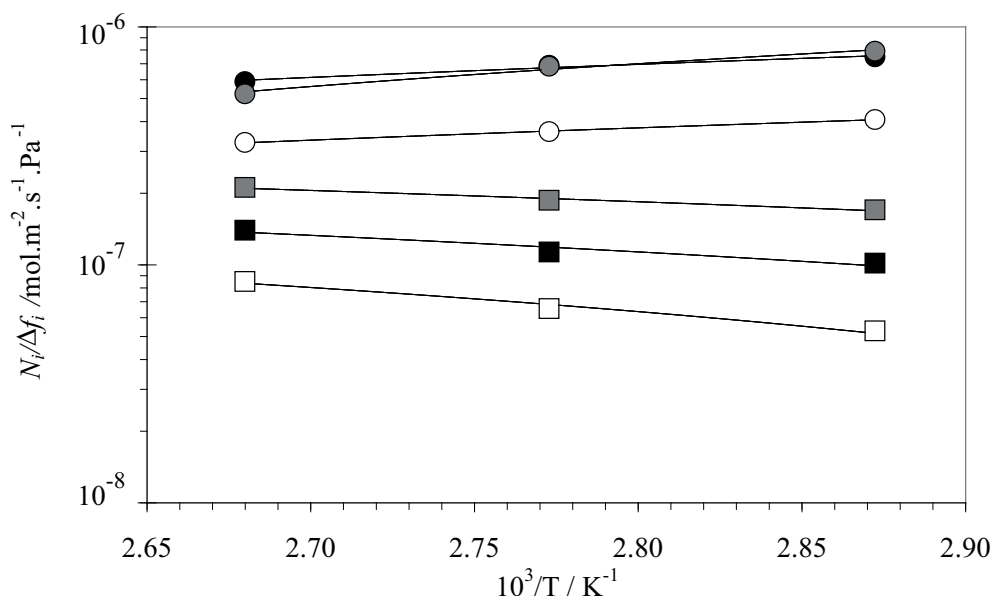


Figure 3.7: Arrhenius plots of M1 (●,■), M2 (○,□), and M2c (◐,◑) for the water (squares) and ethanol (circles) permeance at an ethanol feed concentration of $x = 0.07$. The lines indicate the linear fit according to equation 3.2.

cined membrane, although a higher number of hydrophilic silanol groups is expected in the ozonicated membrane [29]. After the calcination of the ozonicated membrane, M2, at 723 K, the flux is doubled to a value corresponding to the flux across membrane M1 which was initially calcined at 773 K. The observed decrease in the ethanol separation factor is related to the membrane stability, as is discussed later.

3.3.3 Membrane stability

To investigate the membrane stability of M2c, pervaporation experiments were conducted for over 177 h. The temperature was alternated between 373 K and 348 K, where the membrane integrity was evaluated by performing a pressure test. A systematic reduction in flux and selectivity is observed after permeation experiments were conducted at 373 K, at 348 K, on the other hand, the membrane performance appeared to be stable. Figures 3.8 and 3.9 depict the ethanol and water flux, respectively, during the complete experimental program of membrane M2. Figure 3.10 shows the feed ethanol molar fraction, x_e , and the permeate ethanol content, y_e and Figure 3.11 shows the progression of the ethanol separation factor. The initial value of $\alpha_{e,w}$ of

40, decreased to a value of 10 after 100 h of operation at, alternatingly 373 K, 360 K, and 348 K. To determine the membrane performance at lower ethanol concentrations, several measurements at a feed concentration of $x_e = 0.03$ and $T = 348$ K have also been conducted before and right after the calcination step at 723 K. The separation factor and total flux remain fairly constant at this lower ethanol concentration.

To exclude the possibility of hydrolysis of the zeolite, forming silanol groups, membrane M2 was again calcined, this time at 823 K, after 112 h of operation. This did not restore the selectivity of the membrane, as the ethanol separation factor remained constant. The flux, on the other hand, increased by 85%, which is comparable to the increase after the calcination at 723 K. During an additional 30 h of operation at 348 K, the membrane showed stable performance, after which the membrane was again calcined at 823 K, and subsequently at 923 K. These calcination steps did not result in a significant change in either flux (Figures 3.8 and 3.9) or selectivity (Figures 3.10 and 3.11), confirming complete detemplation after the first calcination at 823 K.

The stability of M1 was also examined for 40 h of operation. Since less experiments at 373 K have been conducted, the separation factor has remained closer to the initial value, decreasing from the initial value of 40 to 30 after the first series of experiments at 373 K (Figure 3.15). Analogously to M2, lowering the ethanol feed concentration to $x_e = 0.03$ showed no substantial change in flux (Figures 3.12 and 3.13) or separation factor (Figure 3.15). However, during these measurements a gradual decrease in separation factor and flux is observed. Before the experiments were continued at $x_e = 0.07$, the membrane had been off-line for 98 days. The membrane was stored at room temperature in a sealed container in air atmosphere. After the time off-line, the separation factor had decreased from 27 to 18, while the total flux remained the same at $1.4 \text{ kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$. Calcination of M1 at 823 K showed a similar effect as observed for M2. The total flux increased from 1.2 to $1.8 \text{ kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$, while $\alpha_{e,w}$ showed a small increase from 19 to 21. After the calcination at 823 K, the membrane was again exposed to a measurement at 373 K, which resulted in a decrease in separation factor at 348 K from 21 to 18. Also during the measurements at 373 K, the ethanol flux and separation factor decreased much more rapidly than during the measurements at lower temperatures, while the water flux remained practically constant.

In every experimental series for both membranes, a pressure test was conducted to confirm the integrity of the membrane. No pressure dependency of flux or separation factor was observed, verifying no defects were formed during calcination and

operation. The GC analysis of the feed and the permeate after the complete experimental series did not reveal any build-up of contaminants in the feed or presence of other compounds than in the initial feed, which only contained a small impurity of methanol.

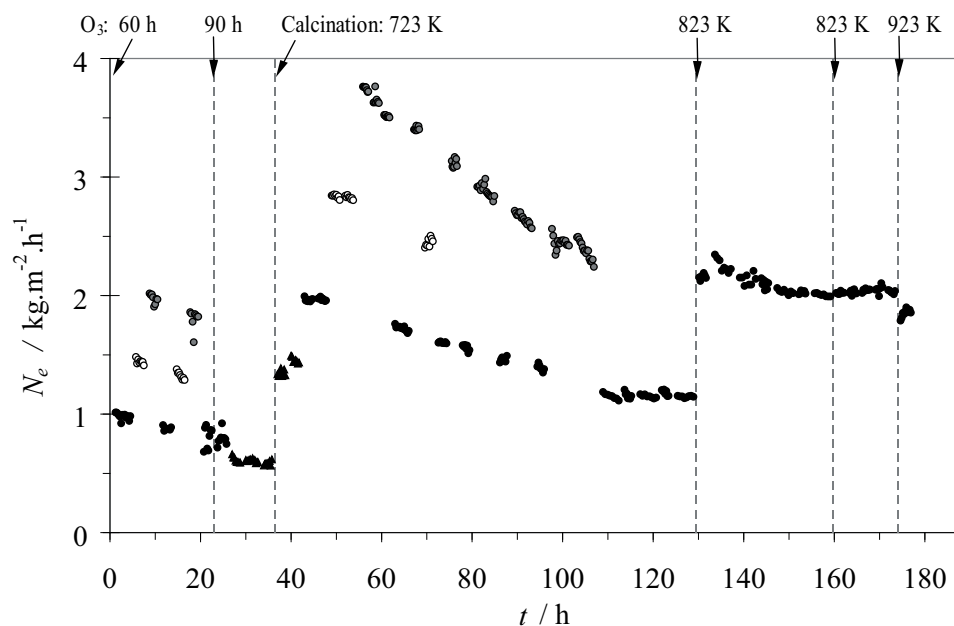


Figure 3.8: Evolution of the ethanol flux at $x_e = 0.07$ and 348 K (●), 360 K (○), and 373 K (●) and at $x_e = 0.03$ and 348 K (▲) for membrane M2. The dashed lines indicate the extra ozonation, and the calcination steps.

3.3.4 Zeolite powder analysis

To determine the mechanism behind the deterioration of the membrane performance in time, analysis of zeolite powders is conducted. The silicalite-1 crystal size is determined by SEM analysis to be $21 \times 13 \times 26 \mu\text{m}$ in the a , b , and c -direction, respectively. The shortest characteristic length is thus comparable to the membrane thickness. To assess the template removal by ozonation, the zeolite powder was ozonicated for up to 60 h, while at intermediate times samples were taken and analyzed by TGA (Figure 3.16). The sharp decrease in mass around 473 K in the TGA curve of the non-detemplated sample is attributed to the oxidation of the template. The mass reduction is decreased with increasing ozonation time, corresponding to

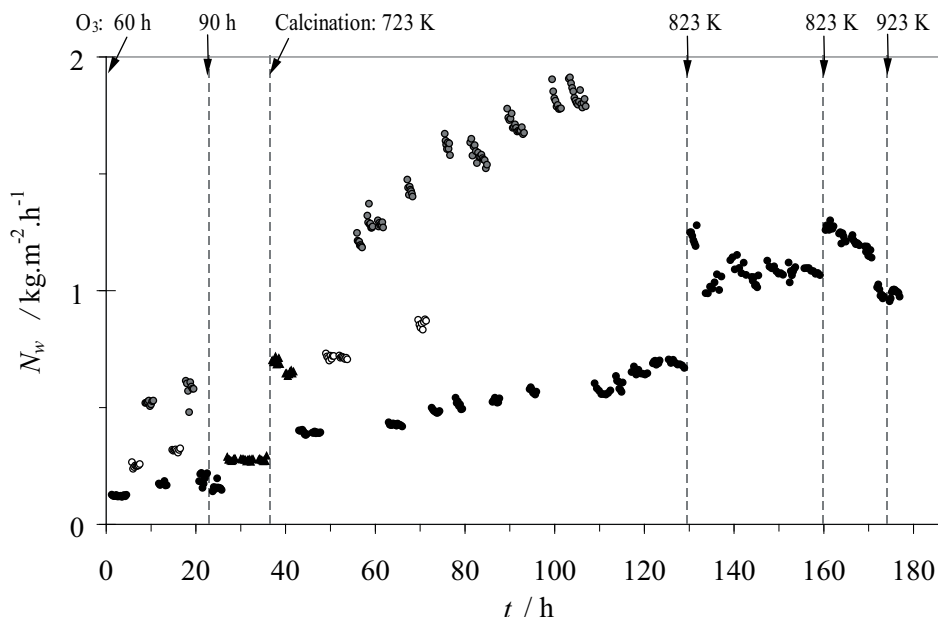


Figure 3.9: Evolution of the water flux at $x_e = 0.07$ and 348 K (●), 360 K (○), and 373 K (●) and at $x_e = 0.03$ and 348 K (▲) for membrane M2. The dashed lines indicate the extra ozonation, and the calcination steps.

the removal of the template. The TGA curves show that the ozonation was essentially complete after 18 h, prolonging the ozonation time to 24 h or 60 h only marginally decreases the mass decrease around the temperature associated with the oxidation of the template. Even after 60 h ozonation a small mass decrease around 723 K is observed, indicating some residual template material, although part of the mass loss can also be attributed to the condensation of silanol groups [30].

Figures 3.17, 3.18, and 3.19 show the DRIFT spectra and TGA curves of calcined and ozonicated silicalite-1 powder and calcined ZSM-5 powder, respectively. Figure 3.17 also includes the data for the uncalcined silicalite-1 sample. The C-H stretching vibrations ($2800\text{--}3000\text{ cm}^{-1}$) and the C-H bending vibration ($1400\text{--}1500\text{ cm}^{-1}$) from the organic template are clearly visible in the as synthesized sample, but are absent in the calcined samples. The removal of the template is also confirmed by TGA, which shows no decrease in mass around 723 K.

The TGA curve of the calcined silicalite-1 sample (Figure 3.17B) shows a limited decrease in mass at temperatures below 400 K, which can be attributed to loss of physisorbed water. After exposure to the water/ethanol mixture the calcined silicalite-1

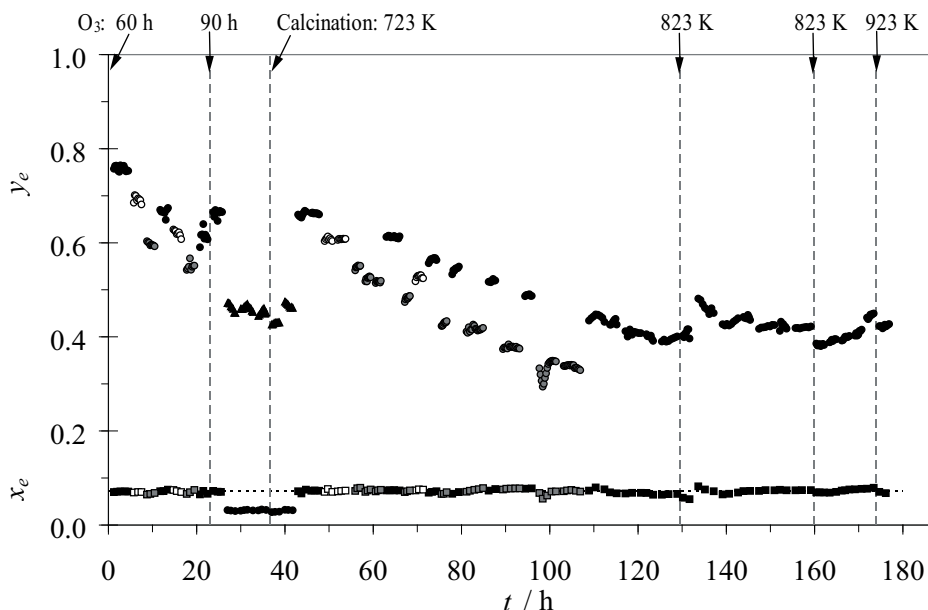


Figure 3.10: Evolution of feed and permeate compositions measured using membrane M2. The permeate ethanol concentration, y_e , at 348 K (●), 360 K (○), and 373 K (◐), and the feed ethanol concentration, x_e , at 348 K (□), 360 K (■), and 373 K (◑) are shown. The dashed lines indicate the extra ozonization, and the calcination steps.

powder show a small change in the DRIFT spectrum at the wavenumbers corresponding to hydrocarbons (Figure 3.17A). There is a reduction in the broad band at 3100–3750 cm^{-1} , which is assigned to adsorbed water. This is in concordance with the TGA curves, which show the disappearance of the initial decrease in mass after the sample has been exposed to the water/ethanol mixture. The changes in the TGA curve and the DRIFT spectrum which occur after exposure to the feed mixture, remain after the samples were calcined at 723 K and 648 K, respectively.

The DRIFT spectra of the ozonicated silicalite-1 sample (Figure 3.18A) show a higher absorbance at 3100–3750 cm^{-1} as compared to the calcined sample, which indicates the higher hydrophilicity due to the increased number of silanol groups. After exposure to ethanol, an increased intensity corresponding to C–H stretching vibrations is observed. These absorbances are more pronounced than for the calcined sample and also remain after heat treatment at 648 K. The terminal silanol groups (3735 cm^{-1}) seem to increase after exposure, and do not disappear after treatment at 648 K. The initial decrease in the TGA curve is not significantly effected by exposure or heat treatment (Figure 3.18B). However, the total mass loss decreases after

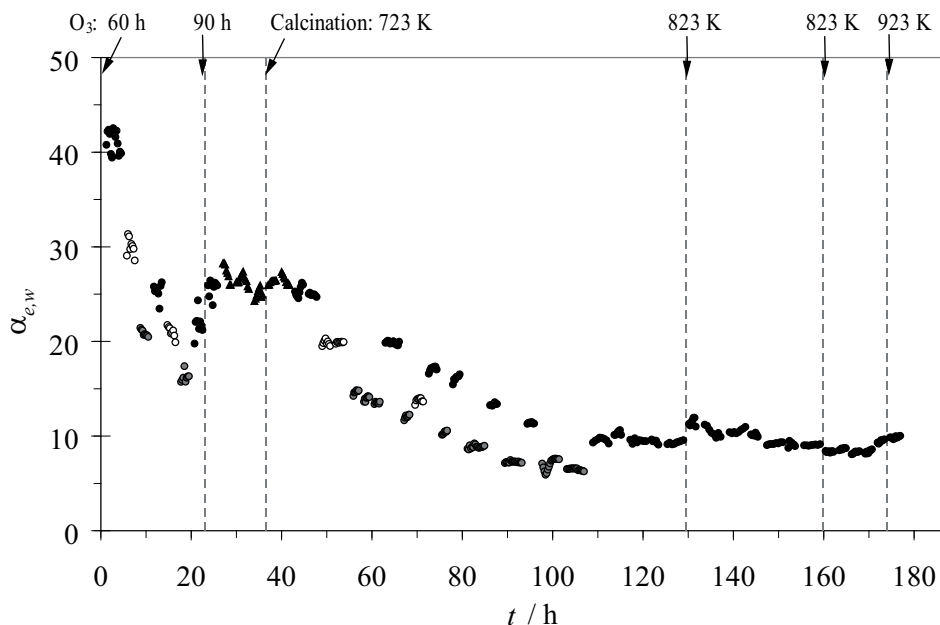


Figure 3.11: Evolution of the ethanol selectivity at $x_e = 0.07$ and 348 K (●), 360 K (○), and 373 K (●) and at $x_e = 0.03$ and 348 K (▲) for membrane M2. The dashed lines indicate the extra ozonation, and the calcination steps.

exposure to the feed mixture and remains after the subsequent heat treatment.

The TGA curve of the ZSM-5 sample shows a large initial mass loss, corresponding to physisorbed water (Figure 3.19B). After the ZSM-5 sample is exposed to the feed mixture, a strong increase in the C-H stretching vibrations is observed (Figure 3.19A). The exposure also results in a decrease of the initial mass loss in the TGA curve, showing the zeolite has become less hydrophilic. As for the ozonicated silicalite-1 sample, the terminal silanol groups seem to increase after exposure to the feed mixture, and remain after heat treatment. After heat treatment the appearance of Brønsted acid sites (3610 cm^{-1} [31]) and a reduction in the intensity of the C-H stretching vibrations are observed, although there are still C-H stretching absorbances visible. The initial decrease in the TGA curve increases after the heat treatment, but is not fully restored to the initial value.

Nitrogen adsorption measurements on detemplated zeolite powder samples were conducted before and after being exposed to a water/ethanol mixture ($x_e = 0.07$) at 373 K for 24 h and then dried for 24 h in air at 373 K and after subsequent heat

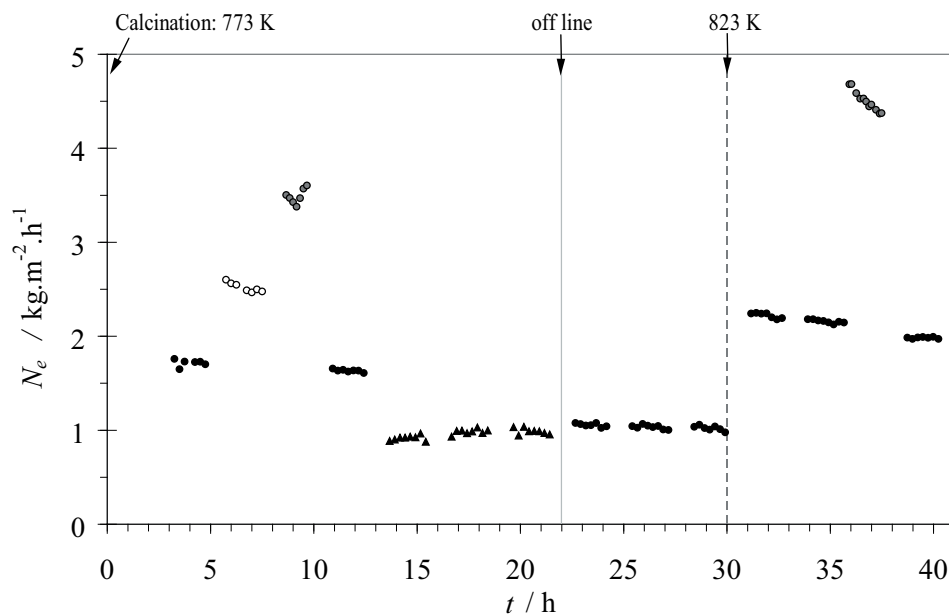


Figure 3.12: Evolution of the ethanol flux at $x_e = 0.07$ and 348 K (●), 360 K (○), and 373 K (●) and at $x_e = 0.03$ and 348 K (▲) for membrane M1. The dashed line indicates the calcination step at 823 K, while the solid line indicated the time off-line for 98 days.

treatment at 723 K for 10 h. No significant changes in BET surface area or micropore volume is observed after these treatments (Table 3.3). The somewhat lower surface area for the ozonicated sample can be attributed to the small amount of residual template material present in the framework, which is in agreement with the TGA and DRIFT data. Figure 3.20 shows the nitrogen isotherms of the samples after exposure and calcination, giving the adsorbed volume of nitrogen, V_{ads} as a function of the ratio of the pressure over the vapor pressure, P/P^0 . Neither the exposure to the feed mixture nor the calcination changed the shape of the measured nitrogen isotherms.

Figures 3.21A, B, and C show the ^{29}Si , ^{13}C and ^{27}Al NMR spectra, respectively. Due to the low amount of carbon in the ethanol exposed samples, the signal-to-noise ratio in the ^{13}C CP MAS NMR measurements is low. For the calcined silicalite-1 sample the carbon content was too low to interpret the spectra. Therefore, only the spectra of the ozonicated silicalite-1 and the ZSM-5 sample are discussed.

In the ^{29}Si MAS NMR spectra (Figure 3.21A) the Q^3 peak ($\delta = -103$ ppm) is ascribed to the $(\text{Si-OH})(\text{Si-O})_3$ and $(\text{Si-O-R})(\text{Si-O})_3$ groups (where R is an alkyl group),

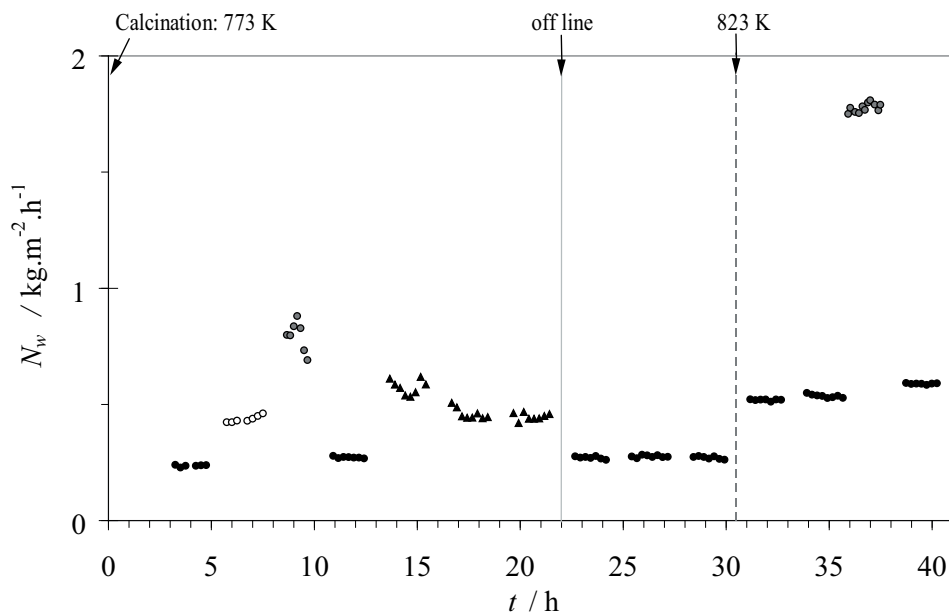


Figure 3.13: Evolution of the water flux at $x_e = 0.07$ and 348 K (●), 360 K (○), and 373 K (●) and at $x_e = 0.03$ and 348 K (▲) for membrane M1. The dashed line indicates the calcination step at 823 K, while the solid line indicated the time off-line for 98 days.

Table 3.3: Nitrogen adsorption data of calcined and ozonicated silicalite-1 and ZSM-5 powder after detemplation and after being exposed to a water/ethanol mixture ($x_e = 0.07$) at 373 K for 24 h and then dried for 24 h in air at 373 K and after subsequent heat treatment at 723 K for 10 h.

Sample	Detemplated		Exposed		Calcined	
	S_{BET} $\text{m}^2.\text{g}^{-1}$	$V_{\text{micropore}}$ $\text{m}^3.\text{kg}^{-1}$	S_{BET} $\text{m}^2.\text{g}^{-1}$	$V_{\text{micropore}}$ $\text{m}^3.\text{kg}^{-1}$	S_{BET} $\text{m}^2.\text{g}^{-1}$	$V_{\text{micropore}}$ $\text{cm}^3.\text{g}^{-1}$
silicalite-1 calc.	453	0.19	419	0.19	439	0.19
silicalite-1 O ₃	352	0.16	400	0.18	383	0.18
ZSM-5	464	0.20	483	0.20	453	0.19

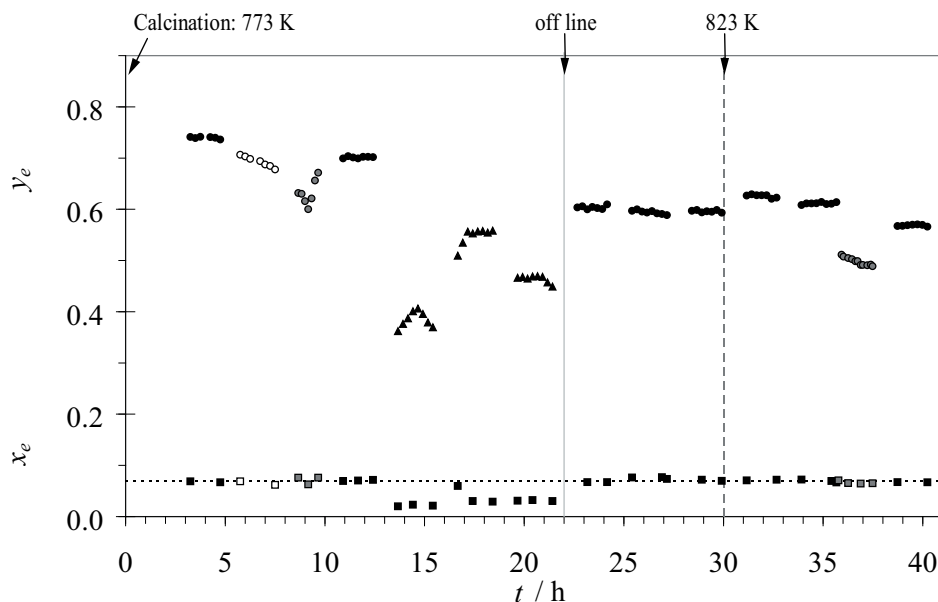


Figure 3.14: Evolution of feed and permeate compositions measured using membrane M1. The permeate ethanol concentration, y_e , at 348 K (●), 360 K (○), and 373 K (●), and the feed ethanol concentration, x_e , at 348 K (□), 360 K (■), and 373 K (■) are shown. The dashed line indicates the calcination step at 823 K, while the solid line indicated the time off-line for 98 days.

while the Q^4 signal ($\delta = -113$ ppm) is ascribed to the $\text{Si}(\text{Si-O})_4$ units [32, 33]. The ZSM-5 sample shows a small peak at 106 ppm, which is ascribed to the $\text{Al}(\text{Si-O})_3$ groups [34] (Figure 3.21A, c). As compared to unexposed samples [16], the ^{29}Si MAS NMR spectra did not reveal any change in the Q^3/Q^4 ratio.

The ^{13}C CP MAS NMR spectra of the ethanol exposed ZSM-5 and ozonicated silicalite-1 samples (Figure 3.21B) show a signal at 61 ppm, which is assigned to terminal ethoxy species ($\text{SiO}(\text{CH}_2\text{CH}_3)$) and the signal around 70 ppm in the ZSM-5 sample can be attributed to surface ethoxy species ($\text{SiO}(\text{CH}_2\text{CH}_3)\text{Al}$) [35]. The signals at 17 ppm are attributed to methyl groups [36, 37].

The signal at 55 ppm in the ^{27}Al MAS NMR spectrum of the ZSM-5 sample (Figure 3.21c) is assigned to framework aluminum, while a small peak at 0 ppm shows the presence of a small amount of extra-framework aluminum [38].

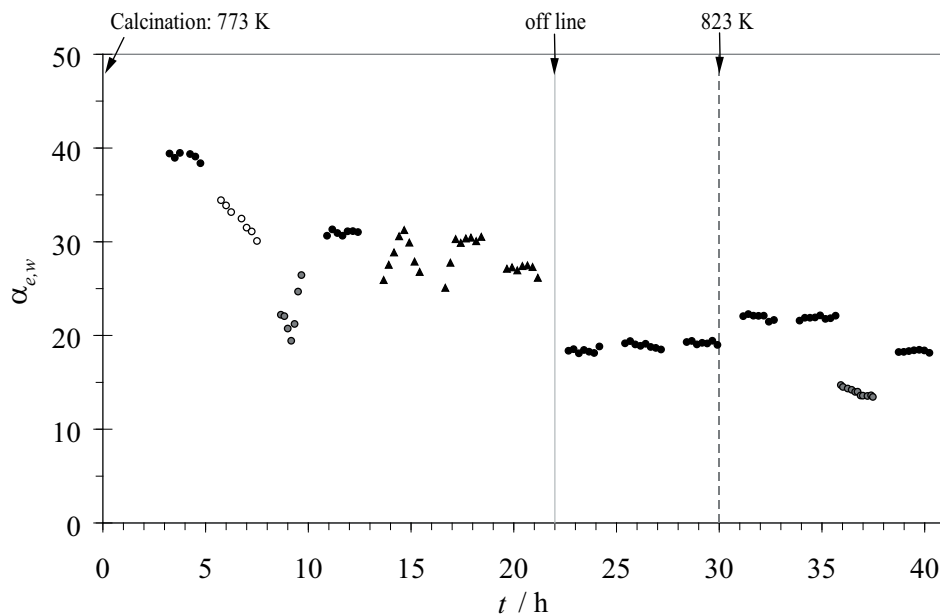


Figure 3.15: Evolution of the ethanol selectivity at $x_e = 0.07$ and 348 K (●), 360 K (○), and 373 K (●) and at $x_e = 0.03$ and 348 K (▲) for membrane M1. The dashed line indicates the calcination step at 823 K, while the solid line indicated the time off-line for 98 days.

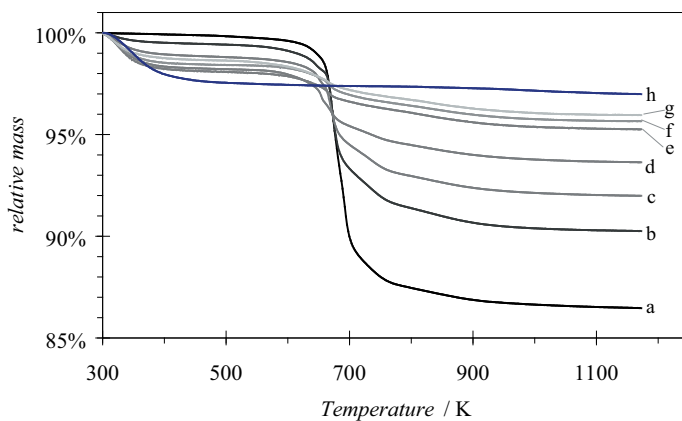


Figure 3.16: TGA curves of silicalite-1 powder ozonicated for (a): 0 h, (b): 2 h, (c): 3.5 h, (d): 8 h, (e): 18 h, (f): 24 h, and (g): 60 h, and (h): calcined at 723 K.

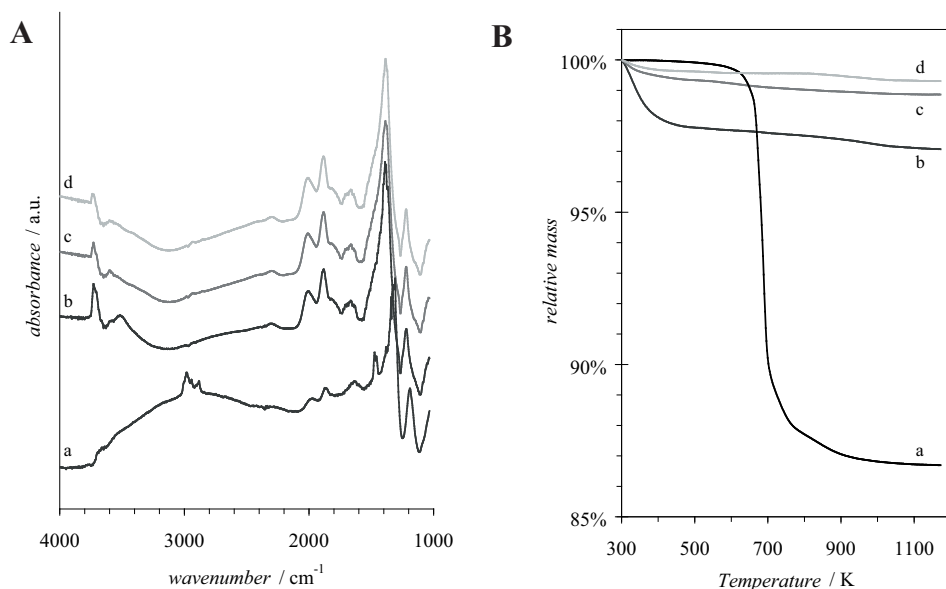


Figure 3.17: (A): DRIFT spectra and (B): TGA curve of silicalite-1 powder measured at 298 K (a): as-synthesized and (b): calcined at 723 K for 6 h, then (c): exposed to a water/ethanol mixture ($x_e = 0.07$) at 373 K for 24 h and then dried for 24 h in air at 373 K and (d): after heat treatment at 648 K (*in situ* DRIFT) or 723 K (in furnace, TGA).

3.4 Discussion

The initial value of $\alpha_{e,w}$ of 40 at 348 K for both membranes is comparable to literature values measured at lower temperatures (Table 3.1). At 348 K, the flux across M2 ($1.1 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) was significantly lower than the flux across M1 ($1.9 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$). After calcination at 723 K, the measured flux through M2c increased to $2.4 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$.

Both the ethanol and the water flux are proportional with the component fugacity difference over the membrane within the applied temperature range (Figure 3.6). The ethanol flux shows a negative deviation from the linear trend at 373 K, and for water the deviation is positive. This corresponds with the irreversible decrease in selectivity at this temperature.

The separation performance of M1 and M2 do not differ significantly (Figure 3.5A). Although M2 is expected to contain a higher number of silanol groups, M1 will also contain silanol groups because of the relatively low calcination temperature [30, 39]. The temperature dependency of the permeance reveals a negative apparent activation energy for ethanol and a positive value for water (Table 3.2). This indi-

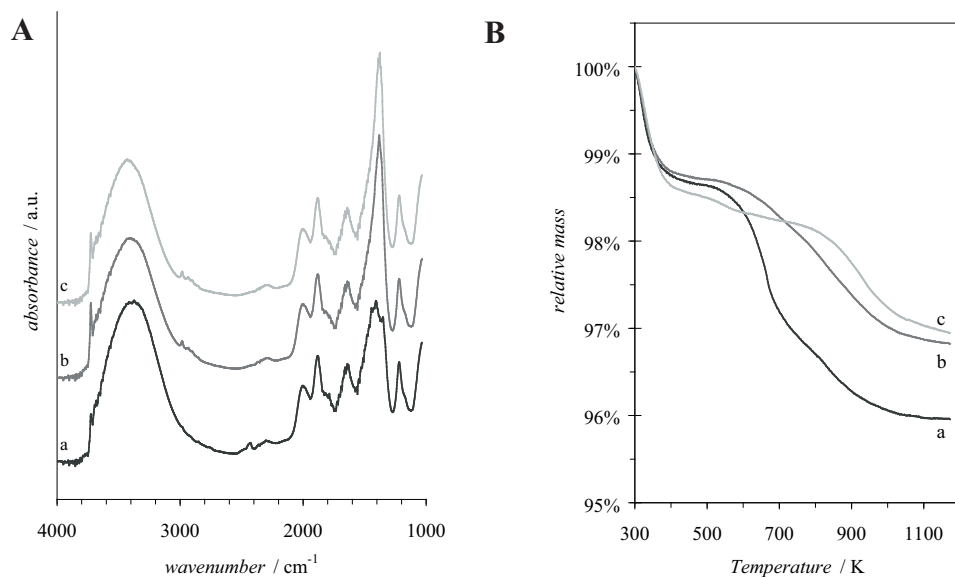


Figure 3.18: (A): DRIFT spectra and (B): TGA curve of silicalite-1 powder measured at 298 K (a): ozonicated for 60 h, (b): exposed to a water/ethanol mixture ($x_e = 0.07$) at 373 K for 24 h and then dried for 24 h in air at 373 K and (c): after heat treatment at 648 K (*in situ* DRIFT) or 723 K (in furnace, TGA).

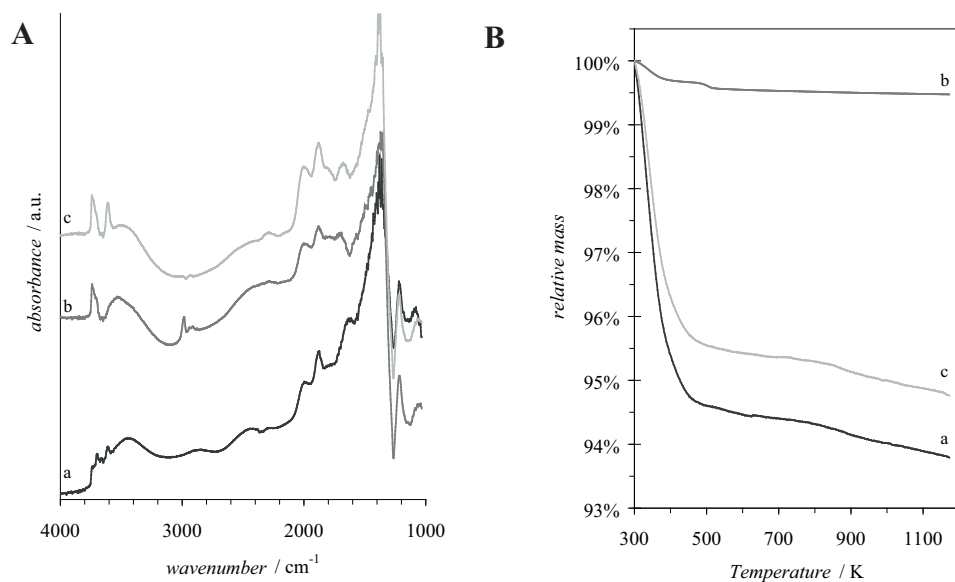


Figure 3.19: (A): DRIFT spectra and (B): TGA curve of ZSM-5 powder with Si/Al = 50 measured at 298 K (a): calcined at 823 K, (b): exposed to a water/ethanol mixture ($x_e = 0.07$) at 373 K for 24 h and then dried for 24 h in air at 373 K and (c): after heat treatment at 648 K (*in situ* DRIFT) or 723 K (in furnace, TGA).

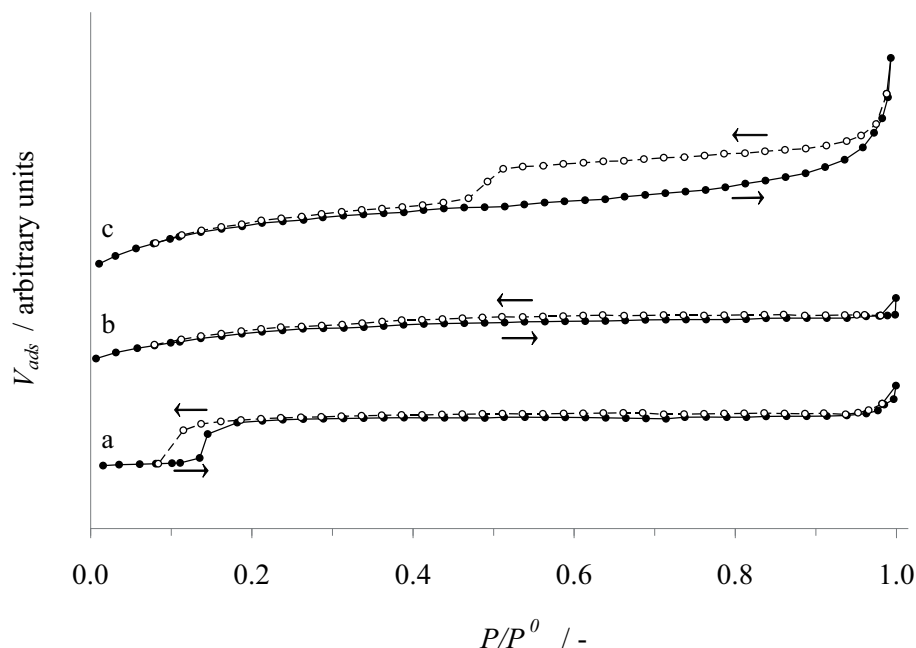


Figure 3.20: Nitrogen adsorption (●) and desorption (○) isotherms at 77 K of (a): silicalite-1 calcined at 723 K, (b): ozonicated silicalite-1, and (c): ZSM-5 (Si/Al = 50) powder after exposure to the feed mixture and subsequent calcination at 723 K. The isotherms were similar to the ones measured before the exposure and calcination.

cates that for water the energy of activation of diffusion dominates over the heat of adsorption, while for the preferentially adsorbing species, ethanol, the heat of adsorption is dominating in the temperature dependence of the permeation [23]. The flux of the ozonicated membrane is approximately half the flux of the membrane calcined at 773 K (Figure 3.5A), indicating the ozonation resulted in a less complete detemplation as compared to the calcination at 773 K.

After a second calcination step at 823 K, both membranes showed almost a doubling of the flux to 2.7 and $3.3 \text{ kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ for M1 and M2, respectively, while no effect on the membrane selectivity is observed. This shows that, also after a calcination at 723 K, there is still template present in the zeolite framework. Although 723 K is sufficient to remove the template from silicalite-1, aluminum containing MFI type zeolites require a higher calcination temperature [40]. The higher temperature required for calcination shows that the membranes contain a certain amount of aluminum, which is leached out of the α -alumina support during synthesis. The aluminum concentration will be the highest close to the support layer [41]. The pres-

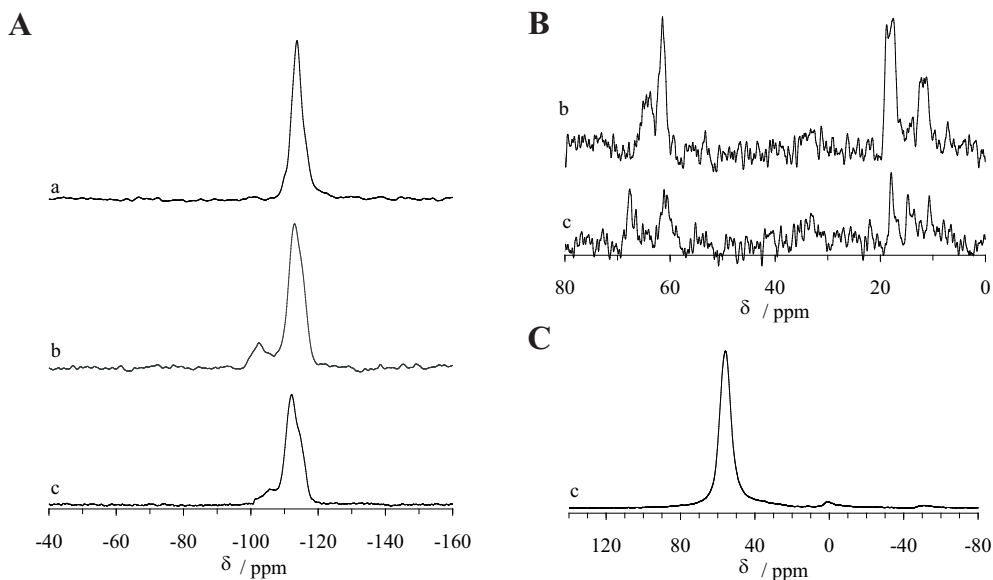


Figure 3.21: (A): ^{29}Si MAS NMR, (B): ^{13}C CP MAS NMR, and (C): ^{27}Al MAS NMR spectra of (a): calcined silicalite-1, (b): ozonicated silicalite-1, and (c): ZSM-5 powder after exposure to a water/ethanol mixture ($x_e = 0.07$) at 373 K for 24 h and then dried for 24 h in air at 373 K.

ence of aluminum also explains the incomplete template removal during ozonation, which is more difficult for aluminum containing zeolites [15].

The decrease in both flux and selectivity is enhanced at higher temperatures. At 348 K the membrane performance only shows a small decrease in time, while at 373 K a significant reduction in ethanol flux (Figures 3.8 and 3.12) and an increase in water flux (Figures 3.9 and 3.13) is observed, leading to a decrease in ethanol separation factor (Figures 3.11 and 3.15). The lower selectivity of the ozonicated membrane after calcination can, therefore, be attributed to the decreased in membrane performance after operation at 373 K.

Several mechanisms can be involved in the change in membrane performance. Although MFI type zeolites exhibit a relatively high hydrothermal stability [42], Andersson *et al.* showed that exposure to water deteriorates silicalite-1 membranes, while ethanol does not reduce the membrane quality [19]. Moreover, the presence of aluminum further decreases the hydrothermal stability of the zeolite [43, 44]. Li *et al.* showed that the limited hydrothermal stability of LTA membranes, resulting in low selectivities and high fluxes in de-watering of ethanol, can be attributed to the dis-

solution of amorphous material in the grain boundaries in pervaporation [20]. This phenomenon would cause defect formation, and therefore increase the flux, while decreasing the selectivity. Since, in this study, both the total flux and the separation factor decrease and no viscous flow contribution is observed, this does not seem the (only) mechanism involved in the observed decrease in membrane performance. Only if the resulting defects are, unlike in the LTA membranes, sufficiently small and hydrophilic to exclude ethanol from passing through, this mechanism could explain the observed changes in performance. Since all-silica zeolites exhibit better crystal intergrowth, resulting in smaller grain boundaries [45], the opening of the grain boundaries, resulting in hydrophilic pathways, could explain the increase in water flux.

Exposure to ethanol vapor has shown to reduce the adsorption capacity of de-boronated [B]MFI zeolite [46]. This effect was attributed to ethanol reacting with residual boron, forming ethylborate species. The adsorption capacity of these zeolites was restored after a heat treatment at 723 K, this was not observed for the selectivity of the membranes in this study.

Ito *et al.* observed deterioration of NaA membranes in alcohol de-watering under pervaporation conditions due to condensation or reaction of organic material [47]. Similar observations were reported by Menendez *et al.* in water removal from a glycerol-acetone reaction [48]. In both these studies it was shown that this type of membranes have increased stability when operated under vapor permeation conditions. If the mechanism of deterioration of membrane performance is a direct consequence of the ethanol reacting with silanol groups and hydrolysis by water, applying vapor permeation is not expected to improve the stability.

MFI zeolites have been used as catalyst for the methanol to olefin process, which can result in dimethyl ether and coke formation. The latter reaction generally occurs at temperatures above 673 K [49]. However, neither the GC analysis of the feed and permeate, nor the ^{13}C CP MAS NMR spectra indicate other products have formed than were present in the feed.

Although the detemplation by ozonation and calcination at 723 K was not complete, the reduction in membrane performance after exposure to 373 K was also observed after complete detemplation for M1 (Figure 3.15). This excludes the possibility that residual template material was involved.

