MASTER'S THESIS

Modification of Silicalite-1 Membranes

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ABSTRACT

In this work Silicalite-1 films were prepared on porous α-alumina micro filtration filters acting as a support using the "seed film method". The films were modified using an aqueous solution of $Ca(NO_3)_2$ in order to obtain a carbon dioxide (CO_2) selective membrane. Two different modification procedures were developed in the present work. The procedures are denoted "evacuation" and "spinning technique".

Single gas permeation and n-hexane porosimetry were used for the characterisation of the membranes. CO_2, nitrogen (N_2), helium (He) and hydrogen (H_2) were used as probe molecules in single gas permeation experiments. n-Hexane porosimetry was used to determine the amount of defects in the membranes. Both modified and unmodified samples were characterized using these techniques.

It was found that a high concentration of $Ca(NO_3)_2$ deteriorated the membrane quality according to porosimetry data. The $CO_2/(H_2, N_2$ or He) permeance ratios became slightly higher after modification of samples modified with a lower salt concentration. However, no significant difference between the two modified methods could be observed with respect to CO_2 selectivity.

It may be thus concluded that CaO was not optimally deposited in the silicalite-1 film. EDS and SEM analysis showed the concentration of Ca varied on the surface but was distributed without aggregates.

1. INTRODUCTION

Approximately 95% of the hydrogen production originates from hydrocarbon raw material. The hydrogen mainly is used as a chemical feedstock for petrochemical, food, electronics and metallurgical industries. Only a small fraction of the produced hydrogen is used as an energy source. It is believed that the implementation of fuel cell systems [1] will increase this fraction. Thus in the future hydrogen may be a valuable energy source.

Hydrogen production processes are confronted with the separation the hydrogen from other gases such as CO_2. However hydrogen separation has high demands on the materials available today such as thermal, solvent and chemical stability [2]. Separation of hydrogen using membrane technology is currently based on Pd alloys or organic polymer membranes. Due to material limitations, organic membranes are not able to fulfil all the requirements the processes.

The usage of inorganic molecular sieves, such as zeolites, would provide a chemically and mechanically stable membrane. Thin zeolite membranes possess high fluxes properties in addition to the shape selectivity of the zeolite compared with organic membranes. Furthermore, zeolites show high thermal stability necessary for long-term separations at elevated temperatures [3]. Hence, zeolite based membranes would possess several advantages over organic polymer membranes.

2. LITERATURE SURVEY

2.1 Zeolites

Zeolites are porous crystalline aluminosilicates. The three-dimensional zeolite network consists of SiO_4 and AlO_4^- terahedra linked together by sharing oxygen atoms [4].

Zeolites may be described with the followings empirical formula:

$$M^{n+}_{2/n} \cdot AlO^-_2 \cdot xSiO_2 \cdot yH_2O \quad [3]$$
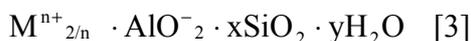
where   M - counterion
              n - counterion valence
              x - silicon/aluminium ratio
              y - content of hydrate water

The aluminium in the zeolite framework renders a negative charge of the framework and this has to be compensated. The counterion may be a metal-, ammonium- or alkylammonium cation. These cations can be replaced by ion exchange.

Zeolites are divided into different structure type groups, which are different in channel geometry [6]. The channels can be elliptical, circular, tubular or contain periodic cavities, straight or zig-zag. The pore structure in zeolites is determined by the framework, composition and cation presence [5]. Zeolites pore sizes are in the range of 3-10 Å. Hence, zeolites are microporous materials according to IUPAC classification.

MFI, A and FAU types are the most common structures in research and industry. The channels in the MFI structure are formed by five-member ring building units linked together (Figure 1.1) [7]. These building units render a framework of sinusoidal channels in the a-direction and straight channels in the b-direction with slightly elliptical pore openings.
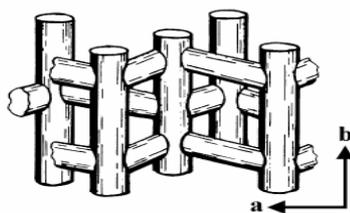

Figure 1.1. The MFI channel system with crystallographic axis.