The DRIFT data show that organic material is deposited in the framework of an aluminum containing MFI zeolite after being exposed to a water/ethanol mixture at

373 K (Figure 3.19). This is also observed for ozonicated silicalite-1, albeit to a lesser extent (Figure 3.18). Also the TGA results indicate that the exposure to the mixture influences the zeolite, reducing the water desorption from the sample. This effects is partially reversible after heat treatment for the aluminum containing sample (Figure 3.19), but not for the calcined and ozonicated silicalite-1 samples (Figures 3.18 and 3.17). The decrease in adsorbed water after exposure to the feed mixture indicates an increased hydrophobicity as compared to the unexposed sample, which is expected to increase the ethanol separation factor. However, the irreversible adsorption of ethanol obstructs the diffusive motion of ethanol molecules, decreasing the effective pore size of the zeolite, which reduces the ethanol selectivity due to molecular sieving. However, since silicalite-1 membranes have been found to show stable operation in pure ethanol permeation [19], it is likely both water and ethanol are involved in the decrease of the membrane performance. Assessment of the membrane stability during pure component water and ethanol pervaporation will give more insight in the effect of each component on the membrane stability.

Although the ^{29}Si MAS NMR spectra do not show an increased Q^3 signal after exposure to the feed mixture, the DRIFT spectra indicate an increase of terminal silanol groups after ethanol exposure in the ozonicated silicalite-1 and the ZSM-5 sample, the calcined silicalite-1 sample shows a reduction at these wavenumbers. If the decrease in ethanol separation factor was caused by hydrolysis of the Si-O-Si bonds which increases the number of hydrophilic silanol groups, this effect would be reversed after heat treatment above 723 K [46]. In this study the selectivity is hardly affected by the calcination steps at 723 K, 823 K and 923 K, which excludes the formation and condensation of silanol groups. Moreover, the zeolite samples are expected to become more hydrophilic after exposure to the feed mixture, while the opposite is concluded from the TGA curves (Figures 3.17, 3.18, and 3.19). However, terminal silanol groups at the crystal surfaces and grain boundaries do not condense and therefore could give a thermally irreverisble increase in hydrophilicity. The mechanism of creating hydrophilc grain boundaries in the membrane can not be confirmed by analysis on loose crystals.

Because the Q^3 signals assigned to $(\text{Si-OH})(\text{Si-O})_3$ and $(\text{Si-O-R})(\text{Si-O})_3$ groups overlap, the ^{29}Si MAS NMR results do not unambiguously show the existence of ethoxy species chemically bound to the framework [33, 33]. Although there is no increase observed in the Q^3 signals after exposure, the ^{13}C CP MAS NMR and DRIFT spectra show the formation of ethoxy species. Because the sample is dried at 373 K,

and the C-H vibrations are still observed in the DRIFT measurements after heat treatment at 648 K, the NMR signals are not expected to originate from physisorbed ethanol. The absence of ^{29}Si MAS signals over the region -6 to -75 ppm indicates there are no Si atoms covalently bonded to a carbon atom [33]. The ^{13}C CP MAS NMR spectra show the ethanol forms ethoxy species with the zeolite framework and in the case of ZSM-5 it also binds to the Brønsted acid sites, which is also confirmed by the disappearance after exposure and re-appearance of the Brønsted acid -OH absorbances in the DRIFT spectra of the ZSM-5 sample after heat treatment, indicating the thermal reversibility of the formed ethoxy species. The irreversible changes observed in the TGA and DRIFT analysis can therefore be attributed to ethoxy groups.

Kawai *et al.* [50] have shown the formation of ethoxy species by the reaction of alcohols with silanol groups in FAU type zeolites predominantly occurs at the outer surface of the zeolite. This mechanism could explain the reduction of the effective pore size, without significantly reducing the effective pore volume or BET surface. Uptake measurements can reveal the influence on the ethoxy species on the sorption kinetics.

The calcined and ozonicated silicalite-1 and the ZSM-5 sample show some distinct differences in the nitrogen adsorption isotherms. The hysteresis loop between $P/P^0 = 0.1$ and 0.2 in the calcined silicalite-1 concerns a phase transition of the adsorbed nitrogen, typical for MFI zeolites [51, 52]. The absence of this sub-step in the ozonicated silicalite-1 and the ZSM-5 sample are attributed to the energetic heterogeneity of the zeolite surface due to the presence of, respectively, silanol groups and aluminum [51]. If residual template material will be present in the zeolite, as the TGA curves of the ozonicated sample suggests (Figure 3.16), this will also result in an energetically inhomogeneous zeolite surface. The hysteresis loop at $P/P^0 = 0.4$ to 0.5 in the ZSM-5 sample is a result of mesoporosity and is often referred to as cavitation or tensile strength effect (TSE) [51, 52]. These results indicate that the incorporation of Al may induce mesoporosity (lower selectivity) while both Al and residual template reduce the homogeneity of the structure.

The decrease after the first series of experiments is more profound for the ozonicated membrane, with a decrease in $\alpha_{e,w}$ from 40 to 25 as compared to the calcined membrane, which showed a decrease in $\alpha_{e,w}$ from 39 to 31 after the first exposure to 373 K. The higher number of silanol groups could be the cause of this faster initial decline in the performance of the ozonicated membrane. However, also after calcination at 823 K, the membrane performance decreased in time, which also suggest

ethoxy formation, possibly combined with hydrolysis, during operation as the cause of the decreased membrane performance.

Although it is not expected at low temperatures and humidity, the observed decrease in ethanol separation factor after the membrane was off-line for 98 days could have been caused by a reaction with residual ethanol and water during time off-line.

XRD analysis, gas permeation measurements and monitoring the change in pore size distribution by means of permporosimetry [53] during operation would give further insight in possible deterioration of the crystal structure, revealing effects of pore plugging and defect formation.

The use of alternative support materials such as porous metal, titania or zirconia will prevent the incorporation of aluminum in the zeolite framework and is therefore expected to enhance the membrane stability. Furthermore, the fast decline in separation performance at 373 K indicates that to ensure stable operation, the use of this type of membranes in ethanol enrichment from aqueous solutions should be limited to low temperatures.

Even after the separation factor has decreased from 40 to 10, the extrapolated fluxes and separation factors using equation 3.1 and Table 3.2 indicate the membrane performance still compares well with values reported in literature (Table 3.1). It should be noted, however, that using equation 3.1 to extrapolate outside the experimentally validated region merely gives an indication of the membrane performance.

3.5 Conclusions

The separation performance of an ozonicated and a calcined multi-channel MFI membrane has been measured in ethanol enrichment from an aqueous solution under pervaporation conditions. The detemplation method does not affect the ethanol separation factor, while the flux through the ozonicated membrane was significantly lower than flux across the calcined membrane, indicating incomplete detemplation.

Ozonication at 473 K and calcination at 723 K and 773 K was not sufficient to remove the template completely, whereas calcination at 823 K resulted in a template free zeolite layer. The incomplete detemplation is attributed to the presence of aluminum in the zeolite layer which is leached from the support layer and incorporated in the zeolite structure during synthesis.

The total flux and the ethanol separation factor remained fairly constant at 348 K, but decreased significantly at a feed temperature of 373 K due to an increase in water

flux, and a decrease in ethanol flux. The ethanol separation factor decreased from 40 to 10 within 177 h of operation at various conditions.

The results indicate the formation of ethoxy species from reactions of ethanol with silanol groups within the zeolite framework combined with creating hydrophilic extra-framework pathways by hydrolysis as the most probable mechanism of deterioration of the membrane performance. Although these ethoxy species increase the hydrophobicity of the zeolite, the decrease in effective pore size results in a decrease in the ethanol separation factor because of molecular sieving. The increase in water flux indicates formation of hydrophilic extra framework pores, which are selective for water. The presence of aluminum in the zeolite framework can further enhance these effects, although ethanol reaction at a Brønsted acid site is expected to be thermally reversible.

The flux will decrease at lower temperatures, but since the measured values after calcination at 823 K are considerably higher than the measured fluxes reported in literature, the performance of this type of high-silica membrane can be considered as good. To ensure stable operation, the use of this type of membranes in ethanol enrichment from aqueous solutions should be limited to low temperatures. The mechanism of deterioration requires further investigation to enable the fabrication of more stable zeolite membranes for these processes.

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Dehydration performance of a hydrophobic DD3R zeolite membrane

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Abstract The all-silica deca dodecasil 3R (DD3R) membrane turns out to be well suited to separate water from organic solvents under pervaporation conditions, despite its hydrophobic character. All-silica zeolites are chemically and hydrothermally more stable than aluminum containing ones and are therefore preferred for membrane applications, including for dehydration, even though these type of membranes are hydrophobic. Permeation of water, ethanol and methanol through a DD3R membrane has been measured at temperatures ranging from 344 K to 398 K. The hydrophobic membrane shows high water fluxes (upto $20 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$). The pure water permeance is insensitive to temperature and is well described assuming weak adsorption. Excellent performance in dewatering ethanol ($N=2 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and $\alpha_{w,e}=1500$ at 373 K and $x_w=0.18$) is observed and the membrane is also able to selectively remove water from methanol ($N=5 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and $\alpha_{w,m}=9$). Water could also be removed from methanol/ethanol/water ($\alpha_{w,e}=1500$, $\alpha_{m,e}=70$ at 373 K) mixtures, even at water feed concentrations below 1.5 mol%.

4.1 Introduction

The polarity of a zeolite is an important parameter determining the transport and separation properties in zeolite packed beds and in zeolite membranes. Conventionally hydrophilic membranes are used for dehydration of solvents. For zeolite membranes this usually implies a low silicon to aluminum ratio. High fluxes and selectivities have been measured in pervaporation and vapor permeation experiments using zeolite membranes with a high aluminum content [1–3]. Sodium LTA (NaA) type of membranes are already being used in industry [3]. FAU type membranes, with a Si/Al ratio of 1.5 - 1.6, have also been used to dehydrate alcohols, albeit with a lower selectivity and flux than the LTA type membranes [4, 5]. Well inter-grown LTA membranes have shown ideal selectivities higher than Knudsen selectivities for He/N₂ and H₂/N₂ [6], however, in LTA membranes a large portion of the flow is through the non-zeolite pores [2, 3, 7]. The mechanism of separation is thus based on preferential adsorption and diffusion through both zeolitic and non-zeolite pores. The high selectivity for water/alcohol mixtures is mainly caused by the preferential adsorption of water. Small defects can even enhance the membrane performance in dehydration because the flux is increased, while the selectivity is maintained due to the strong adsorption in the NaA zeolite [8]. The high aluminum content of these hydrophilic membranes, however, results in reduced chemical and hydrothermal stability [9, 10] and reduced membrane quality, due to inter-crystalline transport [11]. NGK insulators (Japan) has developed thin, defect-free all-silica DD3R zeolite membranes (Si/Al ratio = 980) deposited on an asymmetric α -alumina support [12, 13]. DD3R zeolite membranes are suitable candidates for the separation of small gas molecules, e.g. CO₂/CH₄ [14–16]. Because of the all-silica structure, the DD3R zeolite membrane is chemically and hydrothermally more stable than aluminum containing zeolites and can be used in dehydration of solvents and acids [17]. Den Exter *et al.* have investigated the adsorption of water on DD3R [18] which shows that at moderate pressures the water loading is far below the saturation loading of 8.55 mol·kg⁻¹, confirming its hydrophobic character. This weak adsorption on this hydrophobic material implies that the water separation mechanism in this membrane must differ from that in LTA type membranes. All-silica MFI type zeolite membranes have been used for water removal [19, 20], however, these membranes are based on preferential adsorption due to silanol groups and the mechanism of separation is identical to aluminum containing hydrophilic zeolites. The small pore size of DD3R (3.6 × 4.4 Å) suggests that

water separation from many solvents based on size exclusion is feasible [17]. In this chapter the dehydration performance of a DD3R zeolite membrane under pervaporation conditions is investigated. Pure component and mixture permeation of water, methanol and ethanol are presented. The membrane performance is characterized using permeances and separation factors and modeled using the fugacity difference over the membrane, assuming Henry type adsorption.

4.2 Theory

It has been widely accepted that the mass transport through zeolite membranes is well described using the Maxwell-Stefan equations [15, 21].

$$-\rho \frac{\theta_i}{RT} \frac{\partial \mu_i}{\partial z} = \sum_{\substack{j=1 \\ j \neq i}}^n \frac{q_j N_i - q_i N_j}{q_{i,sat} q_{j,sat} \mathcal{D}_{ij}} + \frac{N_i}{q_{i,sat} \mathcal{D}_{i,M}} \quad i = 1, 2, \dots, n \quad (4.1)$$

With the N_i denoting the flux of component i , $\theta_i = \frac{q_i}{q_{i,sat}}$ is the relative loading, q_i and $q_{i,sat}$ are the loading and saturation loading, respectively. Further, $\mathcal{D}_{i,j}$ and $\mathcal{D}_{i,M}$ are the Maxwell-Stefan diffusion coefficients between the permeating components and between the permeating component and the membrane, respectively. In small pore zeolites the interaction between species within the zeolite can be neglected [22], leaving

$$N_i = -\rho q_{i,sat} \mathcal{D}_{i,M} \frac{\theta_i}{RT} \frac{\partial \mu_i}{\partial z} \quad (4.2)$$

For water in DD3R, its loading is low at moderate pressures [18]. When one assumes the adsorption behavior in the Henry regime ($\theta_i = K_i f_i$), we can write for single component transport [23]

$$N_i = -\rho_i K_i \frac{\mathcal{D}_i}{\delta} \Delta f \quad (4.3)$$

In pervaporation processes the membrane performance is often characterized using the permeance, Π_i , comprising both adsorption and diffusion effects and relating the flux (N_i) to the fugacity difference over the membrane (Δf_i) [23, 24]. When the Poynting factor is neglected and ideal gas behavior is assumed at the permeate side, we can write [23]

$$N_i = -\Pi_i \Delta f_i = -\Pi_i (y_i P_{perm} - x_i \gamma_i P_i^0) \quad (4.4)$$

For a pure component (feed (x_i), and permeate (y_i) molar fraction equals 1), the feed side fugacity thus equals the saturation vapor pressure (P^0), while the permeate side fugacity is equal to the permeate side pressure (P_{perm}).

The temperature dependence of the permeance can be characterized by an apparent activation energy, E_{app} . This parameter comprises both the activation energy for diffusion as well as the enthalpy of adsorption.

$$\Pi_i = \Pi_{i,0} \exp\left(\frac{-E_{app}}{RT}\right) \quad (4.5)$$

To characterize the selectivity of the membrane, the separation factor, α , is used, defined by the following expression [25]

$$\alpha_{i,j} = \frac{y_i x_j}{x_i y_j} \quad (4.6)$$

in which x_i denotes the feed and y_i the permeate molar fraction of component i . The separation factor, as defined in equation 4.6, indicates the selective permeation of one component over another component in a mixture. To account for the pressure drop over the support layers, the Dusty Gas Model (DGM) is used combining viscous flow and Knudsen diffusion [21]. Using the permeate side pressure and the measured flux, the pressure drop over the support layer can be calculated, yielding the actual driving force over the selective layer of the membrane. Although this model neglects the Maxwell slip term [26, 27], it has been shown to give a sufficient description of the mass transport through ceramic supports under pervaporation conditions [28].

$$N^{visc} = -\frac{\varepsilon}{\tau} \frac{d_0^2}{32\eta} \frac{\bar{p}}{RT} \nabla p \quad (4.7)$$

$$N_i^{Kn} = -\frac{\varepsilon}{\tau} \frac{d}{3RT} \sqrt{\frac{8RT}{\pi M_i}} \nabla p_i \quad (4.8)$$

Since the sum of the partial pressures equals the total pressure, Equation 4.7 and 4.8 can be combined. The permeate side pressure and composition is known, as is the flux, therefore, the partial pressure drop over the support layer can be calculated.

4.3 Experimental

4.3.1 Materials

Permeation measurements have been conducted under pervaporation conditions for pure water, methanol and ethanol as well as ethanol/water and methanol/water and

ethanol/methanol/water mixtures. Demineralized water, technical grade ethanol and HPLC pure methanol (J.T. Baker, 99.8%) was used. The membrane used is an all-silica DD3R type zeolite membrane (NGK Insulators, Japan) supported on an α -alumina asymmetric tubular support ($150 \times 12\text{mm}$). Figure 4.1 shows a scanning electron microscopy image of the zeolite membrane.

4.3.2 Equipment

The permeation experiments were conducted using the setup shown in Figure 4.2. The setup consists of a feed vessel, heated by a thermostatic bath, controlling the temperature at the membrane outlet (TIC1). The liquid feed is pumped around between the feed vessel and the membrane module and the pressure in the module (PI1) can be adjusted using a valve (V1). The tubing on the permeate side is electrically traced to allow for experiments at higher permeate pressures. The permeate is condensed using a cold trap, which is cooled using liquid nitrogen. The inerts are removed using a vacuum pump. The setup can be heated to temperatures up to 423 K and can be pressurized up to 16 bar using nitrogen as a pressurizing gas.

4.3.3 Experimental methods

The flux is measured by determining the weight increase in time of the cold trap. The weight is measured every 10-120 min, depending on the flux. When the flux is stabilized the data is collected. To prevent the depletion of the permeating component a dosage pump can be used to add the preferentially permeating component back into the feed vessel. The ethanol/water and methanol/water composition of the feed and permeate is determined by means of densimetry (Anton Paar DMA5000), for low concentrations of water gas chromatography (Chrompack CP9002, FID) and Karl-Fischer titration (Metrohm 756 KF Coulometer) are used to analyse the samples. By measuring the flux at varying feed pressures the viscous flow contribution was found to be negligible at the beginning of the experimental series. The non-selective viscous flow decreases the membrane performance. At the end of the experimental series (after 14 months), the viscous flow contribution for pure water was 1.5% at 2 bar and 10% at 12 bar feed pressure.

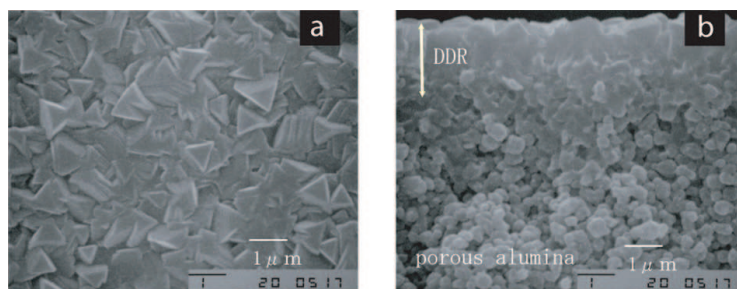


Figure 4.1: Top view (a) and cross section (b) of the NGK DD3R membrane deposited on an α -alumina substrate, observed by scanning electron microscopy.

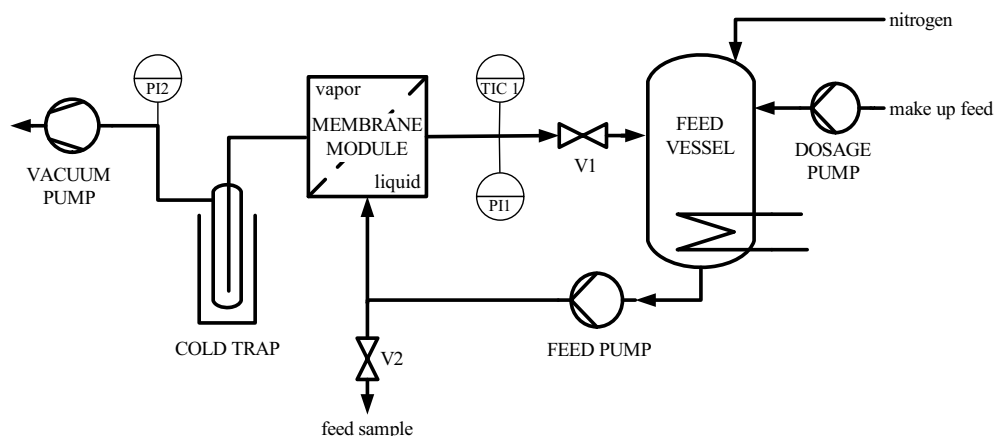


Figure 4.2: Schematic representation of the experimental setup

4.4 Experimental Results and Discussion

4.4.1 Pure component permeation

Pure water permeation up to 398 K has been measured. Figure 4.3 shows the pure water flux as a function of the feed temperature. High fluxes, upto $20 \text{ kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ are obtained. The flux increases with temperature, but the permeance is insensitive to temperature ($E_{app} = -9 \text{ kJ} \cdot \text{mol}^{-1}$, and $\Pi_0 = 4.1 \times 10^{-9} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$), yielding a straight line when plotting the driving force against the flux (Figure 4.6). The flux shows to be insensitive to an increase in permeate pressure up to 80 mbar. The pure methanol flux is an order of magnitude lower than that of pure water and is insensitive to temperature and permeate pressures up to 200 mbar (Figure

4.4); the methanol permeance consequently shows a strong decrease with temperature ($E_{app} = -32 \text{ kJ}\cdot\text{mol}^{-1}$, and $\Pi_0 = 1.3 \times 10^{-9} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$). The ethanol flux in Figure 4.5 is determined with more scattering due to the -even two orders of magnitude- lower values of the flux compared to water. Although the ethanol flux increases with temperature, the ethanol permeance also shows a decrease with temperature ($E_{app} = -24 \text{ kJ}\cdot\text{mol}^{-1}$, and $\Pi_0 = 4.2 \times 10^{-9} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$). If equation (4.4), assuming a constant permeance, would apply for these conditions, plotting the flux against the fugacity difference results in a straight line through the origin. Water permeation can be well described using this model, confirming the assumption of weak adsorption (Figure 4.6). Methanol and ethanol do not comply with this model. The high water fluxes despite of the low adsorption imply the diffusion coefficient of water in DD3R must be high (equation 4.3). Negative apparent activation energies have also been reported for NaA membranes [1] and are assigned to the a heat of adsorption which is larger than the diffusion energy of activation. Clearly, adsorption data are required to properly model the diffusion through the DD3R membrane.

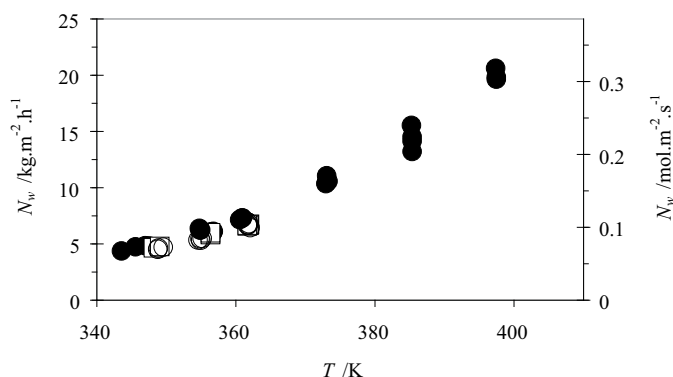


Figure 4.3: Pure water flux versus the feed temperature at different permeate pressures. $P_{perm} = 10 \text{ mbar}$ (●), 50 mbar (□), 80 mbar (○).

4.4.2 Mixture data

The dehydration performance for the DD3R zeolite membrane has been determined for ethanol/water and methanol/water mixtures. The permeate pressure was kept at a value of 10 mbar during the mixture permeation experiments. Figures 4.7 and 4.8 depict the fluxes and compositions measured for the separation of water from

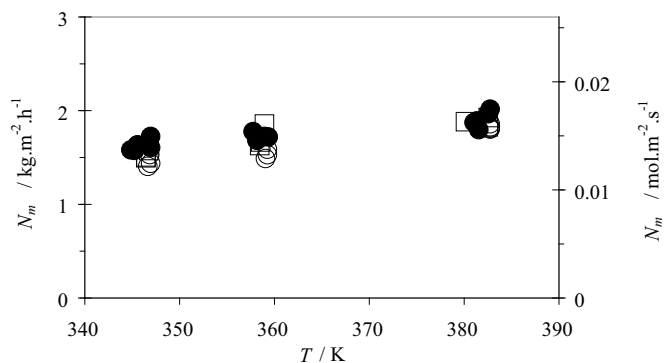


Figure 4.4: Pure methanol flux versus the feed temperature at different permeate pressures. $P_{perm} = 10$ mbar (●), 120 mbar (□), 200 mbar (○).

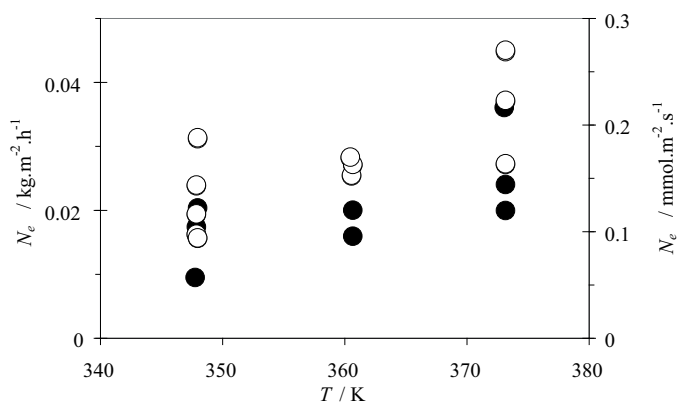


Figure 4.5: Pure ethanol flux versus the feed temperature at different permeate pressures. $P_{perm} = 10$ mbar (●), 200 mbar (○).

ethanol. The separation factor (up to 1500) and total fluxes (up to $2 \text{ kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$) are comparable to reported values for zeolite NaA and T membranes [29]. Figures 4.9 and 4.10 illustrate the fluxes and compositions for methanol dehydration. The fluxes are high ($5 \text{ kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$), but a lower separation factor (up to 9) is observed. The selectivity is lower than for ethanol/water mixtures, since the size selectivity is less pronounced. Figure 4.11 shows the permeances of water, ethanol and methanol in single component permeation and mixtures as a function of the kinetic molecular diameter [30]. The presence of water strongly influences the permeance of ethanol

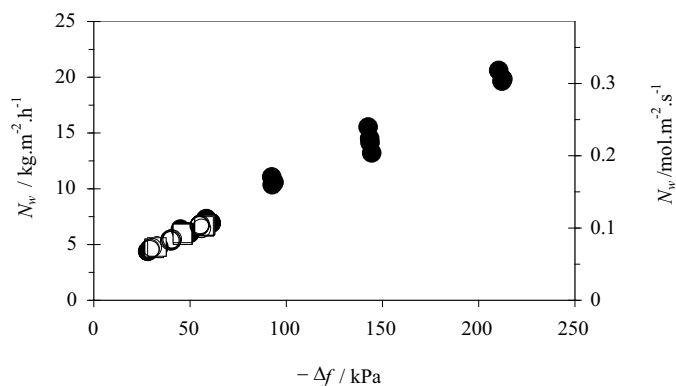


Figure 4.6: Pure water flux versus the fugacity difference in kPa at different permeate pressures. $P_{perm} = 10$ mbar (●), 50 mbar (□), 80 mbar (○).

and vice versa. Both ethanol and water permeance decreases due to the presence of the other component. Methanol and water, however, do not show this effect. This difference in behavior could be due to the difference in the interaction coefficient $\bar{D}_{ij}$ (equation 4.1), although the small pore size of DD3R suggest the interaction term should be negligible [22]. Possibly, the slowly diffusing ethanol molecules inside the cages hinder the accessibility of the cage windows for water, while water could influence the rotational freedom of ethanol, required to fit through the cage window. A more detailed study on adsorption and diffusion of these components is required to explain these phenomena.

4.4.3 Ternary mixtures

Mixtures of ethanol and methanol, containing ~ 1.5 mol% water have been separated at 348 K, 360 K and 373 K. Despite the low water content of the feed, the membrane showed to be able to selectively remove the water. The water content of the permeate ranges from 40 to 50 mol% (Figure 4.13). Figure 4.12 shows the total flux at two compositions ($x_m = 0.30$, $x_w = 0.02$ and $x_m = 0.50$, $x_w = 0.02$). Both methanol and water permeate preferentially over ethanol. The separation factor for water over ethanol increases with temperature from 1000 to 1500 (values similar to the binary mixture), while the water/methanol selectivity is higher than in the binary mixture (15 to 30). The methanol/ethanol separation factor is decreasing slightly with temperature from 70 to 55.

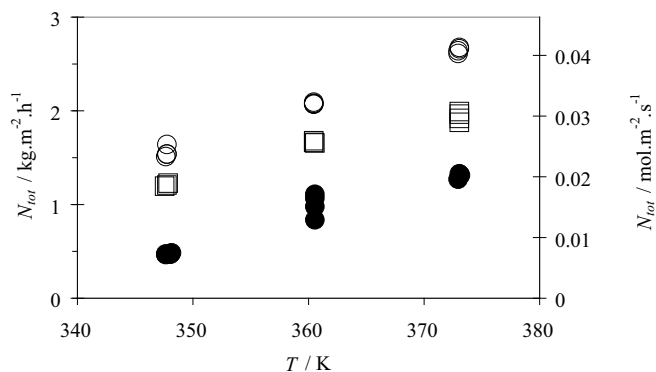


Figure 4.7: Total flux for water/ethanol mixtures for different feed concentrations versus the feed temperature. Molar fractions of water, $x_w = 0.18 \pm 0.08$ (●), 0.34 ± 0.04 (□), and 0.47 ± 0.01 (○).

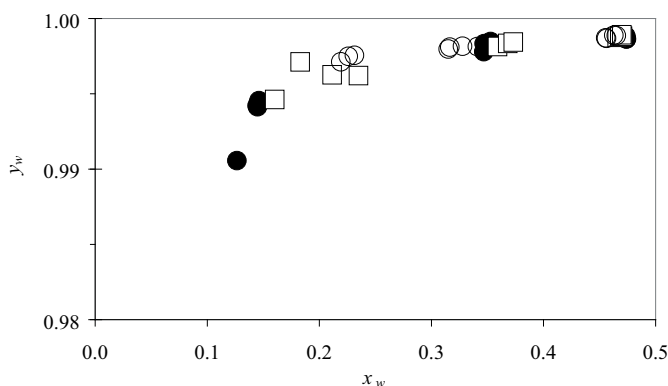


Figure 4.8: Permeate water molar fraction versus the feed water molar fraction for water/ethanol mixtures at $T = 348$ K (●), 360 K (□), and 373 K (○)

A complete interpretation of the presented pervaporation fluxes and selectivities requires detailed insight in the adsorption behavior of the studied components. Nevertheless it is clear that in spite of its low affinity for DD3R, the high permeation of water and its separation from methanol and ethanol is due to the combined effect of a high mobility of water within the DDR framework and a size induced hindered transport of the alcohols.

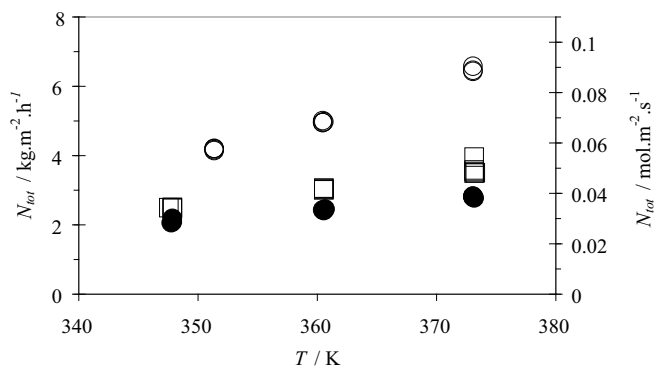


Figure 4.9: Total flux for water/methanol mixture for different feed concentrations versus the feed temperature. Molar fractions of water, $x_w = 0.10 \pm 0.01$ (●), 0.19 ± 0.03 (□), and 0.49 ± 0.01 (○).

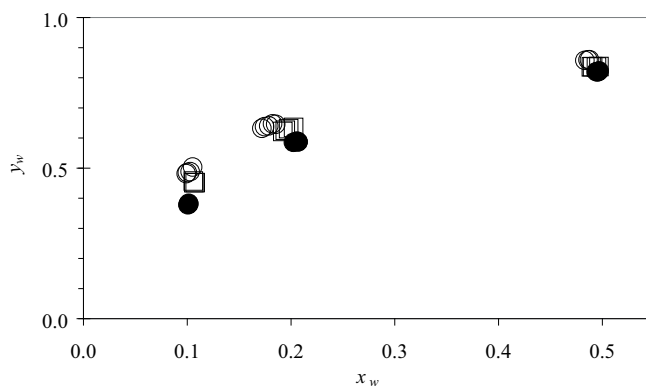


Figure 4.10: Permeate water molar fraction versus the feed water molar fraction for water/methanol mixtures at $T = 348 \text{ K}$ (●), 360 K (□), and 373 K (○)

4.5 Conclusions

Methanol/water and ethanol/water mixtures can successfully be dehydrated using a hydrophobic DD3R zeolite membrane. Mixtures of different compositions and pure component permeation of water, ethanol and methanol have been measured at different temperatures. High fluxes for pure water up to $20 \text{ kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ have been measured at 398 K . Although the adsorption loading of water is low, the weak interaction of water with the zeolite host enables high molecular mobility. The water

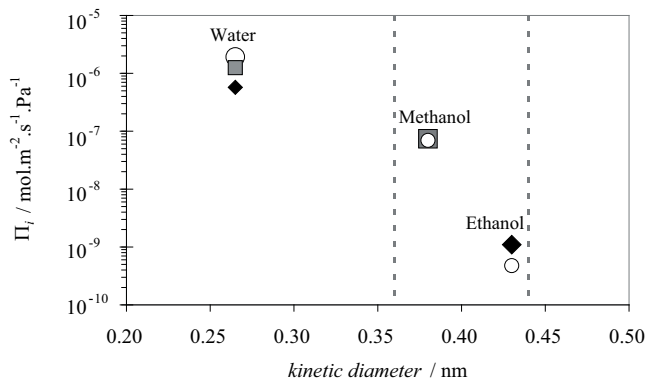


Figure 4.11: Permeances of pure water (○), pure methanol (■) and pure ethanol (◆) and ethanol/water and methanol/water mixtures at $x_w = 0.20$ and $T = 360$ K versus the kinetic molecular diameter. The dashed lines indicate the DD3R pore size..

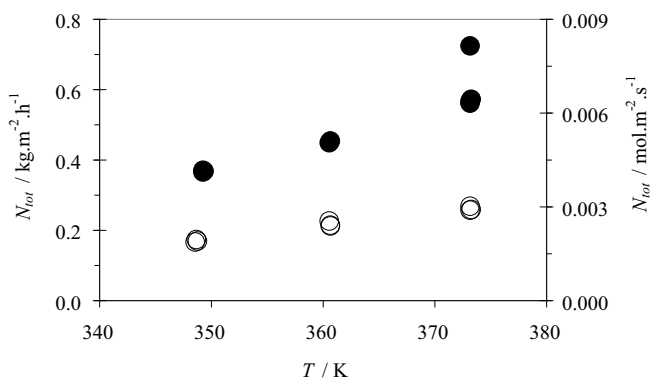


Figure 4.12: Total flux for the ternary mixture of ethanol/methanol/water for two compositions versus the feed temperature. Methanol molar fraction $x_m = 0.3$ (○) and 0.5 (●), Water molar fraction $x_w = 0.018$

flux can be well described using a constant permeance, assuming weak water adsorption. The pure methanol flux is insensitive to temperature at $2 \text{ kg.m}^{-2}.\text{h}^{-1}$, while the ethanol flux increases with temperature up to $0.05 \text{ kg.m}^{-2}.\text{h}^{-1}$ at 373 K . Despite the hydrophobic character of DD3R, selectivities for the dehydration of ethanol up to 1500 are measured with fluxes up to $2 \text{ kg.m}^{-2}.\text{h}^{-1}$. For methanol dehydration, selectivities up to 9 with fluxes up to $5 \text{ kg.m}^{-2}.\text{h}^{-1}$ were observed. Since water does not preferentially adsorb on DD3R, the separation is based purely on size exclusion. The

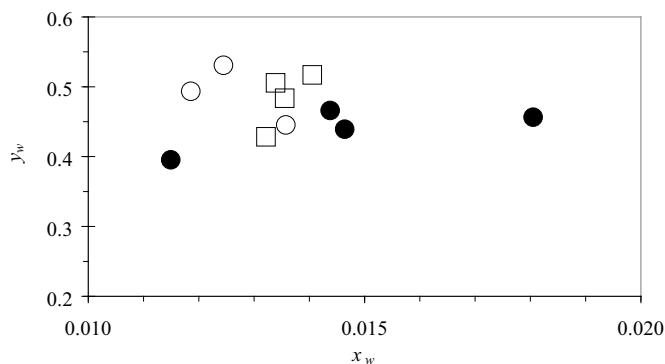


Figure 4.13: Feed water molar fraction versus permeate water molar fraction for ethanol/methanol/water mixtures at 348 K (●), 360 K (□), and 373 K (○).

presence of water has a strong influence on the ethanol permeation and vice versa. Methanol permeation, however, is insensitive to the presence of water. Water at concentrations below 1.5 mol% can still be removed from an ethanol/methanol mixture with a water/ethanol separation factor of 1500, while $\alpha_{m,e} = 70$. The flux and water separation factor in methanol, ethanol and ternary mixtures with water increase with temperature. The high flux and selectivity combined with the superior chemical stability of all-silica zeolites compared to their aluminum containing counterparts make the DD3R membranes a high potential candidate for dewatering of many solvents and acids.

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Adsorption of water, methanol and ethanol in all-silica DD3R: Experiments and simulation

This chapter has, to a large extent, been submitted as:

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Journal of Physical Chemistry C, submitted February 2009

Abstract This study comprises both experimental measurement as well as molecular modeling of adsorption of water, methanol, and ethanol on the hydrophobic all-silica deca dodecasil 3R (DD3R) zeolite. The simulation data are combined with permeation data of these components, measured using a DD3R membrane under pervaporation conditions. The pure component isotherms are measured by vapor phase adsorption and are calculated by Grand-Canonical Monte Carlo (GCMC) simulations. The simulations are conducted using molecular models from literature, without any adjustments. The simulations are in fair agreement with the experimental adsorption data. Computed mixture adsorption isotherms show that the water loading is significantly increased as compared to pure component adsorption. The shape of the computed water isotherm changes from type II to type I when alcohol is present. The loading of both methanol and ethanol at low fugacities is slightly enhanced by the presence of water. The mixture adsorption isotherms are used to calculate the transport diffusivities from pervaporation data. The transport diffusivity of water in DD3R is substantially larger than the diffusivities of both alcohols, but is decreased by an order of magnitude in the presence of methanol or ethanol. In permeation experiments of mixtures, the ethanol diffusivity is also decreased by an order of magnitude while the methanol diffusivity is practically unaffected. The mechanism of separation in the de-watering of alcohols using a hydrophobic DD3R membrane is based on the high diffusivity of water as compared to the alcohols, where especially ethanol suffers from diffusion limitations.

5.1 Introduction

Small pore zeolites have gained increasing interest in the fields of membrane technology and sensor applications. All-silica DD3R has been successfully applied for CO₂/CH₄ separation [1–3] and de-watering of alcohols and other organic solvents [4, 5]. Also hydroxy sodalite (SOD) membranes have been successfully synthesized and tested for water separation [6, 7]. Because of the pronounced size selectivity of these small pore zeolites, they are also well-suited for sensor applications. Dehydration of alcohols is already performed on industrial scale using LTA type zeolite membranes [8, 9]. To design and optimize these type of membrane separation processes, understanding and modeling the behavior of water and alcohols in zeolite membranes is of key importance.

The DDR zeolite topology consists of window-connected cages, which makes this material a member of the group of clathrasils [10]. The crystal structure is built by corner-sharing SiO₄ tetrahedra that are connected to pseudo-hexagonal layers of face-sharing pentagonal dodecahedra (5¹² cages). These layers are stacked in an ABCABC sequence and are interconnected by additional SiO₄ tetrahedra that form six-membered rings between the layers. Thus, two new types of cages arise, a small decahedron, 4³5⁶6¹ cage, and a large 19-hedron, 4³5¹²6¹⁸3 cage (Figure 5.1). By connecting the 19-hedra cavities through a single 8-ring with an aperture of 4.4×3.6 Å, a two-dimensional channel system is formed, which is accessible to small molecules after detemplation by thermal treatment at 773 K - 973 K or ozonation at 473 K [11]. The small decahedron and pentagonal cages are only accessible through 4-ring and 5-ring windows, so they are inaccessible for sorbed molecules. Three different materials with the DDR topology have been reported in the literature: all-silica deca dodecasil 3R (DD3R) [10], sigma-1 [12] and ZSM-58 [13]. For the synthesis of DD3R and sigma-1, 1-adamantanamine (1-ADA) is used as structure directing agent (SDA), while methyltropinium iodide (MTI) is used as SDA in the synthesis of ZSM-58. A DDR unit cell contains six 19-hedra cavities, which each have a volume of approximately 0.35 nm³ [14].

NGK insulators (Japan) have developed a high-silica DD3R zeolite membrane (Si/Al ratio = 980) consisting of a 2 μm zeolite layer deposited on an asymmetric α-alumina support [16, 17]. These membranes have been successfully tested in gas separation experiments, e.g. CO₂/CH₄ [2, 3, 18], and in dehydration of solvents and acids [4, 5]. Adsorption of several gases and vapors on DD3R powder was measured.

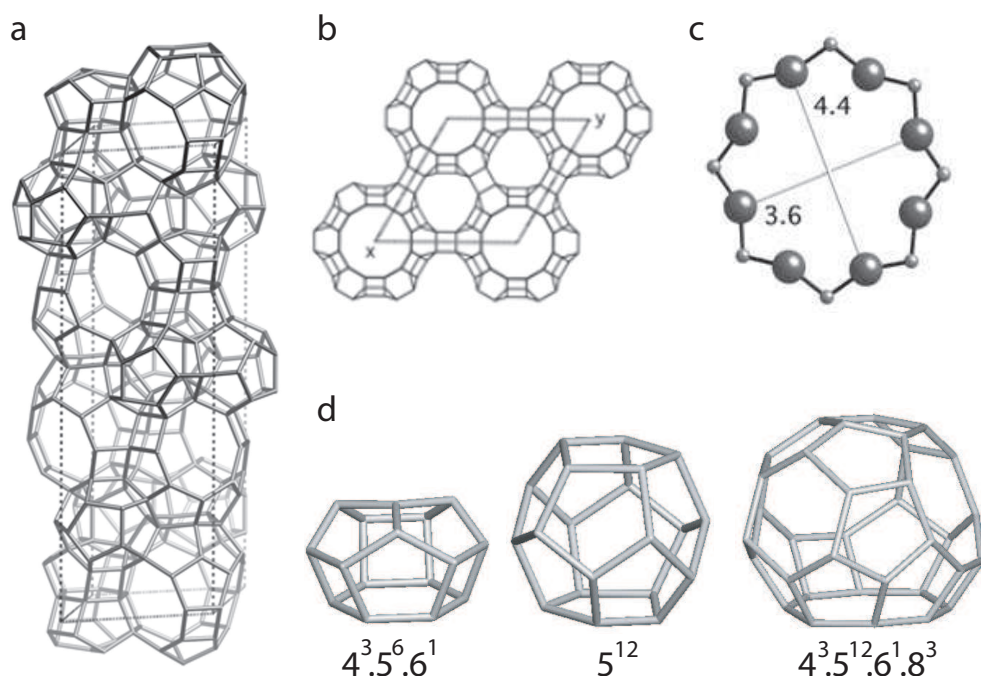


Figure 5.1: The DDR topology unit cell (a): normal to and (b): down on the [001]-plane, (c): the window opening, and (d): the decahedron, pentagonal and 19-hedra cages that build up the structure. Taken from Reference [15].

Zhu *et al.* reported adsorption of several saturated and unsaturated hydrocarbons on DD3R [14, 19]. The DD3R zeolite exhibits selective adsorption of 1,3-butadiene and *trans*-2-butene over 1-butene and *cis*-2-butene, revealing the size and shape selectivity of the DD3R zeolite [14]. Den Exter *et al.* investigated the adsorption of water on DD3R [20] and showed that the zeolite adsorbs water only to a very small extent, confirming its hydrophobic character. Nevertheless, the DD3R membranes have shown to remove water from alcohols at high selectivity under pervaporation conditions [4, 5]. Pervaporation is a mode of operation in membrane separation processes (Figure 5.2), where a liquid mixture is fed to a membrane while a low pressure or gas purge is applied to the permeate side. One or more components from the feed mixture selectively permeate through the membrane, and evaporate into the vapor phase (hence the word 'pervaporation'). In an earlier study [5], we reported pure component permeation fluxes of water, methanol, and ethanol as well as mixtures of these components at temperatures ranging from 344 K to 398 K. The mixture mea-

measurements were conducted at liquid molar feed fractions of water of $x_w = 0.1$ to 0.5, leading to water/ethanol separation factors of up to $\alpha_{w,e} = 1500$ and $\alpha_{w,m} = 9$ for water/methanol.

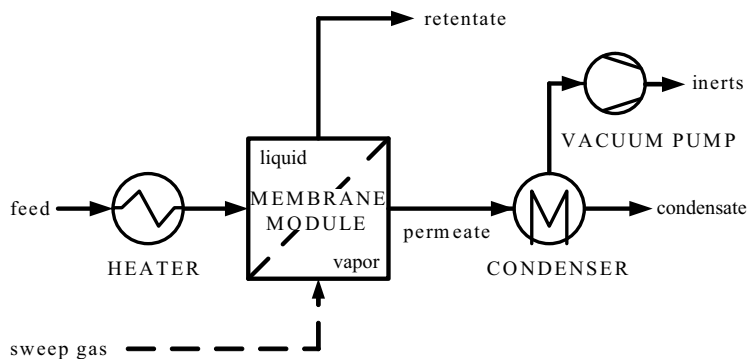


Figure 5.2: Schematic representation of a pervaporation process.

The behavior of water in hydrophobic zeolites is complex and simulation studies on water adsorption and permeation through small pore hydrophobic zeolite membranes, such as DDR, is not extensively studied. Molecular simulations of adsorption and diffusion of several compounds in the DDR structure are reported, but these involve mainly gaseous components, such as CH_4 , CO_2 and N_2 [21–23]. There is a large number of simulation studies on water in hydrophobic zeolites, although the systems considered are nearly exclusively silicalite-1 [24]. Demontis *et al.* demonstrated the complex temperature dependent behavior of water in silicalite-1 by molecular dynamics (MD) simulations including full flexibility of both the water molecules as well as the zeolite framework [25]. Desbiens *et al.* were able to reproduce experimental isotherms of water in silicalite-1 using simple models in GCMC simulations, applying the Tip4P and MSPC/E potentials for water and a rigid zeolite framework [26]. Similar interaction potentials have also been used to study adsorption of water and aromatics in the hydrophilic NaY zeolite [27]. Puibasset *et al.* used the PN-TrAZ water model in GCMC simulations of water in silicalite-1, however, the SPC model describing the confined water had to be adjusted to allow for a quantitative agreement with experimental data. [28]. Fleys *et al.* used the Compass force field to reproduce water adsorption isotherms on silicalite-1 and de-aluminated zeolite Y [29, 30]. The under-prediction of the water loading at low pressures was attributed to crystalline defects, resulting in silanol groups within the zeolite framework. Trzpit

et al. studied the effect of local defects on water adsorption in silicalite-1, enabling qualitative reproduction of the experimentally observed adsorption behavior [31]. A study focused on water in a hydrophobic small pore zeolite is reported by Coudert *et al.*, who studied the behavior of adsorbed water in an all-silica LTA zeolite by means of the Car-Parrinello molecular dynamics method (CPMD) [32].

The adsorption of methanol and ethanol are less comprehensively studied by computational methods. Usually, this adsorption is studied in the presence of water. The works of Vigner-Maeder *et al.* [33] and Pelmeshnikov *et al.* [34] are two pioneering *ab-initio* studies of methanol adsorption in silicalite-1 where the adsorption energies, enthalpies of adsorption, influence of defects and potential maps are calculated. Hinderer *et al.* [35] proposed a Monte Carlo scheme together with a lattice representation of silicalite-1 to study the diffusion of methanol, including the possibility of chemical reactions in the system. Plant *et al.* studied water/methanol diffusion in a NaY zeolite, describing the temperature dependence, the hydrogen bonding and the interaction with the cations [36]. Gupta *et al.* studied water/ethanol adsorption in silicalite-1, indicating the preferential siting of different molecules [37]. Lu *et al.* simulated the adsorption and separation performance of water and methanol mixtures in MFI, MOR, CFI and DON zeolites [38].