Two well-known MFI structures are silicalite-1 and ZSM-5. The difference between them is the aluminium content. ZSM-5 has Si/Al ratio in the range 10-200 [8], when this ratio is more then 200 the material is denoted silicalite-1. Silicalite-1 is a structural analogue to the ZSM-5 zeolite, but due to the fact that silicalite-1 does not contain aluminium or only very small amount this material should only strictly be regarded as a molecular sieve and not as a zeolite.

Zeolites are used in many applications due to its material properties. Examples are ion-exchangers, catalysts, adsorbents and to a small extent as molecular sieve membranes. Thin zeolite films may have a large potential to be used as sensors [7, 9] due to the molecular dimensions of the pores of the zeolites and the ability to adsorb molecules.

For a zeolite based catalyst there are three main shape selective effects:

1. Reactant selectivity: molecules in the feed stream are too large to diffuse into the zeolite pores and react [5].

2. Product selectivity: as above but applicable to product molecules.

3. Restricted transition selectivity: large intermediate compounds will not form due to the limiting pore size [5].

In general, hydrophobicity and thermal stability increases with an increase of the Si/Al ratio, while catalytic activity and ion exchange capacity is decreased. However, the catalytic properties may be undesired in some applications. For instance, when the aim is to separate components, catalytic properties may be detrimental since undesired reactions may occur.

In this work, silicalite-1 membranes were prepared intended for hydrogen and carbon dioxide separation. These show low catalytic activity and inability to ion exchange. Silicalite-1 is also more effective for adsorption of organic molecules than ZSM-5 due to the hydrophobicity of the silicalite-1 material.

2.2 Zeolite membranes

2.2.1 Overview

A membrane is an active or passive barrier for transport of species [10]. A zeolite membrane may be described as a polycrystalline zeolite layer that is able to separate mixtures by adsorption, diffusion or by molecular sieving. Very thin zeolite films are too fragile to be self-supported. Thus the zeolite layer is therefore commonly deposited on discs or a porous support. These supports are usually flat discs or tubular shaped.

A wide range of support materials is available. Examples are amorphous silica, silicon wafers, glass precoated with active silica, aluminium platelets, steel-wool sintered steel composites, porous ceramics, porous α-Al_2O_3, γ-Al_2O_3 membranes, or macroporous α-Al_2O_3 coated by layer of mesoporous γ-Al_2O_3.

The term "good quality" membrane includes high separation factors and permeances, which in practice implies that the zeolite film should be thin and free from defects. The support should also not impose a significant flux resistance that reduce the permeance.

2.2.2 Preparation

2.2.2.1 Preparation of zeolite films membranes

The general preparation procedure involves three main steps [10]:

1. Pre-treatment of the supports in order to clean and/or modify the surface. The support is usually treated with acid, alkali or in an oxidising medium. In some cases aluminium may leach from the support and may thus be incorporated in the zeolite structure during the synthesis. In order to avoid leaching of material the support may be protected using a masking technique [11].

2. The second step involves a synthesis procedure, where a thin layer crystallizes on the top or inside the pores of the support by a hydrothermal treatment of the support in an appropriate synthesis solution. The composition of the synthesis mixture that generally contains a silicon and aluminium source varies depending on the preparation method and zeolite. The structure-directing agent promotes the formation of the zeolite framework.

3. For small pore zeolites, the template is removed by calcinations. This procedure renders the pore structure available for catalytic processes, adsorption, ion exchange and diffusion [12].

The synthesis (2) may be conducted by the main procedures listed below:

- Direct crystallisation (in-situ synthesis): nucleation, crystallisation and film growth occur simultaneously during the hydrothermal treatment.

- Dry gel conversion uses a gel containing necessary components for crystallization. An alumosilicate source is contacted with the support and the crystallization takes place in vapour phase.