Several studies compared the zeolite membrane performance with molecular simulations. Takaba *et al.* employed dual ensemble Monte Carlo (DEMC) simulations to obtain the adsorption and diffusivities of water, ethanol and binary mixtures in pervaporation across a silicalite-1 membrane [39]. Jia *et al.* studied pervaporation of different components and binary mixtures in silicalite-1, zeolite A and chabazite membranes by MD simulations [40]. Furukawa *et al.* used non-equilibrium molecular dynamics (NEMD) simulations to study adsorption of ethanol/water mixtures in a hydrophilic NaA membrane, suggesting that the high selectivity for water is a cooperative effect of the adsorption selectivity and the high diffusivity of water within the zeolite [41]. Yang *et al.* studied methanol/water [42] and ethanol/water [43] permeation across silicalite-1 membranes by combining GCMC and MD simulations in the NVT-ensemble. They were able to qualitatively predict the separation factor and fluxes, while the discrepancies between simulations and measurements were attributed to the existence of crystalline defects in the experimental systems. Modeling an idealized zeolite will always give a discrepancy with real systems, since zeolite crystals often consist of complex inter-grown structures with internal grain boundaries and defects containing silanol groups and varying pore orientation [44].

This study is focused on measuring and simulating adsorption of water, methanol and ethanol on an all-silica DD3R zeolite to elucidate the mechanism of water transport and separation in DD3R zeolite membranes. To the best of our knowledge, no simulation data on these systems and no adsorption data of alcohols on DD3R have been reported before. Pure component vapor phase adsorption data are measured and GCMC simulations are conducted to calculate pure component and mixture isotherms using interaction potentials from literature without further adjustment. The calculated mixture adsorption isotherms are supplemented with permeation data measured under pervaporation conditions to obtain transport diffusivities.

5.2 Experimental methods

5.2.1 Synthesis

To perform adsorption experiments, DD3R crystals were prepared by the method described by Gascon *et al.* [45]. All chemicals were purchased from Aldrich and used as received, without further preliminary purification. The synthesis mixture had the molar ratio of 1-ADA : SiO₂ : ethylenediamine (EDA) : H₂O = 47 : 100 : 404 : 11240 and it was prepared as follows. 1.72 g of 1-ADA (97 wt%) was dissolved in 5.76 g EDA (≥ 99 wt%) and was placed in an ultrasonic bath for 1 h. Water (38 g) was then added rapidly. The mixture was placed in a shaking machine for 1 h. After heating to 368 K for 1 h while stirring, the mixture was cooled down in ice. Aerosil 200 (1.41 g) was then slowly added while the solution was stirred vigorously. The mixture was again heated to 368 K in an open vessel while stirring until the solution became clear (the solution changed from white to almost transparent). As-synthesised DD3R crystals (0.01 g) were added as seeds. The resulting solution is placed in a teflon lined autoclave and heated under hydrothermal conditions (autogenous pressure) to 433 K for 2 days under rotation at 60 rpm. The synthesized samples were calcined at 873 K for 6 h using a heating and cooling rate of 60 K·h⁻¹. The calcination was carried out in static air (Carbolite CSF1100).

The synthesized DD3R crystals are homogeneous diamond-like crystals, as reported by den Exter *et al.* [20]. The size of the crystals is 2.7 μm , measured by laser diffraction and a micropore volume of 0.13 cm³·g⁻¹ was determined by nitrogen adsorption at 77 K using the *t*-plot method [11].

5.2.2 Adsorption

The synthesized zeolite crystals are used for adsorption measurement of water, ethanol and methanol. The single component vapor adsorption (Quantachrome Autosorb-6B) experiments were conducted to determine the adsorption isotherms at different temperatures. Prior to the vapor-phase adsorption measurements, the samples were dried in vacuum at 573 K in order to remove moisture and other volatile components (the weight of the sample after drying is used in the calculations). The adsorption and desorption isotherms were measured at 273 K, 303 K and 333 K, which is the maximum temperature for vapor adsorption in this setup.

5.2.3 Analysis of permeation experiments

Pure component, and mixture permeation of water, ethanol and methanol were previously reported [5]. These permeation measurements were conducted under pervaporation conditions, applying vacuum with a permeate pressure of $p^{perm} = 1$ kPa. In this study we use the pure component measurements as well as measurements of the binary alcohol/water mixtures for comparison and validation of the calculated adsorption data and for calculation of diffusivity data.

The Maxwell-Stefan (M-S) equations are generally used to model mass transport in zeolites and zeolite membranes [46]. They have been successfully applied to several systems [47–49]. These equations balance the driving forces with the friction exerted on molecules and are consistent with the theory of irreversible thermodynamics [50, 51]. In the case of transport through a porous membrane, the membrane can be viewed as a component, M . Using the membrane as frame of reference (choosing the membrane velocity, $v_M = 0$), the M-S equations for an n -component system can be written as [52]

$$-\rho_z \frac{\theta_i \nabla \mu_{i,T}}{RT} = \sum_{\substack{j=1 \\ j \neq i}}^n \frac{(q_j N_i - q_i N_j)}{q_i^{sat} q_j^{sat} \mathcal{D}_{ij}} + \frac{N_i}{q_i^{sat} \mathcal{D}_{iM}} \quad (5.1)$$

Where $\nabla \mu_{i,T}$ denotes the chemical potential gradient at constant temperature as the driving force for mass transport, N_i denotes the molar flux of component i , $\mathcal{D}_{iM}$ is the M-S diffusivity of component i in the microporous membrane, $\mathcal{D}_{ij}$ is the M-S cross-diffusivity that accounts for the interaction between permeating components, and θ_i denotes the fractional loading, defined as the ratio of the loading, q_i over the

saturation loading, q_i^{sat}

$$\theta = \frac{q_i}{q_i^{sat}} \quad (5.2)$$

In small pore zeolites the interaction between species within the zeolite can be neglected (i.e. $\mathcal{D}_{ij} = 0$) [53]. When only transport in the z -direction is considered, equation 5.1 reduces to

$$-\frac{\theta_i}{RT} \frac{d\mu_{i,T}}{dz} = \frac{N_i}{\rho_z q_i^{sat} \mathcal{D}_{iM}} \quad (5.3)$$

The chemical potential gradient can be converted to a gradient in loading, using the thermodynamic correction factor, Γ_{ij} , which relates the fractional loading θ_i to the fugacity, f_i [46].

$$\frac{\theta_i}{RT} \frac{d\mu_{i,T}}{dz} = \Gamma_{ij} \frac{d\theta_i}{dz} \quad (5.4)$$

where

$$\Gamma_{ij} \equiv \frac{\theta_i}{f_i} \frac{\partial f_i}{\partial \theta_j} = \frac{q_j^{sat}}{q_i^{sat}} \frac{q_i}{f_i} \frac{\partial f_i}{\partial q_j} \quad i, j = 1, n \quad (5.5)$$

When the driving force is expressed as the gradient in loading, $\frac{dq_i}{dz} = q_i^{sat} \frac{d\theta_i}{dz}$, the flux can be expressed as [52]

$$N_i = -\rho_z \mathcal{D}_{iM} \left[\Gamma_{ii} \nabla q_i + \Gamma_{ij} \frac{q_i^{sat}}{q_j^{sat}} \nabla q_j \right] \quad (5.6)$$

In single component permeation, the Fickian, or transport diffusivity, D_{iM}^T , can be related to the M-S diffusivity by [54]

$$D_{iM}^T = \Gamma_i \mathcal{D}_{iM} \quad (5.7)$$

For the Langmuir isotherm,

$$q_i = q_i^{sat} \frac{K_i f_i}{1 + K_i f_i} \quad (5.8)$$

the thermodynamic correction factor equals

$$\Gamma_i = \frac{1}{1 - \theta_i} \quad (5.9)$$

When Langmuir adsorption is assumed and the loading dependency of the M-S diffusivity can be described by

$$\mathcal{D}_{iM} = \mathcal{D}_{iM,0} (1 - \theta_i) \quad (5.10)$$

the transport diffusivity in equation 5.7 is equal to the M-S diffusivity [55]. This type of loading dependency is often found for molecules with similar dimensions as the pore size of the zeolite [45, 56].

Combining equations 5.3, 5.5 and 5.7, gives

$$N_i = -\rho_z D_{iM}^T \frac{dq}{dz} \quad (5.11)$$

Integrating dz from the feed side, $z = 0$, to the permeate side, $z = \delta$, and integrating dq_i from the feed side loading, q_i^{feed} , to the permeate side loading, q_i^{perm} , and assuming a constant D_{iM}^T gives the ratio of the flux and the difference in loading as

$$-\frac{N_i}{q_i^{feed} - q_i^{perm}} = \frac{\rho_z}{\delta} D_{iM}^T \quad (5.12)$$

wherein the membrane thickness, δ , and the density of the zeolite, ρ_z , are constant for a specific membrane.

The temperature dependence of the diffusivity is generally described by an Arrhenius type of equation, using an energy of activation, E_A .

$$D_{iM}^T = D_{iM,0}^T \exp\left(-\frac{E_{A,i}}{RT}\right) \quad (5.13)$$

In pervaporation processes, the liquid feed side fugacity, f_i^{feed} , can be calculated using [57]

$$f_i^{feed} = x_i^{feed} \gamma_i p_i^{sat} \phi_i^{sat} \exp\left[\frac{V_{m,i}^l (p - p_i^{sat})}{RT}\right] \quad (5.14)$$

Where x_i^{feed} is the liquid molar fraction and γ_i denotes the activity coefficient in the mixture, p is the system pressure, and $V_{m,i}^l$ is the partial molar volume of component i in the liquid feed. The Antoine equation is used to calculate the vapor pressure, p_i^{sat} , as a function of temperature [58]. The fugacity coefficient ϕ_i^{sat} and the Poynting factor (exponent term in equation 5.14) can be assumed to equal unity at pervaporation conditions. In this study, the activity coefficients were calculated using the NRTL Gibbs excess energy model.

To calculate the adsorption from a given liquid feed, the fugacities are calculated, and these are used as input for the GCMC calculations. The composition can be expressed as the ratio of the component fugacity over the sum of the fugacities of all

species in the mixture

$$\gamma_i = \frac{f_i}{\sum_{j=1}^n f_j} \quad (5.15)$$

As the permeate side is operated at low pressures, it is well approximated by the ideal-gas limit

$$f_i^{perm} = p_i^{perm} = y_i^{perm} p^{perm} \quad (5.16)$$

Therefore, the fugacity ratio, γ_i , equals the vapor molar fraction, y_i , at these conditions.

In experimental studies, the permeation is often described by the permeance, Π_i , defined as the ratio of the flux and the difference in fugacity over the membrane [59]. The temperature dependency of the permeance is then characterized by an apparent energy of activation, E_{app} , which can be seen as the sum of the activation energy of diffusion and the enthalpy of adsorption [54].

5.3 Simulation methods

Adsorption isotherms in confined systems are conveniently computed using GCMC simulations, in which the temperature, the volume and the chemical potential of the system are prescribed. The imposed chemical potential is directly related to the fugacity, which is used as input for the simulations. At high densities, the probability of successfully inserting a molecule in the system is very low. Therefore, the insertion and deletion of molecules in and from the system were performed using the configurational-bias Monte Carlo (CBMC) technique [60] in combination with other MC moves, namely: regrowth, rotation, and translation. In the case of ethanol/water mixtures, identity change moves were also used to increase the performance of the simulation [61]. More details on this simulation technique can be found elsewhere [62, 63]. The saturation loadings were calculated from a single adsorption simulation at a high fugacity. The enthalpies of adsorption were computed as the isosteric heats of adsorption at zero loading using MC simulations in the NVT ensemble [64].

There are several diffusion coefficients that can be used to describe the motion of molecules within a zeolite. Generally, the Fick, or transport diffusivity, D_i^T , is the most intuitive definition of a diffusion coefficient, relating a molar flux to a gradient in concentration [65]. The actual thermodynamic driving force for transport is, however, the gradient in chemical potential [66]. Using the framework of irreversible

thermodynamics, the collective, corrected, or Maxwell-Stefan (M-S) diffusivity, $\bar{D}_i$, can be defined, relating the thermodynamic driving force to a molar flux [54]. The self diffusivity, D_i^S , describes the motion of individual particles and can be related to the mean square displacement of the individual molecules during equilibrium MD simulations by the Einstein relation [67]. The M-S and the transport diffusivity can be obtained from NEMD but also from equilibrium MD simulations by considering the collective motion of molecules [67].

In this study, water is modeled using the Tip5pEw potential [68]. The alcohols were described with the TraPPE force field [69], which was also applied by Jakobtorweihen *et al.* for modeling ethene, propene, and *trans*-2-butene in DD3R [23]. No hydrolysis is expected during the adsorption of these molecules in zeolites under the conditions applied [36, 70]. Intramolecular potentials are included to describe the flexibility of alcohols, while the water molecules are kept rigid. The bond lengths are fixed for all molecules. Bond bending potentials are considered for methanol and ethanol, and a torsion potential is used for ethanol [69].

The crystallographic positions of the zeolite atoms were obtained from X-ray diffraction (XRD) characterization data of the structure [71]. The simulations were performed using $1 \times 2 \times 1$ unit cells with periodic boundary conditions, so that the size of the simulation box was more than twice the Lennard-Jones cut-off radius of 12 Å. To reduce the calculation time, the simulations were performed using a rigid framework [72]. Since the $4^3.5^6.6^1$ and the 5^{12} cages of the DDR structure only contain five membered ring windows, they are inaccessible for sorbed species. To ensure no molecules are adsorbed in these cages during the simulations, they were blocked [23].

The models of Beerdsen *et al.* [73, 74] and Calero *et al.* [75, 76] are used to assign partial charges to the zeolite atoms. The Coulombic interactions were calculated using the Ewald summation with a relative precision of 10^{-6} [77]. The non-Coulombic interactions between non-bonded atoms or atom-groups are modeled using 12-6 Lennard-Jones potentials, truncated and shifted to zero at the cut-off of 12 Å.

The Van der Waals interactions between the adsorbates and the framework are dominated by the dispersive forces between the atom-groups of the sorbed molecules and the oxygen atoms of the zeolite [78, 79]. For this reason, they are modeled through an effective potential that only takes the oxygen atoms of the zeolite structure into account. One set of potential parameters that has been used in previous

studies on water adsorption in zeolites has been implemented [80], together with Lorentz-Berthelot mixing rules in order to account for the rest of the interactions. All parameters for non-bonded interactions used in this work are listed in Table 5.1.

Table 5.1: Force field parameters used in the simulations. The water model has two off-center charges that are labeled M in the table. The name 'alcohol' refers to both methanol and ethanol molecules.

Atom	$\epsilon/k_B/\text{K}$	$\sigma/\text{\AA}$	q/e	Ref.
Si (zeolite)	-	-	2.05	[75]
O (zeolite)	93.53	3.0	-1.025	[80]
O (water)	89.516	3.097	-	[68]
H (water)	-	-	0.241	[68]
M (water)	-	-	-0.241	[68]
CH ₃ (methanol)	98.0	3.75	0.265	[69]
CH ₃ (ethanol)	98.0	3.75	-	[69]
CH ₂ (ethanol)	46.0	3.95	0.265	[69]
O (alcohol)	93.0	3.02	-0.7	[69]
H (alcohol)	-	-	0.435	[69]

5.4 Experimental Results

5.4.1 Single component adsorption

The experimental adsorption and desorption isotherms and calculated adsorption isotherms for water, methanol and ethanol are shown in Figures 5.3, 5.4, and 5.5, respectively. No significant hysteresis effects were observed in the desorption measurements.

Adsorption data for water was previously published by den Exter *et al.* [20]. Our measurements at $T = 333\text{ K}$ and 323 K correspond well with the previous data; whereas at 303 K we find a somewhat lower adsorption loading. The form of the water adsorption isotherms (type II) is consistent with simple BET models valid for free surfaces or fine capillaries with no constraint imposed on the adsorption from the opposite wall. However, it is expected to resemble type IV adsorption when reaching saturation [81]. The calculated water loading, however, under-predicts the experimental values (Figure 5.3). The calculated water isotherms resemble type III adsorption behavior at low fugacities, which is typical for water adsorption on hydrophobic surfaces [82].

The alcohol isotherms show a type I adsorption behavior, which is consistent with Langmuir adsorption (Figures 5.4 and 5.5). The fitted Langmuir parameters, using equation 5.8, are given in Table 5.2. The calculated methanol and ethanol isotherms

show a similar shape and order of magnitude as the experimental data. However, at low methanol fugacities, the loading is under predicted while at higher fugacities the calculated values are higher than the measured data.

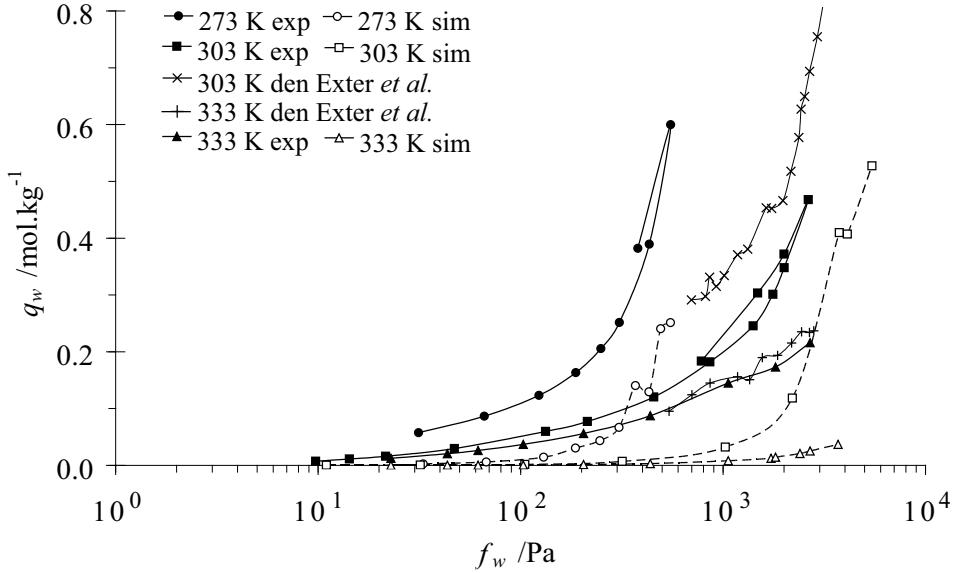


Figure 5.3: Water adsorption isotherms at 273 K (this study, experimental (●) and simulation (○)), 303 K (this study, experimental (■) and simulation (□), and den Exter *et al.* (×)[20]), and at 333 K (this study, experimental (▲) and simulation (△), and den Exter *et al.* (+)[20]). The solid lines and the dashed lines are a guide to eye for the experimental and calculated isotherms, respectively.

Table 5.2: Fitted Langmuir parameters from the measured isotherms of methanol and ethanol on DD3R at 273 K, 303 K, and 333 K.

T / K	Methanol		Ethanol	
	q_i^{sat} / mol.kg ⁻¹	K_i / × 10 ⁻³ Pa.s ⁻¹	q_i^{sat} / mol.kg ⁻¹	K_i / × 10 ⁻³ / Pa.s ⁻¹
273	1.39 ± 0.03	18.18 ± 1.77	1.38 ± 0.03	16.81 ± 1.82
303	1.53 ± 0.03	3.30 ± 0.29	1.51 ± 0.02	3.52 ± 0.29
333	1.60 ± 0.06	0.53 ± 0.05	1.55 ± 0.05	0.70 ± 0.07

The saturation loading is estimated by calculating the loading at a fugacity of 1 GPa and 303 K. This yields a saturation loading of 13.9, 4.2, and 3.8 mol.kg⁻¹ for water, methanol and ethanol, respectively (Figure 5.6), corresponding with 33, 10, and 9 molecules per 19-hedra cage, respectively. The calculated water adsorption

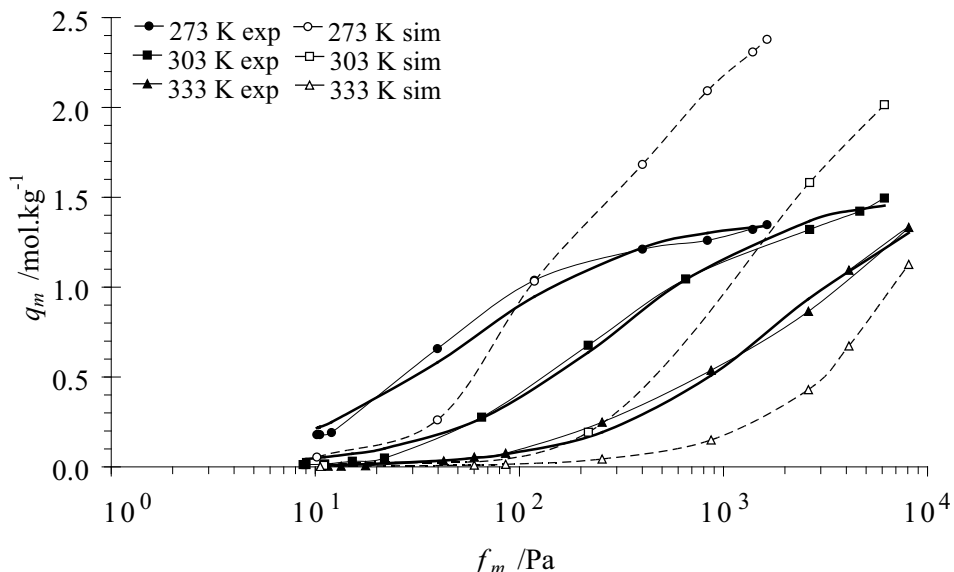


Figure 5.4: Methanol adsorption isotherms at 273 K (experimental (●) and simulation (○)), 303 K (experimental (■) and simulation (□)), and at 333 K (experimental (▲) and simulation (△)). The bold lines indicate the Langmuir fit through the experimental data, the thin solid lines and the dashed lines are a guide to eye for the experimental and calculated isotherms, respectively.

isotherm at 303 K resembles type V behavior. It should be noted that the water loading still showed a slight increase when increasing the fugacity from 100 MPa to 1 GPa, but the increase is within the accuracy of the simulations.

Figures 5.7, 5.8, and 5.9 show snapshots of the simulation box in single component adsorption of water, methanol, and ethanol, respectively, at 360 K and both at low fugacities and at 100 MPa. The hydrogen bridges between the adsorbed molecules are indicated in the figures. The water molecules form clusters inside the 19-hedra cages, whereas methanol, and especially ethanol shows to be more distributed over the DD3R topology.

5.4.2 Mixture adsorption

Mixture adsorption isotherms have been computed at 303 K and 360 K at a constant ratio of the water fugacity, f_w , divided by the sum of the water and the alcohol fugacity, f_a , of $\gamma_w = 0.1, 0.2$ and 0.5 . At low fugacities, this equals the vapor molar fraction, y_w . Figures 5.10 and 5.11 show the mixture adsorption isotherms, together

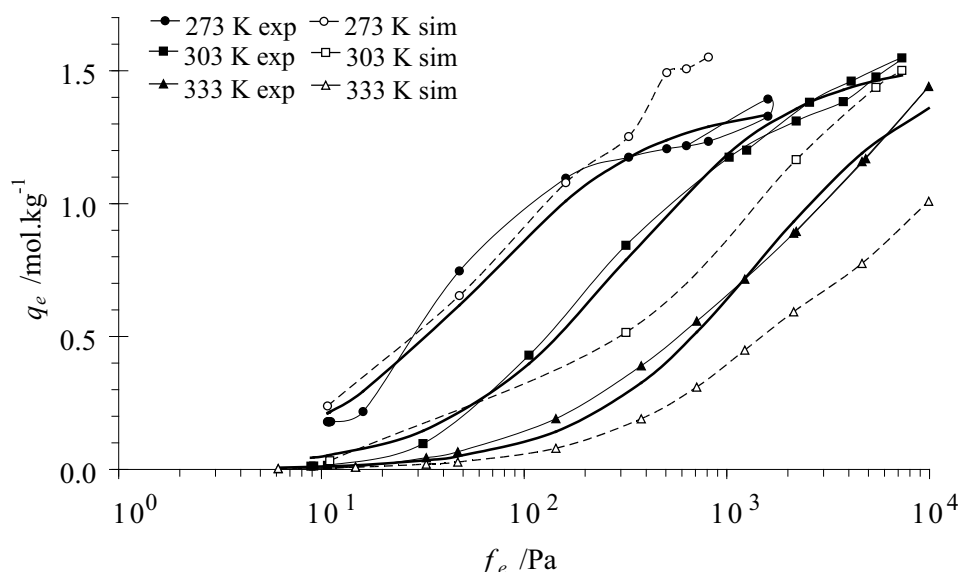


Figure 5.5: Ethanol adsorption isotherms at 273 K (experimental (●) and simulation (○)), 303 K (experimental (■) and simulation (□)), and at 333 K (experimental (▲) and simulation (△)). The bold lines indicate the Langmuir fit through the experimental data, the thin solid lines and the dashed lines are a guide to eye for the experimental and calculated isotherms, respectively.

with the single component isotherms at 303 K for methanol/water and ethanol/water mixtures, respectively. The loading of each component is given as a function of the component fugacity. The isotherms show that, at low fugacities, the loading is increased compared to pure component adsorption for all components. This effect is more pronounced for water adsorption than for the alcohols. The shape of the water isotherm changes from type V to type I, resembling the shape of the alcohol isotherms. For methanol/water mixtures the water loading decreases with water fugacity ratio, while for the ethanol/water mixtures the water loading is insensitive to the water feed fraction between 0.1 and 0.5. The alcohol loading at low fugacity shows a small increase with water fugacity ratio, although the shape of the isotherm remains the same as for single component adsorption.

Figure 5.12 shows the binary adsorption isotherms as a function of the sum of the water and alcohol fugacities up to 180 kPa at 360 K at a constant water fugacity ratio of 0.2, which corresponds to a feed molar fraction of $x_w = 0.5$ and 0.2 for methanol/water and ethanol/water mixtures at 360 K, respectively. These conditions

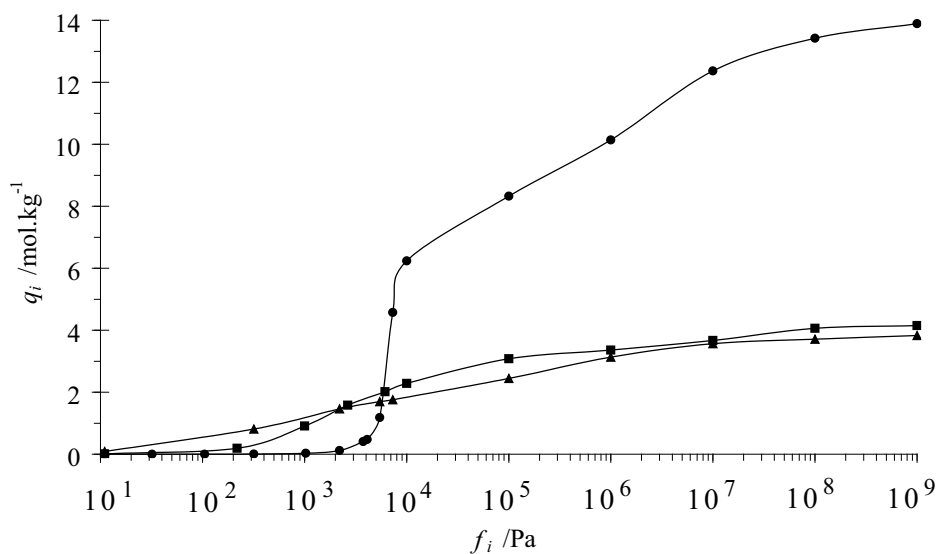


Figure 5.6: Water (●), methanol (■), and ethanol (▲) adsorption isotherms up to 1 GPa at 303 K.

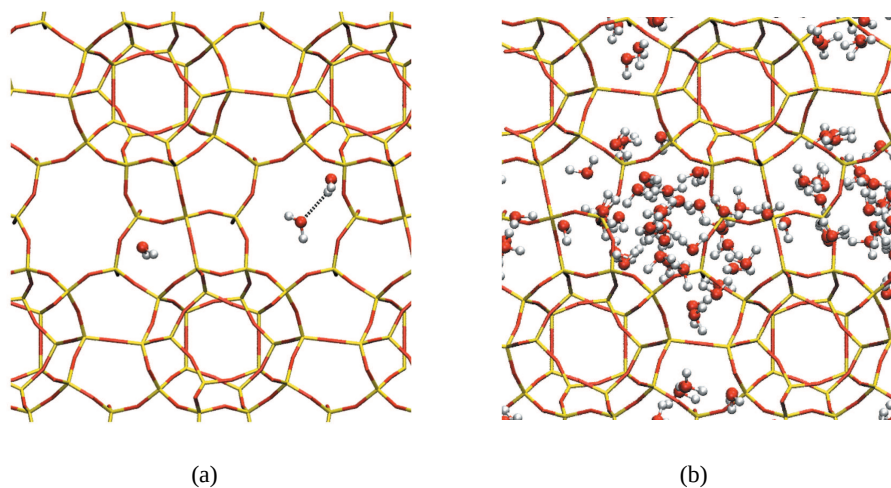


Figure 5.7: Snapshots of single component water adsorption on DD3R at 360 K at (a): 50 kPa and (b): 100 MPa.

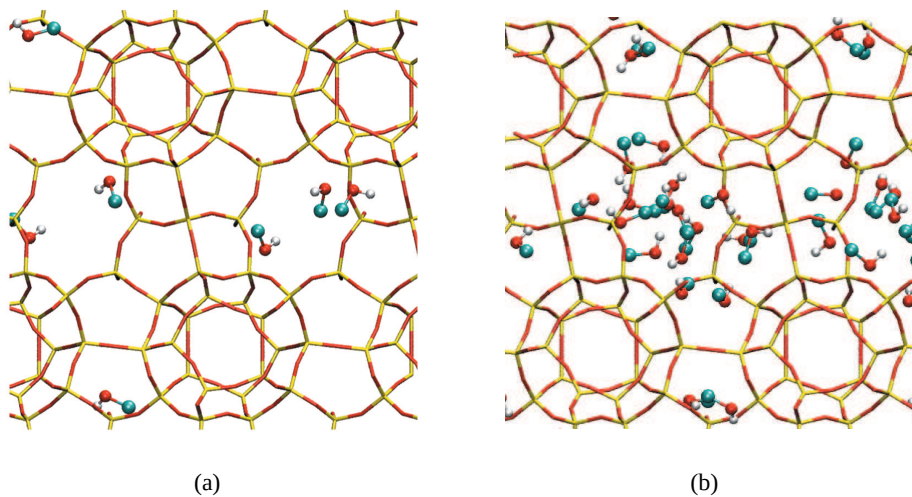


Figure 5.8: Snapshots of single component methanol adsorption on DD3R at 360 K at (a): 15 kPa and (b): 100 MPa.

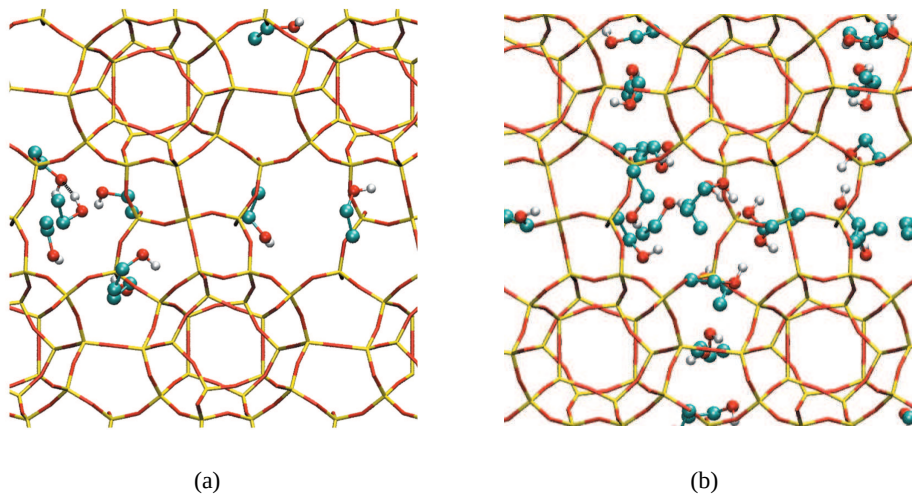


Figure 5.9: Snapshots of single component ethanol adsorption on DD3R at 360 K at (a): 12 kPa and (b): 100 MPa.

correspond to the feed conditions of the conducted pervaporation experiments, which are indicated by the dashed lines. The loading of each component at the feed side under the pervaporation conditions can be directly read from the vertical axis. The calculated water loading remains lower than the alcohol loading within the range of calculated total fugacities. The ethanol loading at the experimental feed condition is lower than that of methanol, while the water loading is equal in both systems.

Figures 5.13a and b show snapshots of the mixture adsorption of methanol/water and ethanol/water, respectively. The figures show a higher loading of the alcohols compared to water. The water molecules show a preferential adsorption in the vicinity of the alcohol groups of the adsorbed methanol and ethanol molecules with which hydrogen bonds are formed.

5.4.3 Combination with permeation data

To elucidate the mechanism of separation of the selective water transport through the hydrophobic DD3R membrane, the simulation data are combined with permeation measurements conducted under pervaporation conditions. To assess the diffusivity of the components, the feed conditions of the pervaporation experiments of pure component and mixture permeation are taken as input to calculate the loading at the feed side. Using equation 5.12, these loadings are used to calculate the transport diffusivities regarding the transport as single component permeation. In the calculations, a zeolite density of $\rho_z = 1700 \text{ kg}\cdot\text{m}^{-3}$ was used, which follows from the unit cell dimensions [15], and a membrane thickness of $2 \text{ }\mu\text{m}$ is assumed.

At the conditions of the pure component permeation experiments, the calculations predict a water loading at the feed side of the membrane which is a factor 2 to 3 lower than for the alcohols (Table 5.3). The calculated feed side loading and the transport diffusivities for the methanol/water and ethanol/water mixtures are listed in Tables 5.4 and 5.5, respectively. The measured permeate side water molar fraction, y_w^{perm} , and the feed composition, x_w^{feed} , are also given, which give a measure for the selectivity. Although the presence of alcohol enhances water adsorption, at the feed conditions of the mixture permeation experiments, the simulation data suggest that the molar water loading is still only half of the alcohol loading.

For mixture permeation at 360 K, the transport diffusivities are given as a function of the feed side composition, x_w (Figure 5.15). The diffusivities were calculated similar to the single component permeation (neglecting Γ_{ij}) and, therefore, only give a first approximation of the actual values. The calculated transport diffusivities of water

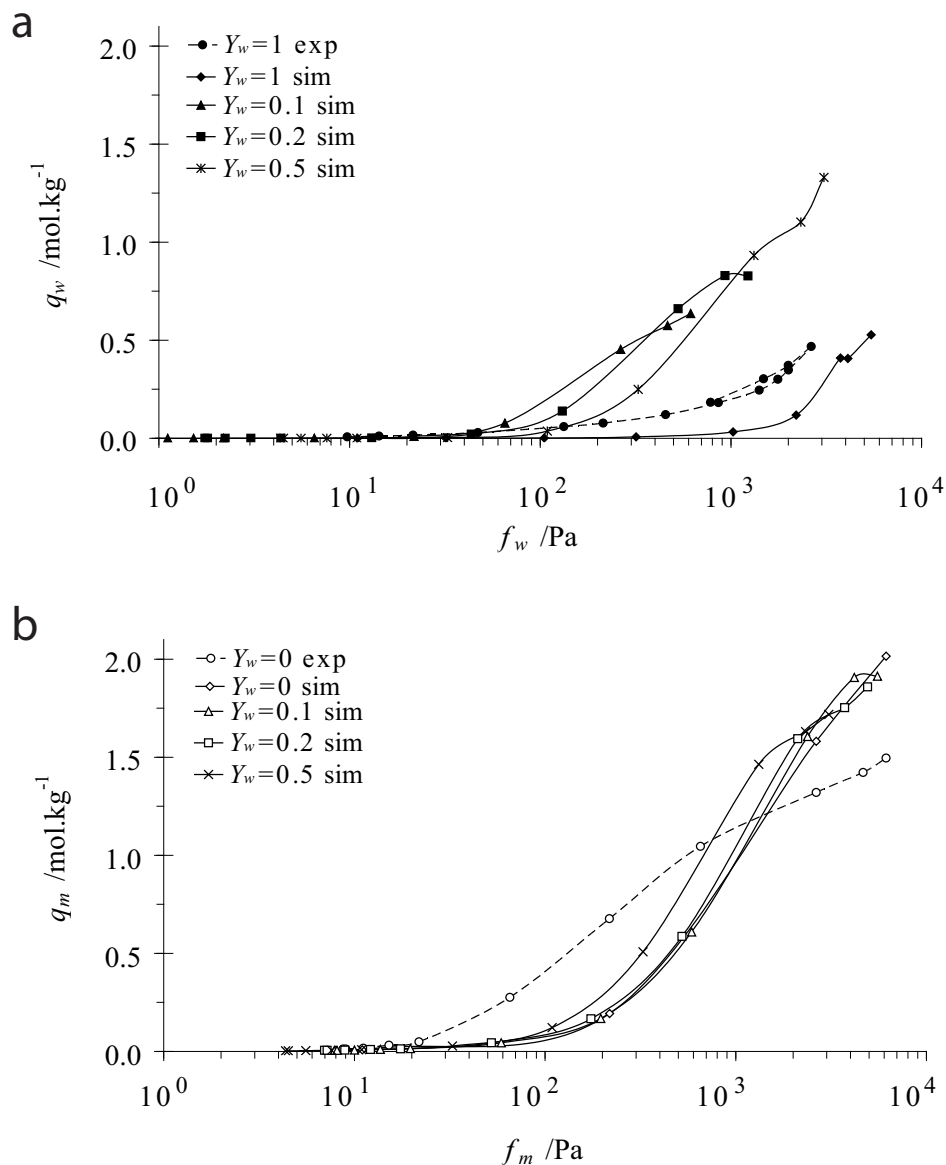


Figure 5.10: Experimental (exp) pure component, and calculated (sim) methanol/water adsorption isotherms at 303 K for water fugacity ratios of $Y_w = 0, 0.1, 0.2, 0.5$ and 1. The loading of (a): water and (b): methanol is shown as a function of the component fugacity. The dashed lines indicate the experimental pure component isotherms. The dashed lines indicate the experimental pure component isotherms.

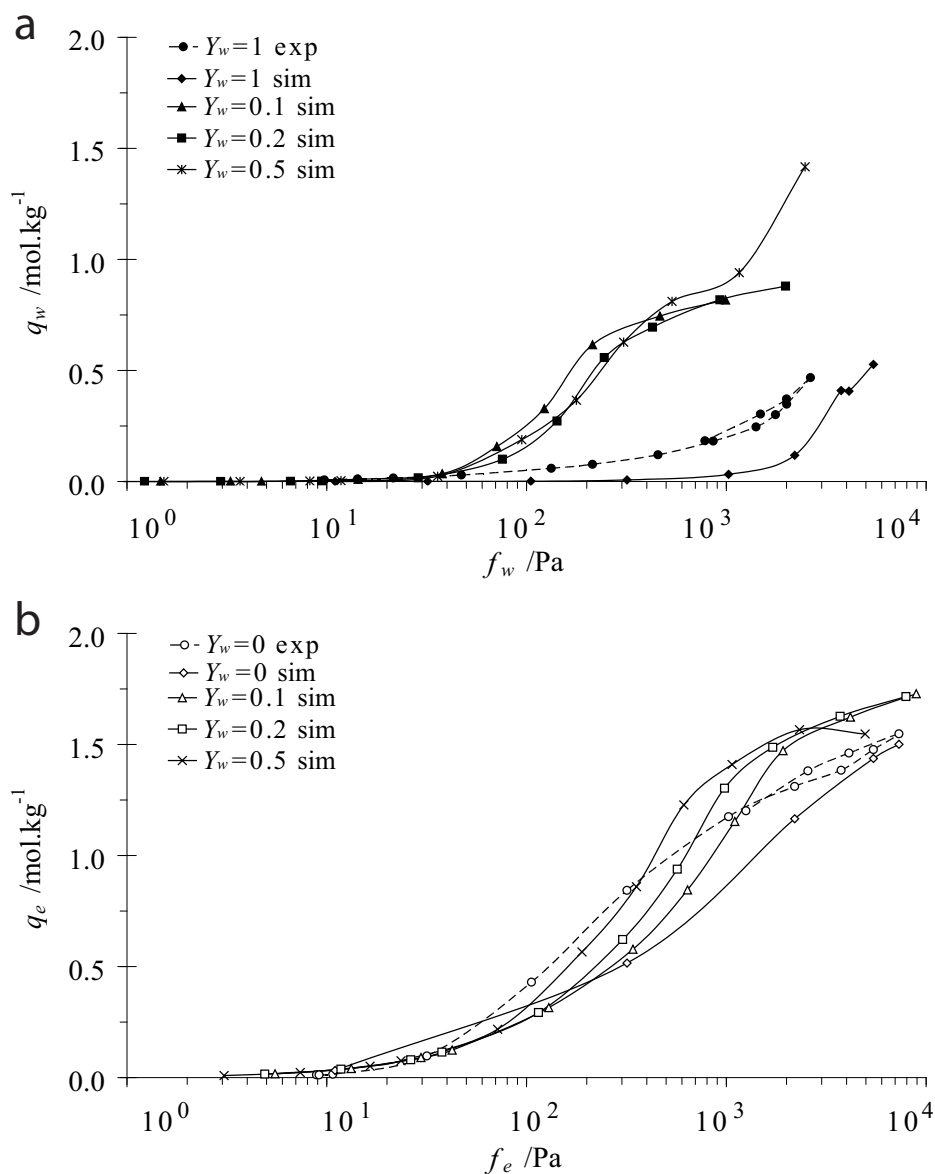


Figure 5.11: Experimental (exp) pure component, and calculated (sim) ethanol/water adsorption isotherms at 303 K for water fugacity ratios of $Y_w = 0, 0.1, 0.2, 0.5$ and 1. The loading of (a): water and (b): ethanol is shown as a function of the component fugacity. The dashed lines indicate the experimental pure component isotherms. The dashed lines indicate the experimental pure component isotherms.

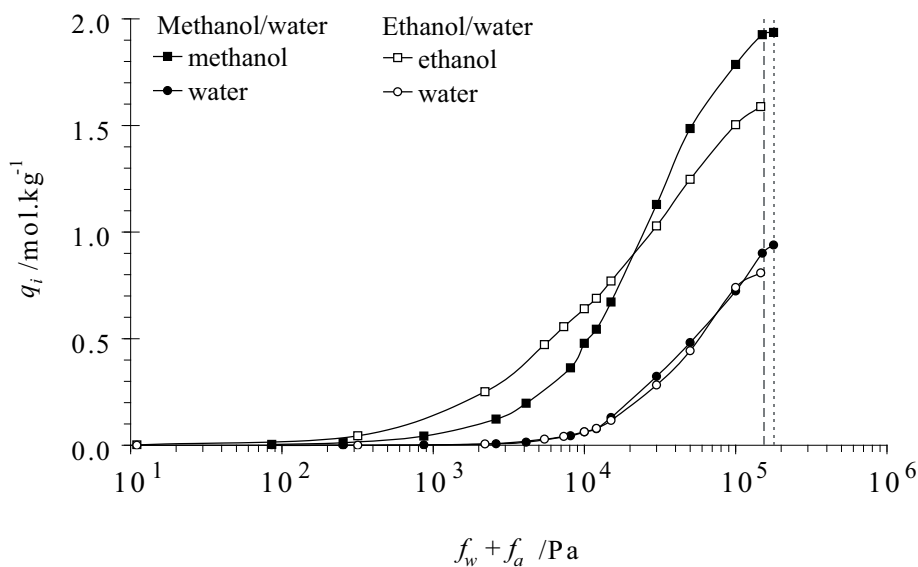


Figure 5.12: Simulated mixture adsorption isotherms of water (●) and methanol (■) in methanol/water mixtures and water (○) and ethanol (□) in ethanol/water mixtures at 360 K and a water feed fugacity ratio of $\gamma_w = 0.2$ as a function of the total fugacity.

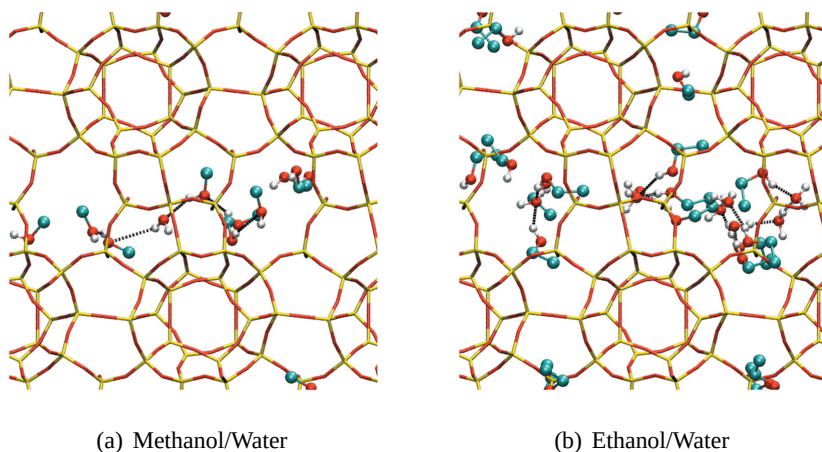


Figure 5.13: Snapshots of (a): methanol/water and (b): ethanol/water mixture adsorption on DD3R at 360 K and 15 kPa.

Table 5.3: Calculated transport diffusivities and pure component loadings at the feed and permeate side for pure component permeation of water, methanol, and ethanol. The permeate side pressure was maintained at 1 kPa.

T / K	q_i^{feed} / mol·kg ⁻¹	q_i^{perm} / mol·kg ⁻¹	D_{iM}^T / m ² ·s ⁻¹
Water			
348	0.87	0.004	7.2×10^{-10}
360	0.97	0.003	9.1×10^{-10}
373	1.11	0.002	12.8×10^{-10}
Methanol			
348	2.46	0.09	5.0×10^{-11}
360	2.39	0.05	5.5×10^{-11}
373	2.36	0.03	6.1×10^{-11}
Ethanol			
348	1.49	0.23	8.4×10^{-13}
360	1.42	0.15	10.4×10^{-13}
373	1.39	0.10	13.7×10^{-13}

are higher than for the alcohols and increase with temperature and concentration. The increase with temperature and concentration also holds for ethanol, while the calculated methanol diffusivity is practically constant.

Table 5.4: Methanol/water feed and permeate side composition and loading and transport diffusivities. The permeate side pressure in the pervaporation experiments is 1.5 kPa.

T / K	x_w^{feed} Ref. [5]	q_w^{feed} / mol·kg ⁻¹	q_m^{feed} / mol·kg ⁻¹	y_w^{perm} Ref. [5]	q_w^{perm} / mol·kg ⁻¹	q_m^{perm} / mol·kg ⁻¹	D_{wM}^T / m ² ·s ⁻¹	D_{mM}^T / m ² ·s ⁻¹
348	0.20	0.69	2.15	0.59	0.011	0.067	2.2×10^{-10}	4.9×10^{-11}
360	0.10	0.42	2.18	0.45	0.062	0.006	2.5×10^{-10}	5.8×10^{-11}
360	0.20	0.59	2.12	0.63	0.031	0.004	3.4×10^{-10}	5.6×10^{-11}
360	0.50	1.00	1.94	0.84	0.015	0.005	5.0×10^{-10}	5.1×10^{-11}
373	0.20	0.59	2.08	0.64	0.002	0.018	4.2×10^{-10}	4.9×10^{-11}

Table 5.5: Ethanol/water feed and permeate side composition and loading, and transport diffusivities. The permeate side pressure in the pervaporation experiments is 1.5 kPa.

T / K	x_w^{feed} [5]	q_w^{feed} / mol·kg ⁻¹	q_m^{feed} / mol·kg ⁻¹	y_w^{perm} [5]	q_w^{perm} / mol·kg ⁻¹	q_m^{perm} / mol·kg ⁻¹	D_{wM}^T / m ² ·s ⁻¹	D_{eM}^T / m ² ·s ⁻¹
348	0.10	0.80	1.63	0.993	0.0056	0.013	0.8×10^{-10}	2.6×10^{-13}
360	0.20	0.83	1.59	0.996	0.0017	0.007	1.6×10^{-10}	3.3×10^{-13}
360	0.30	0.94	1.56	0.998	0.0004	0.004	2.4×10^{-10}	2.5×10^{-13}
373	0.20	0.83	1.53	0.997	0.0043	0.001	2.1×10^{-10}	3.0×10^{-13}

The activation energies of the single component transport diffusivities are calcu-

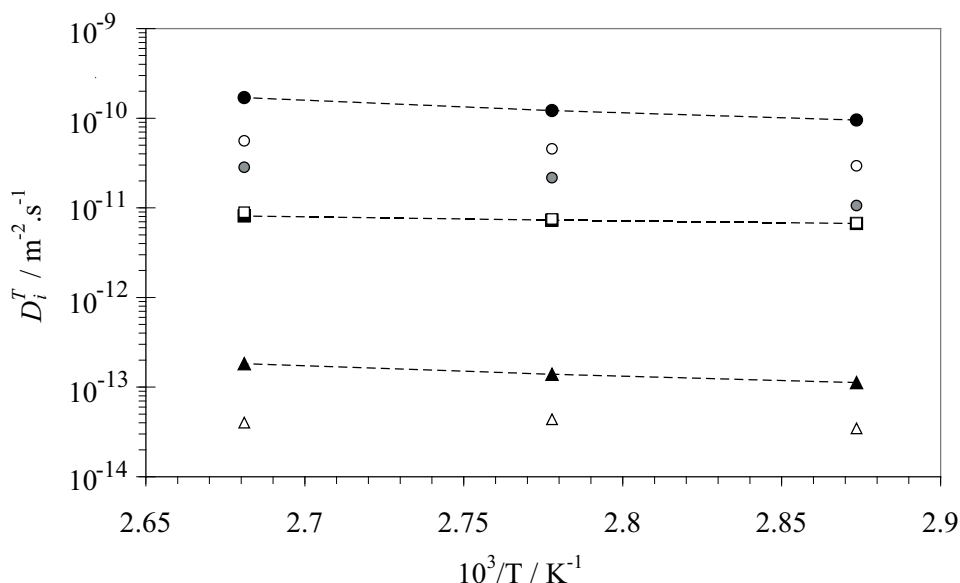


Figure 5.14: The logarithm of the transport diffusivity, D_l^T , calculated as single component diffusion, versus the reciprocal temperature for pure component permeation of water (●), methanol (■), and ethanol (▲), and water (○) and methanol (□) in methanol/water mixtures $x_w = 0.1$, and water (●) and ethanol (△) in ethanol/water mixtures $x_w = 0.2$. The data are also listed in Tables 5.3, 5.4, and 5.5. The dashed lines indicate a linear trend as a guide to the eye.

lated using equation 5.13 and are listed in Table 5.6. The same table also shows the apparent energy of activation calculated from the permeance, as was reported earlier in Reference [5] and the average enthalpies of adsorption calculated as the isosteric heats of adsorption at zero loading at 348 K to 373 K. The enthalpy of adsorption increases with temperature, but the values at 348 K to 373 K only differ by less than 6%.

Table 5.6: Average enthalpies of adsorption computed by GCMC at 348 K to 373 K, the energy of activation for the transport diffusivity and the apparent activation energies of pervaporation as reported in [5] for water, methanol and ethanol on DD3R.

Component	$\Delta_{ads}H$ kJ·mol ⁻¹	E_A kJ·mol ⁻¹	E_{app} [5] kJ·mol ⁻¹
Water	-26.3	24.9	-9.1
Methanol	-39.6	8.2	-32.4
Ethanol	-46.6	20.9	-23.6

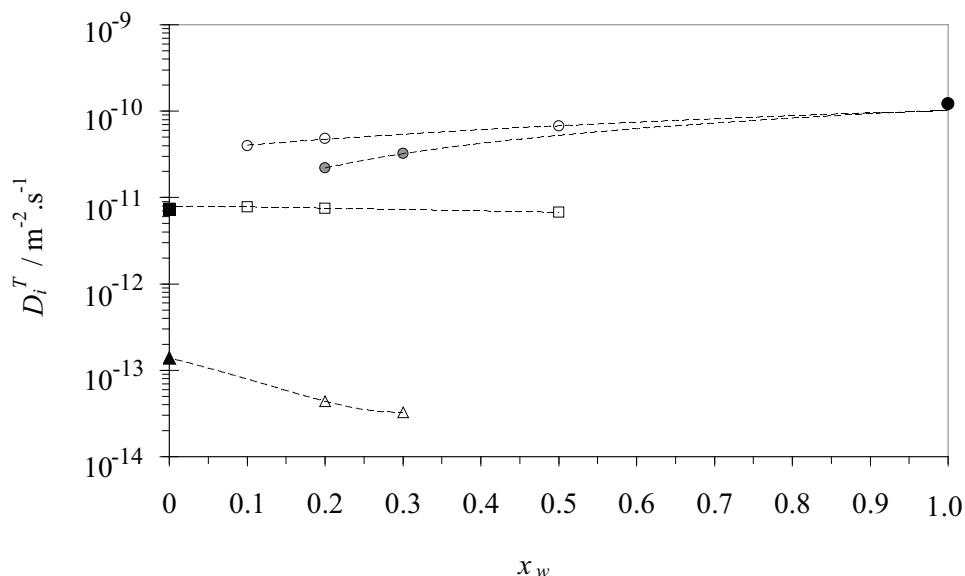


Figure 5.15: The logarithm of the transport diffusivity, D_t^T , calculated as single component diffusion, versus the water feed molar fraction, x_w , for pure component permeation of water (●), methanol (■), and ethanol (▲), and water (○) and methanol (□) in methanol/water mixtures, and water (●) and ethanol (△) in ethanol/water mixtures at 360 K. The data are also listed in Tables 5.3, 5.4, and 5.5. The dashed lines indicate a guide to the eye.

5.5 Discussion

The measured water adsorption isotherms are in fair agreement with the data reported by den Exter *et al.* [52]. The calculated loading under-predicts the actual loading at low fugacities. The measured adsorption resembles type II/IV behavior, while the calculated isotherm corresponds to type III/V (Figures 5.3 and 5.6). This can be partly attributed to the presence of crystalline defects in the zeolite sample, such as silanol groups, which have a strong effect on the water adsorption, especially at the low-end of loadings (and fugacities) [31]. This is also the region, where deviations of the simulations are most apparent. Furthermore, a deviation from the experimental values is expected since the molecular models and force field parameters were taken directly from literature, without further adjustment.

Both the calculated as well as the measured alcohol isotherms resemble type I adsorption. The experimentally determined alcohol loading is fairly well described by a single-site Langmuir adsorption isotherm (Figures 5.4 and 5.5). The Langmuir

adsorption parameters of methanol and ethanol are very similar (Table 5.2). However, the decrease in saturation loading with temperature shows this value does not resemble complete saturation.

The water adsorption is enhanced by the presence of alcohol and vice-versa. This adsorption behavior is comparable to that observed for methanol/water co-adsorption on activated carbon [83, 84]. The increased adsorption in the mixture as compared to single component adsorption is significantly more pronounced for water than for the alcohols. Such an increase in water loading was also observed by Jia *et al.* who conducted molecular simulations for ethanol/water in silicalite-1 [40]. However, in the study on silicalite-1 it was observed that the ethanol loading decreased, while in this study the alcohol loading at constant total fugacity is not significantly affected by the presence of water. This effect can be attributed to water adsorption in the vicinity of the polar OH-groups of the adsorbed alcohols (Figure 5.13). The shape of the water isotherm changes in the presence of the alcohols from a type III/V to a type I, similar to the alcohol adsorption (Figure 5.10a and 5.11a). Because of this complex behavior, the estimation of mixture adsorption behavior from pure component data is not trivial and estimating mixture adsorption from pure component data is not expected to give a good description of the mixture adsorption.

The calculated pure component molar loadings at the feed side of the here considered pervaporation conditions (Table 5.3) reveal that water adsorption increases with feed temperature, whereas the alcohol adsorption decreases. This shows that the increase in vapor pressure for water, and therefore the driving force for adsorption, overcompensates the decrease in the host-guest interaction. This is in agreement with the lower enthalpy of adsorption for water as compared to the alcohols (Table 5.6). At high fugacities (~ 100 kPa), the calculated pure component water adsorption surpasses the alcohol adsorption (Figure 5.6).

The calculated saturation loadings are comparable to values reported for LTA type zeolites, which are 15, 6, and 4 mol $\cdot$ kg $^{-1}$ (204, 82, and 55 molecules per unit cell) for water, methanol, and ethanol, respectively [85, 86]. Adsorption of 1 mol $\cdot$ kg $^{-1}$ in DD3R correspond to 14.4 adsorbed molecules per unit cell, and 2.4 molecules per 19-hedra cage (6 cages per unit cell). In the LTA zeolite structure, which contains only one α -cage and one β -cage per unit cell, 1 mol $\cdot$ kg $^{-1}$ equals 13.6 molecules per unit cell. Since in DDR only the 19-hedra cages are accessible, and in LTA the complete internal void volume is accessible for water, the saturation loading on DD3R is expected to be lower. Corma *et al.* reported a water loading of 0.6 mol $\cdot$ kg $^{-1}$ at 298 K

and 2 kPa on all-silica LTA [87], which is higher than the measured $0.35 \text{ mol}\cdot\text{kg}^{-1}$ on DD3R at 303 K and similar pressure. Coudert *et al.* reported a water saturation loading in the all-silica LTA calculated by GCMC simulations of $1.5 \text{ mol}\cdot\text{kg}^{-1}$ [32], suggesting the pressure at which this loading was calculated was not sufficient to obtain full saturation.

The calculated alcohol saturation using GCMC simulations are higher than the values found by fitting the Langmuir isotherms. This deviation and the increase of the fitted saturation loading with temperature could indicate the Langmuir adsorption isotherm fitted at low pressures does not describe the full adsorption behavior. The fitted saturation loadings (Table 5.2) are similar to reported values obtained by fitting Langmuir isotherms for methane ($1.7 \text{ mol}\cdot\text{kg}^{-1}$) and ethane ($0.8 \text{ mol}\cdot\text{kg}^{-1}$), and lower than for carbon dioxide ($2.8 \text{ mol}\cdot\text{kg}^{-1}$) in DD3R [19, 88]. Both the calculated and experimental values of the ethanol loading are approximately three times higher than reported loadings for ethane [19]. The loadings of methanol and ethanol are also higher than reported loadings for methane, ethane, and ethene on ZSM-58 [89]. The calculated water saturation loading on DD3R is substantially higher than the $6.9 \text{ mol}\cdot\text{kg}^{-1}$ (41 molecules per unit cell) reported for water in silicalite-1, which corresponds to a density inside the zeolite of 85% of the bulk fluid value [26, 28]. To obtain the actual saturation loading of water on DD3R, adsorption measurements over a wide pressure range need to be conducted, as was already reported for water in silicalite-1 [31].

The enthalpies of adsorption show a small increase with temperature, but since the values in the temperature range concerned differ less than 6%, an average value is used (Table 5.6). The calculated values for the alcohols (-40 and $-47 \text{ kJ}\cdot\text{mol}^{-1}$ for methanol and ethanol, respectively) are comparable to values reported for adsorption on silicalite-1 [90]. For water, the computed value of $-26 \text{ kJ}\cdot\text{mol}^{-1}$ was comparable to the $-20 \text{ kJ}\cdot\text{mol}^{-1}$ reported by Fleys *et al.* for silicalite-1. Den Exter obtained an enthalpy of adsorption of $-50 \text{ kJ}\cdot\text{mol}^{-1}$ at zero loading by fitting the experimentally measured water isotherms on DDR (which is in agreement with the data obtained in this study) to a BET isotherm [81].

The sum of the energy of activation, calculated from the transport diffusivities, and the enthalpies of adsorption, obtained by the GCMC simulations, correspond well with the apparent energy of activation calculated from the pure component permeances (Table 5.6). This indicates that the temperature dependency of neither the adsorption nor the diffusion is dominating.

At equal component fugacities, the water loading (represented by the Tip5pEw force field) is similar to that of the alcohols. But, despite the improved water adsorption in the presence of the alcohols, the calculations indicate the water loading at the feed side during pervaporation experiments is at most 50% of the alcohol loading (Tables 5.4 and 5.5). This shows that preferential adsorption is not the cause of the observed separation selectivities of the membrane. Therefore, the high water selectivities obtained in the pervaporation experiments are attributed to the difference in diffusivity.

For methanol and ethanol, the adsorption behavior is consistent with Langmuir adsorption. Moreover, the size of DD3R cage window is similar to the molecular diameters of the alcohols [5]. When assuming a linear loading dependence of the diffusivity (equation 5.10), the calculated transport diffusivity is equal to the M-S diffusivity. For water, the assumption of a constant transport diffusivity over the membrane length is probably not realistic [53]. Nevertheless, the calculated average transport diffusivities give an indication of the diffusive behavior of the different components and mixtures. The calculated transport diffusivities of all components increase with temperature and feed concentration. The calculated pure component transport diffusivity of water is one order of magnitude higher than the methanol diffusivity, and even three orders of magnitude higher than the ethanol diffusivity. This identifies the difference in diffusivity as the major separating mechanism for the de-watering of alcohols using DD3R membranes. The calculated diffusivity of water is lower than reported values for water in silicalite-1 [25], whereas the diffusivity found for methanol is about one order of magnitude higher than the reported value for methane and ethanol has a similar diffusivity as reported for ethylene [89].

The binary thermodynamic factors (Γ_{ij} in equation 5.6) are not taken into account in this study. Therefore, the influence of the binary adsorption on the transport diffusivity is not taken into account. Since the component loading in mixture adsorption is increased this would yield a positive value of Γ_{ij} , which would imply an increase in flux in mixture permeation as compared to pure component permeation, while the opposite is observed. The decrease in flux in mixture permeation experiments is therefore attributed to the decrease in diffusivity. Calculating Γ_{ij} from GCMC simulations or applying mixture adsorption models like the ideal adsorbed solution theory (IAST), will give a more accurate approximation of the mixture diffusivities.

In methanol/water mixture permeation, the methanol diffusivity remains practically unchanged as compared to pure component permeation, while the water diffu-

sivity is reduced with about one order of magnitude. In the ethanol/water system, the diffusivities of both water and ethanol reduce by an order of magnitude as compared to pure component permeation. As the adsorption of the components is increased in the mixture, competitive adsorption does not explain this reduced mixture permeance. The stronger interactions, leading to higher adsorption in the mixtures, combined with steric hindrance of the adsorbed molecules, blocking the cage windows, are likely to reduce the diffusivity, leading to a lower permeance in mixtures. The seemingly unaffected permeance of methanol may be explained by a positive effect of the increased adsorption, balanced by a negative effect of a reduced diffusivity.

To further elucidate this mixture diffusion behavior, MD simulations are currently being conducted. However, it should be noted that the diffusivities obtained in MD simulations assume a perfect crystalline membrane without micro- and macroscopic defects. This will not resemble the actual membrane, which consists of complexly inter-grown crystals with internal and external grain boundaries. Moreover, the DD3R membrane synthesized by NGK insulators, consisted of a thin zeolite layer deposited on an α -alumina support. During the membrane synthesis, aluminum can be leached out of the support material, and be incorporated in the zeolite structure, making the membrane material less hydrophobic than the separately synthesized crystals, and the simulated zeolite framework. Furthermore, despite the high calcination temperature of the DD3R zeolite [11], silanol groups can still be present in the zeolite as crystalline defects. In silicalite-1 it has been observed that up to 8% of the Si is present as Si-OH [91]. These groups linearly increase the framework polarity, and therewith the hydrophilicity [91, 92].

Considering that no force field parameters were fitted here, the calculated adsorption isotherms show a reasonable fit with the experimental adsorption data. To obtain a quantitative result that better matches the experimental isotherms, a refinement of the force field would be required, while taking proper account of the material imperfections, such as silanol groups. The simulation results could also be improved by accounting for framework flexibility. Including framework flexibility has shown to increase the ethanol/water loading in silicalite-1 without affecting the sorption selectivity [40].

5.6 Conclusions

Adsorption isotherms for water, methanol and ethanol on all-silica DD3R have been measured by single-component vapor phase adsorption and calculated by GCMC simulations. The measured alcohol adsorption can be described by a single-site Langmuir adsorption isotherm. The MC simulations were able to qualitatively reproduce the adsorption behavior of the experimental isotherms. For water, the adsorption resembles type II adsorption. The water loading is under-predicted by the calculations at pressures up to 2.5 kPa. The calculated loadings at high pressures of all the components are higher than reported values for gases in DDR type zeolites and are comparable to loadings on LTA type zeolites. The molecular models and force field parameters were taken directly from literature without further adjustment. Nevertheless, the order of magnitude and the shape of the pure component isotherms resemble the experimental data well.

Mixture adsorption isotherms have been computed and combined with permeation data measured under pervaporation conditions. The calculated mixture isotherms show that the loading of both alcohols and water at constant component fugacity increases as compared to pure component adsorption. Moreover, the shape of the water isotherm changes from type IV to type I. The decrease in water and ethanol permeance in the mixture as compared to pure component permeation is not caused by competitive adsorption. The increase in loading in mixture adsorption is significantly more profound for water than for the alcohols, but this does not lead to selective water adsorption at the feed conditions of the pervaporation experiments.

The transport diffusivities calculated from the permeation data and the calculated mixture isotherms show that the water diffusivity is one to three orders of magnitude higher than those of the alcohols. The selective water transport through DD3R zeolite membranes can be explained by the higher diffusivity of water in the hydrophobic DD3R.

List of symbols.

symbol	name	unit
c	concentration	$\text{mol}\cdot\text{m}^{-3}$
D^s	self diffusivity	$\text{m}^2\cdot\text{s}^{-1}$
D^T	transport diffusivity	$\text{m}^2\cdot\text{s}^{-1}$
$\mathcal{D}$	M-S diffusivity	$\text{m}^2\cdot\text{s}^{-1}$
E_A	energy of activation for diffusion	$\text{J}\cdot\text{mol}^{-1}$
E_{app}	apparent energy of activation	$\text{J}\cdot\text{mol}^{-1}$
f	fugacity	Pa

List of symbols. (continued)

symbol	name	unit
$\Delta_{ads}H$	adsorption enthalpy	$\text{J}\cdot\text{mol}^{-1}$
K	Langmuir adsorption parameter	Pa^{-1}
k_B	Boltzmann constant	$\text{m}^2\cdot\text{kg}\cdot\text{s}^{-2}\cdot\text{K}^{-1}$
N	molar flux	$\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$
M	molar mass	$\text{kg}\cdot\text{mol}^{-1}$
p	pressure	Pa
p^{sat}	vapor pressure	Pa
q	equilibrium loading	$\text{mol}\cdot\text{kg}^{-1}$
q^{sat}	saturation loading	$\text{mol}\cdot\text{kg}^{-1}$
R	gas constant	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
T	temperature	K
V_m	partial molar volume	$\text{m}^3\cdot\text{mol}^{-1}$
x	liquid molar fraction	—
y	vapor molar fraction	—
z	length coordinate	m
δ	membrane thickness	m
ε	Lennard-Jones energy parameter	J
Γ	thermodynamic correction factor	
γ	activity coefficient	
σ	Lennard-Jones size parameter	m
θ	fractional loading	
μ	chemical potential	$\text{J}\cdot\text{mol}^{-1}$
ρ	density	$\text{kg}\cdot\text{m}^{-3}$
Π	permeance	$\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$
ϕ^{sat}	fugacity coefficient	—
Υ	fugacity ratio	—
sub and super scripts		
l	liquid	
$_{exp}$	experimental	
$_{feed}$	feed side	
$_{perm}$	permeate side	
$_{pred}$	predicted	
a	alcohol	
e	ethanol	
i	component i	
M	membrane	
m	methanol	
w	water	
z	zeolite	

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A non-equilibrium thermodynamics approach to model mass and heat transport for water pervaporation through a zeolite membrane

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Abstract Pervaporation through zeolite membranes involves local heat effects and combined heat and mass transport. The current state-of-the-art Maxwell-Stefan (M-S) models do not take these effects into account. In this study, transport equations for the coupled heat and mass transport through a zeolite membrane are derived from the framework of non-equilibrium thermodynamics (NET). Moreover, the assumption of equilibrium between the adjacent bulk phases at the feed and permeate sides of the zeolite layer is abandoned in favor of local equilibrium. The equations have been used to model pervaporation of water through a 2 μm thick NaA type zeolite membrane, deposited on an asymmetric α -alumina support, at a feed temperature of 348 K. Assuming a flux of $10 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ($0.15 \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$), the transport through the zeolite layer, as well as the liquid feed side boundary layer and the support layers is modeled. The activity, fugacity, and temperature profiles are calculated with and without taking coupling effects and surfaces into account. The profiles show distinct differences between the two cases. Including the surface effects leads to discontinuities in the activity and temperature at the membrane interfaces. A significantly higher temperature drop of 1.3 K is calculated across the zeolite, compared to 0.4 K when surface and coupling effects are not accounted for. The calculated decrease in temperature over the zeolite layer is dominated by the surfaces. This could indicate that temperature polarization is, to a large extent, a surface effect. The heat flux induces an extra driving force for mass transport, reducing the activity difference over the membrane. A positive jump in activity is observed at the interfaces, revealing the mass transport across the interfaces is governed by the coupling with the heat flux. The support layers contribute significantly to the total mass transport resistance.

6.1 Introduction

The transport through zeolite membranes is generally described following an adsorption-diffusion mechanism, where molecules first diffuse from the bulk feed to the zeolite surface. Next, they adsorb to the sites on the zeolite surface and in the zeolite pores. The adsorbed molecules diffuse through the zeolite, driven by the chemical potential gradient within the pore. At the permeate side of the membrane, molecules desorb from the zeolite and into the support pores to the bulk permeate [1]. Non-equilibrium thermodynamics in the form of the M-S equations, are generally used to model mass transport in zeolites and zeolite membranes [2]. They have been successfully applied to several systems [3–5]. The equations balance the driving forces with the friction exerted on molecules [6]. The M-S equations have also been used to model gas and vapor permeation [7–9] and pervaporation processes in zeolite [10] and silica [11] membranes.

Pervaporation is a mode of operation in membrane separation processes (Figure 6.1), where a liquid mixture is fed to a membrane, whereas the permeate side is in gaseous, either by maintaining a low pressure or by introducing a purge gas. One or more components from the mixture selectively permeate through the membrane, and effectively evaporate into the vapor phase. The phase-change enthalpy of the permeating components can be added by pre-heating the liquid feed. In the case of a large membrane surface area, intermediate heating steps are required. Temperature polarization is a local temperature drop at the membrane surface due to evaporation of the permeating components. This effect has been observed in pervaporation processes and has a detrimental effect on the membrane performance [12].

Zeolites are microporous aluminosilicates, and are generally chemically and thermally robust. Zeolite membranes are also well suited for pervaporation processes, which is already a commercially applied process [13, 14]. Because zeolites have a uniform crystalline porous structure, and don't swell, they are well suited for modeling studies [15]. Adsorption in a zeolite from the vapor phase is usually physisorption and is therefore an exothermic, non-activated process [10]. When a component adsorbs from the liquid phase, the net enthalpy change is derived from the adsorption enthalpy and the phase-change enthalpy. In current modeling it is generally assumed that the membrane has a uniform temperature [16]. However, the adsorption and desorption step and the phase change of the permeating substance during transport from the feed to the permeate side of the membrane impose strong local heat effects,

which can result in large local temperature gradients. The combined heat and mass transport in current modeling studies only involve a reduction in the driving force due to temperature polarization on the liquid side, and incorporate the temperature dependency of adsorption equilibria and diffusivities [11, 17].

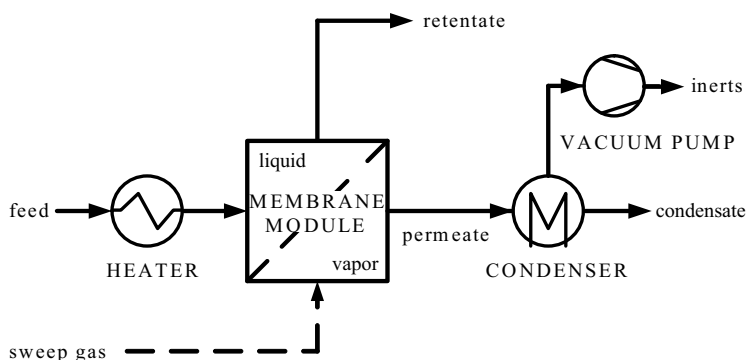


Figure 6.1: Schematic representation of a pervaporation process

The theory of non-equilibrium thermodynamics (NET) is based on the assumption of local equilibrium and linear flux-force relations. Furthermore, NET is the only theory capable of describing coupling between fluxes. These coupling effects have shown to be essential to correctly describe the dissipation of energy in polymer fuel cells [18]. It has been shown that in a membrane/permeant system, the coupling effects can differ greatly from that in a continuous system [19]. However, to our knowledge, there are no studies on the coupling between mass and heat transport in pervaporation processes.

In current modeling of zeolite transport, equilibrium between any two adjacent phases is assumed, i.e. the adsorbed phase in the zeolite is assumed to be in equilibrium with the bulk fluid at the zeolite surface. Only recently, Kjelstrup and Bedeaux [20, 21] abandoned the assumption of equilibrium across the interfaces and defined the interface properties using local equilibrium instead. Inzoli *et al.* have concluded from a non-equilibrium molecular dynamics study on the adsorption of n-butane on a silicalite-1 membrane, that the surface is rate-limiting to heat transfer and that transport in zeolites should include a thermal driving force, in addition to the chemical driving force [22].

In this study we use the framework of NET and the dividing surface to derive transport equations for pervaporation. For simplicity, the equations for a single com-

ponent system are described, but the generalization to a multi-component system is straight-forward. The equations shall be applied to calculate the activity and temperature profiles across a hydrophilic NaA zeolite membrane during pure water pervaporation. The chosen process conditions and physical properties are based on experimental data. NaA is the sodium form of the LTA type zeolite, a highly hydrophilic zeolite with small pores, that has shown to give high water fluxes under pervaporation conditions [23]. This type of membrane is already being used on commercial scale for de-watering of solvents under pervaporation conditions [13, 14]. Although NaA membranes often contain defects and pinholes [24], for simplicity, we will assume a perfect crystalline, defect-free zeolite layer.

To show the effect of considering the coupling and surface effects on mass and heat transport, the temperature, fugacity and activity profiles across the zeolite membrane will be calculated (NET model) and compared to a model where no coupling and no surface effects are taken into account (no coupling, no surfaces (nCnS) model). The terminology will follow that introduced by Kjelstrup and Bedeaux [25].

6.2 Non-equilibrium thermodynamics description of transport

Figure 6.2 gives a schematic representation of the mass and heat fluxes observed in a pervaporation process. Using the framework of NET and the concept of the dividing surface, the transport of mass through the zeolite membrane can be divided into five steps

1. diffusion from the bulk to the liquid/zeolite interface
2. transfer across the liquid/zeolite surface
3. diffusion through the zeolite layer
4. transfer across zeolite/support surface
5. diffusion into the bulk permeate through the support pores

In Figure 6.2 the mass flux, J_i , is directed from left to right, following the above mentioned five steps. At the liquid/zeolite interfaces (step 2), the adsorption into the

zeolitic pores takes place, releasing the enthalpy of adsorption as heat. At the zeolite/support interface, the permeating molecules desorb into the gas phase, requiring the enthalpy of desorption. By neglecting the temperature dependence of the enthalpy and the heat capacity, the observable heat flux, J'_q , only changes at the interfaces, where the permeating water undergoes an enthalpy change. The enthalpy change at the liquid/zeolite interface is denoted by $\Delta_{l/z}H_i$. Since we assume steady state operation, the mass flux, is constant throughout the whole system. The energy balance over the liquid/zeolite interface, relating the observable heat flux in the zeolite layer, J'^z_q , to the heat flux in the liquid boundary layer, J'^l_q , then becomes

$$J'^z_q = J'^l_q - J_i \Delta_{l,z} H_i \quad (6.1)$$

At the zeolite/support interface, an enthalpy change, $\Delta_{z,sup}H_i$, occurs. The observable heat flux in the support, J'^{sup}_q , can be related to the heat flux in the zeolite layer, J'^z_q , by the energy balance

$$J'^{sup}_q = J'^z_q - J_i \Delta_{z,sup} H_i \quad (6.2)$$

The double arrows in between the heat and mass flux in Figure 6.2, indicate the coupling between these heat fluxes and the mass flux.

The entropy production rate in the absence of a chemical reaction, is obtained as the sum of the product of the thermodynamic driving forces and conjugate fluxes. When linear relations between the fluxes and the driving forces are assumed this results in [25]

$$\sigma = J'_q \left(-\frac{\nabla T}{T^2} \right) + J_i \left(-\frac{\nabla \mu_{i,T}}{T} \right) \quad (6.3)$$

The driving forces can be written in local-linear form using the resistivities, r_{ij} . For combined mass and heat transport this results in

$$-\frac{\nabla \mu_{i,T}}{T} = r_{\mu\mu} J_i + r_{\mu q} J'_q \quad (6.4)$$

$$-\frac{\nabla T}{T^2} = r_{q\mu} J_i + r_{qq} J'_q \quad (6.5)$$

The component molar flux, J_i , can be written as $c_i v_i$, where $c_i = cx_i$ denotes the concentration of component i . In equation 6.4, $\nabla \mu_{i,T}$ denotes the chemical potential gradient at constant temperature as the driving force for mass transport. In the case of transport through a porous membrane, the membrane can be viewed as a component,

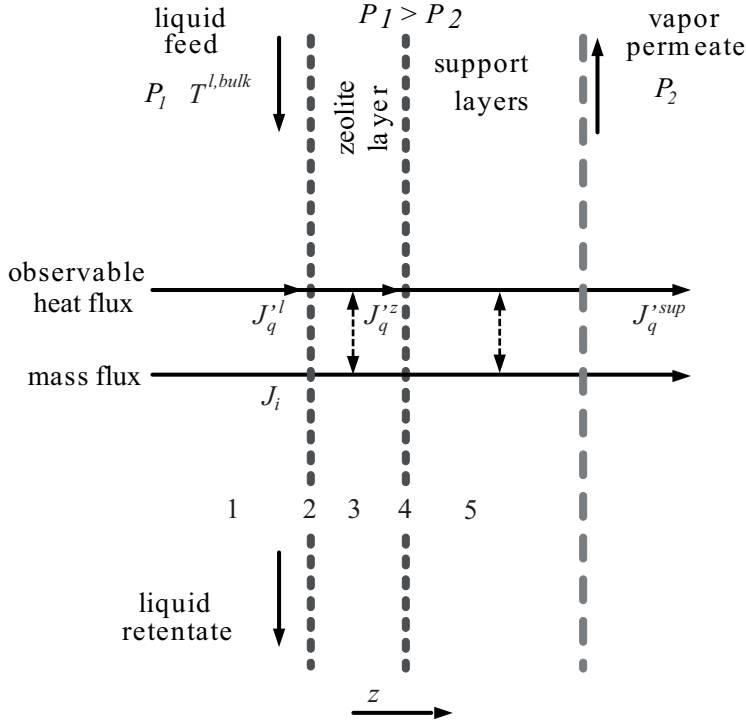


Figure 6.2: Coupling of mass and heat transport in a membrane under pervaporation conditions.

M. Using the membrane as frame of reference, the velocity, v_M , equals zero. The thermal resistivity is related to the Fourier thermal conductivity by [26]

$$r_{qq} = \frac{1}{\lambda T^2} \quad (6.6)$$

By defining a diffusivity, describing the interaction between the membrane and a permeating compound, $\mathcal{D}_{iM}$, as

$$\frac{R}{c\mathcal{D}_{iM}} = r_{iM} - \frac{r_{Mq}r_{iq}}{r_{qq}} \quad (6.7)$$

we can write the coupled transport equations in a form comparable to the Maxwell-Stefan equations, often used for membrane transport modeling [1].

$$-\frac{\nabla \mu_{i,T}}{RT} = \frac{J_i}{c_i \mathcal{D}_{iM}^{eff}} - \frac{q_i^*}{RT^2} \nabla T \quad (6.8)$$

$$-\lambda \nabla T = -q_i^* J_i + J'_q \quad (6.9)$$

where $\mathcal{D}_{iM}^{eff}$ is an effective diffusivity defined as the ratio of the diffusivity describing the interaction between the membrane, M , and component i , and the molar fraction of the membrane, x_M [2], as

$$\mathcal{D}_{iM}^{eff} \equiv \frac{\mathcal{D}_{iM}}{x_M} \quad (6.10)$$

and J'_q again denotes the measurable heat flux. The coupling is described by the heat of transfer, q_i^* , which is defined as

$$q_i^* \equiv \left(\frac{J'_q}{J_i} \right)_{dT=0} = -\frac{r_{q\mu}}{r_{qq}} \quad (6.11)$$

Equations 6.8 and 6.9 describe the combined mass and heat transport in the zeolite layer. Under isothermal conditions, equation 6.8 reduces to

$$-\frac{\nabla \mu_{i,T}}{RT} = \frac{J_i}{c_i \mathcal{D}_{iM}^{eff}} \quad (6.12)$$

This equation is often referred to as the M-S equation [2]. When equation 6.12 is to be applied to non-isothermal conditions, an error is made because then the coupling terms are omitted. In this study, we will show the influence of neglecting the coupling terms on the calculated temperature and activity profiles. Moreover, we will investigate the influence of taking the coupled mass and heat transfer across the membrane interfaces into account.

6.2.1 Coupled heat and mass transport across interfaces

Recently Bedeaux and Kjelstrup introduced transport equations across surfaces which incorporate coupling between heat and mass transport [20, 25]. The interface was considered as a separate thermodynamic system between the two adjacent phases. Although the system is always at local equilibrium, the assumption of global equilibrium (requesting the temperature and chemical potential to be continuous) was abandoned. In pervaporation processes, there is a phase change at the membrane surfaces, where the species adsorb from the liquid phase, and at the permeate side, where the adsorbed species desorb into the vapor phase. The adsorption and desorption also induce heat effects at these surfaces.

Figure 6.3 gives a schematic representation of a dividing surface and the standard notation, as used by Kjelstrup and Bedeaux [25]. This notation is based on the two

phases (i and o) adjacent to the surface, s : e.g. the molar flux from the i -side across the surface, s , is denoted by $J_i^{i,o}$. Or alternatively stated, the first superscript indicates the phase on one side of the surface and the second superscript indicates the adjacent phase.

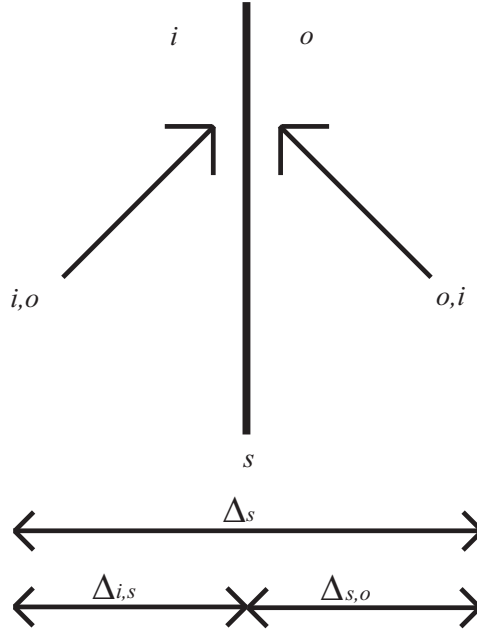


Figure 6.3: Standard notation for transport across surfaces [25].

For a surface with heat and single component mass transport, the surface excess entropy production, σ^s , can be written as [25]

$$\begin{aligned} \sigma^s = & J_q^{i,o} \left(\Delta_{i,s} \frac{1}{T} \right) + J_q^{o,i} \left(\Delta_{s,o} \frac{1}{T} \right) \\ & + J_i^{i,o} \left(-\frac{1}{T_s} \Delta_{i,s} \mu_{j,T} \right) + J_i^{o,i} \left(-\frac{1}{T_s} \Delta_{s,o} \mu_{j,T} \right) \end{aligned} \quad (6.13)$$

At steady state, there is no accumulation of mass at the interfaces, hence, $J_i^{o,i} = J_i^{i,o}$. In the measurable heat flux, however, there is a discontinuity at the interfaces (equations 6.1 and 6.2), due to the macroscopically discrete nature of the surface. Therefore, derivatives in equations 6.8 and 6.9 are here replaced by differences. We can choose to eliminate either $J_q^{i,o}$ or $J_q^{o,i}$, because they are inter-linked by the energy balances. If we assume feed conditions are known, and we want to calculate the

temperature and activity difference over the interface, it is best to eliminate $J_q^{i,o}$. For a one-component system in steady state, equation 6.13 then reduces to [25]

$$\sigma^s = J_q^{o,i} \Delta_{i,o} \frac{1}{T} - J_i \frac{\Delta_{i,o} \mu_T(T^i)}{T^i} \quad (6.14)$$

From the linear flux force relations the transport equations for heat and mass of a single component over the surface, after some algebra and using the Gibbs-Duhem relation and the Onsager relations, it follows [25]

$$-\Delta_{i,o} T = T^i T^o r_{qq}^s (J_q^{o,i} - q_i^{*s,o} J_i) \quad (6.15)$$

$$-\frac{\Delta_{i,o} \mu_T(T^i)}{T^i} = r_{\mu\mu}^s J_i - r_{qq}^s q_i^{*s,o} J_q^{o,i} \quad (6.16)$$

The chemical potential is here defined at T^i , which is the temperature on the left hand side of the surface (Figure 6.3). Equations 6.15 and 6.16 can be used to define the resistivity coefficients, $r_{\mu\mu}^s$ and r_{qq}^s . These are properties of the surface, and correlate the discrete difference in, respectively, chemical potential and temperature over the interface to the mass and heat fluxes across the surface.

The heat of transfer, $q_i^{*s,o}$ is defined as

$$q_i^{*s,o} \equiv \left(\frac{J_q^{o,i}}{J_i} \right)_{\Delta_{i,o} T=0} \quad (6.17)$$

The $q_i^{*s,o}$ and the corresponding value with $J_q^{i,o}$, $q_i^{*s,i}$, are inter-related by

$$q_i^{*s,o} - q_i^{*s,i} = -\Delta_{i,o} H_i \quad (6.18)$$

The chemical potential can be written as a function of the activity by

$$\mu_i = \mu_i^0 + RT \ln(a_i) \quad (6.19)$$

Where μ_i^0 is the chemical potential at the reference state, which can be a function of temperature and a_i denotes the activity of component i , which is defined as the ratio of the fugacity at local conditions and the fugacity at the reference state.

$$a_i = \frac{f_i}{f_i^0} \quad (6.20)$$

Combining equation 6.19 with equation 6.16, we can now write the difference in chemical potential over the surface as

$$-\frac{\Delta_{i,o}\mu_T(T^i)}{T^i} = R\ln\left(\frac{a_i^{i,o}(T^i)}{a_i^{o,i}(T^i)}\right) = r_{\mu\mu}^s J_i - r_{qq}^s q_i^{*s,o} J_q'^{o,i} \quad (6.21)$$

For the reference state in equation 6.20, we choose the fugacity of a liquid in equilibrium with a vapor at local temperature. Using the Gibbs-Helmholtz relation combined with equation 6.19, we can correct the activity at the *o*-side of the surface defined at T^i , $a_i^{o,i}(T^i)$ to the activity at the local temperature, $a_i^{o,i}(T^o)$, by

$$R\ln\left(\frac{a_i^{o,i}(T^o)}{a_i^{o,i}(T^i)}\right) = (h_i^o - h_i^0) \left(\frac{\Delta_{i,o}T}{T^i T^o}\right) \quad (6.22)$$

where h_i^o and h_i^0 are the partial molar enthalpies of component *i* on the *o*-side of the surface, and at the reference state, respectively. As in equation 6.20, the reference state is a liquid in equilibrium with a vapor at local temperature. So, when the surface resistivities and the heat flux out of the surface are known, the temperature and fugacity differences over the membrane can be determined, using equations 6.15, 6.21 and 6.22.

6.2.2 Heat and mass transport through the multi-layer system

In this section the equations for the above combined heat and mass transport are adapted to a single component pervaporation process, consisting of diffusion through the liquid boundary layer, a zeolite membrane and a porous support. The transport equations are presented according to the different steps which the permeating molecules undergo, as shown in Figure 6.2.

6.2.2.1 Transport in the liquid boundary layer

All transfers in the liquid phase can be assumed to take place in the laminar boundary layer [27] (step 1 in Figure 6.2). For single component bulk diffusion, there is no gradient in chemical potential. The heat flux, in the absence of a driving force for mass transport, can be described by the Fourier equation,

$$-\lambda \nabla T = J_q' \quad (6.23)$$

When the heat flux within the boundary layer is constant, the temperature as a function of the laminar film thickness, z , becomes

$$T(z) = T^{l,bulk} - \frac{J_q^l}{\lambda} z \quad (6.24)$$

This sets the z -coordinate at zero at the liquid bulk phase, or at $\delta_{T,film}$, at the liquid/zeolite surface.

6.2.2.2 Transport through the zeolite layer

The adsorbed species diffusing through zeolitic pores (step 3 in Figure 6.2) experience a strong interaction with the pore walls. The dominating diffusion mechanism in this case is configurational or zeolitic diffusion. The driving force for mass transport is the chemical potential gradient, which can be expressed as the gradient in fractional loading of the adsorbed species, θ_i , using [2]

$$\theta_i \frac{\nabla \mu_{i,T}}{RT} = \Gamma_{iM} \nabla \theta_i \quad (6.25)$$

The interaction with the pore walls is expressed by the so-called thermodynamic correction factor, Γ_{iM} , which can be determined from equilibrium experiments. It is defined by the Darken equation [6], which for single component diffusion can be written as

$$\Gamma_{iM} = \frac{\partial \ln f_i}{\partial \ln \theta_i} = \frac{\theta_i}{f_i} \frac{\partial f_i}{\partial \theta_i} \quad (6.26)$$

Combining equation 6.25 with equation 6.8, and writing the concentration c_i as $\rho_z q_i^{sat} \theta_i$, we find

$$-\Gamma_{iM} \nabla \theta_i = \frac{J_i}{\rho_z q_i^{sat} D_{iM}^{eff}(\theta)} - \frac{q_i^{*z}}{RT^2} \nabla T \quad (6.27)$$

Where ρ_z is the zeolite density, q_i^{sat} is the saturation loading, and θ_i denotes the fractional loading inside the zeolite pores.

When the coupling terms are neglected, the transport in the zeolite layer, equation 6.27 reduces to

$$-\Gamma_{iM} \nabla \theta_i = \frac{J_i}{\rho_z q_i^{sat} D_{iM}^{eff}(\theta)} \quad (6.28)$$

We now have equations 6.27 and 6.9 to describe the coupled heat and mass transfer (NET model), and equations 6.28 and 6.23 to describe non-coupled heat and mass transfer of a single component in a zeolite (nCnS model). Comparing the two sets

of equations, we see equation that 6.27 can be seen as the M-S equations (equation 6.28) with an extra term describing the molar flux caused by the temperature gradient, while equation 6.9 can be seen as the Fourier equation (equation 6.23) with an extra term describing the coupling effects.

6.2.2.3 Transport across the liquid/zeolite interface

The molecules at the membrane surface transfer to an adsorbed phase, over the liquid/zeolite interface (step 2 in Figure 6.2). Since the feed temperature is known, and the temperature at the liquid/zeolite interface was determined using equation 6.24, the temperature difference over the interface can be calculated using equation 6.15. Using the calculated temperature difference and by combining equation 6.21 with 6.22, we can find the activity difference over the surface using

$$R \ln \left(\frac{a_i^{i,o}(T^i)}{a_i^{o,i}(T^o)} \right) = r_{\mu\mu}^s J_i - r_{qq}^s q_i^{*s,o} J_q'^{o,i} - (h_i^o - h_i^0) \left(\frac{\Delta_{i,o} T}{T^i T^o} \right) \quad (6.29)$$

Where, at the liquid/zeolite interface, the *i*-side denotes the liquid phase, while the *o*-side is the adsorbed phase in the zeolite.

6.2.2.4 Transport across the zeolite/support interface

From equation 6.27 and 6.9 the conditions at the *i*-side of the zeolite/support interface are calculated. Therefore, equation 6.15 and 6.29 for the liquid/zeolite interface can also be applied to calculate the temperature and activity difference across the zeolite/support interface (step 4 in Figure 6.2). In the equations the *i*-side now denotes the adsorbed phase in the zeolite, and *o*-side is the gaseous phase in the support material.

6.2.2.5 Transport through the porous support material

After the permeating molecules have been transferred across the zeolite/support interface, they diffuse through the support pores toward the bulk permeate gas phase (step 5 in Figure 6.2). The resistance in the support layer of a ceramic membrane can have a profound contribution to the total mass transport resistance [28, 29]. Most modeling on transport in membranes is based on the dusty gas model (DGM) [2, 28]. Although the model neglects the Maxwell slip term [30, 31], it has been shown to model the

transport in porous media with relative high accuracy, therefore the use of the DGM is widely accepted. In the DGM, the membrane is considered as a pseudo species in the mixture which is motionless and of infinite molar mass. The flux through the support is described by a combination of Knudsen diffusion and viscous flow. The viscous flow is not molecular diffusion, and therefore has no coupling effects. Using equation 6.8, the coupling between mass and heat flux can be incorporated in the Knudsen flow. When the support is assumed to have cylindrical pores, the molar flux in the porous support can be written as

$$J_i = -c_{i,pore} \mathcal{D}_{isup}^{Kn,eff} \frac{\nabla \mu_{i,T}}{RT} + \frac{c_{i,pore} \mathcal{D}_{isup}^{Kn,eff} q_i^{*sup}}{RT^2} \nabla T - \frac{\varepsilon}{\tau} \frac{c_{i,pore} d_p^2}{32\eta} \nabla P \quad (6.30)$$

Where $c_{i,pore}$ is the concentration of component i in the support pores and $\mathcal{D}_{isup}^{Kn,eff}$ is the effective Knudsen diffusivity, given by [2].

$$\mathcal{D}_{isup}^{Kn,eff} = \frac{\varepsilon}{\tau} \frac{d_0}{3} \sqrt{\frac{8RT}{\pi M_i}} \quad (6.31)$$

For a single component gas on the low pressure permeate side of the membrane, the ideal gas law can be applied. By substituting equation 6.19 in equation 6.30, whereby the fugacity of the permeating component equals the pressure, the pressure drop over the support can be written as

$$-\nabla P = \frac{J_i - \frac{c_{i,pore} \mathcal{D}_{isup}^{Kn,eff} q_i^{*sup}}{RT^2} \nabla T}{\frac{c_{i,pore} \mathcal{D}_{isup}^{Kn,eff}}{P} + \frac{\varepsilon}{\tau} \frac{c_{i,pore} d_p^2}{32\eta}} \quad (6.32)$$

Analogously to the zeolite layer, equation 6.9 is used to describe the heat transport through the support, using the heat of transport of the permeating component inside the support layer, q_i^{*sup} . For the temperature gradient in the support we can write

$$J'_q{}^{sup} = -\lambda \frac{\partial T}{\partial z} + q_i^{*sup} J_i \quad (6.33)$$

When the coupling between heat and mass transport is neglected, equation 6.32 simplifies to

$$-\nabla P = \frac{J_i}{\frac{c_{i,pore} \mathcal{D}_{isup}^{Kn,eff}}{P} + \frac{\varepsilon}{\tau} \frac{c_{i,pore} d_p^2}{32\eta}} \quad (6.34)$$

Equation 6.32 describes the coupled mass transport in the porous support (NET model), while the non-coupled mass transport is described by equation 6.34 (nCnS

model). The coupled heat transport in the support layers is described by equation 6.33 (NET model), which, for the nCnS model, again reduces to the Fourier equation when the coupling is neglected.