- In the wash coating procedure the zeolite coating is deposited on the support from a wash coat solution. The solution contains a binder based on alumina and silica. After the wash coating, support is calcined in order to bond the crystalline material to the support. The binder material distributes the zeolite film uncontinuously on the support surface and also reduces the size of the openings of the zeolite pores. This reduction increases mass transfer resistance in certain applications.

-New methods for preparation of thin films are the seeded growth methods. Small crystallite crystals, attached to the support are hydrothermally treated in appropriative synthesis solution to form a thin continuous layer.

In the present work silicalite-1 membranes were prepared using a seeded growth method [14, 15], on porous α-alumina disc acting as supports. The membranes were characterised and evaluated using single gas permeations and n-hexane porosimetry measurements.

2.2.2.2 Modification of zeolite membranes

Zeolites can serve as hosts for small metal clusters, metal oxides or sulphides. A metal containing modifying agent can passivate the external surface and control the pore opening size of the zeolite. The pore structure of zeolites may be modified by numerous methods, such as ion exchange and impregnation.

Ion exchange is a reversible chemical reaction, in which ions may be exchanged between two interacting phases. Ion exchange shows high and even dispersion. In case of silicalite-1 material the impregnation method is the most appropriate, since silicalite-1 has a low ion exchange capacity. Even though the method may yield large metal particles in the zeolite material.

The impregnation technique may be classified into two methods [6]. In the first method the sample is submerged into an excess quantity of modifying solution. A more accurate way to modify is to spray the sample with the solution. The volume should preferably be slightly less then what is needed fully wet the material. Unfortunately this method is inappropriate for thin zeolite membranes, due to the difficulty of adding the liquid in a proper amount. The second method is to place the sample into a vessel in most cases under vacuum with an aqueous metal salt solution of known concentration [16-20]. By varying the initial concentration of the salt solution the metal content in the final catalyst may be controlled. The solvent is removed by evaporation and finally the as-modified materials are calcined.

In the present work, samples were modified by the impregnation technique with a $Ca(NO_3)_2 \cdot 4H_2O$ solution in order to achieve a CO_2 selective membrane. The CaO,

obtained after calcinations, in the pore structure would cause partial or full blockage of the pores, depending on the concentration and dispersion of initial modifying solution. The gas permeances will be affected by the CaO. Since the CO_2 is able to chemisorb on CaO and form $CaCO_3$. Thus it is possible for CO_2 to permeate through the pores.

2.2.3 Defects and characterisation of defects

Defects in zeolite films are in general classified as microscopic or macroscopic defects. Defects, with a size exceeding 500 Å are classified as macro-defects. These defects are probably formed during the calcination of the as-synthesised material when the template molecules are combusted [10]. It is believed that this procedure causes a compression tension and expansion in the zeolite film [22]. Incomplete/uneven seeding and insufficient hydrothermal treatment may also result in macroscopic defects. Meso-sized defects (within the range of 20-500 Å) and intra crystalline defects (with size < 20 Å) are probably formed during the preparation procedure.

The amount of defects in the zeolite film may be estimated with n-hexane porosimetry. Porosimetry is based on measuring the flow of a noncondensable gas as a function of partial pressure of a condensable species (such as n-hexane) [14, 23]. A helium flow through the membrane is induced with an absolute pressure difference. The flow of pure helium (p/p_0=0) is the sum of permeances through both micropores (zeolite) and larger pores (defects). A condensable vapour, such as n-hexane, is subsequently mixed with He at a low partial pressure (i.e. p/p_0=0.025). The n-hexane adsorbs in the smallest pores and results in a blockage of He flow through the zeolite pores. If the partial pressure of n-hexane is increased further, n-hexane continues to occupy the zeolitic pores and reduce the He flow through the membrane by condensing in lager pores and blocking those for helium transport. Thus a flow of He through the sample indicates an imperfectability of the membrane at higher partial pressures of n-hexane.