6.3 Calculations

To illustrate the impact of the surface and the coupling effects on a pervaporation process, the equations presented in the previous sections were applied to model pure water pervaporation through a NaA zeolite membrane, deposited on an asymmetric α -alumina support. In the calculations we considered a membrane with a zeolite layer thickness of $2\ \mu\text{m}$ deposited on an three-layer asymmetric α -alumina layer. Although there are not many values of pure water permeation reported, a flux of $10\ \text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ($0.15\ \text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) pure water was assumed at a feed temperature of 348 K. A similar flux has been measured for pure water pervaporation in an all-silica DD3R zeolite membrane at a temperature of 398 K [32]. The values of the membrane thickness, feed temperature and flux represent the performance of a high performance NaA membrane [29].

6.3.1 Estimation of transport parameters

In this section, the parameters, required to solve the presented transport equations for water pervaporation through a LTA-type membrane, are estimated. The sequence in which the estimated parameters are presented follows the different steps denoted in Figure 6.2.

6.3.1.1 The liquid boundary layer

To obtain the boundary layer thickness, δ_T , we assumed turbulent flow ($Re = 50 \times 10^3$) and a geometric length, l_{geo} , of $5 \times 10^{-3}\ \text{m}$, which is a typical value for the inner radius of a zeolite membrane tube. The Nusselt number, Nu , for turbulent flow in a tube was determined using the Dittus-Boelter correlation [33]

$$Nu = 0.023Re^{4/5}Pr^{0.3} \quad (6.35)$$

δ_T is then determined using [33]

$$Nu = \frac{\frac{\lambda}{\delta_T}l_{geo}}{\lambda} = \frac{l_{geo}}{\delta_T} \quad (6.36)$$

Using equation 6.35 and 6.36, a laminar film thickness of $28.4 \mu\text{m}$ was calculated. This value was then used as a boundary condition in equation 6.24 to calculate the temperature profile across the liquid boundary layer.

6.3.1.2 Zeolite layer: adsorption

Water adsorbed in hydrophilic zeolites has a density and diffusion behavior in between that of a solid and a liquid [34, 35]. In hydrophobic zeolites the behavior of adsorbed water lies in between that of a liquid and a vapor [36]. For the estimation of adsorption and diffusion parameters we used results from molecular simulation and experimental data.

Water adsorption on NaA was described by a single-site Langmuir adsorption behavior [34].

$$\theta_w = \frac{q_w^{eq}}{q_w^{sat}} = \frac{K_w f_w}{1 + K_w f_w} \quad (6.37)$$

The Antoine equation was used to correlate the vapor pressure, P_w^{sat} , to the temperature [37]. The liquid fugacity was then determined by [38]

$$f_w = P_w^{sat} \phi_w^{sat} \exp \left[\frac{V_{m,w}^l (P - P_w^{sat})}{RT} \right] \quad (6.38)$$

The fugacity coefficient ϕ_w^{sat} is unity for the conditions considered. The adsorbed water in the zeolite layer is transported through the membrane and finally desorbs into the support layer. At the liquid/zeolite interface, the enthalpy change $\Delta_{l,z}H_w$ is the adsorption enthalpy of water on NaA, $-18 \text{ kJ}\cdot\text{mol}^{-1}$. At the zeolite/support interface, the desorption step is accompanied by a phase change, this results in an enthalpy change, $\Delta_{z,sup}H_w$ of $65 \text{ kJ}\cdot\text{mol}^{-1}$ [39]. Table 6.1 gives the values of the adsorption parameters used in the calculations. Because of the steep adsorption isotherm, the loading of water in the highly hydrophilic zeolite is close to saturation at all positions in the membrane.

Table 6.1: Parameters for adsorption of water on a NaA type zeolite.

parameter	value	unit	reference
K_w	10^{-3}	Pa^{-1}	[40]
q_w^{sat}	15	$\text{mol}_w\cdot\text{kg}_z^{-1}$	[40]
$\Delta_{l,z}H_w$	-18×10^3	$\text{J}\cdot\text{mol}^{-1}$	[39]
$\Delta_{z,sup}H_w$	65×10^3	$\text{J}\cdot\text{mol}^{-1}$	[39]

6.3.1.3 Zeolite layer: diffusion

The diffusivities of adsorbed species in zeolites with cage like structures are often a strong function of the loading [41, 42]. To model the loading dependency of the diffusivity, the Reed - Ehrlich formulation was used [43]. This method relates the diffusivity to the loading via [44]

$$\mathcal{D}_{w,M}^{eff} = \alpha_3 \frac{(1 + \varepsilon)^{11}}{(1 + \varepsilon/\phi)^{12}} \quad (6.39)$$

wherein ϕ and ε are defined as

$$\phi = \alpha_1 \exp(\alpha_2 \theta) \quad (6.40)$$

$$\varepsilon = \frac{(\beta - 1 + 2\theta)\phi}{2(1 - \theta)} \quad (6.41)$$

with

$$\beta = \sqrt{1 - 4\theta(1 - \theta)(1 - 1/\phi)} \quad (6.42)$$

The Reed-Ehrlich equations were fitted to NEMD data of water diffusion in NaA [45]. Table 6.2 shows the fitted parameters for calculating the water diffusivity. Since, in this system, the loading is always close to saturation, the calculated values of $\mathcal{D}_{iM}^{eff}$ are $\sim 4 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ and do not differ significantly over the membrane thickness.

Table 6.2: Fitted Reed-Ehrlich parameters for NEMD data [45] of water diffusivity in a NaA type zeolite.

parameter	value	unit
α_1	1.22	$\text{m}^2 \cdot \text{s}^{-1}$
α_2	0.165	
α_3	3.05×10^{-10}	

6.3.1.4 Zeolite layer: heat of transfer

The adsorbed phase in the zeolite is assumed to resemble liquid-like properties. For the heat of transfer of water in the zeolite we used the same estimation which was used by Kjelstrup *et al.* for water in a polymer fuel cell [25].

$$q_w^{*z} = -S_w T \quad (6.43)$$

where S_w is the entropy of the adsorbed phase, which in this case is assumed to be equal to the liquid entropy of water, $S_{w,l}$. The calculated heat of transfer is - 6.3 J·mol⁻¹, which lies in a range of values found for q_w^{*z} of butane in a silicalite-1 membrane [22].

6.3.1.5 Zeolite layer: thermal conductivity

We assumed the effective thermal conductivity, λ_{eff} , to be a linear combination of the volume fractions, v_i , and the thermal conductivities, λ_i , of the sorbent and sorbate species.

$$\lambda_{eff} = \sum_{i=1}^n v_i \lambda_i \quad (6.44)$$

The volume fraction of adsorbed water in a zeolite can be written as a function of the fractional loading as

$$v_w = \frac{\theta_w q_w^{sat} M_w \rho_w}{\rho_z + \theta_w q_w^{sat} M_w \rho_w} \quad (6.45)$$

The thermal conductivities used in the calculations are shown in Table 6.3. Using these data, an effective thermal conductivity of the zeolite layer, λ_{eff}^z , is found to be $\sim 0.6 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$.

Table 6.3: Thermal conductivity data and densities for water, NaA zeolite and an α -alumina support.

parameter	value	unit	reference
$\lambda_{w,l}$	0.65	$\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$	[46]
$\lambda_{w,g}$	~ 0	$\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$	[46]
λ_z	0.10	$\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$	[47]
λ_{sup}	30	$\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$	[46]
ρ_w	1000	$\text{kg} \cdot \text{m}^{-3}$	[46]
ρ_z	1415	$\text{kg} \cdot \text{m}^{-3}$	[48]

6.3.1.6 Dividing surfaces

At the dividing surfaces, the values for $q_w^{*s,o}$ were estimated as a fraction of the enthalpy difference across the surface [49].

$$q_w^{*s,o} = -k \Delta_{i,o} H_w \quad (6.46)$$

Previous studies on vapor-liquid equilibria, gave k in equation 6.46 equal to 0.3 for the vapor side of the interface [50]. The values of $q_w^{*s,o}$ for the liquid zeolite ($q_w^{*l,z}$)

and the zeolite/support ($q_w^{*z,sup}$) interfaces, using $k = 0.3$, are listed in Table 6.4. The enthalpy differences, used in equation 6.46, are listed in Table 6.1.

Because of the novelty of the concept of the dividing surface, the required transport parameters are not readily available. The resistivities (r_{qq}^s and $r_{\mu\mu}^s$) of the surface were assumed to be the same at the liquid/zeolite and the zeolite/support interfaces. The values were estimated based on work of Xu *et al.* who performed non-equilibrium molecular dynamics (NEMD) simulations of a vapor-liquid interface for argon-like particles [51].

Table 6.4: Parameters used for transport across the liquid/zeolite and zeolite/support interfaces.

parameter	value	unit	reference
$q_w^{*l,z}$	5.4×10^3	$\text{J} \cdot \text{mol}^{-1}$	[39, 49]
$q_w^{*z,sup}$	-19.5×10^3	$\text{J} \cdot \text{mol}^{-1}$	[39, 49]
r_{qq}^s	6×10^{-10}	$\text{m}^2 \cdot \text{s} \cdot \text{J}^{-1} \cdot \text{K}^{-1}$	[51]
$r_{\mu\mu}^s$	5×10^{-4}	$\text{J} \cdot \text{m}^2 \cdot \text{s} \cdot \text{mol}^{-2} \cdot \text{K}^{-1}$	[51]

6.3.1.7 Support layers: diffusion

In our model the zeolite layer is deposited on an asymmetric α -alumina support, which consists of three layers with increasing thickness and pore size from the membrane side to the permeate side. The values used for the calculation are typical values [52, 53], given in Table 6.5. These data include the porosity, ε , the tortuosity, τ , the layer thickness, δ , of the support material, and the average pore diameter, d_p , estimated from the α -alumina particle size, d_{part} , using [54]

$$d_p = \frac{2}{3} \frac{d_{part} \varepsilon}{1 - \varepsilon} \quad (6.47)$$

Table 6.5: Parameters for the asymmetric α -alumina support.

parameter	value	unit
ε	0.4	
τ	3	
$\delta_{sup,1}$	13×10^{-6}	m
$d_{p,1}$	0.22×10^{-6}	m
$\delta_{sup,2}$	70×10^{-6}	m
$d_{p,2}$	1.1×10^{-6}	m
$\delta_{sup,3}$	1.75×10^{-3}	m
$d_{p,3}$	5.4×10^{-6}	m

Using these data we find Knudsen diffusivities of 6.1×10^{-6} , 3.1×10^{-5} , and $1.5 \times 10^{-4} \text{ m}^2 \cdot \text{s}^{-1}$, and viscous flow contribution of 10%, 20%, and 60% for layer one, two, and three, respectively.

6.3.1.8 Support layers: heat of transfer

The low pressure gas inside the support layer mainly resembles Knudsen behavior [28]. Rastogi *et al.* have obtained expressions from kinetic theory for describing the linear transport equations for thermo-osmosis of a Knudsen gas [19]. The heat of transfer of a Knudsen gas was estimated by

$$q_i^{*Kn} = -\frac{RT}{2} \quad (6.48)$$

The value of q_w^{*Kn} in the support layers is typically $\sim -1.4 \times 10^3 \text{ J} \cdot \text{mol}^{-1}$, which is substantially higher than in the absorbed phase in the zeolite.

6.3.1.9 Support layers: thermal conductivity

Also in the support layers, equation 6.44 was used to determine the overall thermal conductivity. The volume fraction of the low pressure vapor in the porous structure is equal to the porosity, ε . The thermal conductivity in the support is dominated by the conductivity of α -alumina, so the conductivity of the low pressure vapor was neglected ($\lambda_{w,g} = 0$). Using equation 6.44 and the data in Table 6.5 and 6.3 the effective thermal conductivity in the support was calculated. Equations 6.32 and 6.9 were then used to calculate activity and temperature profiles in the support.

The data in Table 6.3 yields a typical value of $\lambda_{eff}^{sup} = 18 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$.

6.3.2 Solution procedure

To single out the influence of the coupling and surface effects on mass and heat transport, the transport equations have also been solved while neglecting the surface and coupling effects (i.e. r_{qq}^s , $r_{\mu\mu}^s$, and all heats of transfer, q_i^* , are zero), which resulted in a model consisting of the M-S equations describing mass transport, and the Fourier equation describing heat transport. Since there is no heat supply possible after the water has passed the zeolite/support interface, we have set the heat flux inside the support, J_q^{sup} , equal to zero. From this equation, it is then evident that when the coupling is neglected, the nCnS model will predict no temperature gradient

in the support. The boundary conditions used in the calculations are listed in Table 6.6.

Table 6.6: Boundary conditions used in the model, giving the feed temperature, mass flux, and observable heat flux in the support layer.

parameter	symbol	value	unit
feed temperature	$T^{l,bulk}$	348	K
molar water flux	J_w	0.15	$\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$
heat flux in support layers	J_q^{sup}	0	$\text{J}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$

We have considered a one-dimensional system, with transport in the z -direction, as depicted in Figure 6.2. The equations were solved in the sequence of transport, using Matlab (ode45).

Using equation 6.1, 6.2, and 6.33, the heat fluxes in each layer were calculated for a given steady state molar water flux, J_w . The temperature and activity gradients in each layer were calculated using the presented equations for the NET model and the nCnS model. From the temperature and activity gradients the activity, fugacity and temperature profiles were obtained.

In the NET model, equations 6.8 and 6.9 were used to model the mass and heat transport in the homogeneous phase, and equations 6.21, 6.22 and 6.15 were used to describe transfer across the surfaces. By neglecting the coupling effects and the contribution of the interfaces, the model was simplified to equations 6.12 and 6.23, which is referred to as the nCnS model.

6.4 Results

For the water feed temperature of 348 K, and a flux of $0.15 \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$, the profiles for activity, fugacity and temperature were calculated. The activity is the ratio of the fugacity at local conditions and the fugacity at the reference state, a pure component liquid at the local temperature. Figures 6.4, 6.6 and 6.8 show the temperature, fugacity and activity profiles in the complete membrane system, including laminar liquid film and support layers. In these figures the length coordinate Δz , is given in logarithmic scale. Figures 6.5, 6.7, and 6.9 give an enlargement of the profiles in the $2 \mu\text{m}$ zeolite layer and at the dividing surfaces.

With the saturated liquid as the reference state, it follows that the activity in the liquid boundary layer is always unity, which corresponds to the absence of a driving

force for mass transfer. The enthalpy at the reference state is therefore equal to the liquid enthalpy. For the enthalpy differences in equation 6.22 this now yields the enthalpy of adsorption at the liquid/zeolite interface and the heat of evaporation at the zeolite/support interface.

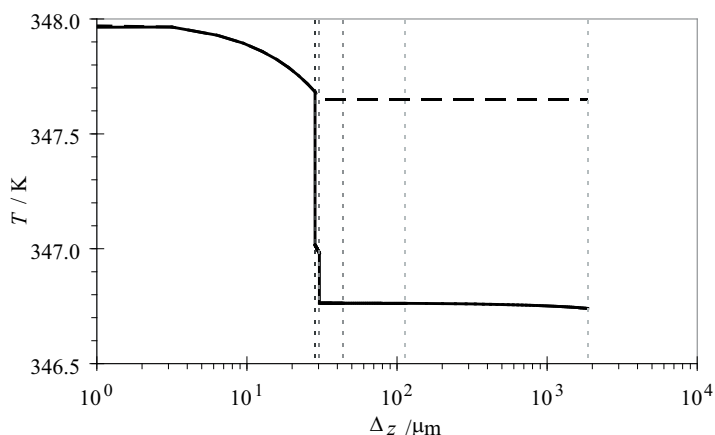


Figure 6.4: Temperature profile across the liquid film, zeolite layer and the α -alumina support, calculated using the NET model (solid line) and the nCnS model (dashed line). The vertical dashed lines indicate, from left to right, the liquid/zeolite interface, the zeolite/support interface and the boundary of the different support layers.

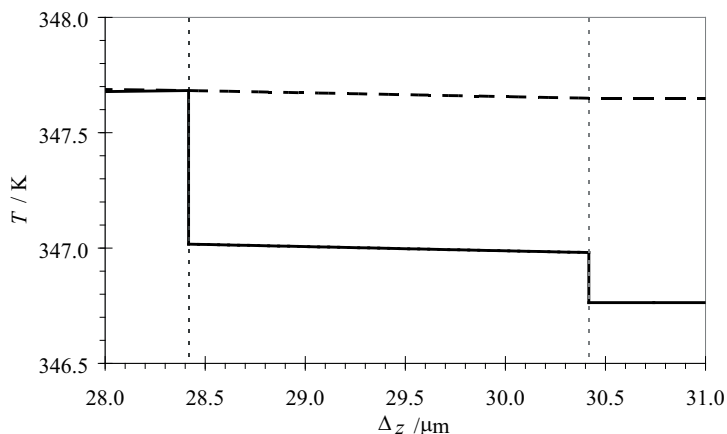


Figure 6.5: Temperature profile across the zeolite layer and the dividing surfaces calculated using the NET model (solid line) and the nCnS model (dashed line). The figure is an enlargement of Figure 6.4. The vertical dashed lines indicate the liquid/zeolite interface and the zeolite/support interface.

Figure 6.4 shows a temperature difference over the membrane system of 1.3 K is calculated using the NET model. Neglecting the coupling effects, results in more than a three fold lower total temperature difference (0.4 K). The largest temperature drop is observed at the interfaces (Figure 6.5).

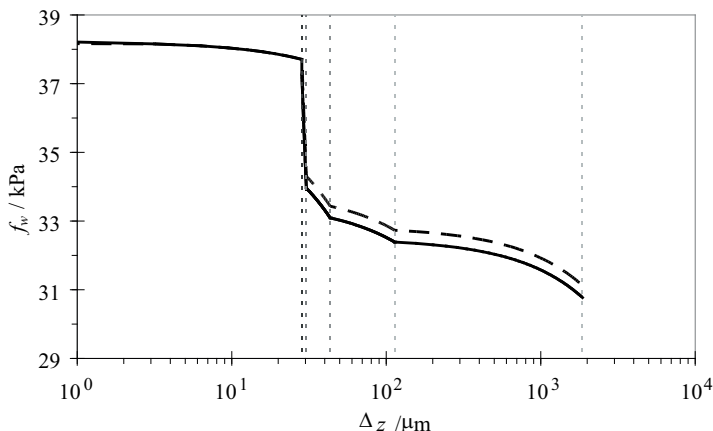


Figure 6.6: Profile of the fugacity of water across the liquid film, zeolite layer, the α -alumina support, calculated using the NET model (solid line) and the nCnS model (dashed line). The vertical dashed lines indicate, from left to right, the liquid/zeolite interface, the zeolite/support interface and the boundary of the different support layers.

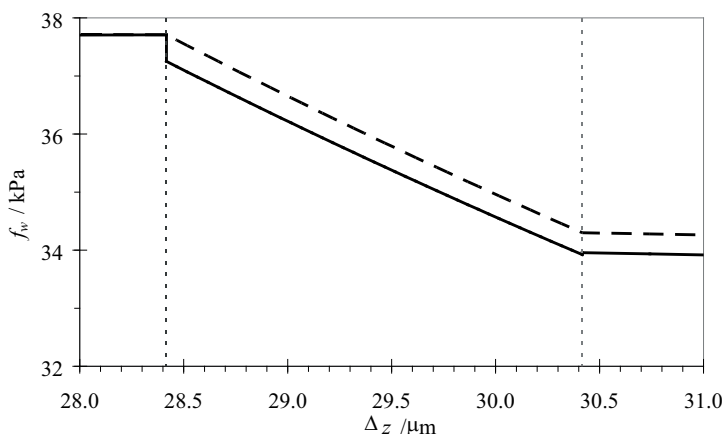


Figure 6.7: Profile of the fugacity of water across the zeolite layer and the dividing surfaces calculated using the NET model (solid line) and the nCnS model (dashed line). The figure is an enlargement of Figure 6.6. The vertical dashed lines indicate the liquid/zeolite interface and the zeolite/support interface.

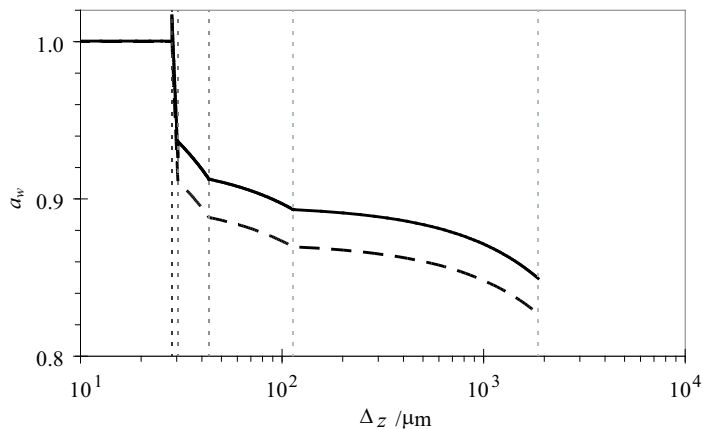


Figure 6.8: Profile of the activity of water across the liquid film, zeolite layer, the α -alumina support, calculated using the NET model (solid line) and the nCnS model (dashed line). The vertical dashed lines indicate, from left to right, the liquid/zeolite interface, the zeolite/support interface and the boundary of the different support layers.

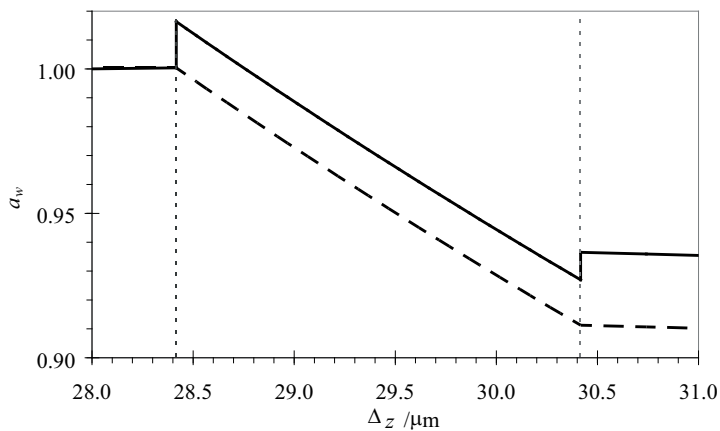


Figure 6.9: Profile of the activity of water across the zeolite layer and the dividing surfaces calculated using the NET model (solid line) and the nCnS model (dashed line). The figure is an enlargement of Figure 6.8. The vertical dashed lines indicate the liquid/zeolite interface and the zeolite/support interface.

Figure 6.9 shows that at the liquid/zeolite and the zeolite support interfaces, the activity increases with, respectively, 11% and 6% of the total difference. The fugacity shows a drop at the liquid/zeolite interface of 6%, while at the zeolite/support interface, there is a small positive jump in fugacity (-0.5%).

Table 6.7 gives an overview of the relative contributions of the laminar boundary layer, the zeolite layer, and the support layers, as well as the surfaces, to the total temperature, fugacity and activity difference over the total system for both the case of incorporating (NET model) as well as neglecting (nCnS model) surfaces and coupling effects.

Table 6.7: Relative contributions to temperature and fugacity difference over the membrane system at $T = 348$ K, $J_w = 0.15 \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$, and $J_q^{sup} = 0 \text{ J}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$.

Layer	NET model			nCnS model		
	$\frac{\Delta_{layer} T}{\Delta_{tot} T}$	$\frac{\Delta_{layer} f}{\Delta_{tot} f}$	$\frac{\Delta_{layer} a}{\Delta_{tot} a}$	$\frac{\Delta_{layer} T}{\Delta_{tot} T}$	$\frac{\Delta_{layer} f}{\Delta_{tot} f}$	$\frac{\Delta_{layer} a}{\Delta_{tot} a}$
liquid film	25.2%	6.8%	0.0%	90.5%	7.1%	0.0%
surface liquid/zeolite	52.9%	6.1%	-10.6%			
zeolite layer	2.9%	44.7%	59.2%	9.5%	48.1%	51.4%
surface zeolite/support	17.2%	-0.5%	-6.3%			
support layers	1.8%	32.8%	57.7%	0.0%	44.8%	48.6%
total difference	-1.3 K	-7.4 kPa	-0.15	-0.35 K	-7.1 kPa	-0.17

Calculations have shown that neglecting the viscous flow term in the support increases the activity and fugacity drop over the membrane by 70% and 52%, respectively.

When the heat flux in the support, J_q^{sup} , is chosen larger than zero, the temperature and fugacity difference over the membrane increase. Because of the positive coupling between the heat and mass flux, the activity difference decreases with increasing heat flux. This suggests the possibility of enhancing the mass flux by generating a heat flux across the membrane, which can be done by cooling the permeate side of the membrane. The effect of the heat flux inducing mass transfer is singled out under thermal osmosis conditions [19, 25], meaning the mass flux is set to zero, while a positive heat flux is imposed on the system. In this system, this results in a positive activity difference over the membrane, showing the heat flux induces a driving force for mass flux in the direction of the heat flux.

At mass fluxes above $0.73 \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$, the permeate side activity becomes zero, marking the maximum flux physically attainable in this system.

6.5 Discussion

The profiles in Figures 6.4, 6.6 and 6.8 illustrate the impact of taking the surface effects and the coupling between mass and heat transport into account on a practical system. Since many of the transport parameters are estimated based on different systems, the comparison between these models is meant as a qualitative measure for the impact of the surface and coupling effects. The activity represents a measure for the driving force for mass transport at constant temperature and pressure, while the fugacity can be seen as a corrected pressure, which in the support equals the actual pressure. The profiles for the nCnS and the NET models show distinct differences, particularly for the temperature profiles.

Figure 6.5 clearly shows that the discontinuity in the temperature at the liquid/zeolite and zeolite/support interface. The temperature drop at the surfaces dominates the temperature drop over the zeolite layer. At both surfaces a drop in temperature is observed, despite the fact that at the feed side an exothermic process occurs. This shows that the temperature difference over the surface is dominated by the value of r_{qq}^s . Approximately 70% of the temperature drop over the whole system is generated at the surfaces. Using these parameters, it was found that the liquid/zeolite surface has a higher contribution than the zeolite/support surface.

The total fugacity and activity difference over the system is similar for the NET and the nCnS model (Table 6.7). The discontinuities are also observed in the fugacity and activity profiles (Figures 6.7 and 6.9), albeit much smaller than for the temperature. The positive jumps in activity at the interfaces reveal that there is a molar flux across the surfaces against the activity difference. This means that, at the interfaces, the mass transport is driven by the temperature gradient.

For the NET and the nCnS model, the fugacity and temperature difference over the laminar boundary layer are equal (0.5 kPa and 0.3 K, respectively). However, the liquid/zeolite interface causes an additional 0.7 K temperature drop. This could indicate that temperature polarization effects are not only limited by conduction in the liquid phase, but also by the surface resistance. Because in the single component liquid phase there is no driving force for mass transport, the NET model and the nCnS model are described with the same equations in the liquid boundary layer. For a multi-component system, this will not be the case.

The support layers contribute significantly to the overall mass transport resistances figures 6.8). This holds for both the NET and the nCnS model. Since the heat

flux on the permeate side, J_q^{sup} , is set to zero, the temperature gradient in the support in Figure 6.4 is only caused by the coupling effects. The temperature difference over the support predicted by the nCnS model is, evidently, zero, while the coupling effects in the NET model cause a small temperature difference. The heat of transfer is estimated based on a pure Knudsen gas, the actual value of the heat of transfer in the support could be lower, reducing the coupling effect in the support.

The temperature dependency of the adsorption and diffusion is not taken into account in this model. The absolute temperature differences are limited to a few Kelvin and the highly hydrophilic zeolite will be close to saturation in the case of pure water feed within this temperature range. The temperature dependency of diffusivity and loading are therefore expected to be negligible. In the case of gas permeation, or water transport through an apolar membrane, these temperature dependencies are expected to be of more importance.

In practice, conduction at the permeate side of the membrane could induce a heat flux deviating from the assumed value of zero. Moreover, when the condensation of the permeate vapor would occur close to the permeate membrane surface, the heat flux would be determined by the mass flux and the heat of condensation. Nevertheless, unless heat is added on the permeate side there would be a positive deviation from zero, enhancing the mass flux through the coupling effects. This effect was observed doing simulating thermal osmosis experiments, which showed the possibility of enhancing the flux in pervaporation processes by increasing the temperature gradient over the membrane. This has interesting technical consequences.

Because of the novelty of the concept of the dividing surface, the available transport parameters are limited. For the system of water in a zeolite membrane there are no experimental or simulation results available yet which give the surface properties and the coupling constants. Although the transport parameters are estimated based on simulation data and theory, and the values correspond to values found for other systems, actual data are not available. The values for q_i^* at the interfaces and of the adsorbed phase, and the values of $r_{\mu\mu}^s$ and r_{qq}^s should be determined by experiments [55, 56] or molecular simulations [22, 57] to give a better description of the transport in this system.

6.6 Conclusions

Based on the theory of non-equilibrium thermodynamics, transport equations for coupled mass and heat transport are derived. The calculated activity, fugacity and temperature profiles are compared to a model neglecting surface and coupling effects. Taking coupling and surface effects into account, reveals discontinuities in temperature, activity and fugacity at the liquid/zeolite and zeolite/support interfaces. The positive jump in activity shows that the transfer across the interfaces can be governed by the temperature gradient. The temperature difference over the zeolite layer was here dominated by the interfaces. This could indicate that temperature polarization occurring in pervaporation processes could, to a large extent, be caused by surface effects. The calculated total activity difference over the membrane was lower when coupling effects were considered. The influence of the support on the overall mass transport resistance is significant for both cases.

Increasing the temperature gradient across the membrane, decreases the activity gradient. This shows the possibility of enhancing the mass flux by generating an energy sink at the permeate side of the membrane.

The transport parameters used to model this system are, to a large extent, estimates based on data of different systems. Molecular simulations or thermal osmosis experiments can provide better estimates for these transport parameters.

List of symbols.

symbol	name	unit
a	activity	
c	concentration	$\text{mol}\cdot\text{m}^{-3}$
$d_{p,A}$	pore diameter in material A	m
d_{part}	particle diameter	m
$\mathcal{D}_{ij}$	M-S diffusivity of component i in j	$\text{m}^2\cdot\text{s}^{-1}$
f	fugacity	Pa
$H_{A,i}$	enthalpy of component i in phase A	$\text{J}\cdot\text{mol}^{-1}$
J	molar flux	$\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$
J'_q	observable heat flux	$\text{W}\cdot\text{m}^{-2}$
K	Langmuir adsorption parameter	Pa^{-1}
M_i	molar mass of component i	$\text{kg}\cdot\text{mol}^{-1}$
P	pressure	Pa
P^{sat}	vapor pressure of component i	Pa
q^*	heat of transfer of component i	$\text{J}\cdot\text{mol}^{-1}$
q^{eq}	equilibrium loading	$\text{mol}\cdot\text{kg}^{-1}$
q^{sat}	saturation loading	$\text{mol}\cdot\text{kg}^{-1}$
R	gas constant	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
r_{ij}	resistivity coefficient	

List of symbols. (continued)

symbol	name	unit
$S_{i,A}$	entropy of component i in phase A	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
T	temperature	K
V_m	partial molar volume	$\text{m}^3\cdot\text{mol}^{-1}$
v	volume fraction	—
x	molar fraction	—
z	length coordinate	m
δ_A	thickness of layer A	m
ε	porosity	—
η	viscosity	$\text{Pa}\cdot\text{s}$
Γ	thermodynamic correction factor	
θ	fractional loading of component i	
λ	heat conductivity of component i	$\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
μ	chemical potential of component i	$\text{J}\cdot\text{mol}^{-1}$
ρ	density	$\text{kg}\cdot\text{m}^{-3}$
σ	entropy production in a homogeneous phase	$\text{J}\cdot\text{s}^{-1}\cdot\text{K}^{-1}\cdot\text{m}^{-3}$
σ^s	surface entropy production	$\text{J}\cdot\text{s}^{-1}\cdot\text{K}^{-1}\cdot\text{m}^{-2}$
τ	tortuosity	—
v	velocity	$\text{m}\cdot\text{s}^{-1}$
ϕ^{sat}	fugacity coefficient	—
sub and super scripts		
eff	effective	
l	liquid	
sup	support material	
z	zeolite	
i	component i	
q	heat	
w	water	
μ	molar	
Kn	Knudsen	
i	i-side of interface	
o	o-side of interface	
s	surface	
0	at standard state	
l,z	liquid/zeolite interface	
z,sup	zeolite/support interface	

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Detemplation of DDR type zeolites by ozonation

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Abstract Ozonation is a technique which can be used to remove the template from zeolites at much lower temperatures than conventional calcination. The template removal by ozonation has been investigated for small pore zeolites of the DDR topology. The pore size of the DDR type zeolites (4.4×3.6 Å) is smaller than the molecular diameter of ozone (4.6 Å). The detemplation of these zeolites confirms the assumption of ozone breaking down into radicals at the zeolite surface before diffusing through the pore system. All-silica DDR (DD3R), all-silica ZSM-58 and aluminum containing NaZSM-58 (Si/Al=170) have been synthesized. The crystal size distributions of the materials show the DD3R crystals have an average size of 2.7 μm , while the ZSM-58 sample consists of 6.1 μm hexagonal shaped crystals. The NaZSM-58 material consists of globular aggregates of 36 μm , consisting of small 1 μm primary particles. The ozonation was carried out at 473 K using $6 \times 10^{-3} \text{ m}^3 \cdot \text{h}^{-1}$ (STP) of a mixture of 80 $\text{g} \cdot \text{m}^{-3}$ (STP) ozone in oxygen. DD3R was completely detemplated in 38 h of ozonation, showing porosity characteristics equal to that of a calcined sample. The all-silica ZSM-58 and NaZSM-58 samples were detemplated for 75% in 38 h and 90% in 8 h, respectively, as compared to the calcined samples. The incomplete detemplation is expected to be due to the larger size of the SDA for ZSM-58 (MTI) compared to the SDA for DD3R (1-ADA). The lower template removal of the all-silica ZSM-58 is attributed to the larger crystal size.

7.1 Introduction

Small pore zeolites have gained increasing interest in the fields of membrane technology and sensor applications. All-silica deca-dodecasil 3R (DD3R) has been successfully applied for CO_2/CH_4 separation [1–3] and de-watering of alcohols and other organic solvents [4, 5]. Dehydration of alcohols is already done on industrial scale using zeolite LTA type membranes [6]. Also hydroxy sodalite (SOD) membranes have been successfully synthesized and tested for absolute water separation [7]. Because of the pronounced size selectivity of these small pore zeolites, they are also well suited for sensor applications.

Most zeolites require an organic structure directing agent (SDA) for a successful synthesis. After the synthesis, this organic molecule needs to be removed from the zeolite structure. Conventionally this is done by calcination at temperatures between 623 K and 973 K. High detemplation temperatures are very undesired in fragile materials with unusual framework compositions, or in applications such as membranes or coating of sensors, or other materials with a low dielectric constant. In the case of coatings and membranes, heating can lead to crack formation. Even when applying low heating rates the chance of creating defects is profound. Moreover, many sensor materials are not capable of withstanding the high temperatures required for template removal.

Several low temperature detemplation techniques have been developed [8–12]. In this chapter, we will apply ozonation, in which a zeolite is contacted with an oxygen/ozone mixture at elevated temperatures. At these temperatures, ozone decomposes into atomic oxygen and radical species, which are highly reactive oxidants [12–14]. Heng *et al.* have successfully detemplated MFI type zeolite membranes using 50–100 g·m⁻³ (STP) ozone in oxygen at temperatures up to 473 K [12]. Where standard conditions are defined at 293 K and 1.01 bar. Ozonation has also been successfully applied for coke removal from MFI and FAU type zeolites [15–17]. Because of the mild thermal conditions, this method is well suited for detemplating zeolite coatings on temperature sensitive substrates; or for detemplating membranes. Although it is suggested that the decomposition of ozone into radical species takes place at the zeolite surface [17], and the formed radicals diffuse into the pore system, oxidizing the template, this mechanism has not been proven yet.

This chapter focuses on applying ozonation to remove the template from different zeolites of the DDR framework topology. The structure of DDR consists

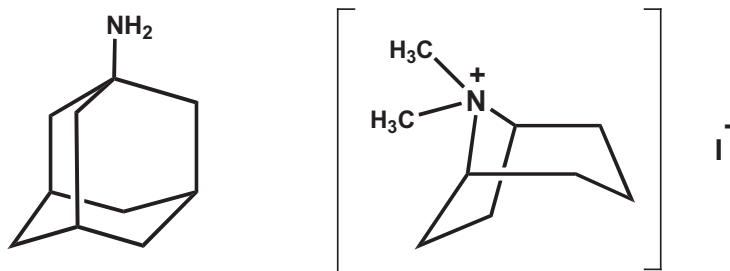


Figure 7.1: Structure directing agents used in the synthesis of zeolites with the DDR topology: 1-adamantanamine (left) and methyltropinium Iodide (right)

of window-connected cages, which makes this material a member of the group of clathrasils [18]. The crystal structure is built by corner-sharing SiO_4 tetrahedra that are connected to pseudo-hexagonal layers of face-sharing pentagonal dodecahedra (5^{12} cages). These layers are stacked in an ABCABC sequence and are interconnected by additional SiO_4 tetrahedra that form six-membered rings between the layers. Thus, two new types of cages arise, a small decahedron, $4^35^66^1$ cage, and a large 19-hedron, $4^35^{12}6^18^3$ cage. By connecting the 19-hedra cavities through a single 8-ring with an aperture of $4.4 \times 3.6 \text{ \AA}$, a two-dimensional channel system is formed, which is accessible to small molecules after thermal treatment at 773 K - 973 K. Three different materials with the DDR topology have been reported in the literature: all-silica deca dodecasil 3R (DD3R) [18], sigma-1 [19] and ZSM-58 [20]. For the synthesis of DD3R and sigma-1, 1-adamantanamine (1-ADA) is used as SDA, while methyltropinium iodide (MTI) is used as SDA in the synthesis of ZSM-58 (Figure 7.1). The small pore size of DDR materials excludes ozone from entering the pores, since the molecular diameter of ozone is larger than the DDR pore window [21]. Since the molecular diameter of oxygen ($3.4 \text{ \AA}$), atomic oxygen ($1.4 \text{ \AA}$) and many radical (i.e. $\text{OH}\cdot$ or $\text{CH}_3\cdot$) species are smaller than the DDR pore window, successful detemplation of these zeolite types would confirm the proposed mechanism of ozone degradation at the zeolite surface, and the diffusion of the active radical species. Moreover, the detemplation of the same structure topology but with two different SDA's and both all-silica and aluminum containing frameworks would demonstrate the range of applicability of this technique.

7.2 Experimental methods

7.2.1 Synthesis

All the chemicals were purchased from Aldrich and used as received, without further preliminary purification. DD3R crystals were prepared by the method described elsewhere [22]. The synthesis mixture has the molar ratio of 1-ADA : SiO₂ : ethylenediamine (EDA) : H₂O = 47 : 100 : 404 : 11240 and it was prepared as follows. 1.72 g of 1-ADA (97 wt%) was dissolved in 5.76 g EDA ($\geq$ 99 wt%) and was placed in an ultrasonic bath for 1 h. Water (38 g) was then added rapidly. The mixture was placed in a shaking machine for 1 h. After heating to 368 K for 1 h while stirring, the mixture was cooled down in ice. Aerosil 200 (1.41 g) was then slowly added while the solution was stirred vigorously. The mixture was again heated to 368 K in an open vessel while stirring until the solution became clear (the solution changed from white to almost transparent). As-synthesised DD3R crystals (0.01 g) were added as seeds. The resulting solution is placed in a teflon lined autoclave and heated under hydrothermal conditions (autogenous pressure) to 433 K for 2 days under rotation at 60 rpm.

For the synthesis of ZSM-58 [20], first the SDA, methyltropinium iodide (MTI), was prepared by adding 25.1 g methyl iodide (99 wt%) dropwise to a solution of 25.0 g tropine (98 wt%) in 100 g ethanol at 273 K under stirring and keeping the suspension under reflux for 72 h. After cooling and filtration, the resulting crystalline MTI was washed with 100 g ethanol and dried at 353 K. The synthesis mixture is characterized by a molar ratio of MTI : SiO₂ : Al₂O₃ : Na₂O : H₂O = 17.5 : 70 : x : 11.5 : 2800, where the amount of alumina, x , depends on the desired Si/Al ratio. The Si/Al ratio of the zeolite is equal to that of the synthesis mixture and can be varied between infinite and 70, corresponding to an x between 0 and 0.125. In this case 0 and 0.051 are used for the all-silica ZSM-58 and the NaZSM-58, respectively. The synthesis mixture was prepared as follows: 10 g of Ludox HS-40 was added to a solution of 4.7 g MTI in 8.7 g H₂O and stood overnight while stirring (solution A). 0.78 g sodium hydroxide and the corresponding amount of sodium aluminate (Al₂O₃: 50-56 wt%, Na₂O: 40-45 wt%) were dissolved in 33.3 g H₂O (solution B). The resulting solution (A+B) is stirred for 30 min, placed in a teflon lined autoclave and heated under hydrothermal conditions (autogeneous pressure) to 433 K under rotation at 60 rpm for 48 h in the case of all-silica ZSM-58, and 7 days in the case of NaZSM-58.

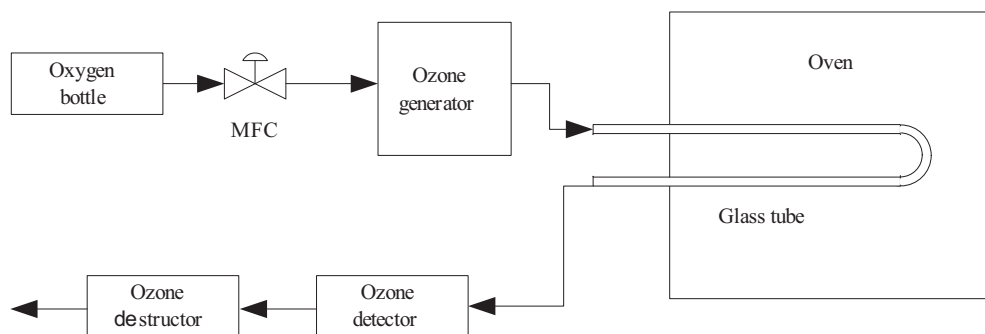


Figure 7.2: Schematic illustration of ozonation setup

7.2.2 Template removal

7.2.2.1 Calcination

As a reference, the synthesized samples are thermally calcined at 823 K to 973 K for 6 to 16 h using a heating and cooling rate of $60 \text{ K} \cdot \text{h}^{-1}$ in static air (Carbolite CSF1100). The sample is placed in a ceramic dish, which is placed inside the oven.

7.2.2.2 Ozonation

The detemplation is carried out by ozonation in a glass u-tube (diameter 6 mm and length 900 mm), placed in a programmable oven (Binder FP53) which is kept at a temperature of 473 K. A zeolite sample (0.2 - 1 g) is placed, as a thin layer, inside the glass tube. After a certain amount of time, part of the zeolite sample is taken out after which the ozonation is continued. Dry oxygen from a gas cylinder is passed through a Corona discharge ozone generator (A2Z Ozone Systems, SOZ-16GLAB). The inlet pressure of oxygen at the ozone generator is set at 1.5 bar. Using a mass flow controller (Bronkhorst Hi-Tech B.V.), the zeolite sample is exposed to a flow of $6 \times 10^{-3} \text{ m}^3 \cdot \text{h}^{-1}$ (STP) dry oxygen containing $80 \text{ g} \cdot \text{m}^{-3}$ (STP) of ozone where normal conditions are 298 K and 1.01 bar. The ozone concentration at the outlet of the oven is monitored using an ozone detector (Lenntech, BMT 964) after which it is sent through a manganese dioxide/copper oxide catalytic ozone destructor. Figure 7.2 gives a schematic representation of the setup used for ozonation. Before ozonation, the system is flushed with pure oxygen at 473 K to ensure a water-free atmosphere.

7.2.3 Characterization

The crystal morphology is examined by scanning electron microscopy (SEM) (Philips XL20). X-ray Diffraction (XRD) is used to verify the crystal structure (Bruker-AXS D5005). Elementary analysis is done by inductively coupled plasma optical emission spectrometry (ICP-OES) (PerkinElmer Optima 3000 DV). The crystal size distribution (CSD) is measured in water by Laser diffraction (Microtrac S3500), assuming a refractive index of the zeolite of 1.5. Ultra-sound of 40 W was applied for 300 s to break up any agglomerates of crystals before performing the CSD measurement. The determined size is an average since the crystal shape is anisotropic, as can be seen from the SEM micrographs.

The degree of detemplation is determined using several measurement techniques; (differential) thermogravimetric analysis/differential thermal analysis (DTG/TGA/DTA) (Mettler Toledo, TGA/SDTA 851e) measuring the mass decrease upon heating in air upto 1173 K with a heating rate of $600 \text{ K}\cdot\text{h}^{-1}$ and Diffuse reflectance infrared Fourier transform spectrometry (DRIFT) (Thermo Nicolet, Nexus) using KBr as background. The adsorption capacity of a zeolite is generally described by a BET surface area. To determine the BET surface and to confirm the removal of the SDA from the zeolite framework, nitrogen adsorption tests were conducted (Quantachrome Autosorb-6B). Prior to the nitrogen gas-adsorption measurements, the samples were dried in vacuum at 573 K in order to remove present moisture and other volatile components (the weight of the sample after drying is used in the calculations). The nitrogen adsorption and desorption isotherms were measured at 77 K. The BET method was used to calculate the specific surface area of the samples, the t-plot method was applied to determine the micropore volume, while the total pore volume was obtained at $p/p^0=0.99$. The DD3R structure was also examined by ^{29}Si Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) (Bruker Avance 400). The NMR measurements were conducted using a 4 mm zirconium holder at 298 K with a frequency of 79.449 MHz, a relaxation delay of 15 s and a spinning frequency of 11 kHz. The chemical shifts were referenced with respect to tetramethylsilane (TMS).

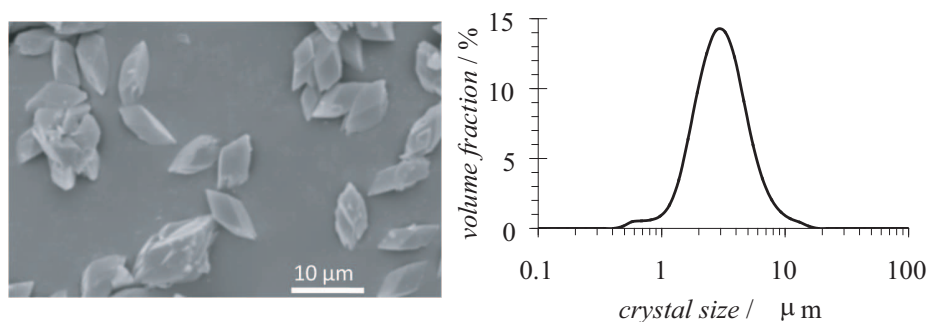


Figure 7.3: SEM micrograph and CSD of DD3R crystals after 300 s of ultra-sound, showing small diamond shaped crystals, which give a single peak at 2.7 μm .

7.3 Experimental Results

7.3.1 Characterization

Figures 7.3 to 7.5 show SEM micrographs and CSD data of the synthesized zeolite samples. The crystal structure of the samples is confirmed by XRD. Figure 7.6 shows the XRD patterns of the calcined samples. It is noteworthy that the relative intensity of the characteristic peaks of the DDR topology differ for the three materials. In the case of NaZSM-58 and DD3R the most intense peak is located at $2\theta = 17^\circ$, but this peak is less intense for the all-silica ZSM-58 sample. In all three cases, the intensity of all peaks below $2\theta = 15^\circ$ increases considerably after calcination, as reported by den Exter *et al.* [23].

The DD3R sample reveals homogeneous diamond-like crystals, as reported by den Exter *et al.* [23], while the CSD measurements show a single peak at 2.7 μm (Figure 7.3). It is interesting that, as reported by Ernst and Weitkamp [20], a change in the crystal morphology of ZSM-58 occurs when aluminum is incorporated in the framework. In the all-silica sample, hexagonal crystals are found, the CSD measurement shows a narrow peak at 6.1 μm (Figure 7.4). In the aluminum containing sample spheres are formed, but also small diamond shaped crystals can be distinguished on top of the particles, as reported by Olson *et al.* [24]. These spheres appear to be agglomerates of smaller particles. The CSD before applying ultra-sound shows a peak at 36 μm , however, after ultra-sonic treatment, the peak shifts to 1 μm (Figure 7.5).

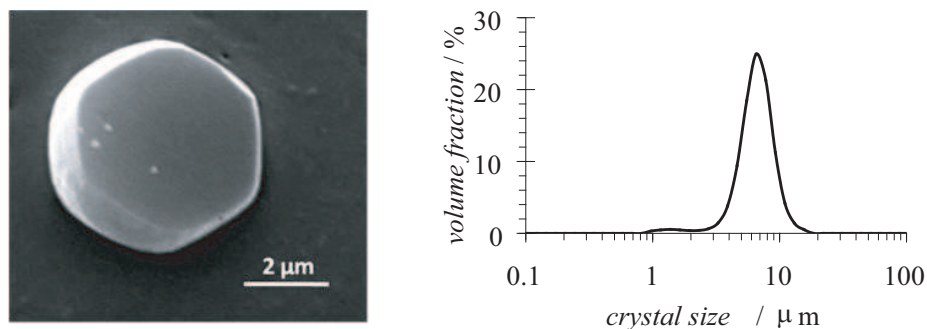


Figure 7.4: SEM micrograph and CSD of ZSM-58 crystals after 300 s of ultra-sound, showing hexagonal crystals of 6.1 μm .

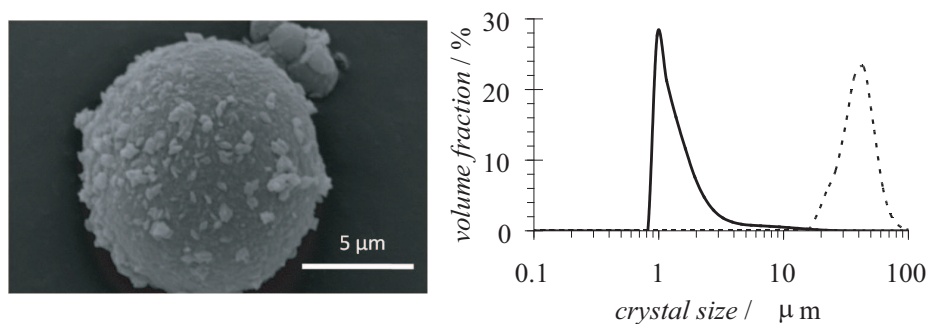


Figure 7.5: SEM micrograph and CSD of NaZSM-58 (Si/Al=170) crystals before (dashed line) and after (solid line) 300 s of ultra-sound, showing the aggregates consisting of small crystals, giving an initial peak at 36 μm and 1 μm after ultra-sound treatment.

7.3.2 Detemplation

Figure 7.7 shows the ozone concentration measured at the oven outlet at different temperatures using an empty tube and a flow of $6 \times 10^{-3} \text{ m}^3 \cdot \text{h}^{-1}$ (STP) oxygen/ozone mixture. The ozone concentration sharply decreases above 433 K. When a zeolite sample is placed inside the reactor, the outlet ozone concentration is lower than for an empty tube and increases gradually during detemplation.

The DD3R sample was ozonicated at 473 K for 18 and 38 h, the thermal calcination was done at 873 K for 6 h using a heating and cooling rate of $60 \text{ K} \cdot \text{h}^{-1}$. The TGA shows the progression of detemplation with ozonication time (Figure 7.8). Although a small decrease in mass is still observed in the ozonicated sample, the DTA shows no exothermic peak, confirming the complete removal of template (Fig-

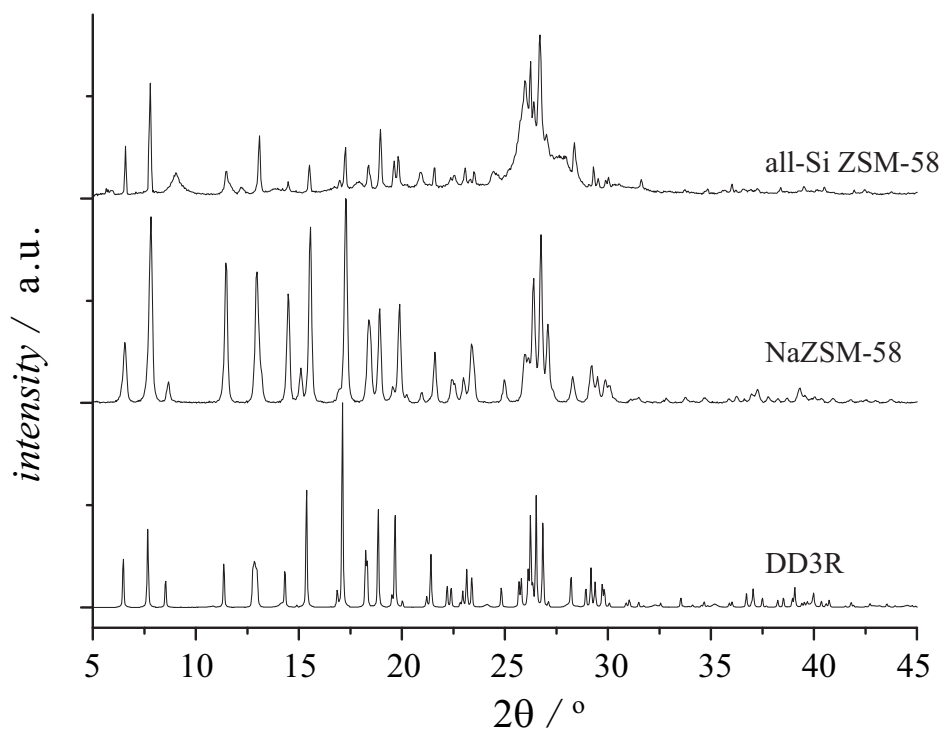


Figure 7.6: XRD patterns of DD3R, ZSM-58 and NaZSM-58 after calcination in air at 973 K (ZSM-58) and 873 K (DD3R) for 6 h.

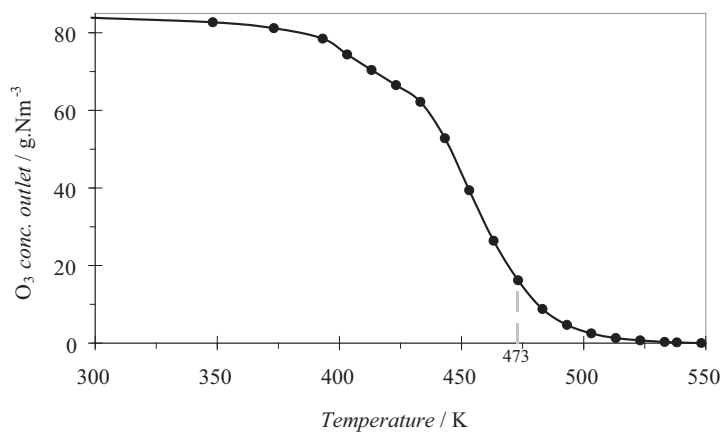


Figure 7.7: Ozone concentration in $6 \times 10^{-3} \text{ m}^3 \cdot \text{h}^{-1}$ (STP) oxygen/ozone mixture measured at the outlet of the glass reactor as a function of the oven temperature

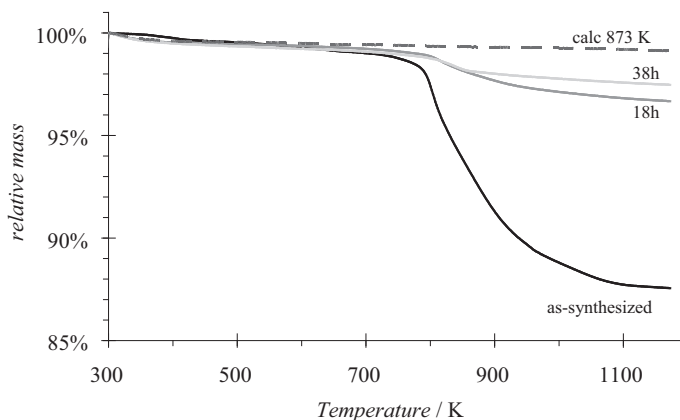


Figure 7.8: TGA of DD3R: as-synthesized, calcined (at 873 K for 6 h using a heating and cooling rate of $60 \text{ K}\cdot\text{h}^{-1}$) and ozonicated after 18 and 38 h at 473 K.

ure 7.9). For the DRIFT measurement DD3R samples ozonicated for 8, 24 and 32 h are compared. In the DRIFT spectra (Figure 7.10), the absorbance between 800 and 1300 cm^{-1} changes after ozonation and calcination. The absorbance at 810, 1010 and 1900 cm^{-1} increases, while the absorbance at 1230 cm^{-1} decreases. The C-H stretching vibrations ($2800\text{--}3000 \text{ cm}^{-1}$) and the C-H bending vibration ($1400\text{--}1500 \text{ cm}^{-1}$) are clearly visible in the as synthesized sample, but are strongly reduced after ozonation and are not visible in the calcined sample. The absorbances at 2920 and 2850 cm^{-1} , which are present in the as-synthesized sample correspond to the peaks observed in the spectrum for 1-ADA [25]. Although there is a small residual absorbance at 2970 cm^{-1} of the ozonicated sample, the nitrogen adsorption data confirm the complete template removal. The nitrogen isotherms show type 1 behavior with high uptake at low pressures. At moderate and high pressure, hardly any nitrogen uptake is observed suggesting the absence of a significant contribution of both meso- and small macropores. The ozonicated and the thermally calcined sample are purely microporous and show identical porosity characteristics. Surface area, pore volume and micropore contribution are within the experimental error of the setup (Table 7.1).

The NaZSM-58 sample was ozonicated at 473 K for up to 30 h. After 8 h no further mass loss was observed (Figure 7.11). As reference, the NaZSM-58 has been calcined at 823 K for 16 h and at 973 K for 6 h using a heating/cooling rate of $60 \text{ K}\cdot\text{h}^{-1}$. Figure 7.12 shows the DRIFT spectra of the as synthesized, ozoni-

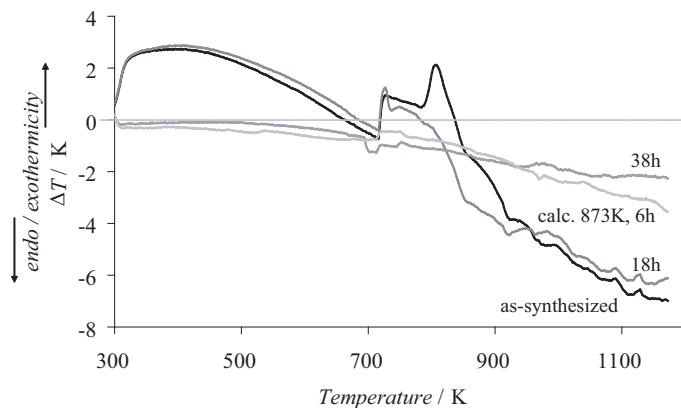


Figure 7.9: DTA of DD3R: as-synthesized, calcined (at 873 K for 6 h using a heating and cooling rate of $60 \text{ K}\cdot\text{h}^{-1}$) and ozonicated after 18 and 38 h at 473 K.

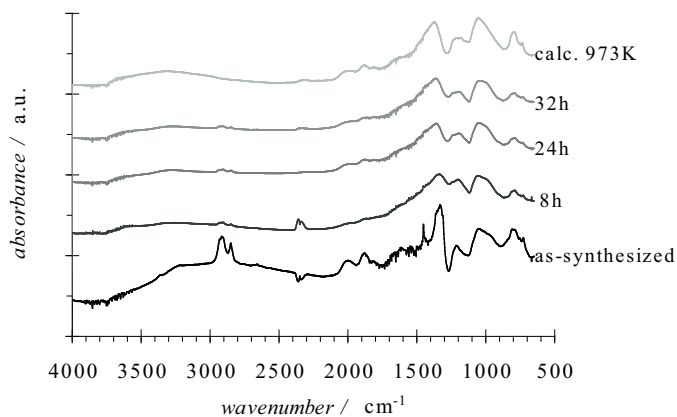


Figure 7.10: DRIFT spectra of DD3R: as-synthesized, calcined (at 973 K for 6 h using a heating and cooling rate of $60 \text{ K}\cdot\text{h}^{-1}$) and ozonicated after 8 and 24 and 32 h at 473 K.

cated and calcined samples. The disappearance of the absorbances indicating the C-H stretching and bending vibrations corresponding to the organic template in the as-synthesized crystals after ozonation, confirm the detemplation. The sharp peak at 1320 cm^{-1} decreases, broadens and shifts to 1370 cm^{-1} after 8 h of ozonation and for the calcined sample. After 24 h of ozonation the absorbance at 1370 cm^{-1} is further reduced. The ozonicated samples show a higher absorbance at 950 cm^{-1} compared to the calcined sample.

The all-silica ZSM-58 was ozonicated at 473 K for 38 h. After 38 h, no further detemplation occurs. The calcined sample shows a more pronounced initial mass decay compared to the ozonicated samples (Figure 7.13). The ozonicated samples still show a mass decrease of 4% between 600 K and 900 K, indicating that part of the template is still present in the framework, also condensation of silanol groups could contribute to this mass loss. The DRIFT spectra (Figure 7.14) show after 18 h of ozonation the C-H stretching and the C-H bending vibrations are of comparable intensity as the calcined sample. An increase in the absorbance between 3200 and 3700 cm^{-1} , and at 1630 cm^{-1} for the ozonicated sample is observed, corresponding to physisorbed water. The calcined sample shows a lower absorbance at these wavenumbers and also at 950 cm^{-1} , which corresponds to silanol nests. The nitrogen adsorption data are shown in Table 7.1. The nitrogen adsorption (Table 7.1) shows the ZSM-58 samples are purely microporous and show very similar porosity characteristics to the DD3R sample. The micropore volume and BET surface of the ozonicated and calcined samples are similar for DD3R, but somewhat lower for the ZSM-58 samples.

The ^{29}Si MAS NMR spectra of DD3R (Figure 7.15) only show clear signals in the Q^4 region (-105 to -120 ppm), which correspond to the $\text{Si}(\text{OSi})_4$ groups of the zeolite framework. The ozonicated sample shows a slight increase in the Q^3 region (-90 to -105 ppm), which is attributed to silanol groups [26]. The spectrum of the calcined sample shows a signal at -109 ppm , which is not visible as a separate signal in the ozonicated sample but is part of the broader band at -111 ppm . The signals at -111 , -117 , -119 , and -121 ppm are visible in both samples.

7.4 Discussion

The applied ozone concentration is within the range of 50 to $100\text{ g}\cdot\text{m}^{-3}$ (STP) suggested by Heng *et al.* [12]. Since the outlet flow still contains ozone, the ozone

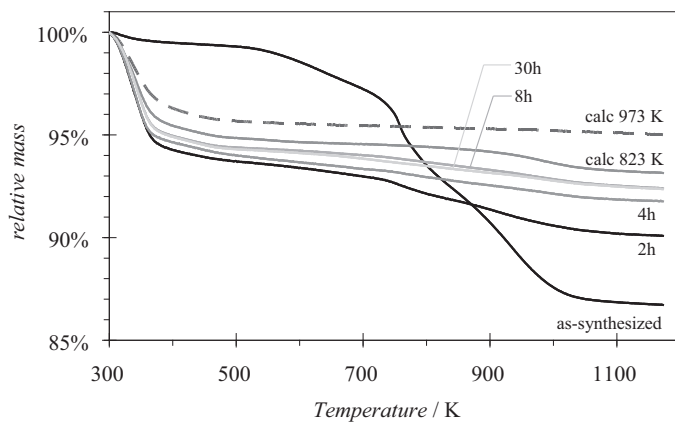


Figure 7.11: TGA of NaZSM-58: as-synthesized, calcined for 16 h at 823 K and for 6 h at 973 K using a heating and cooling rate of $60 \text{ K}\cdot\text{h}^{-1}$), and ozonicated after 2, 4, 8 and 24 h at 473 K.

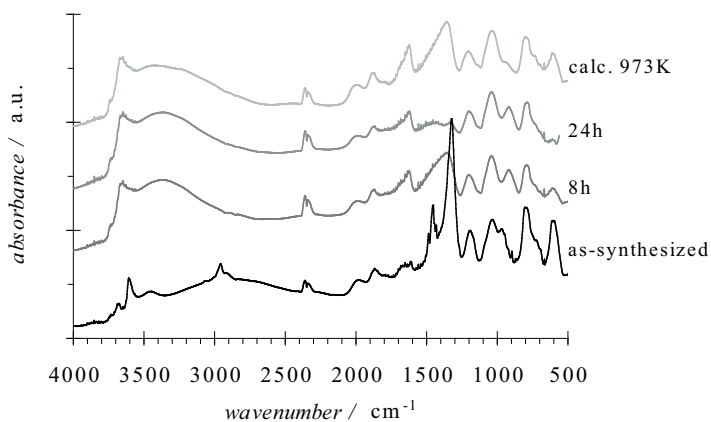


Figure 7.12: DRIFT spectra of NaZSM-58: as-synthesized, calcined (at 973 K for 6 h using a heating and cooling rate of $60 \text{ K}\cdot\text{h}^{-1}$) and ozonicated after 8 and 24 h at 473 K.

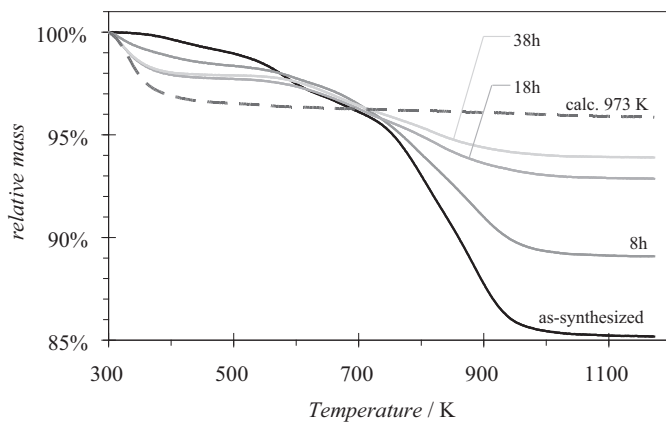


Figure 7.13: TGA of all-silica ZSM-58: as-synthesized, calcined (at 973 K for 6 h using a heating and cooling rate of $60 \text{ K}\cdot\text{h}^{-1}$) and ozonicated after 18, 24, 30 and 50 h at 473 K and 18 and 32 h at 523 K (dashed lines).

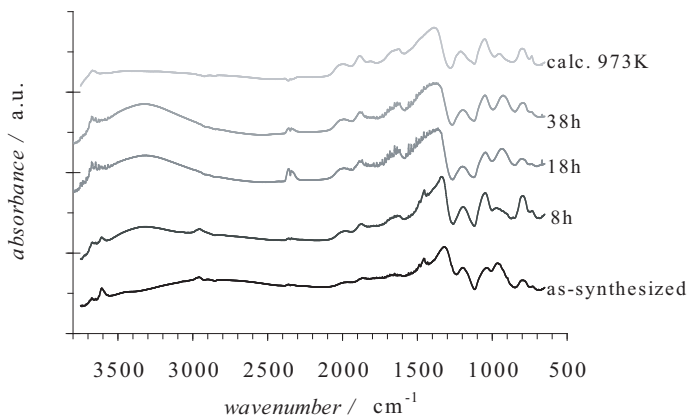
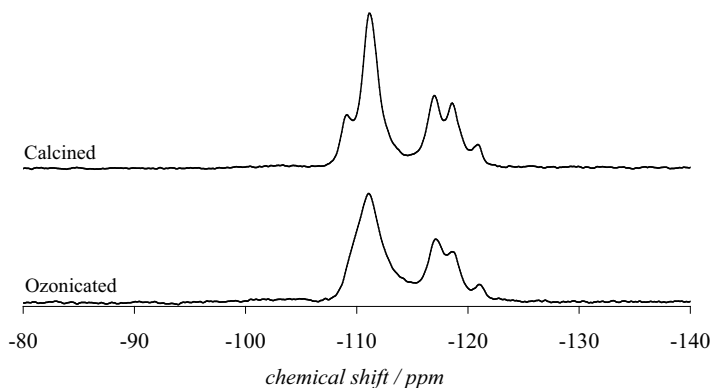


Figure 7.14: DRIFT spectra of all-silica ZSM-58: as-synthesized and calcined (at 973 K for 6 h using a heating and cooling rate of $60 \text{ K}\cdot\text{h}^{-1}$) and ozonicated after 50 h at 473 K.

Table 7.1: Nitrogen adsorption characterization of DD3R, all-silica ZSM-58 and NaZSM-58 after ozonation and calcination

Sample	Temp. K	Time h	S_{BET} $m^2 \cdot g^{-1}$	Ext. area $m^2 \cdot g^{-1}$	Micropore vol. $cm^3 \cdot g^{-1}$	Tot. pore vol. $cm^3 \cdot g^{-1}$
DD3R						
Ozonicated	473	38	327	9	0.13	0.15
Calcined	873	6	331	14	0.13	0.16
ZSM-58						
Ozonicated	473	18	270	13	0.10	0.12
	473	38	301	25	0.11	0.15
Calcined	973	6	397	7	0.16	0.17
NaZSM-58						
Ozonicated	473	30	319	18	0.12	0.15
Calcined	823	16	310	19	0.12	0.15
	973	6	348	17	0.14	0.16

**Figure 7.15:** ^{29}Si MAS NMR spectra of DD3R: calcined (at 873 K for 6 h using a heating and cooling rate of $60 \text{ K} \cdot \text{h}^{-1}$) and ozonicated for 38 h at 473 K.

concentration can be further reduced to economically optimize the process. A higher temperature results in faster decomposition of the ozone (Figure 7.7), however, due to the short life time of the radical species further increasing the temperature can eventually have a detrimental effect on the detemplation process. The mechanism describing the thermal decomposition of ozone [13, 27] reduces to a second-order dependence on the ozone concentration, for both high and low concentrations of ozone in oxygen. Zaslowsky *et al.* [27] noted that impurities in the oxygen (except water) and the presence of other materials (such as mercury or vacuum grease) dramatically

increased the decomposition rate and gave non-reproducible results. The presence of the zeolite and the reactions of the radical species with the organic template makes the ozonation a complex process of which the exact mechanism is not easy to elucidate. The nitrogen adsorption data (table 7.1) of all the samples prove them to be microporous with very similar porosity characteristics. The ozonicated and calcined DD3R samples have identical micropore volumes. From these data it can be concluded that complete detemplation is achieved in 38 h, but from the TGA and DRIFT data of the DD3R sample it can be assumed the complete detemplation can likely be achieved in less than 38 h. The ozonicated all-silica ZSM-58 shows a 30% lower micropore volume than the calcined sample. This is comparable to the difference in mass loss above 473 K (25%). For the NaZSM-58 sample, nitrogen adsorption test shows that surface area, pore volume and micropore contribution are slightly higher for the sample calcined at 973 K than for the ozonicated and calcined at 823 K sample, which is consistent with the TGA and the DRIFT data. The micropore volumes of the ozonicated sample and the sample calcined at 823 K are 14% lower compared to the sample calcined at 973 K. The larger size of MTI compared to 1-ADA, combined with the larger crystal size of the all-silica ZSM-58 could be the cause of the incomplete detemplation.

According to Ernst and Weitkamp [20] calcination at 813 K for 16 h should be sufficient to remove the template. Calcination of zeolites at higher temperatures can cause collapse of the framework due to dealumination [28]. For the Si/Al ratio of 170, however, XRD analysis shows that the crystal structure is preserved during calcination at 973 K for 6 h. It should be noted, however, that at lower Si/Al ratio the high-temperature calcination could result in dealumination.

The DRIFT spectra of the all-silica DD3R sample do not show significant increase in the absorbances corresponding to physisorbed water ($3200 - 3700\text{ cm}^{-1}$ and 1630 cm^{-1}) after detemplation. The ^{29}Si MAS NMR measurements confirm this, as the spectra show no significant Q^3 signal which is attributed to silanol groups. Although there is a slight increase in the Q^3 signal in the ozonicated sample compared to the calcined sample. The DRIFT spectra of the all-silica ZSM-58 shows an increased intensity in the $3200 - 3700\text{ cm}^{-1}$ region for the ozonicated samples but not for the calcined sample, whereas the more hydrophilic NaZSM-58 shows an increase of these intensities for both the ozonicated and calcined samples. The higher peak at 950 cm^{-1} of the ozonicated NaZSM-58 and all-silica ZSM-58 samples compared to the calcined sample can be assigned to silanol nests which are condensed dur-

ing calcination, but retained at the lower temperatures of ozonation. Although this effect is not observed with the all-silica DD3R sample. The adsorbance assigned to SiO_2 -overtone (1800 and 2100 cm^{-1}) are visible in all detemplated samples. For the all-silica ZSM-58 sample these peaks develop during detemplation, while for the aluminum containing NaZSM-58 these peaks are already visible in the as-synthesized sample. For the DD3R sample, the as-synthesized as well as calcined sample show these peaks, while the ozonicated samples show a development of these peaks over time. These changes as well as the changes in the adsorbances between 950 and 1200 cm^{-1} , which are assigned to silicon oxide vibrations, can be due to small changes in the crystal structure during detemplation. The doublet at 2370 cm^{-1} , in all samples, corresponds to CO_2 and varies due to the variation of CO_2 in the atmosphere during measurement of the samples. The water adsorption on NaZSM-58 is also reflected in the TGA data, where the initial mass loss (up to 473 K) from the detemplated samples is due to desorption of water. The ozonicated samples show a larger initial decrease of mass, which can be explained by the higher hydrophilicity due to the presence of silanol groups. The mass loss of the ozonicated samples at temperatures above 723 K and above 823 K for the sample calcined at 823 K and can be (partly) due to condensation of silanol groups [9]. To assess the detemplation only the mass loss corresponding to the loss of the template should be considered. The difference in mass loss above 473 K for the sample calcined at 973 K compared to the ozonicated and 823 K calcined sample is 10%, which corresponds to the difference in BET surface (10%) and micropore volume (14%) measured by nitrogen adsorption.

Contrary to the ozonicated NaZSM58, the ozonicated all-silica samples show a lower initial mass decrease compared to the calcined one. The mass decrease of the all-silica ZSM-58 between 600 K and 750 K is similar for the as-synthesized sample as for the ozonicated samples, indicating part of the template molecules are still present in the framework.

The all-silica ZSM-58 and the aluminum containing ZSM-58 zeolite have the same SDA and show similar TGA curves of the as-synthesized samples. Although the NaZSM-58 is more hydrophilic than the all-silica ZSM-58, as is evident from the DRIFT spectra, the TGA curves of the calcined samples are similar. The all-silica ZSM-58 and NaZSM-58 samples show an initial mass decrease (up to 473 K) associated with the loss of physisorbed water of, respectively, 3% and 4%. The DD3R sample only shows a mass loss of less than 1% in this temperature range. This could

indicate the pores of ZSM-58 are more accessible compared to DD3R.

Tiscornia *et al.* have attempted to use ozone to detemplate ITQ-29 (all-silica LTA) membranes, however, only 40% of the template could be removed [29]. Since the membrane thickness is only 5 μm , the diffusion path length is not expected to be the cause of the incomplete detemplation. The temperature required for detemplation is similar to the DDR type zeolites calcined in this study. Regarding the results of this work, the incomplete detemplation could be explained by the applied low ozone concentration of 50 ppmv (0.1 $\text{g}\cdot\text{m}^{-3}$ (STP)) and the bigger size of the templates used for the synthesis of ITQ-29.

7.5 Conclusions

The detemplation of zeolites by ozonation is a very suitable technique for detemplation of membranes and coated sensors. The low temperatures required will give less thermal stress and will allow detemplation of zeolite coatings on temperature sensitive substrates. The low temperatures during ozonation also preserve the silanol groups within the zeolite structure. The small pore zeolites, DD3R and ZM58 have been synthesized and detemplated using ozone at mild thermal conditions. The ozonation was carried out at 473 K using a flow of $6 \times 10^{-3} \text{ m}^3\cdot\text{h}^{-1}$ (STP) oxygen containing 80 $\text{g}\cdot\text{m}^{-3}$ (STP) of ozone.

The DD3R crystals are diamond shaped particles with an average size of 2.7 μm . The ZSM-58 material consists of a mixture of 6.1 μm hexagonal shaped crystals. The NaZSM-58 material consists of globular aggregates of 36 μm , consisting of small 1 μm primary particles. DD3R could be completely detemplated in 38 h of ozonation. No further detemplation of the all-silica ZSM-58, and NaZSM-58 occurred after 38 and 8 h, respectively. The porosity characteristics of the ozonicated sample were equal to that of the calcined sample, confirming complete template removal and no loss of micro porosity. The ZSM-58 samples were not completely detemplated and showed a lower BET surface area by 25% (all-silica ZSM-58) and 10% (NaZSM-58) as compared to the thermally calcined samples. This difference can be attributed to the larger size of MTI compared to 1-ADA, combined with the larger crystal size of the all-silica ZSM-58.

Since ozone has a larger molecular diameter than the pore size of these zeolites, the detemplation confirms the assumption of the degradation of ozone at the outer zeolite surface, and the diffusion of radical species causing the degradation of the

template.

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Detemplation of [B]MFI zeolite crystals by ozonation

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Abstract Silanol nests within zeolites can be used as catalytic centres, or to facilitate T atom insertion. Deboronation provides a way of increasing the number of silanol nests. However, at high calcination temperatures, required to remove the templates, the silanol nests are condensed. Using ozone, the temperature required for calcination can be decreased drastically. Boron containing MFI type zeolite powder ([B]MFI) has been successfully detemplated by means of ozonation. After 18 h at 473 K under a flow of oxygen containing $80 \text{ g} \cdot \text{m}^{-3}$ (STP) ozone, the template molecules are removed, while 80% of the boron is retained in the framework. The detemplation is confirmed by TGA as well as DRIFT analysis. The boron can subsequently be leached out using a HCl solution leaving silanol nests. ^{29}Si Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) shows the ozonicated and deboronated [B]MFI sample exhibits an increased number of silanol groups (13 (Si-OH)/u.c.) compared to conventionally deboronated [B]MFI (9 (Si-OH)/u.c.) and ozonicated silicalite-1 (8 (Si-OH)/u.c.). This method provides a faster and easier way of synthesizing MFI zeolite with a larger number of silanol groups, than previously developed methods, even without leaching of boron.

8.1 Introduction

Conventionally, the conversion of cyclohexanone oxime to ϵ -Caprolactam is done through the Beckmann rearrangement with oleum or sulfuric acid as a reaction medium. Sulfuric acid is then neutralized with ammonia, which results in the production of large amounts of ammonium sulfate as a by-product. Recently, Sumitomo Chemical Co. developed the vapor-phase Beckmann rearrangement process using a zeolite as a catalyst instead [1–4]. High-silica MFI type zeolites have shown to be well suited, especially due to the presence of silanol nests as defect sites [3]. At present, silicalite-1 is used as a commercial catalyst. In order to further increase the amount of H-bonded silanols, the deboronation of [B]MFI catalysts can be performed through post-synthesis modifications [5]. Hoelderich *et al.* have investigated the vapour phase Beckmann rearrangement on [B]MFI zeolites through several post-synthesis modifications [4]. The good catalytic performance is a consequence of the high concentration of comparably weak acidic sites on the external surface of the zeolite. Their results indicate an enhancement in catalytic performance of [B]MFI upon treating with basic or acid solutions at different concentrations [2, 4]. Conventional thermal calcination methods cause the loss of framework boron. Several non-thermal detemplation techniques have been developed using nitric acid and hydrogen peroxide [6], ozone [7], Fenton chemistry [8] or short-wavelength UV-light [9]. Maesen *et al.* have investigated the detemplation of [B]MFI using oxygen plasma [10]. After 28 days of plasma treatment less than 50% of the template was removed, moreover part the framework boron was lost due to hydrolysis with ambient water. In the protonated form, the boron is coordinated trigonally within the framework as the proton forms a silanol group with the (Si-O) unit. Sodium as the counter-ion causes the boron to attain a tetrahedral coordination [11]. De Ruiter *et al.* have developed a calcination procedure which prevents the loss of framework boron. This method comprises calcination under NH_3 atmosphere at 723 K, followed by an ion exchange step using a NaBr solution and calcination under oxygen at 823 K. Subsequently, boron is leached out, leaving silanol nests consisting of four silanol groups [5]. The silanol nests in the deboronated MFI structure ([de-B]MFI) can also be used to re-incorporate other *T*-atoms, such as Ti or Si [12]. Although this method is effective, it is laborious and time consuming. It has been shown that ozone/oxygen mixtures can be used to remove coke deposition in MFI and FAU type zeolites at mild thermal conditions [13–15]. Under similar conditions also thin MFI zeolite membranes have

been detemplated [7]. Because this detemplation procedure is done at much lower temperatures than conventional calcination, we suspect that the boron is preserved in the framework. Even if extraction of boron occurred during ozonation, this would not lead to loss of silanol nests, since the condensation of the silanol groups takes place at higher temperatures [5, 6]. In this chapter we investigate the detemplation of [B]MFI zeolite powder using ozonation. After detemplation the boron can be leached out from the framework, leaving silanol nests. The amount of silanol groups is then determined using ^{29}Si MAS NMR.

8.2 Experimental methods

Boron containing MFI type zeolite powder is prepared by in-situ hydrothermal crystallization at 458K for 24 h in a Teflon-lined autoclave, according to the following recipe: 4.44 TPAOH : 19.46 SiO_2 : 1.55 $\text{B}(\text{OH})_3$: 500 H_2O [16, 17]. Ludox AS-40 (Aldrich) is used as the silica source, Boric acid (99.99%, Sigma Aldrich) as boron source, as structure directing agent tetrapropylammoniumhydroxide (TPAOH) (1 M solution in water) is used, sodium hydroxide (97.6%, VWR) is added for pH adjustment and demineralized water is used as solvent. After synthesis the crystals are filtered, rinsed with water and dried over night at 373 K. The synthesis mixture contains a Si/B ratio of 12.5, while inductively coupled plasma - optical emission spectrometry (ICP-OES) (Perkin Elmer Optima 3000 DV) shows the zeolite powder contains ~ 2 B/u.c, corresponding to a Si/B of ~ 50 . Silicalite-1 crystals were synthesized according to Noble *et al.* [18]. The detemplation is carried out by ozonation in a glass u-tube (diameter 6mm, length 900 mm), placed in a programmable oven (Binder FP53) which is kept at a temperature of 473 K (Figure 8.1). Dry oxygen from a gas cylinder is passed through a Corona discharge ozone generator (A2Z Ozone Systems, SOZ-16GLAB). Using a mass flow controller (Bronkhorst Hi-Tech B.V.), 400 mg [B]MFI zeolite powder is exposed to a flow of $12 \times 10^{-3} \text{ m}^3 \cdot \text{h}^{-1}$ (STP) dry oxygen containing $80 \text{ g} \cdot \text{m}^{-3}$ (STP) of ozone, where standard conditions are 298 K and 1.01 bar. The ozone concentration is monitored using an ozone detector (Lenntech, BMT 964) after which it is sent through a manganese dioxide/copper oxide catalytic ozone destructor. Prior to feeding the ozone, the system is flushed with pure oxygen at 473 K to ensure a water-free atmosphere. Because of the mild thermal conditions during ozonation, the silanol groups that stem from crystalline defects are not condensed and remain present in the framework. When the ozoni-

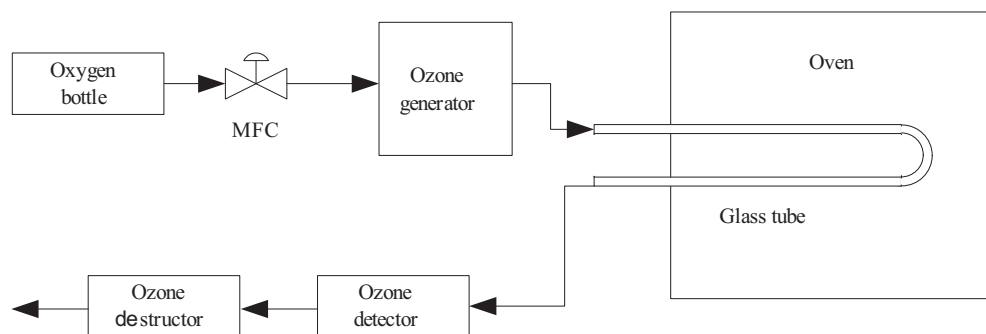


Figure 8.1: Schematic illustration of ozonation setup.

cated [B]MFI crystals are treated with HCl solution ($\text{pH} = 1$) at 373 K for 24 h, the boron can be leached out of the framework, leaving four more silanol groups per removed boron atom [5]. The amount of silanol groups is quantified using ^{29}Si Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) (Bruker Avance 400). The NMR measurements were conducted using a 4 mm zirconium holder at 298 K with a frequency of 79.449 MHz, a relaxation delay of 15 s and a spinning frequency of 11 kHz. The chemical shifts were referenced with respect to tetramethylsilane (TMS).

The degree of detemplation is determined by thermogravimetric analysis (TGA) (Mettler Toledo, TGA/SDTA 851e) measuring the mass decrease upon heating in air up to 1173 K with a heating rate of $600 \text{ K}\cdot\text{h}^{-1}$, and by Diffuse reflectance infrared Fourier transform spectrometry (DRIFT) (Thermo Nicolet, Nexus) using KBr as background. The morphology and crystal structure of the samples was examined using scanning electron microscopy (SEM)(Phillips XL20) and X-Ray Diffraction (XRD) analysis (Bruker-AXS D5005). Also nitrogen adsorption tests were conducted (Quantachrome Autosorb-6B) to confirm the removal of the SDA from the zeolite framework. Prior to the nitrogen gas-adsorption measurements, the samples were dried in vacuum at 523 K in order to remove present moisture and other volatile components (the weight of the sample after drying is used in the calculations). The nitrogen adsorption and desorption isotherms were measured at 77 K.

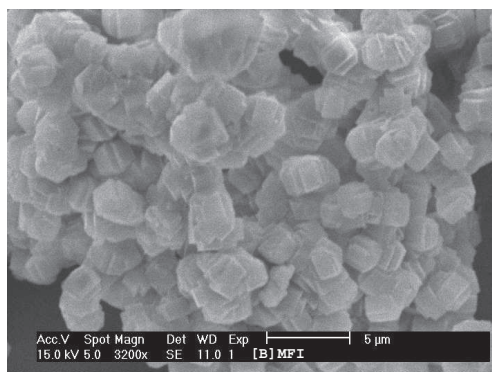


Figure 8.2: SEM micrograph of the as-synthesized [B]MFI crystals showing aggregates of small crystals.

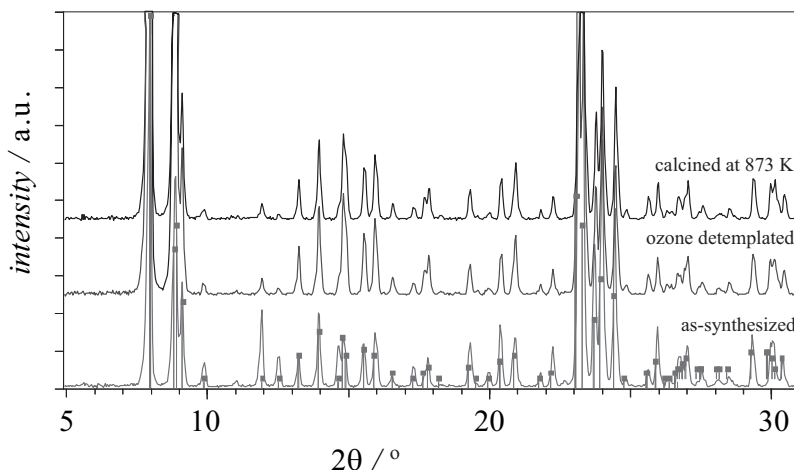


Figure 8.3: XRD spectra of the [B]MFI crystals confirming the MFI structure, the 18 h ozone detemplated pattern is equal to the thermally calcined sample. The squares indicate the MFI reference reflections.

8.3 Experimental results

The SEM micrograph of the zeolite powder shows that the material consists of agglomerates of small crystals (Figure 8.2). XRD analysis confirms the preservation of the MFI structure of the zeolite (Figure 8.3) during ozonation.

Figure 8.4 shows the DRIFT spectra of the sample as-synthesized, the ozone detemplated sample before and after deboronation, and the sample that was detemplated according to the recipe of de Ruiter *et al.* [5] as well as an ozonicated silicalite-1 sample. In these spectra, the C-H stretching vibrations (2981 , 2943 and 2883 cm^{-1}) and

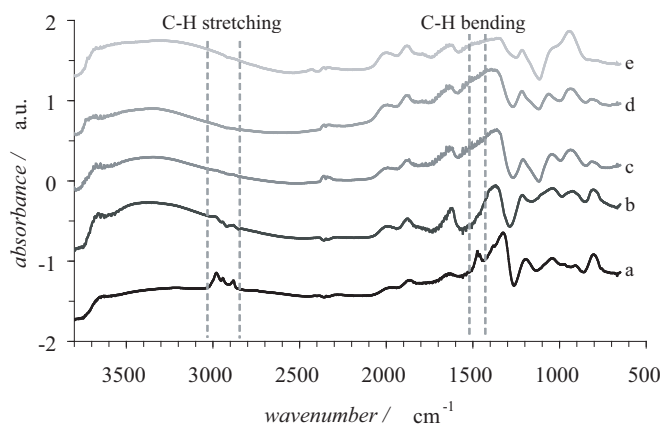


Figure 8.4: DRIFT spectra of [B]MFI: as-synthesized (a), ozonicated for 18 h at 473 K before (b) and after de-boronation (c), deRuiter detemplated and deboronated (d), and silicalite-1 ozonicated for 18 h at 473 K (e).

the C-H bending vibration (1473 , 1459 and 1382 cm^{-1}) corresponding to the organic template in the as-synthesized crystals, have vanished after 18 h of ozonation. Furthermore, a broad band is observed in the range of $3200\text{--}3700\text{ cm}^{-1}$, corresponding to perturbed OH groups, the peak at 950 cm^{-1} corresponds to silanol nests. The TGA curves of the detemplated samples (Figure 8.5) show an initial mass decrease due to the loss of physisorbed water. The as-synthesized sample shows a large mass decrease between 650 K and 750 K , corresponding to the oxidation of TPA. The sample detemplated according to de Ruiter *et al.* shows practically no mass loss in this temperature range. Although the mass loss in this region decreases with ozonation time, the ozonicated samples still show a small decrease in mass. Nitrogen adsorption experiments (Table 8.1) reveal that the ozonicated sample and the sample calcined according to the method developed by de Ruiter *et al.* show identical porosity characteristics, confirming complete detemplation by ozonation.

Table 8.1: Porosity characteristics of [B]MFI after ozonation and detemplation according to de Ruiter *et al.* determined by nitrogen adsorption.

Detemp. method	Temp. /K	S_{BET} / $\text{m}^2\cdot\text{g}^{-1}$	Ext. area / $\text{m}^2\cdot\text{g}^{-1}$	Micropore vol. / $\text{cm}^3\cdot\text{g}^{-1}$	Tot. pore vol. / $\text{cm}^3\cdot\text{g}^{-1}$
deRuiter	823	311	36	0.14	0.18
Ozonication	423	322	21	0.15	0.17

ICP-OES shows 80% of the boron is preserved in the zeolite framework after

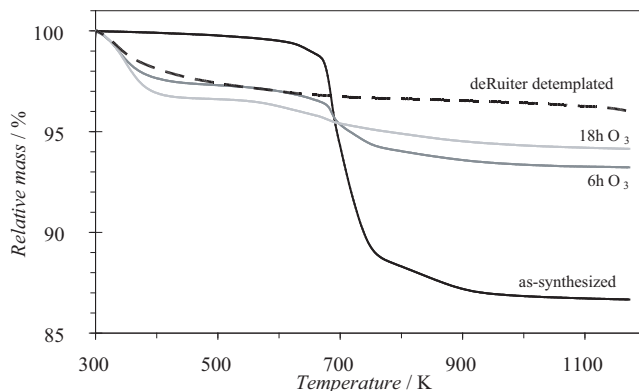


Figure 8.5: TGA and DTGA curves of [B]MFI: As-synthesized, detemplated according to de Ruiter *et al.* and ozonicated for 6 and 18 h.

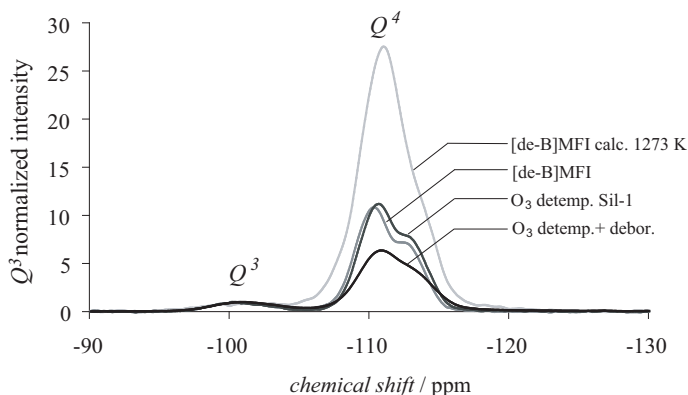


Figure 8.6: ^{29}Si MAS NMR Q^3 normalized intensities of [de-B]MFI treated at 423 K and 1273 K, ozonicated silicalite-1 and ozonicated and deboronated [B]MFI

ozonation, the loss of framework boron has been attributed to hydrolyzation with ambient water [10]. After leaching of the boron using HCl solution, the number of silanol groups in the zeolite structure is determined using ^{29}Si MAS NMR (Figure 8.6). For comparison, the ^{29}Si MAS NMR spectra of ozonicated silicalite-1, as well as [de-B]MFI according to the method developed by de Ruiter *et al.*[5] before and after heat treatment at 1273 K, are shown. The NMR spectra are normalized by the Q^3 intensity. The Q^3 signal in the ^{29}Si MAS NMR spectra ($\delta = -103$ ppm) is ascribed

to the $(\text{Si-OH})(\text{Si-O})_3$ groups, while the Q^4 signal ($\delta = -113$ ppm) is ascribed to the $\text{Si}(\text{Si-O})_4$ units [19]. The right shoulder of the Q^4 peak increases with increasing Q^3 intensity. For the normalized intensities, shown in Figure 8.6, a lower Q^4 signal corresponds to a higher amount of silanol groups. The ozonicated silicalite-1 sample and the [de-B]MFI sample both show a similar Q^4 intensity, while the ozonicated and deboronated [B]MFI sample shows a higher amount of silanol groups. The MFI structure contains 96 T -atoms per unit cell [20], so the number of silanol groups equals $96/(Q^4/Q^3 + 1)$. Because of the small error, we neglect the effect of the reduction in T -atoms by deboronation. The Q^4/Q^3 ratios and the number of silanol groups per unit cell, calculated from that number are shown in Table 8.2.

Table 8.2: Q^4/Q^3 ratios and the number of silanol groups per unit cell for [B]MFI detemplated and deboronated and ozonicated silicalite-1

Sample	Detemp. method	Temp. /K	Q^4/Q^3	Si – OH /u.c.
[de-B]MFI	deRuiter	423	9.8	8.9
[de-B]MFI-calc.	deRuiter	1273	21.9	4.2
[de-B]MFI	Ozonication	473	6.3	13.2
Silicalite-1	Ozonication	473	11.0	8.0

8.4 Discussion

The results of our analysis indicate that after 18 h of ozonation at 473 K, the template is removed from the zeolite. Nitrogen adsorption (Table 8.1) shows identical porosity characteristics of the ozonicated and the calcined sample. The signals in the DRIFT spectra corresponding to the template are significantly reduced. Furthermore, the TG analysis (Figure 8.5) shows no evident mass decrease around 700 K, typical for the oxidation of TPA. The larger decrease in mass between 300 K and 400 K of the ozonicated sample compared to the sample detemplated according to the method developed by de Ruiter *et al.* [5] may be assigned to higher amounts of water adsorbed in the ozonicated sample due to the higher number of silanol groups present.