2.3 Application of zeolite membranes

Modified zeolite films may be used in gas separation processes. For instance metal incorporated membranes may be used in hydrogen recovery from industrial processes. Steam reforming of natural gas or hydrocarbon materials, is today the most economical way for hydrogen production. The process is a series of chemical reactions where the final product is a mixture of hydrogen and carbon dioxide. current processes, CO_2 is removed from the product by adsorption. The hydrogen may be a very important energy source in the future since fuel cells are developed as an alternative to the ordinary gasoline engine. However fuel cells requires very pure hydrogen for a long time usage. Thus zeolite membranes are interesting candidates for accomplish this task due to their material properties.

3. EXPERIMENTAL PART

3.1 Preparation

Zeolite films were prepared on asymmetric porous α-alumina discs with a diameter of 25 mm from Inocermic GmbH. The supports have a large-pore body (3 μm pore size) with 3 mm thickness and small pore (100 nm pore size) top layer with 30 μm thickness.

At the division of chemical technology at Luleå University of Technology a new method for preparation of thin zeolite membranes has been developed. The method includes a protection of the support prior to the synthesis of the zeolite film. The idea of the masking step is to reduce the leaching of aluminium from support material and undesirable growth of zeolite material inside the pores of the support. Growth of zeolite species in the interior of support increases the mass transfer resistance and is belived to facilitate the defect formation during calcination [13, 14]. The membranes were prepared as described in [13] and outlined below (Figure 3.1)

3.1.1 Masking technique

The supports were initially rinsed with acetone and filtered (0.1μm) ethanol, and subsequently dried at 200°C. After drying the samples were cooled to room temperature. A mixture of polymethylemetacrylate (PMMA) dissolved in acetone was applied on the top layer of the substrate (A). This layer will protect the surface from wax deposition during the procedure. The viscosity of the PMMA/acetone solution also inhibits the penetration into the porous support. The PMMA coating is subsequently dried at room temperature overnight and heated with 1°C/h at atmospheric pressure to the final temperature of 150°C.
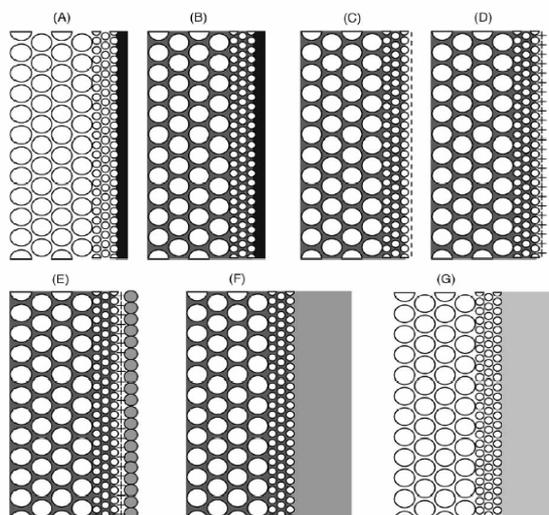

Figure 3.1. The top surface of the porous support is coated with a PMMA layer (A). The porous support is then filled with wax (B). Afterwards the PMMA is dissolved in acetone leaving one surface available for seeding(C). The masked substrate is then treated with cationic polymer solution (D) and to facilitate electrostatic seed adsorption (E). The seeded substrate is hydrothermally treated and the seeds crystals are grown into a dense continuous film (F). The samples are calcined in order to remove the wax, cationic polymer and template molecules from the sample (G).

At 150°C the PMMA coated substrates were impregnated with molten polyethylene wax (B) (melting point 120°C) under vacuum. The PMMA coated surface was facing downwards during the process. The pressure was increased to

atmospheric after 1h and the supports were wiped with paper to remove the excess of wax from the external surface and cooled to room temperature. The substrates were finally rinsed in acetone for one week in order to remove the PMMA top layer in order to obtain one surface available for seeding. The acetone was changed at least once a day.

3.1.2 Seeding

The supports were rinsed in ethanol in order to remove dust and then five times in a filtered (0.1μm) 0.1 M NH_3 solution. A filtered (0.8 μm) cationic polymer solution (0.4% Redifloc 4150, Eka Chemicals AB, Sweden) of pH=8.0 was added for 10 min in order to obtain positively charged surface (D). In order to remove the excess of polymer solution the substrates were rinsed in a filtered (0.1μm) 0.1M NH_3 solution. The supports were subsequently immersed in a silicalite-1 seed sol, prepared according to Persson at al, [27]. The negatively charged seed crystals were thus adsorbed by electrostatic forces on the support surface (E). The samples were finally rinsed five times in a filtered (0.1μm) 0.1M NH_3 solution in order to remove the excess of seeds.

3.1.3 Hydrothermal treatment

The seeded supports were placed in polypropylene tubes almost vertical to avoid gas accumulation on the support surface due to the boiling of the synthesis solution during hydrothermal treatment. The seeded surface was facing downwards to avoid sedimentation of crystals on the growing film surface. The hydrothermal treatment was conducted at 100°C for 30 h in a clear synthesis solution with the following molar composition $3TPAOH:25SiO_2:1500H_2O:100EtOH$ (F).

After cooling, the samples were rinsed in a 0.1M ammonia solution. The coated membranes were calcined at 500°C for 6 h using heating rate of 0.2°C/min and a cooling rate 0.3°C/min (G).

3.2 Permeation measurements

3.2.1 Porosimetry

n-Hexane porosimetry was used to characterize the size and amount of defects and estimate the contribution of micropores to the overall flux through the membrane [8, 28]. A principal scheme of the porosimetry unit is illustrated in Figure 3.2. The membrane is placed in the stainless steel cell (Figure 3.3). Graphite gaskets with an inner diameter of 19 mm were used for sealing. Prior to measurement, the membrane was heated to 300ºC overnight in order to remove adsorbed compounds in the zeolite. The feed to the membrane was controlled by two mass flow controllers (MFC), which were used to adjust the relative pressure of the hydrocarbon present in the saturators. Pure He ($p/p_0=0$), partially saturated He ($0<p/p_0<1$) or fully-saturated He ($p/p_0=1$) was applied to the. A condenser, connected on the permeate side of the membrane, removed most of the condensable species from thepermeate prior to flow measurement. The flow through the membrane was measured using a soap bubble flow meter.
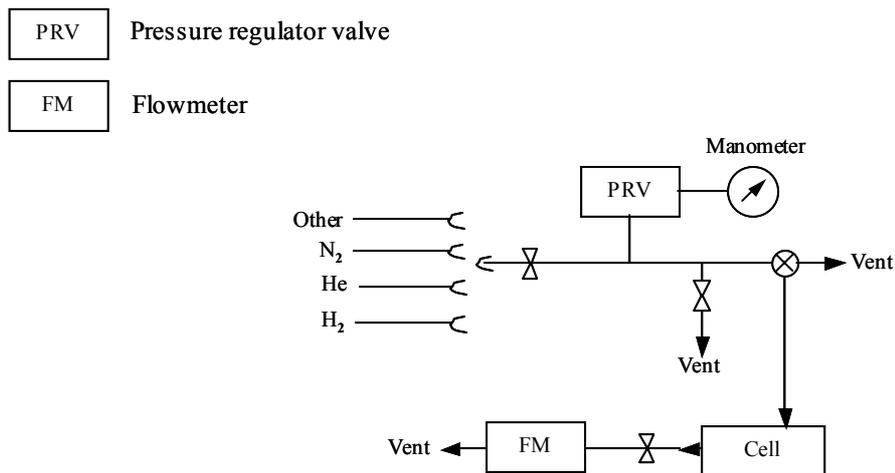
Figure 3.2. Porosimetry unit.

Figure 3.3. Stainless steel cell for porosimetry measurements.