The silanol groups formed after the loss of boron are not condensed because of the mild thermal conditions. The increased number of silanol groups of the ozonicated sample, measured by ^{29}Si MAS NMR confirms this. Also the DRIFT spectrum (Figure 8.4) of the ozonicated and deboronated sample shows a higher intensity

of the absorbances corresponding to silanol groups as compared to the ozonicated [B]MFI sample and the [de-B]MFI sample. The Q^4/Q^3 ratio of the ^{29}Si MAS NMR spectrum equals the ratio of (Si-O)/(Si-OH) units. Figure 8.6 shows the [de-B]MFI sample which was heated to 1273 K contains the lowest number of silanol groups (4 (Si-OH)/unit cell). The ozonicated silicalite-1 and the [de-B]MFI sample show similar Q^4/Q^3 ratios corresponding to, respectively, 8 and 9 (Si-OH)/unit cell. This corresponds to the initial boron content of 2 boron per unit cell. The combination of ozone detemplation and deboronation yields the highest number of silanol groups (13 (Si-OH)/unit cell). The DRIFT spectra show the increase in silanol nests of the deboronated sample as compared to the boron containing one. Also the ozonicated silicalite-1 sample shows a high intensity at 950 cm^{-1} , typical for silanol nests. ^1H -NMR could give more insight in the difference type of silanol groups [5].

Ozonication provides a faster and easier manner compared to previously developed methods [5, 10] to detemplate boron containing MFI type zeolites, without loss of silanol groups. The time required for calcination is considerably shorter using ozone as compared to using oxygen plasma [10]. Although not all the boron is preserved in the framework, ozonation is less laborious than the calcination method developed by the Ruiter *et al.* [5]. This study may facilitate further developments in catalysis, e.g. for the Beckmann rearrangement reaction.

8.5 Conclusions

[B]MFI crystals have been successfully detemplated using a $12 \times 10^{-3}\text{ m}^3\cdot\text{h}^{-1}$ (STP) feed of $80\text{ g}\cdot\text{m}^{-3}$ (STP) of ozone in oxygen at 473 K for 18 h. The complete removal of the template molecules is confirmed by nitrogen adsorption, DRIFT and TGA. After ozonation, 80% of the framework boron was retained while, at the low temperatures at which the ozone detemplation is conducted, there is no condensation of silanol groups during detemplation. This method provides an easy and fast manner to detemplate [B]MFI zeolites with limited loss of framework boron and without the loss of silanol groups. ^{29}Si MAS NMR shows that, even when applied to silicalite-1, ozonation yields a high number of silanol groups within the zeolite framework. The amount of silanol groups is even further increased by combining ozonation and deboronation compared to either ozonation or deboronation.

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Manufacturing of a silicalite-1-Metglas composite sensor: Solving the detemplation issue through ozonation

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The Analyst, submitted April 2009

Abstract

New selective gas sensors utilizing a *b*-oriented silicalite-1 layer-Metglas assembly are presented. The sensors have been prepared by coating a magnetoelastic Metglas ribbon with an oriented, thin silicalite-1 zeolite layer. The thickness of the zeolite layer is that of a single crystal and the crystals are oriented in the *b*-direction, meaning the straight channels are perpendicular to the sensor surface, as confirmed by X-ray diffraction (XRD) analysis. Since the Curie temperature of the Metglas material is below the temperature required for conventional thermal calcination methods for silicalite-1, this method of detemplation can not be applied. The silicalite-1 coating was successfully detemplated by means of ozonation at 473 K, opening the possibility of applying templated zeolite coatings on sensors materials with limited thermal stability. This significantly increases the number of zeolite types that can be used for this application. These sensors operate by monitoring the resonance frequency of the zeolite coated Metglas ribbon in response to concentration changes of a component in the gas phase. The sensor showed an increase in resonance frequency when exposed to carbon dioxide and n-butane as compared to exposure to air, while it showed negligible response to the presence of iso-butane, indicating sensing selectivity.

9.1 Introduction

Chemical and biochemical sensors are becoming of great importance in industrial applications. Many sensors are based on selective adsorption or absorption of certain analytes from gas or liquid environment. The significant parameters determining the performance of these sensors are selectivity, sensitivity, reversibility and response time. The mechanism of sensing can be based on the selective alteration of various sensor properties, such as: electrochemical, electronic, optical, acoustic or other properties.

Magnetoelastic sensors are magnetostrictive materials that, in response to an externally applied magnetic field impulse, emit a magnetic flux with a characteristic resonance frequency. These type of sensors efficiently convert magnetic energy into elastic energy, which acts to mechanically deform the sensor. As the sensor mechanically deforms, it generates magnetic flux which allows wireless detection by a pick-up coil or, when the amplitude of the signal is sufficiently high, by acoustic monitoring [1]. Magneto-elastic sensors have the advantage that they are monitored remotely, without the need for direct physical connections such as wires or cables, nor line-of-sight alignment as needed with optical detection methods [2]. Metglas [3] ribbons are composed of amorphous iron- and nickel-based alloy metals, which are well suited as a platform for magnetoelastic sensors. Depending upon the application, magnetoelastic sensors can be sized from micrometer to millimeter size, and have very low material costs, allowing for their use on a disposable basis. Metglas material has already been used in various sensing applications, such as positioning [4], strain [5], humidity [6], liquid viscosity and density [7], flow rate, and temperature [1] sensing. By applying a suitable deformation of the Metglas material, it can respond to changes in ambient pressure [8] and by applying a responsive polymer coating on the Metglas material, it can be made sensitive to pH [1], or to the presence of glucose [2] or ammonia [9]. Coating these sensors with a zeolite layer can make the material selective for various gaseous species. A magnetoelastic Metglas ribbon coated with a FAU type zeolite layer has been successfully applied as a carbon dioxide sensor [10]. Zeolites provide a large internal surface area, which leads to a high adsorption capacity. The Metglas-zeolite composite combines the magnetoelastic properties of the Metglas with the adsorption selectivity of the zeolite [10, 11]. This provides a great potential for making selective sensors for many compounds, as the zeolite type can be adjusted to the required analyte.

At small mass loads, the increase in the adsorbed mass correlates linearly with a negative shift in the resonance frequency of the Metglas sensor [1]. However, it has been observed that the adsorption of gases in the zeolite coating on the sensor can influence the elastic properties of the film, resulting in signals deviating from the expected negative linear behavior [12].

As the zeolite coating increases in thickness, so does the response time because of an increase in mass transport resistance, as was shown for ZSM-5 zeolite [13] and polymer films [9]. In order to decrease the response time, the zeolite layer should be thin, and oriented with its channels perpendicular to the sensor surface, preferably without grain boundaries in the mass transport direction [14]. Decreasing the thickness of the zeolite coating, on the other hand, reduces the adsorbed amount of gas molecules, leading to a smaller frequency shift [9]. Clearly, there is an optimum in the thickness of the zeolite coating. Moreover, strong adhesion between zeolite layer and sensor is needed for good durability.

Over the past years, several sensor materials have been successfully combined with coatings of zeolites [15–17] or mesoporous silicates [15, 18]. Coating of oxygen selective sensors with a zeolite film has shown to improve the detection of oxygen due to molecular sieving and adsorption selectivity of the zeolite layer [19]. Zeolite coated on attenuated total reflection (ATR) spectroscopy crystals have been reported as selective gas sensors and have been used to study the adsorption behavior of thin zeolite films [20–23]. Zeolite layers, deposited by dip-coating, have been used to introduce chemical selectivity into surface acoustic wave (SAW) devices [24]. Vilaseca *et al.* coated semiconductor gas sensors with MFI and LTA layers making them selective for several gases and vapors [17]. Mintova *et al.* have reported a thin LTA-type zeolite coating grown on a quartz crystal micro-balance as a humidity sensor [25]. Allendorf *et al.* showed that a microcantilever coated with a layer of a metal organic framework (MOF) material yields a sensor for water, methanol and ethanol vapor [26]. Many zeolites, and particularly all-silica types (such as silicalite-1) are usually synthesized using a template-assisted synthesis [27, 28]. To make the pores of the zeolite layer accessible, it is necessary to remove the organic template after synthesis. Conventionally, the template is removed by calcination in air at temperatures between 623 K and 973 K. However, many sensor materials are not capable of withstanding the high temperatures required for this template removal. The piezoelectric properties of α -quartz, used in SAW devices and microbalances, degrade at temperatures above 573 K [29]. Metglas has a Curie temperature of 620 K, but the magnetoelastic

properties of these materials shatter at temperatures above 573 K [30]. Currently, this drastically limits the number of zeolite types that can be applied as coating material for these types of sensors. Several non-thermal detemplation techniques have been developed. Masuda *et al.* have used nitric acid and hydrogen peroxide in detemplating a silicalite-1 membrane [31]. Heng *et al.* used a mixture of oxygen and 50 to 100 g·m⁻³ (STP) ozone at elevated temperatures (473 K) to remove the template from silicalite-1 and ZSM-5 membranes [32]. Melian Cabrera *et al.* have successfully detemplated zeolite beta crystals under mild conditions by means of Fenton chemistry, using hydrogen peroxide and an iron salt [33]. Fenton chemistry [34] is the reaction of OH radicals with an organic molecule. The radicals are formed by a reaction between hydrogen peroxide and a Fenton reagent (Fe²⁺/Fe³⁺). Parikh *et al.* have detemplated a thin silicalite film (<500 nm) using short-wavelength UV-light (184-257 nm) [35] and Maesen *et al.* have investigated the detemplation of [B]MFI using oxygen plasma [36]. In detemplation by means of ozonation, the oxidants are highly reactive atomic oxygen and radical species which are formed by the decomposition of ozone at elevated temperatures [32]. Ozonation has already been successfully applied to detemplate silicalite-1 and ZSM-5 membranes [32] and [B]ZSM-5 [37] and DDR [38] type zeolite powder at temperatures around 473 K, well below the temperature limit of the Metglas material. In this study, new selective gas sensors utilizing a monocrystal-thin *b*-oriented silicalite-1-layer-Metglas assembly are presented. A synthesis procedure for the *b*-oriented coating has been developed and combined with a novel detemplation technique. The thin and oriented layer is intended to reduce the response time of the sensors by minimizing the mass transport resistance. By applying ozonation, the silicalite-1 coating was detemplated at mild thermal conditions, preventing the loss of the magnetoelastic properties of the Metglas material. The resonance frequency of the Metglas strip in relation to the amount of adsorbed gases in the *b*-oriented silicalite-1 coating is measured to determine the sensor performance.

9.2 Methods

9.2.1 Synthesis and detemplation

The *b*-oriented silicalite-1 layer was synthesized on both sides of a 6 × 2 × 0.03 mm Metglas 2826 MB (Fe₄₀N₃₈Mo₄B₁₈) magnetoelastic ribbon (Dacpol, Poland [39] and

Allied Signal [3]). Before the synthesis, organic residues were removed by cleaning the Metglas ribbon with acetone. A synthesis mixture was prepared by mixing tetrapropylammonium hydroxide (TPA, Aldrich, 1 M in water), de-ionised water and tetraethylortho silicate (TEOS, 98%, Aldrich), resulting in a synthesis mixture composition of 107.7 SiO₂ : 32.68 TPA : 32.68 OH : 12000 H₂O. The reaction mixture was aged with stirring for 1.5 hours prior to synthesis. The Metglas ribbons were placed vertically in a 55 ml Teflon-lined autoclave and placed in a convection oven at 453 K for 70 to 150 min. After synthesis, the autoclaves were cooled with water and the zeolite coated ribbons were rinsed with water and dried over night at room temperature.

Due to the upper temperature limit for Metglas sensor of 573 K [30], ozone detemplation was applied to detemplate the zeolite layer of the coated sensors. The experimental setup and methods for the ozonation procedure are described elsewhere [37, 38]. The ozonation was carried out for 2 h, in a stainless steel module, using a flow of $6 \times 10^{-3} \text{ m}^3 \cdot \text{h}^{-1}$ (STP) of oxygen containing 80 g·m⁻³ (STP) ozone (37×10^3 ppmv) at 473 K with a heating and cooling rate of 60 K·h⁻¹, where standard conditions are 298 K and 1.01 bar. The oxygen was fed to the ozone generator from a gas cylinder. The outlet pressure of the oxygen cylinder was always set at 1.5-2 bar gauge and the flow was regulated with a mass flow controller.

9.2.2 Analysis and testing

An optical microscope, Olympus BH2, was used for the estimation of macroscopic integrity and coverage and the presence of cracks in the layer before and after calcination. The crystal morphology and the layer thickness of the silicalite-1 coating was examined by scanning electron microscopy (SEM) (Philips XL20). The silicalite-1 crystal structure and the orientation were determined by XRD. The measurements were performed on a Bruker-AXS D5005 Theta-Theta diffractometer, equipped with a graphite monochromator in the diffracted beam using CuK α wavelength. The $\theta - 2\theta$ scans were made in the range of 5 to 85 ° with a stepsize of 0.05 ° and a counting time per step of 0.5 s. The detemplation of the ozonicated sensor was investigated by means of diffuse reflectance infrared Fourier transform spectrometry (DRIFT) (Thermo Nicolet, Nexus), using KBr as background. Both the XRD as well as the DRIFT analysis did not involve any pre-treatment of the sample.

The response of the sensors was measured by monitoring the difference in resonance frequency during the exposure of the samples to different gases [10, 12]. To

remove any adsorbed molecules from the zeolite layer, prior to any sensing experiments, the sensors were kept overnight in contact with a N_2 stream at room temperature. This gentle cleaning was performed to mimic use at practical conditions. The measurements were carried out at room temperature and atmospheric pressure. The methods of measurement and the experimental setup used are described elsewhere [10]. During the sensing measurements, the sensor was placed in a 2.5 cm long glass tube, in which the measured gases were set to flow. A magnetoelastic resonator excited the sensor with a time-varying magnetic field and recorded the voltage induced by the sensor's vibrations using a detection coil. The shift in the resonance frequency was measured while the sensor was alternatingly exposed to an air and an analyte gas flow. Three different gases, namely CO_2 , n-butane, and iso-butane were used as analytes.

9.3 Results

The silicalite-1 layer thickness was controlled by adjusting the time of hydrothermal synthesis. Figures 9.1a-f show top views and cross-sections of the sensors coated with silicalite-1, after different crystallization times. The cross section was prepared by etching away a small portion of the coating at the edge of the film with hydrofluoric acid. The SEM micrographs confirm complete coverage of the sensor's surface. Individual crystals grow on the surface of the sensor with their largest flat surfaces (*a-c* plane) parallel to the surface of the sensor. The visible crystals are primary monocrystals, unlike the more composite crystals which are observed at crystal sizes larger than $\sim 1 \mu m$ [40]. Due to the anisotropic growth of silicalite-1 crystals, the sensor can be covered with a thin continuous layer of zeolite crystals. The fastest growing direction of silicalite-1 (*c*-direction) is parallel to the sensor surface, while the slowest growing *b*-direction is perpendicular to the sensor surface. After 90 min of in-situ crystallization, the sensor was fully covered with an ~ 800 nm thick, well inter-grown mono-layer of *b*-oriented silicalite-1 crystals.

The silicalite-1 crystal structure and orientation was confirmed by XRD (Figure 9.2). Mainly peaks corresponding to (0*k*0) planes appear in XDR analysis, confirming that the straight channels of the crystals are perpendicular to the substrate surface. At higher 2θ , also peaks corresponding to the (*h*00) plane are observed, these become more apparent at increasing synthesis time. Prolonging the crystallization time above 90 min, results in a multi-layer of inter-grown *a* and *b* oriented silicalite-1

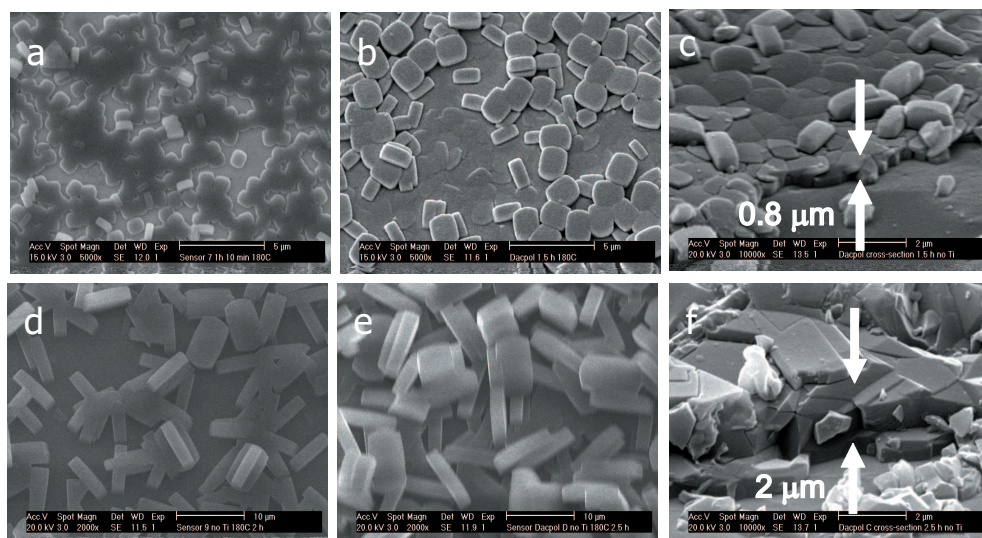


Figure 9.1: SEM micrographs of *b*-oriented Metglas-silicalite-1 composite sensor. Synthesis time: 70 min top view (a); 90 min top view (b) and cross section (c); 120 min top view (d); 150 min top view (e) and cross section (f).

crystals. Silicalite-1 crystals forming the primary sensor coating are still predominantly *b*-oriented. With further increasing crystallization time, deposition of loose crystals from the solution on top of silicalite-1 mono-layer occurs, resulting in reflections corresponding to random crystal orientation. Even at the increased synthesis time, the silicalite-1 layer is predominantly *b*-oriented. All further measurements are conducted on a sensor with a zeolite coating with 90 min synthesis time.

The ozonation was carried out using a flow of $6 \times 10^{-3} \text{ m}^3 \cdot \text{h}^{-1}$ (STP) of $80 \text{ g} \cdot \text{m}^{-3}$ (STP) ozone in oxygen at 473 K for 2 h. To assess the degree of template removal, DRIFT analysis of the zeolite coated sensors was performed (Figure 9.3). The absorbances corresponding to C-H stretching vibrations (2981 , 2943 and 2883 cm^{-1}) and the C-H deformation (bending) vibrations (1473 , 1459 and 1382 cm^{-1}) are apparent in the spectrum of the as-synthesized sample, but are significantly reduced in the spectra of the detemplated sample. Increasing the ozonation time from 2 to 28 h did not result in a further decrease of these absorbances. The ozonicated sensor showed a broad peak in the adsorbance at wavenumbers ranging from 3200 to 3700 cm^{-1} and an absorbance at 1600 cm^{-1} , corresponding to adsorbed water and indicating an appreciable accessibility of the pore space of the silicalite-1 layer. Although there is still a weak signal corresponding to C-H vibrations, the selective

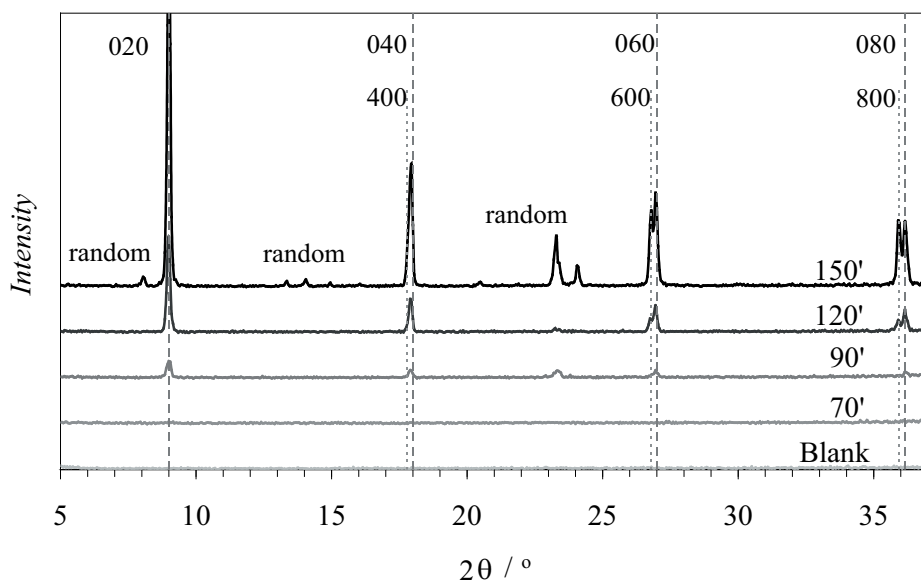


Figure 9.2: XRD patterns of silicalite-1 on Metglas ribbon, after different synthesized times. The dashed lines indicate the angle at the $0k0$ and the dotted lines indicate the $h00$ planes. The reflections assigned to the randomly orientated crystals deposited on the oriented layer are also indicated.

response of the sensor to CO_2 and n-butane, indicated sufficient detemplation.

To show the reversible sensing capacity of the Metglas-silicalite-1 composite, the response of the sensor was measured at 298 K and atmospheric pressure, as a function of time during alternating exposure to air and, either, CO_2 (Figure 9.4), or n-butane (Figure 9.5), or iso-butane (Figure 9.6) environment. All these analyte gases are able to adsorb in the silicalite-1 pores (Table 9.1). Switching from air to a CO_2 gas flow increases the resonance frequency. The same effect is observed when switching from an air to an n-butane and iso-butane environment, with only a small observed change in resonance frequency in the latter case. The sensor shows a longer response time for n-butane than for CO_2 and the resonance frequency in air does not return to its initial value after exposure to n-butane. The resulting shift in the resonance frequency in air shows a slight decrease in time.

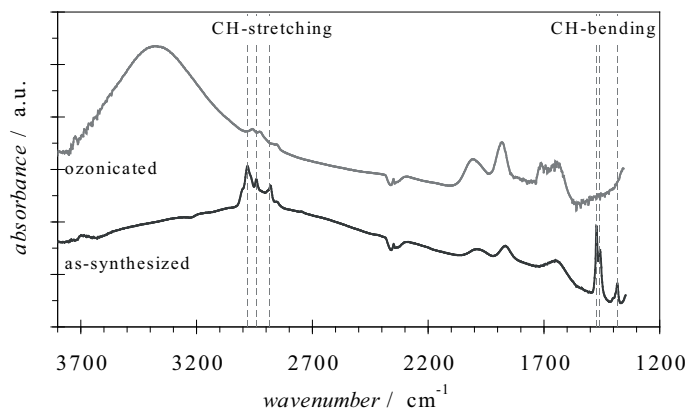


Figure 9.3: DRIFT spectra of a *b*-oriented Metglas-silicalite-1 composite sensor (90 min synthesis time) before and after ozonation for 2 h at 473 K, using a flow of $12 \times 10^{-3} \text{ m}^3 \cdot \text{h}^{-1}$ (STP) O_2 containing $80 \text{ g} \cdot \text{m}^{-3}$ (STP) O_3 . The dashed lines indicate the C-H stretching and bending vibrations.

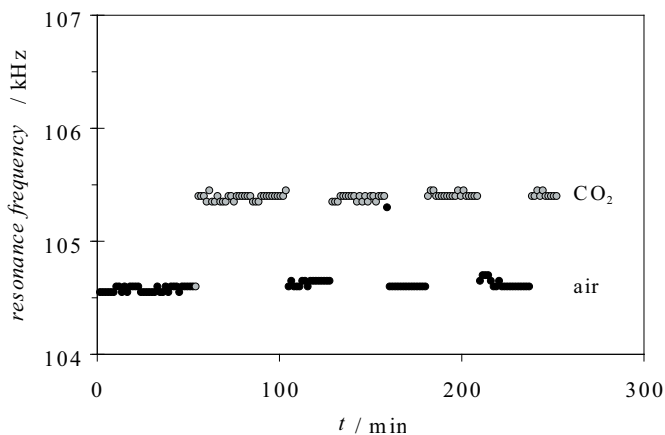


Figure 9.4: Response of the sensor (90 min synthesis time) as a function of time when alternatingly exposed to air (●) and CO_2 (○) flow, measured at 298 K and 101.3 kPa.

Table 9.1: Adsorption loading, q_i , and diffusivities, D_i , of CO_2 , n-butane and iso-butane at 303 K and 100 kPa.

component	M_i $/ \text{g} \cdot \text{mol}^{-1}$	q_i $/ \text{mol} \cdot \text{kg}^{-1}$	q_i $/ \text{g} \cdot \text{kg}^{-1}$	D_i $\text{m}^2 \cdot \text{s}^{-1}$	reference
CO_2	44	1.6	70	2.2×10^{-10}	[41, 42]
n-butane	58	1.7	99	5.0×10^{-10}	[42, 43]
iso-butane	58	1.4	81	6.4×10^{-13}	[42, 43]

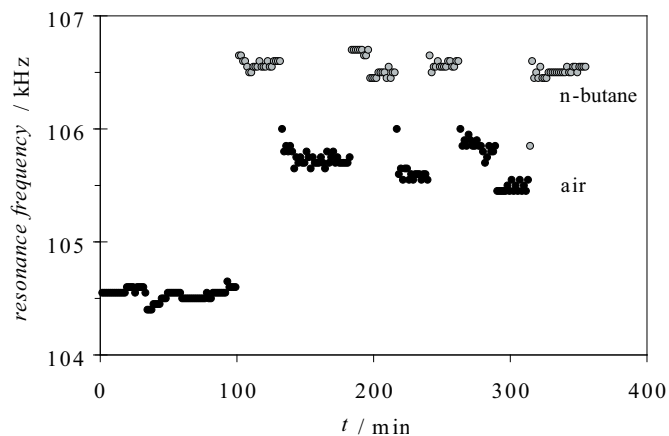


Figure 9.5: Response of the sensor (90 min synthesis time) as a function of time when alternatingly exposed to air (●) and n-butane (○) flow, measured at 298 K and 101.3 kPa.

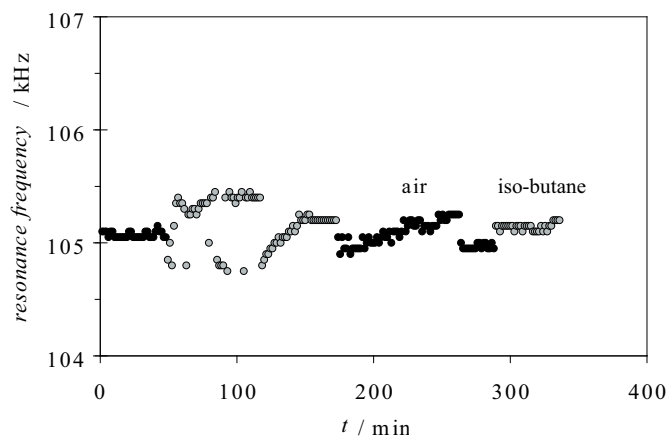


Figure 9.6: Response of the sensor (90 min synthesis time) as a function of time when alternatingly exposed to air (●) and iso-butane flow (○), measured at 298 K and 101.3 kPa.

9.4 Discussion

To cover the Metglas ribbons with a closed mono-layer of *b*-oriented silicalite-1 crystals, 90 min of synthesis time is required. At longer synthesis times, also *a*-oriented and, eventually, some randomly oriented crystals are observed by both SEM micrographs (Figure 9.1d and e) and XRD analysis (Figure 9.2), although the zeolite layer remains predominantly *b*-oriented.

Essentially complete removal of the template molecules from the zeolite coating of the sensors by the ozone treatment was confirmed by DRIFT analysis (Figure 9.3). After 2 h of ozonation, the intensities indicating the presence of the organic template were significantly reduced. The ozonicated sensor shows increased absorbances corresponding to water ($3200\text{--}3700\text{ cm}^{-1}$). Since an ozonicated zeolite contains a larger amount of silanol groups as compared to a calcined zeolite [37], an increased adsorption of water in the detemplated zeolite is expected. The increased number of silanol groups in ozonicated silicalite-1 can also have an impact on the adsorption and diffusion behavior of analyte species in the zeolite layer.

The *b*-oriented Metglas-silicalite-1 sensor was able to repeatedly sense CO_2 when alternately exposed to an air and a CO_2 flow. Figure 9.4 shows a good reproducibility in the dynamic behavior of CO_2 detection. The measured resonance frequency of the Metglas-silicalite-1 composite was stable and depended only on the environment (air or CO_2). The measured shift in resonance frequency during adsorption of CO_2 is less than that of *n*-butane, which is in concordance with the difference in loading at ambient conditions (Table 9.1). The adsorption of CO_2 and *n*-butane results in an increase in resonance frequency, as compared to exposure to air. Although this is an effect opposite to what is expected from an increase in mass, this behavior has been observed before and can be explained by the change in the elastic properties of the detemplated zeolite with loading of adsorbed species [12]. The change in elastic properties of the zeolite is temperature dependent and alters the response of the sensor, to an extent that can surpass the effect of mass increase.

To assess the selectivity of the silicalite-1 coated Metglas sensor, its responses to iso-butane (diameter $5\text{ \AA}$) and *n*-butane (diameter $4.3\text{ \AA}$) was measured. Although, at moderate conditions, *n*-butane adsorbs to higher loadings than iso-butane, both isomers are able to adsorb into the silicalite-1 pores (diameter $5.4\text{ \AA}$) [43–45]. The diffusivity of *n*-butane in silicalite-1 is three orders of magnitude higher than that of iso-butane (Table 9.1), indicating that the diffusion can be the limiting factor to the

response of iso-butane.

The sensor showed a clear response to n-butane, while no significant response during exposure to iso-butane was observed (Figures 9.5 and 9.6) showing the selectivity of the sensor. The difference in the resonance frequencies measured does not correspond to the expected difference in mass loads (Table 9.1). This indicates that the sensor's response is not only determined by the mass load of the adsorbed analyte.

Because of the large difference in diffusivities of iso-butane and n-butane, the difference in response of the sensor could purely be a kinetic effect. Prolonging the sensing experiments would reveal if this is the case. Since iso-butane and n-butane adsorb at different locations within the zeolite structure [45], this can result in a different impact on the zeolite's elastic properties. Therefore, the effect of mass increase, and the effect of change in elastic properties could cancel out in the case of iso-butane.

The reversible transition of the crystal symmetry with temperature of the zeolite layer anchored to the Metglas surface can induce stress, altering the sensor's response and adsorption properties [46]. Detemplation can also induce stress on the zeolite-sensor assembly since MFI type zeolites change symmetry group after template removal [47]. It has been shown that, after detemplation, a *b*-oriented silicalite-1 layer contracts, while an *a*-oriented layer expands in the direction parallel to the surface on which it is coated [48]. This anisotropic deformation shows that the induced stress on the Metglas-zeolite composite is strongly dependent on the orientation of the zeolite layer. Thin and oriented zeolite films can have different properties than zeolite powder [23, 49]. This is attributed to the induced stress, which can also influence the the adsorption capacity of the zeolite layer [22].

The adsorption of large molecules, such as naphthalene (diameter 5.8 Å) in MFI requires a deformation of the zeolite structure [50]. But also adsorption of smaller species, including iso-butane and n-butane, can induce deformation of the zeolite structure which has shown to alter the performance of zeolite membranes [51]. Molecular dynamics simulations have shown that the influence of framework flexibility has a larger influence on the diffusivity of iso-butane as compared to n-butane [52]. The adsorption of p-xylene in a thin oriented silicalite-1 film coated on an ATR crystal has been shown to differ from bulk adsorption, showing a lower saturation loading and the shape of the isotherm, while the adsorption of n-hexane was similar as on zeolite powder [22]. The discrepancy in the adsorption behavior of p-xylene was

attributed to the effect of silanol groups, grain boundaries, and induced strain in the crystals anchored to the substrate [22]. Comparing XRD analysis before and after template removal for the coated sensor and bulk zeolite material would reveal the stress induced by the template removal. Also, measuring the frequency response during ozonation would yield information on the stress induced during detemplation.

The thin layer of the zeolite only allows for a small amount of adsorbed mass. Increasing the layer thickness would increase the adsorbed amount, but also the response time [9]. Moreover, an increased thickness reduces the anisotropy of the layer (Figure 9.2), which could reduce the deviation in elastic properties of the zeolite layer, as compared to bulk zeolite material. This might eventually lead to a frequency response of the sensor which decreases with adsorbed mass. Measurements at different analyte concentrations and temperatures as well as determining the effect of the zeolite layer thickness can further elucidate the observed responses to the analyte gases. Measuring the frequency response during ozonation would allow direct insight in the progress of the detemplation process and the stress induced by removal of the template.

It should be noted that a small amount of residual template material left in the framework (Figure 9.3) could cause an extra mass transport barrier, further reducing the uptake of iso-butane. This could be verified by coating the sensors with aluminum containing MFI type zeolites which can be synthesized without a template [53] or with templates which are more easily removed than TPA [27].

A shift is observed in the measured resonance frequency of the sensor in air after initial exposure to n-butane. This effect can be attributed to incomplete desorption of n-butane. Since the sensing experiments are carried out at relatively low temperature and atmospheric pressure, the hydrocarbons adsorb strongly to the zeolite [43]. The strong adsorption can result in a slow and incomplete desorption under the applied conditions. Moreover, the switching times between gases could be insufficient to completely reach saturation or desorption. Increasing the time in between shifts, or increasing the temperature to promote desorption could improve the consistency of the measurements.

9.5 Conclusions

Novel gas sensors have been manufactured by applying a mono-crystalline-thin, *b*-oriented silicalite-1 film on a magnetoelastic Metglas ribbon. Ozonation at 473 K

was successfully applied to detemplate the zeolite coating without losing the magnetoelastic properties of the Metglas material. This enables the use of templated zeolite coatings on sensors which are vulnerable to high temperatures, so that the number of zeolite types that can be used for this application is significantly increased. The Metglas-silicalite-1 composite combines the selective adsorption capacity of the zeolite coating with the magnetoelastic property of the Metglas alloy to convert mass loads of adsorbed gases into measurable shifts in the sensor's resonance frequency. The sensors have shown to successfully detect CO₂ in air, and are able to distinguish between iso-butane and n-butane. A shift in the resonance frequency in air is observed after an initial exposure to n-butane, indicating partial irreversible desorption. The higher number of silanol groups of ozonicated silicalite-1 can influence the adsorption and diffusion behavior of analyte species. The weak response to iso-butane can be caused by canceling out of the effect of mass increase and change in elastic properties of the zeolite. Also diffusive limitations, possibly enhanced by the reduced flexibility of the anchored silicalite-1 crystals and residual template material within the zeolite framework can play a role.

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Characterization and dynamic optimization of membrane assisted crystallization of adipic acid

This chapter is submitted as:

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Abstract The concept of membrane assisted crystallization using reverse osmosis (MaC-RO) shows a high potential in decreasing energy conversion as compared to evaporative crystallization. A setup has been constructed for MaC-RO, using two separate loops for membrane separation and crystallization. In this study we focus on the characterization of the membrane performance in solvent removal from an aqueous adipic acid solution under reverse osmosis conditions. A semi-empirical model was developed for the flux as a function of temperature, concentration and pressure difference across the membrane. The presence of adipic acid strongly reduces the flux at the same feed temperature and pressure, as compared to the flux from a pure water feed. This effect could be attributed to competitive adsorption on the membrane surface and, to a lesser extent, concentration polarization. For a batch MaC-RO process a dynamic optimization was conducted by changing the operational policy (membrane feed pressure, flow rate and temperature). The energy conversion is minimized while maintaining a high, prior optimized product yield, defined as the volume based mean size. The so-determined optimal operational policy results in a 6 times lower energy conversion as compared to evaporative crystallization with a final mean size that closely corresponds to the maximum mean size that can be achieved in a crystallizer with ideal control of supersaturation. This study demonstrates the potential of the concept of MaC-RO in terms of control over product quality and reduction of energy conversion.

10.1 Introduction

Membrane assisted crystallization (MaC) offers an interesting opportunity to generate supersaturation by removing the solvent from a crystallizer. It constitutes an alternative to conventional evaporative crystallization processes, which have high energy demands. By using membranes instead of a boiling zone for solvent removal, the surface area available for solvent removal per unit crystallizer volume can be increase. Since membranes can, in principle, be placed at any location in a crystallizer vessel, areas of low supersaturation can be chosen as membrane location to reduce the gradients in supersaturation within the crystallizer. This can lead to smaller and more efficient equipment. In terms of operational flexibility, it has been shown that application of membranes within a task based design framework for crystallization processes showed an increase in operational flexibility [1]. Finally, the use of membranes enables operation at low temperatures and outside boiling conditions, increasing flexibility for design and allowing crystallization of thermally labile compounds [2, 3].

The number of studies on the combination of membranes and crystallization has been increasing over the last decade. These studies emphasize not only the high potential of the concept, but also the main challenges in process design and operation. The main focus has been on two modes of operation, namely MaC using reverse osmosis (MaC-RO) and membrane distillation (MaC-MD), of which the latter method received most attention. Although MD is generally less affected by polarization effects than RO and is not limited by the osmotic pressure [4], the MD process involves a phase change and thus requires the enthalpy of vaporization, making the energy demand comparable to evaporation processes [5]. Therefore, MaC-RO has a higher potential in reducing the energy requirements, as an alternative to conventional evaporative crystallizers [6, 7]. For MD to be energetically competitive with RO, MD membranes should be approximately 100 times more permeable than current commercial membranes [4]. Moreover, MD requires the use of hydrophobic microporous membranes for water removal, making these materials more susceptible for nucleation of organophilic compounds on the membrane surface. Furthermore, due to the evaporation in MD, the temperature decrease along the membrane increases the local supersaturation, which increases the risk of scale formation on the membrane surface.

The high potential of MaC-RO to control the generation of supersaturation was recognized by Azoury *et al.* [8], who applied MaC-RO for the precipitation of cal-

cium oxalate, but they also concluded that fouling of the membrane needs to be prevented for successful operation. Fouling of the membrane induces a decline in flux which is proportional to the blocked surface area [9, 10]. Furthermore, excessive fouling has shown to reduce the long-term stability of membranes [11, 12]. To reduce crystal growth on the membrane surface in an MaC-MD process to produce NaCl crystals, Curcio *et al.* [13] separated the membrane module from the crystallizer vessel. Although the results confirmed the potential of MaC-MD for redesigning traditional crystallizers, crystal deposition inside the membrane remained a major obstacle. Weckesser *et al.* found MaC-MD enabled better control over product quality in crystallization from a NaCl/KCl/water solution [14]. Tun *et al.* [15] produced Na₂SO₄ and NaCl crystals, also by means of MaC-MD. Although reasonable mass fluxes were obtained, temperature and concentration polarization and crystal formation on the membrane surface were identified as limiting factors. Gryta *et al.* observed membrane wetting induced by salt deposition inside the pores, which eventually leads to loss of selectivity [16]. Concentration polarization has shown to have a significant detrimental effect on the membrane performance in MaC-MD of NaCl [16]. Polarization effects can also lead to a critical supersaturation at the membrane surface, above which crystallization on the membrane surface can occur, causing a significant drop in flux [15]. Generally, the design of membrane processes is aimed at minimizing scaling and polarization effects [17]. However, several studies claim to utilize the membrane as a template to induce heterogeneous nucleation [2, 18–21]. As a general observation, however, it is stressed by these studies that polarization effects need to be minimized and scaling ought to be prevented in order to ensure successful operation of membrane assisted crystallization processes.

In this study, MaC-RO of adipic acid (AA) is investigated experimentally and by modeling and optimizing the process operation. The concept of MaC-RO offers additional process actuators and design variables compared to conventional evaporative or cooling crystallization. To investigate the potential of this technique, an experimental program was conducted in order to characterize the membrane performance as a function of temperature, pressure and solute concentration. Thereafter, a dynamic optimization of the MaC-RO process, focused on optimizing product quality under minimal energy conversion by manipulating the operational policy is conducted.

10.2 Experimental methods and materials

A schematic drawing of the experimental setup is given in Figure 10.1. The setup consists of a crystallizer vessel connected to a buffer vessel which was used to increase the concentration of the solute. Two liquid circulation loops were used (loop A and loop B) with individual flow rates, pressure levels, and temperatures. Loop A ($F_{C,i}$ and $F_{C,o}$) circulated a liquid stream between the crystallizer and the buffer vessel at relatively low flow rate. To prevent scaling, circulation loop B ($F_{M,i}$ and $F_{M,o}$), feeding the membrane from the buffer vessel, was set at a higher temperature than the temperature of the crystallizer. The supersaturation at the membrane surface is in this way reduced. Moreover, loop B was operated at high flow rates ($Re \approx 20,000$) to minimize polarization effects. Since loop B was kept at constant temperature, this large flow did not need to be cooled or heated for every pass through the membrane module.

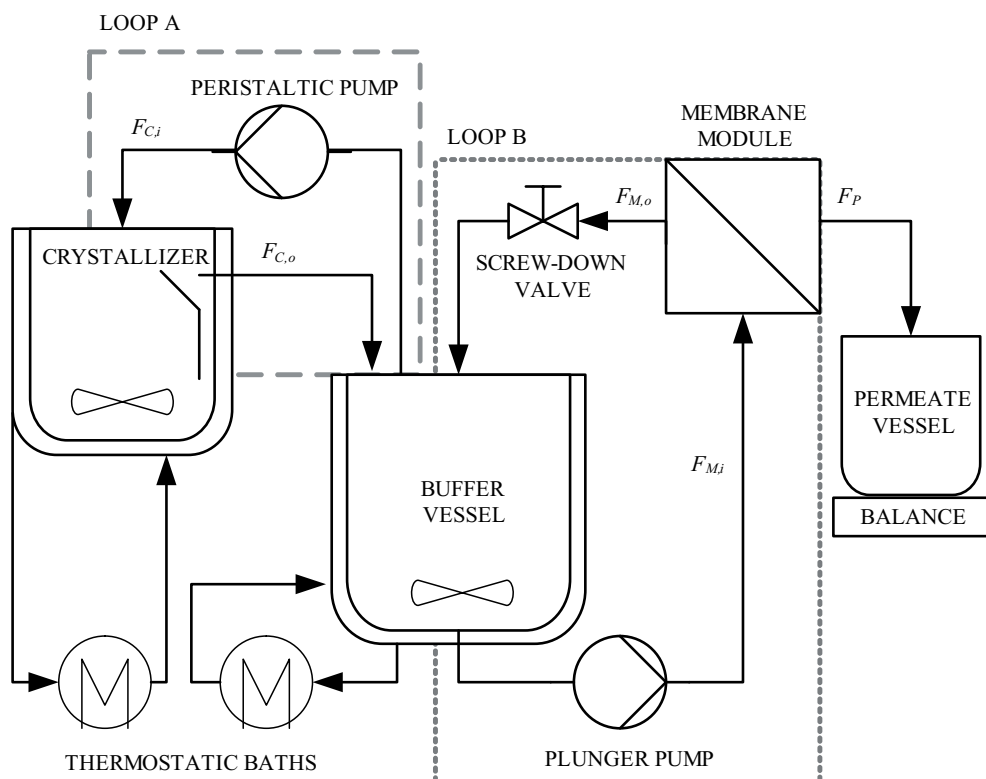


Figure 10.1: Schematic representation of the membrane assisted crystallization setup

A stirred 5-l jacketed vessel with a draft-tube was used as crystallizer, wherein a funnel combined with an overflow was placed to prevent the crystals from flowing out of the vessel and to maintain constant liquid level. The buffer vessel was a 10-l jacketed vessel in which mixing was provided by a tangential inlet of the flow returning from the membrane module. The buffer vessel as well as the tubing in loop B, were jacketed and were connected to a thermostatic bath (Lauda RK8KP) which was connected to an external Pt-100 to control the temperature inside the vessel. The solution in the buffer vessel was pumped through the membrane module with a reciprocal pump with three plungers (Cat Pumps 5CP6221), which allowed for control of both pressure and flow rate. The setup was operated at retentate side pressure of the membrane module up to 40 bar, which could be adjusted using a pressure indicator and a screw-down valve after the membrane module. The pressure of 40 bar was sufficient to obtain reasonable fluxes, since the molar solubility of adipic acid is low resulting in osmotic pressure of the membrane feed which are always below 30 bar [22]. In loop B, the flow rate was maintained at $3.3 \times 10^{-4} \text{ m}^3 \cdot \text{s}^{-1}$ ($20 \text{ l} \cdot \text{min}^{-1}$). A pulsation dampener (Cat Pumps 6028) was installed to minimize fluctuations in flow and pressure. A shell and tube type reverse osmosis membrane module (ITT Aquious MIC-RO 240) was used with a total surface area of 0.024 m^2 . The module was mounted with polyamide membranes (ITT Aquious AFC99) with an apparent retention for NaCl of 99% and a normal operational range of $3 < pH < 11$ and $273 \text{ K} < T < 343 \text{ K}$. The module contained two membrane tubes with a length of 0.3 m and an inner diameter of 0.01 m. The feed flow, $F_{M,i}$, was introduced at the tube side, while at the permeate side the liquid, F_p , was allowed to flow out of the module into the permeate vessel. The permeate vessel was placed on a balance (Mettler PM30) to measure the weight increase of the vessel due to solvent permeation through the membrane.

Using this setup, a characterization of the membrane performance has been conducted at temperatures ranging from 293 K to 333 K and a retentate side pressure of 10 to 40 bar. In these experiments only loop B was used, where the buffer vessel was filled with water, or an adipic acid solution with a concentration of $164 < c_{AA}^B < 342 \text{ mol} \cdot \text{m}^{-3}$. Because of the high flow rate in loop B compared to the permeate flow, the retentate side concentration, c_{AA}^R , was assumed to be constant, and equal to the buffer vessel concentration, c_{AA}^B .

10.3 Modeling membrane transport in MaC

10.3.1 Reverse osmosis

Figure 10.2 gives a schematic figure of a reverse osmosis process. Both the retentate side (R) and the permeate side (P) are in the liquid phase. A pressure difference is applied over the membrane, resulting in a chemical potential difference, which is the driving force for mass transport.