Figure 3.4. Stainless steel cell for single gas permeation measurements.

3.2.2 Single gas measurements

Single gas experiments were carried out after calcination or drying of the samples. A schematic of the permeation unit is illustrated in the Figure 3.4 [18]. The membranes were removed from the furnace at 110°C after the calcination or drying procedure and mounted in a stainless steel cell (Figure 3.4) under a flow of dry nitrogen. This procedure prevents moisture adsorption from the surrounding air. Rubber gaskets with inner diameter 22 mm were used for single gas experiments at room temperature, and graphite gaskets were used for measurements at elevated temperatures (up to 300°C). For measurements at elevated temperatures the cell was placed in to a heating mantle equipped with a temperature controller.

The feed pressure was varied in the range from 0.5 to 2.0 bar absolute pressure in order to reveal any adsorption effects. The permeate was kept at 1 bar absolute pressure and the flow was measured with a soap bubble flow meter. Helium, nitrogen, hydrogen and carbon dioxide were used as probe gases.

Figure 3.5 Single gas permeation unit.

3.4 Membrane modification

The modification was carried out using two different techniques described below. Prior to modification the membranes were calcined at 500°C with a heating and cooling rate of 1°C/min. Initially, the membranes were cooled in air and later in a dry nitrogen atmosphere.

3.4.1. Modification by evacuation technique

Membranes modified with the evacuation technique were either:
- removed from the furnace at 110°C and submerged into a preheated (100°C) water solution of $Ca(NO_3)_2 \cdot 4H_2O$.

- removed from the furnace at 25°C and immersed into a modifying solution at room temperature. The membrane was placed in a plastic tube, containing the modifying solution, with the film surface downwards. The samples were impregnated under vacuum at room temperature to obtain the salt inside the pores of the zeolite. However, the modifying solution was also transferred into the porous support. The membranes were subsequently rinsed in distilled water, dried and calcined to form CaO.

3.4.2. Modification by spinning technique

The membranes were also modified with spinning technique. A stream of dry nitrogen was fed to the beaker that contained the membranes during the calcination. This in order to prevent adsorption of unwanted species such as water in the zeolite during cooling after the calcination. When the temperature in the furnace reached 25°C, the beaker was removed from the furnace. A few drops of $Ca(NO_3)_2 \cdot 4H_2O$ solution were placed on the top surface of the dry membranes. The membranes were immediately spinned at 10 000 rpm to obtain an even distribution of salt in the zeolite film and to remove the excess of water from the membrane surface. The samples were finally calcined in order to obtain the CaO modified structure.

3.3 Additional membrane characterisation

A Philips XL 30 Scanning electron microscopy (SEM) equipped with a LaB_6 electron emission source was used to study the film morphology. The samples were fixed on aluminium holders using conductive carbon glue and coated with a thin layer of gold prior to investigation. EDS data were recorded with an Oxford Instruments ISIS Ge energy dispersive X-ray detector attached to the SEM.

4. RESULTS AND DISCUSSION

4.1 The evacuation technique

Table 4.1. Summary Table of modified membranes. Membranes superscripted with 1 were immersed in preheated solution (100°C) and impregnated at 25°C.

Sample	Modification technique	Concentration of $Ca(NO_3)_2 \cdot 4H_2O$, wt. %	Temperature of modification, °C
FCJ10[#]	Evacuation	5	100/25[1]
FCJ9[#]	Evacuation	10	100/25[1]
LCV26[#]	Evacuation	distilled water	25
LCV27[#]	Evacuation	1	25