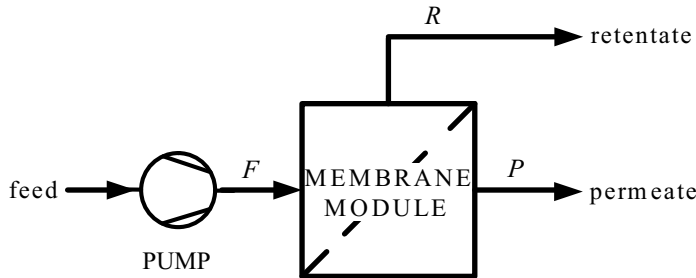


Figure 10.2: Schematic representation of a reverse osmosis process

In RO, the selectivity is often expressed as a retention factor. In the case of the retention of adipic acid the retention factor, R_{AA} , is defined as [23]

$$R_{AA} = 1 - \frac{c_{AA}^P}{c_{AA}^R} \quad (10.1)$$

For selective water permeation from an adipic acid solution through a an RO membrane, the chemical potential difference across the membrane can be related to the pressure difference by [24, 25]

$$-\frac{\Delta\mu_w}{RT} = \ln\left(\frac{x_w^P\gamma_w^P}{x_w^R\gamma_w^R}\right) + \frac{1}{RT} \int_{P^R}^{P^P} v_{0,w} dP \quad (10.2)$$

where $v_{0,w}$ denotes the water partial molar volume at the permeate side. At equilibrium and when the permeate is assumed to be pure water, and the pressure dependency of $v_{0,w}$ is neglected, this yields the osmotic pressure, $\Delta\pi$ [25].

$$\Delta\pi = \int_{P^P}^{P^R} dP = \frac{RT}{v_{0,w}} \ln(x_w^R\gamma_w^R) \quad (10.3)$$

At low adipic acid concentrations, equation 10.3 can be approximated by

$$\Delta\pi = \frac{RT}{v_{0,w}} x_{AA}^R \quad (10.4)$$

10.3.2 Modeling of the permeate flux

At high water selectivities, the permeation of adipic acid can be neglected. Using the same assumptions that lead to equation 10.4 and assuming a linear relation between the water molar flux and a difference in chemical potential and Henry type of solution behavior of water in the membrane material, the pressure difference, ΔP , can be related to the water flux across the membrane, N_w , by the solution diffusion model [25].

$$N_w = \frac{K_{wM} \mathcal{D}_{wM}}{RT d_M} (\Delta P - \Delta \pi) = P_w (\Delta P - \Delta \pi) \quad (10.5)$$

The permeance, P_w , comprises the membrane thickness, d_M , and the solubility, K_{wM} , and diffusivity, $\mathcal{D}_{wM}$, of the permeating component in the membrane. Both K_{wM} and $\mathcal{D}_{wM}$ are temperature dependent parameters, which can be described by an Arrhenius type of equation [26]. Where the temperature dependencies of the solubility and diffusivity are related to the heat of solution, $\Delta_s H_{wM}$, and the activation energy of diffusion, E_A , respectively.

$$K_{wM} = K_{wM,0} \exp\left(\frac{-\Delta_s H_{wM}}{RT}\right) \quad (10.6)$$

$$\mathcal{D}_{wM} = \mathcal{D}_{wM,0} \exp\left(\frac{-E_A}{RT}\right) \quad (10.7)$$

These temperature dependencies can be combined in an apparent activation energy, E_{app} , describing the temperature dependency of the permeance by

$$P_w = \frac{P_{0,w}}{T} \exp\left(\frac{-E_{app}}{RT}\right) \quad (10.8)$$

By substituting equation 10.8 into equation 10.5 we find

$$\ln\left(\frac{N_w T}{\Delta P - \Delta \pi}\right) = \ln(P_{0,w}) + \left(\frac{-E_{app}}{R}\right) \frac{1}{T} \quad (10.9)$$

The permeance can also be dependent on the solvent feed concentration. This is a complex relation, which involves the interaction of adipic acid with the membrane material, and the influence on the water solubility. Rautenbach *et al.* found that the total concentration adsorbed in the membrane can be assumed constant and the adsorption can be described by a Langmuir isotherm [27]. This implies the adsorbed

adipic acid can partly block the membrane, decreasing the effective surface area for water transport. The concentration dependency of $P_{0,w}$ can then be written as [28]

$$P_{0,w}^{eff} = P_{0,w} \left(\frac{1}{1 + K_0 c_{AA}} \right) \quad (10.10)$$

10.3.3 Concentration polarization

Concentration polarization is the increase of the concentration of the retained components at the membrane surface, reducing the driving force for the selectively permeating species. Minimizing this effect is one of the main challenges in the MaC concept. Since the MaC process is operated close to saturation, an increase in concentration can lead to scale formation on the membrane surface. In the case of highly selective membranes, polarization can have a profound detrimental effect on the membrane performance. Assuring turbulent conditions at the retentate side of the membrane module can significantly reduce polarization effects [17]. Figure 10.3 gives a schematic representation of the concentration profile near the membrane surface, showing an increase in the adipic acid concentration at the membrane surface (c_{AA}^M) compared to the bulk concentration (c_{AA}^R).

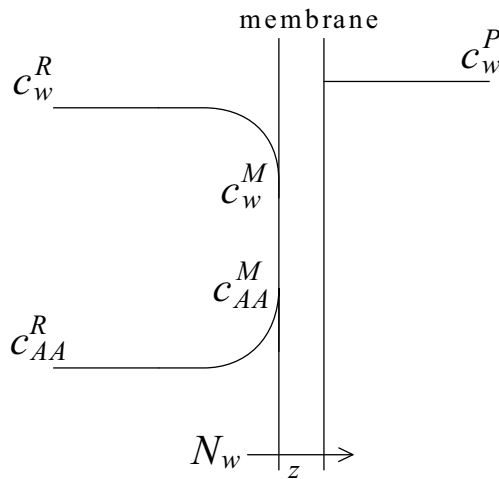


Figure 10.3: Schematic representation the concentration profiles of water and adipic acid near the membrane surface.

When the liquid feed is in a turbulent flow regime, the mass transport resistance can be assumed to be in the laminar boundary layer close to the membrane surface.

For the water and adipic acid flux in the liquid boundary layer, we can adopt the Maxwell-Stefan equations in a simplified form [29]

$$\frac{dx_w}{dz} = \frac{x_{AA}N_w - x_wN_{AA}}{c\mathcal{D}_{w,s}} \quad (10.11)$$

$$\frac{dx_{AA}}{dz} = \frac{x_wN_{AA} - x_{AA}N_w}{c\mathcal{D}_{AAw}} \quad (10.12)$$

Where z is the length-coordinate in the direction of transport and c is the total concentration in the system which, at low solute concentrations, can be assumed equal to the molar density of the solvent, water. The diffusivity of adipic acid in water is denoted by $\mathcal{D}_{AAw}$, while $\mathcal{D}_{w,s}$ denotes the self diffusion coefficient of water, which can be used because of the low solubility of adipic acid. At these low concentrations, the total concentration, c , can be assumed to be molar density of water. When the membrane is assumed to be highly selective for water ($N_{AA} = 0$), we can find the concentration gradient of adipic acid in the boundary layer by integrating equation 10.12 over the linearized boundary layer thickness, δ . Since the adipic acid concentration, $c_{AA} = c x_{AA}$ an expression for the adipic acid concentration at the membrane surface, c_{AA}^M , can now be found.

$$c_{AA}^M = c_{AA}^R \exp\left(\frac{N_w \delta}{c\mathcal{D}_{AAw}}\right) \quad (10.13)$$

The diffusivity of adipic acid in water can be expressed as a function of temperature as [30]

$$\mathcal{D}_{AAw} = (-53.735 + (0.205/K) T) 10^{-10} \text{ m}^2 \cdot \text{s}^{-1} \quad (10.14)$$

The effective boundary layer thickness, δ , depends on the geometry of the membrane module and can vary over the length of the membrane. The boundary layer thickness for a turbulent fluid flowing in a pipe, the Chilton-Colburn relation can be applied to the Dittus-Boelter correlation [31]

$$Sh = 0.023 Re^{4/5} Pr^{1/3} \quad (10.15)$$

Where the Reynolds ($Re = \rho v d / \eta$) and Prandtl ($Pr = \eta / (\rho \mathcal{D})$) numbers are related to the Sherwood number, defined as

$$Sh = \frac{\frac{k}{\delta} l_{geo}}{k} = \frac{l_{geo}}{\delta} \quad (10.16)$$

For the geometric length, l_{geo} , the radius of the membrane tube can be used (5×10^{-3} m).

Using equations 10.5, 10.8, 10.14, and 10.13, the water flux can be related to the pressure difference across the membrane and retentate side concentration

$$N_w = \frac{P_{0,w}^{eff}}{T} \exp\left(\frac{-E_{app}}{RT}\right) (\Delta P - RT c_{AA}^M) \quad (10.17)$$

10.3.4 Model validation

To characterize the membrane performance and determine the transport parameters, the flux across the membrane was measured for an aqueous feed, as well as for adipic acid solutions of different concentration at different temperatures and pressures. The adipic acid concentration was kept below saturation during the experiments to reduce the chance of scale formation on the membrane. Figure 10.4 shows the water flux as a function of the pressure difference across the membrane. For each temperature, the measured fluxes showed a linear trend with the pressure, which is in agreement with equation 10.17. For the aqueous adipic acid solution feed, a similar linear trend was observed (Figure 10.5). The intercept of the pressure-axis, however, is no longer zero, but corresponded to the osmotic pressure of the solution. Table 10.1 shows an overview of the osmotic pressures calculated from the concentration in the buffer vessel and the extrapolated intercept from Figure 10.5. From equation 10.5, it follows that the permeance, P_w , equals the slope of the flux as function of the pressure difference across the membrane, $\frac{dN_{tot}}{d\Delta P}$. The maximum pressure is set to 40 bar as the pressure difference is constraint by the mechanical strength of the membrane and the membrane module.

Table 10.1: Osmotic pressures at different temperatures and retentate side concentrations, calculated assuming $c_{AA}^R = c_{AA}^B$, using equation 10.4 and extrapolated to the intercept of the pressure-axis in Figure 10.5 and the permeances, P_w , as the slopes, $\frac{dN_{tot}}{d\Delta P}$ from Figure 10.5.

T / K	c_{AA}^B / $\text{mol} \cdot \text{m}^{-3}$	$\Delta \pi$ / bar		P_w $\text{kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$
		extrapolated	calculated	
313	164	3.8	4.3	5.9
313	253	6.5	6.6	5.6
323	164	3.4	4.4	6.3
323	253	6.0	6.8	6.2
323	342	8.7	9.1	6.1
333	164	2.4	4.5	6.5
333	253	5.6	7.0	6.4

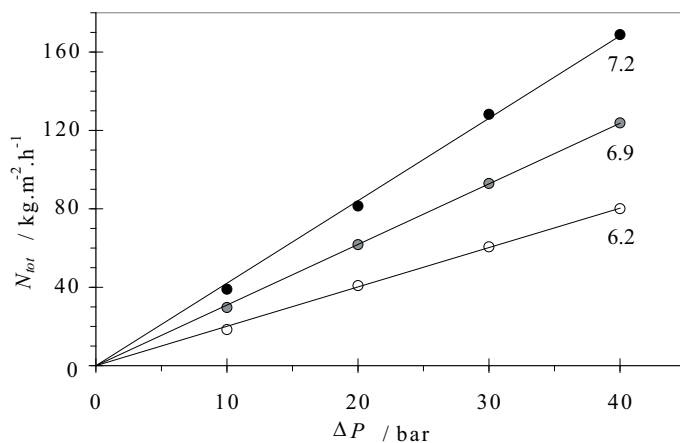


Figure 10.4: Pure water flux versus the pressure difference over the membrane at 298 K (○), 308 K (◐), and 323 K (●). The numbers indicate the permeance, $P_w/\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$, as the slope of the lines, $\frac{dN_{tot}}{d\Delta P}$.

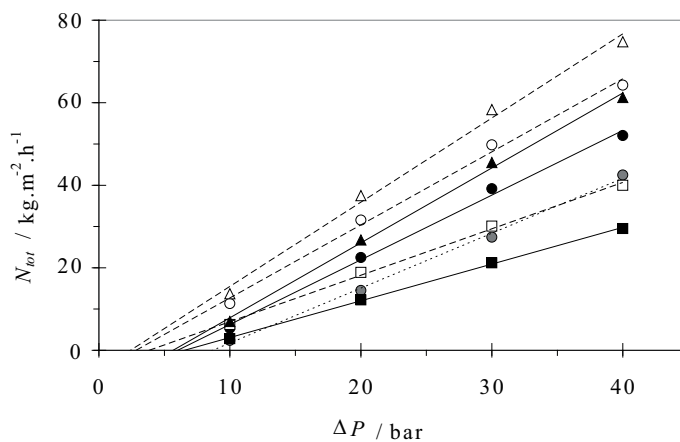


Figure 10.5: Total flux for adipic acid solutions of $164\text{ mol}\cdot\text{m}^{-3}$ (open symbols, dashed line), $253\text{ mol}\cdot\text{m}^{-3}$ (closed symbols, solid line) and $342\text{ mol}\cdot\text{m}^{-3}$ (grey symbols, dotted line) versus the pressure difference over the membrane at 313 K (□), 323 K (○), and 333 K (△).

The adipic acid in the permeate has been measured, and an average retention factor of $R_{AA} = 0.994$ was determined. A small decrease in retention was observed with increasing temperature. Nevertheless, the lowest measured retention factor was above 0.98, validating the assumption of pure water permeation.

The linear relations between the fluxes and pressure difference (Figure 10.5) indicate concentration polarization does not have a profound influence on the flux, as that would result in a deviation from the linear trend. The good correspondence of the osmotic pressures calculated from the bulk concentration with the value extrapolated from the permeation measurements (Table 10.1) also confirm this.

The values of the permeance of pure water (Figure 10.4) and of adipic acid solution (Table 10.1) show an increase of the permeance with temperature, and a decrease with adipic acid concentration. The concentration dependency of the flux is described by equation 10.10, where K_0 is fitted to the experimental data. Figure 10.6 shows the measured data in comparison to correlations using equation 10.9. On the y-axis the term $N_{tot}/(\Delta P - \Delta \pi)$ are taken from Table 10.1. The data is adequately correlated by the transport model confirming that the temperature dependency of the permeance can be described by equation 10.8 for all measured conditions.

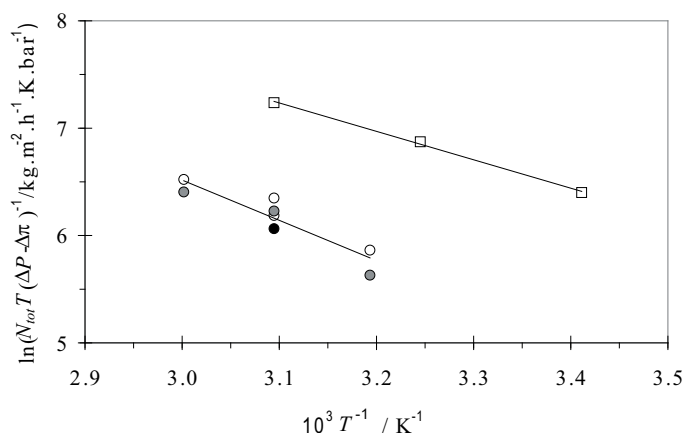


Figure 10.6: Arrhenius plot of pure water feed ($\square$) and adipic acid solution feed at $164 \text{ mol} \cdot \text{m}^{-3}$ ($\circ$), $253 \text{ mol} \cdot \text{m}^{-3}$ ($\bullet$), and $342 \text{ mol} \cdot \text{m}^{-3}$ ($\bullet$).

The measured water fluxes from a pure water and an adipic acid solution feed are used to fit the pre-exponential factor, $P_{w,0}$, the apparent activation energy, E_{app} , and the Langmuir adsorption parameter, K_0 , in equation 10.17 using general PROCess

Modeling System (gPROMS Modelbuilder 3.1.4, PSE Ltd., London, UK). The fitted parameters are listed in Table 10.2. The boundary layer thickness, $\delta = 8.49 \times 10^{-6}$ m, is calculated using equations 10.15 and 10.16 and is assumed to be constant over the length coordinate of the membrane. From the feed temperatures, an average diffusivity of $1.25 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ was calculated and the physical properties of the mixture are approximated by pure water properties ($\eta = 10^{-3} \text{ Pa} \cdot \text{s}$, $\rho = 10^3 \text{ kg} \cdot \text{m}^{-3}$), resulting in a concentration at the membrane surface which is 1% to 10% higher than the bulk concentration, depending on the flux.

Table 10.2: Fitted parameters, including 95% confidence interval, for the permeance pre-exponential factor and activation energy for the water permeation from a pure water and adipic acid solution ($164 \leq c \leq 342 \text{ mol} \cdot \text{m}^{-3}$) feed, at $293 \leq T \leq 333 \text{ K}$ and $10 \leq \Delta P \leq 40 \text{ bar}$.

parameter	value	unit
$P_{w,0}$	$(7.9 \pm 1.1) \times 10^7$	$\text{kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \text{bar}^{-1}$
E_{app}	$(29.2 \pm 0.4) \times 10^3$	$\text{J} \cdot \text{mol}^{-1}$
K_0	$(9.2 \pm 0.4) \times 10^{-3}$	$\text{m}^3 \cdot \text{mol}^{-1}$

The calculated permeance is comparable to literature data for water permeation across other RO membranes [23]. Figure 10.7 shows a parity plot of the fitted data, showing the water flux is well described by equation 10.17, with the pre-exponential factor, the apparent activation energy and the Langmuir adsorption parameter as fitting parameters (Table 10.2).

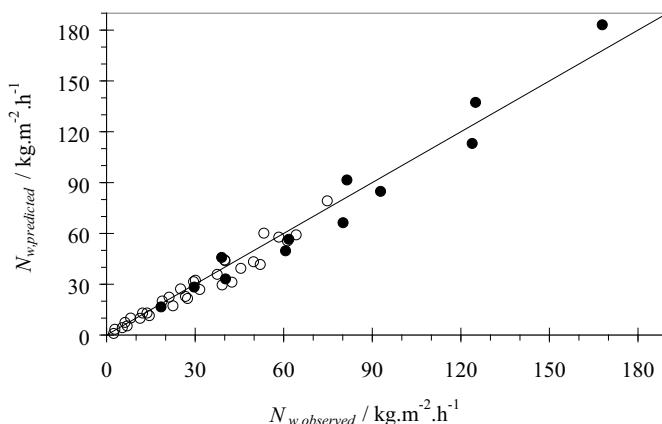


Figure 10.7: Parity plot of the predicted and observed total flux for a pure water feed at temperatures of 293 K, 308 K, and 323 K (●) and adipic acid solutions of 164, 253 and 342 $\text{mol} \cdot \text{m}^{-3}$ at temperatures of 313 K, 323 K, and 333 K (○), at $\Delta P = 10$ to 40 bar

The correlation found for the flux as a function of temperature, pressure and concentration is valid within the range of measured conditions but is also assumed to be suited for extrapolation to higher concentrations below saturation and higher or lower temperatures within the recommended operation range of the membrane. It should be noted that MaC-RO will usually be operated at higher concentrations and temperatures than conventional RO. The operating conditions (temperature and pH) in our experiments are close to the boundaries of the operational range of the polyamide membranes, this can influence the long term stability of the process. The process could be further optimized by using membranes which show less interaction with adipic acid, reducing the effect of competitive adsorption.

10.4 Dynamic optimization of MaC-RO of adipic acid

10.4.1 Modeling of batch MaC-RO

To explore the potential of the MaC-RO concept in improving the control over crystalline product quality, a model of a batch wise membrane assisted crystallization process as illustrated in Figure 10.1 was set up.

In general, the quality of crystalline products is not only determined by purity, but also by properties such as shape, polymorphic form and crystal size distribution (CSD). The focus of this optimization study will be on size distribution as, generally speaking, it determines to a large extent the cost of downstream processes and also the functionality of the final product. The dynamic development of the number density distribution, n , describing the CSD, is given by the population balance [32]:

$$\frac{dn}{dt} + G \frac{dn}{dL} = 0 \quad (10.18)$$

with

$$n(L, t = 0) = 0 \quad (10.19)$$

$$n(L = 0, t) = \frac{B_0}{G} \quad (10.20)$$

$$n(L = L_w, t) = 0 \quad (10.21)$$

The growth rate, G , can be seen as a velocity in the direction of the length coordinate, L . When G is assumed to be independent of length, it can be described by a power law function

$$G = k_G \sigma^k \quad (10.22)$$

Where k_G denotes the growth rate constant, and σ is the relative supersaturation. Mohan *et al.* estimated the kinetic parameters in equation 10.22 for describing crystal growth at different temperatures [33]. The relative supersaturation is defined as

$$\sigma = \frac{w_{AA}^C - w_{AA}^{sat}}{w_{AA}^{sat}} \quad (10.23)$$

where w_{AA} denotes the mass fraction of adipic acid, which is related to the molar concentration, c , by

$$w_{AA} = \frac{c_{AA}M_{AA}}{c_{AA}M_{AA} + c_wM_w} \approx \frac{c_{AA}M_{AA}}{\rho_w} \quad (10.24)$$

The solubility behavior of adipic acid in water is described by

$$w_{AA}^{sat}(T) = w_{AA}^{sat}(T_{min}) \exp[\alpha(T - T_{min})] \quad (10.25)$$

where α is an empirical parameter which was fitted to experimental solubility data, obtained from literature [34].

Nucleation was assumed to introduce particles at zero length only, while agglomeration and breakage processes were neglected. The population balance can be classified as a hyperbolic partial differential equation, which is challenging to solve from a numerical point of view. The model equations will be used for an inverse problem, as an optimal operating profile will be calculated from a desired outcome. Therefore, instead of solving the full population balance, only the first four moments of the distribution are considered, transforming the original partial differential algebraic equation (PDAE) system into an ordinary differential algebraic equation (ODAE) system, in which the moments, m_i , of the CSD are defined as

$$m_i = \int_{L=0}^{L=L_\omega} L^i n dL \quad i = 0, 1, 2, 3, 4 \quad (10.26)$$

The numerical value of the first four moments can easily span ~ 12 orders of magnitude, which will result in an ill-defined optimization problem. Therefore, the moments are scaled with the growth rate constant, k_G . Substitution of equation 10.26 into the population balance 10.18, gives the moment equations describing the dynamic development of the first four moments of the CSD as

$$\frac{d\chi_0}{dt} = \beta, \quad \chi_0 = m_0 k_G^3 \quad (10.27)$$

$$\frac{d\chi_1}{dt} = \sigma^k \chi_0, \quad \chi_1 = m_1 k_G^2 \quad (10.28)$$

$$\frac{d\chi_2}{dt} = 2\sigma^k \chi_1, \quad \chi_2 = m_2 k_G \quad (10.29)$$

$$\frac{d\chi_3}{dt} = 3\sigma^k \chi_2, \quad \chi_3 = m_3 \quad (10.30)$$

$$\frac{d\chi_4}{dt} = 4\sigma^k \chi_3, \quad \chi_4 = m_4 k_G^{-1} \quad (10.31)$$

Where χ_0 to χ_4 represent the scaled moments, β denotes the scaled nucleation rate, given by

$$\beta = B_0 k_G^3 \quad (10.32)$$

Wherein B_0 denotes the nucleation rate. In this study, only secondary nucleation is taken into account, making the model only valid within the metastable zone. It is assumed that effective seeding keeps the supersaturation within the metastable zone. A power law function is used relating the nucleation rate to the relative supersaturation and solid content [35]

$$B_0 = k_B \sigma^i \left[(1 - \varepsilon) \frac{\rho_S}{M_{AA}} \right]^j \quad (10.33)$$

Typical values for the kinetic parameters k_B , i , and j are taken from literature [36].

The component balance for the crystallization vessel (loop A) is given by

$$\frac{d [\rho_L V_C w_{AA}^C \varepsilon + (1 - \varepsilon) V_C \rho_S]}{dt} = F_{C,i} \rho_L w_{AA}^R - F_{C,o} \rho_L w_{AA}^C \quad (10.34)$$

and the total mass balance is expressed in terms of the solid volume fraction, $k_V \chi_3$, as

$$-k_V \frac{d\chi_3}{dt} = \frac{\rho_L (F_{C,i} - F_{C,o})}{V_C (\rho_L - \rho_S)} \quad (10.35)$$

where ρ_L denotes the liquid density, which is assumed to be constant. The liquid volumetric flow into the crystallizer, $F_{C,i}$, is controlled and the liquid fraction, ε , can be related to the third moment of the size distribution by

$$\varepsilon = 1 - k_V \chi_3 \quad (10.36)$$

The model is completed by describing the component and the total mass balance for loop B, given by

$$\frac{d (w_{AA}^F V_B \rho_L)}{dt} = \rho_L F_{C,o} w_{AA}^C - \rho_L w_{AA}^F F_{C,i} \quad (10.37)$$

$$\rho_L \frac{dV_B}{dt} = \rho_L F_{C,o} - \rho_L F_{C,i} - N_w A \quad (10.38)$$

The energy requirement of the process is the sum of the pump duty, the heating capacity needed to heat the crystallizer outlet flow as well as the initial volume of the buffer vessel. Because the temperature and concentration changes are small, a constant heat capacity and liquid density are assumed, giving

$$E_{tot} = \int_{t=0}^{t=t_f} \frac{F_{C,O}(t) \Delta P(t)}{\eta} \cdot dt + C_{pL} \rho_L (T_B - T_C) \left[\int_{t=0}^{t=t_f} F_{C,O}(t) \cdot dt + V_B(t=0) \right] \quad (10.39)$$

10.4.2 Objective functions and constraints

The water mass flux across the membrane, N_w , can be manipulated by changing the pressure or temperature in the membrane module, as described by equation 10.17. The model was implemented in gPROMS Modelbuilder (v. 3.1.4, PSE Ltd., London, UK) with parameter settings as given in Tables 10.2 and 10.3. To reduce the difference in order of magnitude of the parameters, the time scale is set to hours, the energy conversion to kWh, and the pressure to bar. The initial condition in the buffer vessel corresponds to a clear liquid with a concentration saturated at T_C . In the crystallization vessel a seed population of 8 g is introduced with a log-normal distribution characterized by a volume-based mean size of $172 \mu\text{m}$ and standard deviation of $35 \mu\text{m}$ from which the initial moments are derived.

The objective of the dynamic optimization is to produce crystals with a volume-based maximum mean size from a given seed population within a certain time at minimum energy conversion. Two sequential dynamic optimizations are performed to achieve this objective, first optimizing the volume-based mean size and, subsequently, minimizing the energy conversion. The flow rate between loop A and B (Figure 10.1), $F_{C,i}$, and the pressure in loop B, ΔP , are taken as time-dependent continuous-manipulated variables, while the temperature and initial volume of loop B ($V_B(t=0)$ and T_B) are chosen as time invariant manipulated variables. The constant time horizon t_f is divided into 125 equally spaced intervals for optimization of the time dependent manipulated variables. The objective function of the first optimization problem (labeled as OP1), maximizing the volume-based mean size, $\frac{m_4}{m_3}$, is

stated as

$$\max_{\Delta P(t), F_{BC}(t), T_B, V_B(t=0)} \frac{m_4(t=t_f)}{m_3(t=t_f)} \quad (10.40)$$

while the second optimization problem (labeled as OP2) minimizes the total energy conversion, E_{tot} , according to the objective function

$$\min_{\Delta P(t), F_{BC}(t), T_B, V_B(t=0)} E_{tot} \quad (10.41)$$

The constraints in both OP1 and OP2 are given by

$$0 < \Delta P(t) < 40 \quad t \in [0, t_f] \quad (10.42)$$

$$10^{-4} < F_{C,i}(t) < 0.1 \quad t \in [0, t_f] \quad (10.43)$$

$$T_C < T_B < 343 \quad (10.44)$$

$$0 < V_B < V_C \quad (10.45)$$

$$w_{AA}^{sat}(T_C) < w_{AA}^M(t) < w_{AA}^{sat}(T_B) \quad t \in [0, t_f] \quad (10.46)$$

The obtained maximum value of the mean size, resulting from OP1, sets a constraint on mean size for the second optimization (OP2) which minimizes the energy conversion required to achieve this maximum mean size. In addition to the constraints stated before (equations 10.42-10.46), a constraint on mean size is added to equation 10.41, using the maximum mean size which is found from equation 10.40, giving

$$\frac{m_4(t=t_f)}{m_3(t=t_f)} \geq \max \text{OP1} \quad (10.47)$$

Note that there are several manipulated variables that can affect the supersaturation profile in the crystallization vessel ($F_{C,i}$, ΔP , $V_B(t=0)$, and T_B). Different values or trajectories of these variables might lead to the same or similar supersaturation profile and, therefore, final mean size. But they can have a completely different impact on energy conversion. Hence, the optima found in OP1 and OP2 can differ substantially.

10.4.3 Results and discussion

The optimal values for mean size, total energy requirement and time invariant control variables are given in Table 10.4. The optimal trajectories of the applied pressure in the membrane module and volumetric flow rate between loop A and B are depicted in Figure 10.8 for both OP1 and OP2. The development of supersaturation and concentration in the buffer vessel and at the membrane surface are shown in Figure 10.9.

Table 10.3: Parameter settings dynamic optimization study

parameter	value	unit	physical meaning
V_C	0.005	m^3	Fixed volume crystallization vessel
A	0.0240	m^2	Membrane surface area
T_{min}	283	K	Minimum temperature solubility curve [34]
w_{AA}^{min}	0.0108	$\text{kg} \cdot \text{kg}^{-1}$	saturated concentration at T_{min}
T_C	313	K	Temperature crystallization vessel (loop A)
w_{AA}^{sat}	0.0490	$\text{kg} \cdot \text{kg}^{-1}$	Saturated concentration at T_C
C_p	2420	$\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$	Heat capacity of the liquid
M_{AA}	0.146	$\text{kg} \cdot \text{mol}^{-1}$	Molecular weight adipic acid
k_G	4.57×10^{-3}	$\text{m} \cdot \text{h}^{-1}$	Growth rate proportionality constant [33]
k	0.85	—	growth rate exponential constant [33]
k_B	2.5×10^{12}	$\# \cdot \text{mol}^{-1} \text{h}^{-1}$	Nucleation rate proportionality constant [36]. Estimated power number of the stirrer is 0.4
i	2	—	Nucleation rate exponential constant
j	1	—	Nucleation rate exponential constant
ρ_L	1000	$\text{kg} \cdot \text{m}^{-3}$	Density liquid phase
ρ_S	1344	$\text{kg} \cdot \text{m}^{-3}$	Density solid phase
k_V	$\pi/6$	—	shape factor [34]
α	0.0519	-	exponential factor solubility curve
θ	0.7	-	Pump efficiency
t_f	5.0	h	final batch time

In OP1, Both the applied pressure and flow rate work together to maximize the final mean size. In general, the strategy is to keep the supersaturation below a certain threshold (Figure 10.9), above which secondary nucleation, which has a higher order dependency on supersaturation compared to crystal growth, becomes dominating. In the very beginning of the batch both pressure and flow rate are high for a short time to quickly generate supersaturation in the crystallization vessel until the threshold for nucleation is reached (Figure 10.9). In the next phase of the batch, a low pressure and low flow rate are applied to gradually increase supersaturation as the surface area of the crystal population is still relatively small. Simultaneously, the concentration in the buffer vessel steadily increases (Figure 10.9) to store supersaturation for later use. It should be noted that the flow rate is low, but not constrained by the imposed minimum value in equation 10.43. In the final phase of the batch, both the applied pressure and the concentration in the buffer vessel reach a maximum. At this moment, the flow rate is sharply increased to generate a final, high supply of supersaturation with corresponding high growth rate and also a high nucleation. The high nucleation rate hardly affects the mean size because the mean size is volume, rather than number based and the large amount of crystals that are produced in the last moment of

the batch have a small volume. The experimental policy described is referred to in literature as a late growth operating policy and is the direct result of the chosen objective function, which is based on higher moments (volume-based mean size) [37]. An objective function based on lower moments (number based mean size) will result in a different optimal supersaturation trajectory.

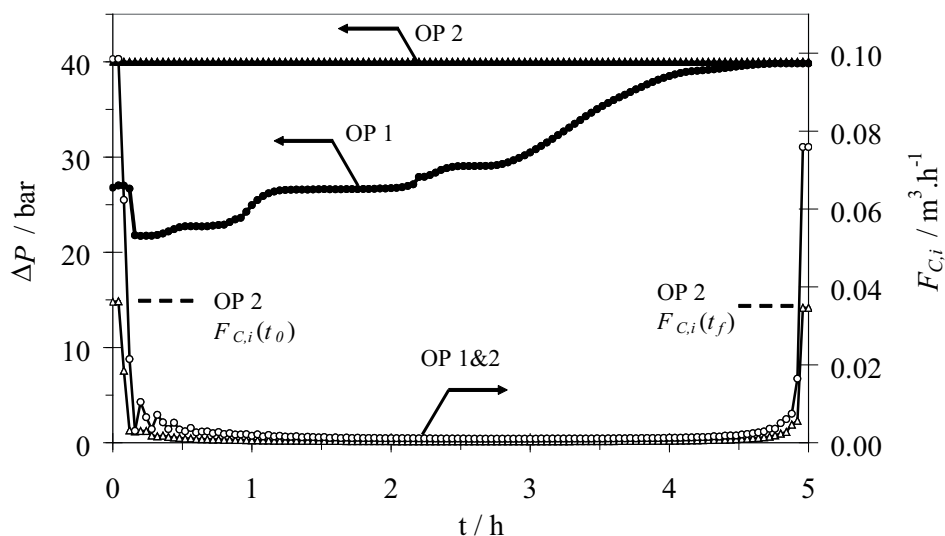


Figure 10.8: Optimal trajectories of manipulated variables ΔP (OP1 (●), OP2 (▲)) and $F_{C,i}$ (OP1 (○), OP2 (△)). OP1 and OP2 refer to the first and second optimization problem, respectively (equations 10.40 and 10.41). Note that the optimal trajectories for the crystallizer inlet flow rate are almost identical for both optimization problems with exception of the start and final value (indicated by dashed arrows).

In OP2, the total energy conversion is reduced by a factor three as compared to OP1. Comparing the profiles of OP1 and OP2 (Figure 10.8) shows that the minimization of the energy conversion for the same final mean size results in a more prominent use of different process actuators (ΔP , $F_{C,i}$, T_B , and V_B). In OP2 the pressure is used to its full extent to generate supersaturation, it is at a maximum value throughout the complete batch (Figure 10.8). The flow rate between loop A and B shows a similar trend for both optimization problems. The optimal values for $F_{C,i}$ determined in OP1 and OP2 differ at the very beginning and in the last phase of the batch. OP2 results in a lower optimal flow rate as high flow rates increase pump duty and heating capacity. At lower flow rates, a higher concentration in the buffer vessel is needed to supply

the same amount of supersaturation to the crystallization vessel (Figure 10.9). The increase in concentration is limited by the constraint (equation 10.46), keeping the concentration at the membrane surface below the saturated value to prevent scaling on the membrane surface. The minimization of the energy conversion also results in a lower temperature, T_B . In OP1 and OP2, the concentration polarization results in an increase of concentration of 3 to 8% at the membrane surface as compared to the bulk concentration. This is within the range of the experimentally measured data. Note that the optimal supersaturation profiles for both optimization problems are almost identical. Supersaturation is the driving force for both nucleation and growth and therefore determines the development of the seed population.

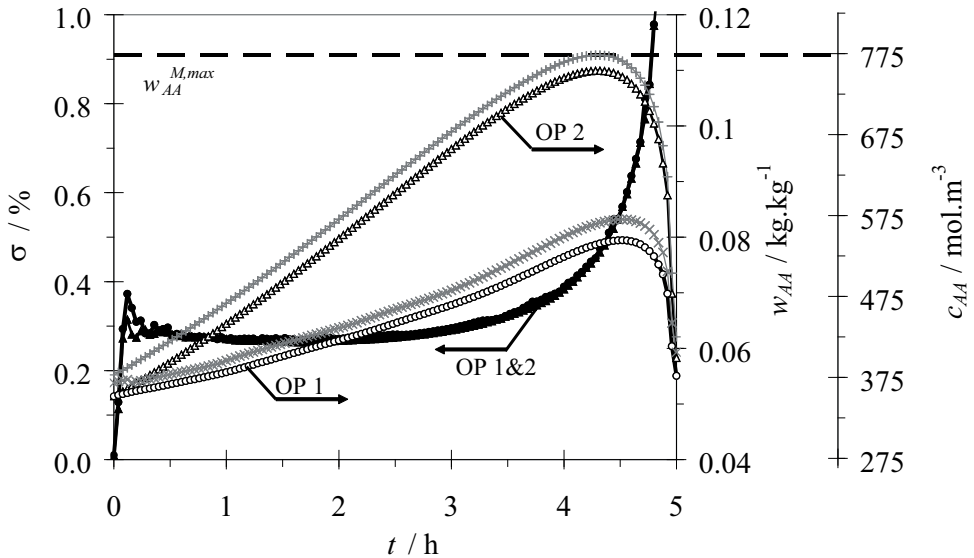


Figure 10.9: Trajectories of supersaturation (OP1 (●), OP2 (▲)) and the concentration at the membrane surface, w_{AA}^M and c_{AA}^M , (OP1 (×), OP2 (+)) and the bulk concentration, w_{AA}^B and c_{AA}^B , (OP1 (○), OP2 (△)). OP1 and OP2 refer to the first and second optimization problem, respectively (equations 10.40 and 10.41). Note that the supersaturation profiles for both cases are almost identical. The horizontal dashed line indicates the saturated concentration at the membrane surface for OP2

The model that is being optimized has a strong non-linear character due to both crystallization kinetics and the model describing the permeation through the membrane. The fact that two completely different operational policies lead to the same mean size raises the question whether the found maximum mean size is a true maximum. To verify the maximum mean size calculated in OP1, a third optimization (labeled OP3) is performed, which only involves the moment equations (equations

10.27 to 10.31), following the objective function

$$\max_{\sigma(t)} \frac{m_4(t = t_f)}{m_3(t = t_f)} \quad (10.48)$$

In other words, we assume that we can generate any supersaturation profile in the crystallization vessel to optimize mean size. It provides an upper value for the mean size compared to previous optimization problems since in case of objective function of OP3 (equation 10.48) less constraints are imposed. Figure 10.10 shows the found optimal supersaturation profile combined with the development of mean size during the batch. For comparison, Figure 10.10 also contains the results obtained from OP2, showing that the profiles of both OP2 and OP3 are almost identical. Closer inspection of Figures 10.9 and 10.10 shows that in OP1 and OP2 the supersaturation shows a sharp initial increase to the optimal trajectory. The time needed to reach this optimum trajectory is mainly determined by equipment limitations (e.g. available membrane surface area) and properties of the seed population. For the remainder of the batch, the supersaturation profiles of OP1 and OP2 follow the optimal trajectory (OP3) with the exception of the very end of the batch time, which is again a region constrained by equipment limitations.

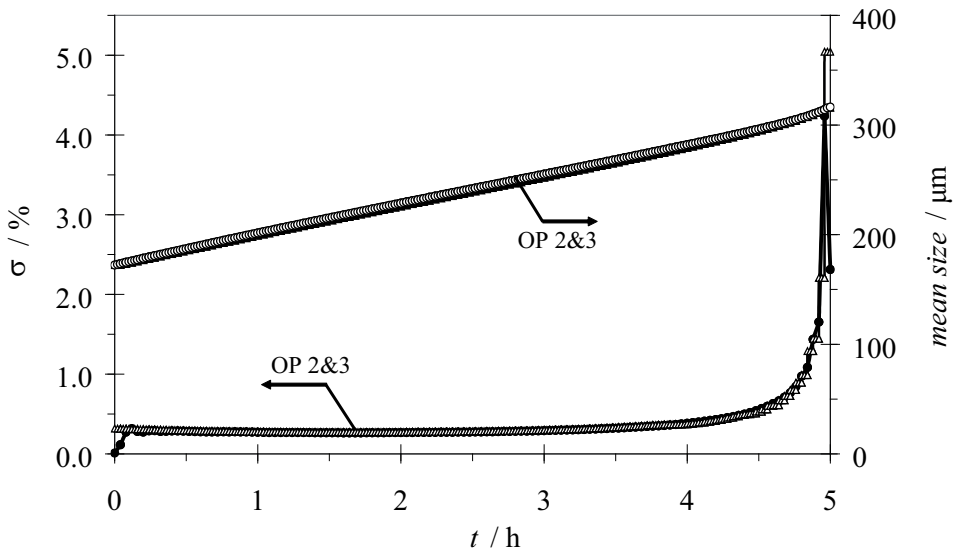


Figure 10.10: trajectories of supersaturation (OP2 (●), OP3 (△)) and mean size (OP2 (▲), OP3 (○)).

Table 10.4: Values for time invariant variables for both optimization problems

Parameter	Objective function		Unit
	equation 10.40	equation 10.41	
Mean size ($t = t_f$)	315.8	315.8	μm
E_{tot}	0.58	0.21	kWh
$V_B(t = 0)$	0.0050	0.0040	m^3
T_B	341.9	335.3	K

Note that the concentration and temperature in the buffer vessel are outside the experimentally validated region of the membrane characterization experiments. However, since the concentration is kept below saturation, and the temperature within the operating window of the membrane, the correlation describing the membrane performance is assumed to be valid at the conditions concerned.

Due to the high number of possible process actuators in the MaC-RO process, different operational policies can lead to the same optimal supersaturation profile for maximization of final volume-based mean size. In our case, the profiles of OP1 are, to a certain extent, dictated by the initial values since no additional constraints or objectives are imposed. In OP2 such an additional objective involving energy minimization is imposed. As was already observed and characterized for the membrane transport, both temperature and pressure can be utilized to manipulate the flux and, therefore, supersaturation. The temperature has a significant impact on energy conversion as the duty of the heat exchanger contributes to a large extent to the total energy requirement of the process. The energy conversion is minimized by applying a high pressure in combination with a low temperature difference between crystallization vessel and buffer vessel. This difference should be high enough to prevent supersaturation close to the membrane surface, as was assured in this study. A strong temperature dependency of the solubility allows for a small temperature difference between the buffer vessel and the crystallizer, while maintaining a concentration below saturation at the membrane surface. Therefore, MaC is most attractive for systems with a strong dependency of temperature on supersaturation.

It should be kept in mind that the optimized energy requirement is significantly lower compared to a conventional evaporative crystallization process, which is one of the strong points of the MaC-RO concept. At minimum energy conversion, the total yield at the end of the batch is 113 g with a total permeate volume of 3.0 kg, using 0.21 kWh (756 kJ). To obtain the same crystal yield by evaporating the corresponding amount of solvent at $T_C = 313$ K (2.2 kg) requires 1.4 kWh (4956 kJ), showing the

energy conversion for evaporative crystallization or MaC-MD in this system is over 6 times higher than that for MaC-RO. Note that the difference in solvent removal for the same yield is due to the increased final concentration in the buffer vessel. This difference does not apply for continuous operation, which would further increase the difference in energy conversion. It should be noted, however, that because of the steep dependency of the solubility of adipic acid on temperature, cooling crystallization would be applied for this system in favor of evaporative crystallization. Comparing the energy conversion of MaC-RO with cooling crystallization, however, is not trivial since cooling crystallization inevitably leads to different mass streams. Since also cooling does not involve the energy intensive liquid vapor phase change, it is expected that cooling crystallization performs competitive from an energy point of view. Generally, cooling crystallization requires less investment costs, as the high pressure RO system is avoided. The MaC-RO process on the other hand, has the additional benefit of being efficient in treating feed streams available at low temperatures and with a low solute concentration, leading to higher yields per volume of solvent. MaC-RO could also be combined with cooling crystallization, where the membrane process can increase the product yield, either by in-situ removal of the solvent or recovering of product from the waste stream.

Finally, it should be noted that the objective functions used in the optimizations did not contain any elements regarding capital costs. For the design of a real-life process, a trade-off has to be made involving product quality, and energy and investment costs. Whichever is more important is often case specific. However, the proposed models and methods in this work can easily be extended to optimize other specific cases.

10.5 Conclusions

The membrane performance in a MaC-RO process of adipic acid has been assessed and the feasibility of the MaC-RO process has been investigated by dynamic optimization of final mean size with minimal energy conversion.

A MaC-RO setup has been designed and constructed, which can be operated at pressures upto 40 bar, while maintaining an elevated temperature in the membrane module as compared to the crystallizer temperature.

High selectivities were obtained for water removal from an adipic acid solution, justifying the assumption of pure water permeation for mass transport modeling. The

water flux from a pure water feed and adipic acid solutions is well described by a model, correlating the flux to the pressure difference over the membrane and the osmotic pressure on the membrane retentate side (equation 10.17) using three fitting parameters. The temperature effect can be described by an Arrhenius type equation, using the apparent energy of activation as fitting parameter. The decrease in permeance in the presence of adipic acid can be described by assuming competitive Langmuir adsorption of adipic acid and water on the membrane surface, decreasing the effective surface area for water transport, and, to a lesser extent by polarization effects.

Dynamic optimization of final mean size with minimum energy conversion by manipulating the operational policy of the batch MaC-RO process reveals that different operational policies can approximate the ideal supersaturation profile very closely. This indicates the MaC-RO system has a high degree of flexibility for design and control. The optimal operational policy was obtained by performing two consecutive optimization, yielding a maximum mean size and, subsequently, minimum energy requirements. The found optimal operational policy operates the system at maximum pressure difference across the membrane. The flow rate between the membrane and the crystallization vessel is used to deliver the optimal amount of supersaturation to the crystal population. The concentration at the membrane surface can be constrained to prevent scaling and osmotic pressures exceeding the pump pressure. As this is easier in moderately soluble substances with a strong temperature dependency of the solubility, such as adipic acid, these systems are most attractive for the MaC-RO process.

The energy conversion of the optimized system is 6 times lower for MaC-RO compared to evaporative crystallization or MaC-MD, while approximating the ideal supersaturation profile very closely.

This study demonstrates the potential of the MaC-RO concept to reduce energy conversion and improve control over crystalline product quality. Future studies will focus on conducting crystallization experiments using the constructed setup to verify the modeling results and on determining the operating window of the MaC-RO process.

List of symbols.

symbol	name	unit
A	membrane surface area	m^2
B_0	nucleation rate	$\text{m}^3 \cdot \text{h}^{-1}$

List of symbols. (continued)

symbol	name	unit
c	total molar concentration	$\text{mol}\cdot\text{m}^{-3}$
c_i	concentration of component i	$\text{mol}\cdot\text{m}^{-3}$
$\mathcal{D}_{ij}$	diffusivity of i in j	$\text{m}^2\cdot\text{s}^{-1}$
E	energy conversion	kWh
E_{app}	apparent activation energy	$\text{J}\cdot\text{mol}^{-1}$
E_A	activation energy for diffusion	$\text{J}\cdot\text{mol}^{-1}$
F	volumetric flow rate	$\text{m}^3\cdot\text{h}^{-1}$
K_{ij}	solubility of i in j	—
K_0	Langmuir adsorption parameter	$\text{l}\cdot\text{mol}^{-1}$
L	crystal growth length coordinate	m
l_{geo}	geometric length	m
M_i	molar mass of component i	$\text{kg}\cdot\text{mol}^{-1}$
m_i	i^{th} moment	$\text{m}^i\cdot\text{m}^{-3}$
N_i	flux	$\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ $\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$
n	density distribution	—
P	pressure	Pa
P_l	permeance	$\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$ $\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$
$P_{0,i}$	pre-exponential factor	$\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$ $\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$
R	ideal gas constant	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
R_i	retention factor of component i	—
T	temperature	K
t	time	h
V	volume	m^3
$v_{0,i}$	partial molar volume	$\text{m}^{-3}\text{mol}^{-1}$
w	weight fraction	—
x	molar fraction	—
z	length coordinate	m
β	scaled nucleation rate	h^{-4}
$\Delta\pi$	osmotic pressure	Pa
$\Delta_s H_{ij}$	enthalpy of solution of i in j	$\text{J}\cdot\text{mol}^{-1}$
δ	effective boundary layer thickness	m
ε	liquid fraction	—
γ_i	activity coefficient of component i	—
ρ	density	$\text{kg}\cdot\text{m}^{-3}$
χ	scaled moment	
sub and super scripts		
B	buffer vessel	
C	crystallizer	
M	at membrane surface	
P	permeate	
R	retentate	
i	in	
o	out	
w	water	

List of symbols. (continued)

symbol	name	unit
AA	adipic acid	
eff	effective	
tot	total	

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Curriculum vitae

Jelan Kuhn was born in Amsterdam, the 9th of June 1980. After finishing his high school (HAVO) at the Lek & Linge College in Culemborg he started the bachelor Chemical Engineering at the HTS Chemische Technologie of the Hogeschool van Utrecht in 1997. During this education he did internships at Akzo Nobel Catalysts (now Albemarle) in Amsterdam, Bammensgroep S&T in Maarssen, and Akzo Nobel Central Research in Arnhem.



After completing the study in 2001 he decided to further develop in the field of chemical engineering, by following the Master of Science program in Chemical Engineering at the Eindhoven University of Technology. He obtained his MSc degree in 2004, after doing a graduation assignment in the Process Development group on multi-phase flow in ceramic membranes. In 2004 he started his PhD project at the Delft University of Technology within the Delft Center for Sustainable Industrial Processes (DCSIP). He worked at the Process & Energy Department of the faculty 3ME and the Ceramic Membrane Center, The Pore, of the faculty TNW. During the project he has coached 8 MSc students, 6 BSc students, and 2 interns. The research results described in this thesis have been published in various international journals and presented at various refereed conferences in the field of chemical engineering, zeolites, and Membrane technology.

Since March 2009, Jelán is employed at the BASF in Ludwigshafen, where he is part of the Membrane Team of the GCT/C Process Engineering department.

List of publications

Papers

J. Kuhn, K. Yajima, T. Tomita, J. Gross, and F. Kapteijn

Dehydration performance of a hydrophobic DD3R zeolite membrane

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J. Kuhn, M. Motegh, J. Gross, and F. Kapteijn

Detemplation of [B]MFI zeolite crystals by ozonation

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J. Kuhn, J. Gascon, J. Gross, and F. Kapteijn

Detemplation of DDR type zeolites by ozonation

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Membrane assisted crystallization
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