Table 4.1 gives the modification procedure for samples LCV27, FCJ9 and FCJ10. FCJ9 and FCJ10 were removed from the furnace at 110°C and immersed in a preheated solution (100°C) whereas LCV27 and LCV26 were removed from the furnace at room temperature. LCV26 was treated in the same way as LCV27 with the difference that no salt was added only distilled water. The evacuation was carried out at 25°C for all samples. Figure 4.1 shows that the porosimetry pattern before and after modification of LCV27 is very similar. It can thus be concluded that no significant mount of defects were formed after modification and calcination of LCV27 according to porosimetry data. FCJ9 and FCJ10 became very defective after the modification according to the porosimetry data shown in Figure 4.2. Unfortunately the sample labelling disappeared from FCJ9 and FCJ10 during the modification treatments. Thus FCJ[#2] in the figure 4.2 denotes either the modified FCJ9 or FCJ10. SEM images showed that both the zeolite film and the support cracked during the process. Parts of the zeolite film dissolved or peeled off during the treatment. However, it hasn't been investigated in which step the defect formation occur. The defects may be formed during immersion into the modification at 100°C and/or during the calcination. Large crystals were found in the cracks within the support. These crystals were probably CaO or $Ca(NO_3)_2$. Thus it is possible that the high concentration resulted in a too large amount of salt in the zeolite or in the pores of the support, which resulted in crack formation during calcinations.
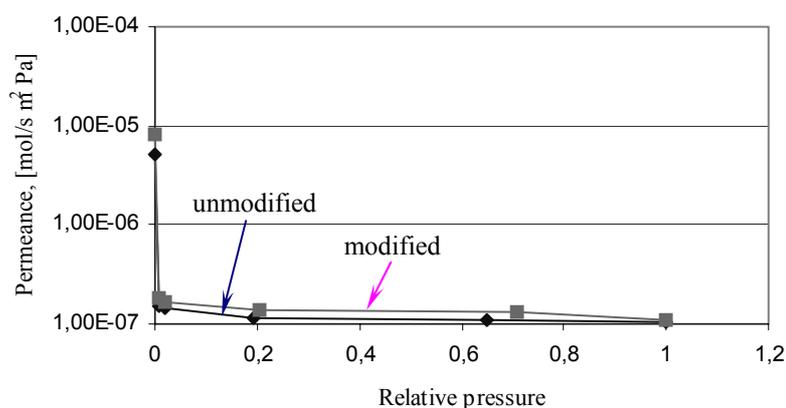

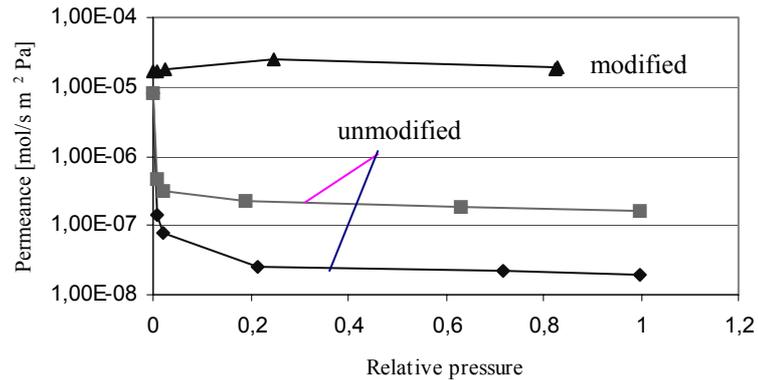Figure 4.1 Porosimetry data for LCV27, modified with evacuation technique

Figure 4.2 Porosimetry data for FCJ10 and FCJ9 membranes.

The results of FCJ9 and FCJ10 indicated that the evacuation method might deteriorate the membranes. In order investigate this LCV26 was modified with distilled water as stated previously. Porosimetry data given in Figure 4.3 indicated that no significant negative effect of the modification was observed. Both LCV26 and LCV27 are of similar quality both before and after modification. Hence, the impregnation of modifying solution into the membrane with the evacuation technique is not the cause of the defect formation in FCJ9 and FCJ10. Thus it is likely that the defect formation in the film and the support was caused by either the high salt concentration in the solution or the immersion of the membranes into the 100°C solution.
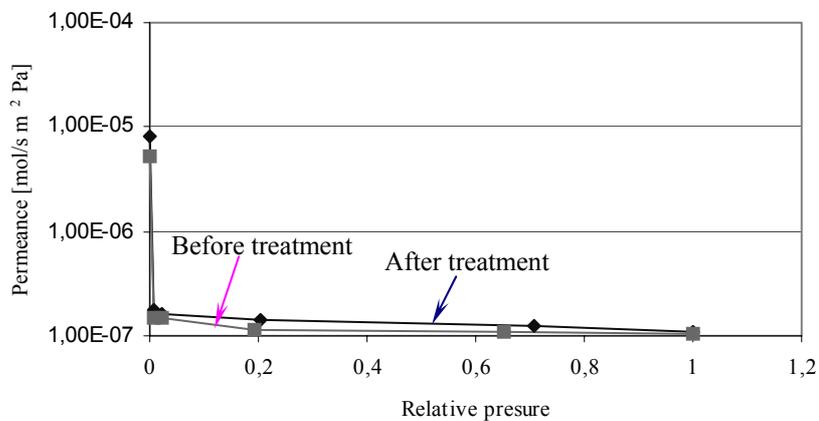

Figure 4.3. Porosimetry data for LCV26, modified evacuated with distilled water at room temperature.

Single gas permeation results for selected samples, modified by the evacuation technique, are given in Table 4.2. As may be seen from the table, modification by this technique did not yield in any obvious changes in the CO_2/H_2 selectivity for sample LCV26 and LCV27. For samples FCJ9 and FCJ10 the ratios decreased and permeances increased after the modification. This indicates that these samples became more defective after the modification procedure. It can be concluded that evacuation technique did not incorporate the proper amount of CaO inside the zeolite pores. This statement is justified by samples LCV26 and 27 that was not significantly affected by the modification procedure. Thus a more effective way to impregnate CaO directly in

the zeolite pores and prevent deposition of CaO in the support material has to be developed.

Table 4.2. Single gas permeation data measured with one bar pressure difference for selected membranes (unmodified and modified by impregnation). Symbols [#1] and [#2] denotes the modified FCJ membranes, since the name labels disappeared during modification treatments.

Sample	H_2 Permeance	Permeance ratios		
	/[10-7 mol/(s m^2 Pa)]	H_2/ He	CO_2/ H_2	CO_2/N_2
FCJ9	242	2.46	0.83	1.27
FCJ10	201	2.4	0.84	1.28
FCJ[#1]	229	1.56	0.29	0.89
FCJ[#2]	254	1.55	0.29	0.87
LCV26	229	2.37	0.64	1.56
LCV26[#]	213	2.28	0.7	1.16
LCV27	225	2.33	0.66	1.17
LCV27[#]	205	2.3	0.72	1.23

4.2 Membrane modification by spinning technique

The spinning technique was developed to obtain a better deposition of salt into the zeolite pores in order to avoid penetration of salt into the support as discussed previously.

Dry membranes were modified by the spinning technique as described in the experimental part. Samples were impregnated using a solution with a lower concentration of $Ca(NO_3)_2$ (1 and 2 wt. %), than in previous experiments. This to avoid cracking of the zeolite film caused by to the formation of large CaO crystals during calcinations. Table 4.3 gives a summary of the modification conditions uses for selected samples.

Table 4.3. Summary Table of modified membranes

Sample	Modification technique	Concentration of $Ca(NO_3)_2 \cdot 4H_2O$, wt. %	Temperature of modification, ^0C
LCV26[#*+]	ET+ST	0 ÷ and 2	25
LCV27[#*+]	ET+ST	2	25
LCV28[*]	ST	1	25
LCV28[**+]	two step ST	2	25

[+]- cooling in N_2 atmosphere after calcination

It should be mentioned that the zeolite can preferentially adsorb water from the modifying solution. Thus the Ca will probably remain at the film top surface. In order to avoid a preferred adsorption of water and to improve the distribution of the modifying solution another solvent such as methanol may be used in the future.

A slightly blue colour was observed after the modification procedure on the top surface on a few samples. A possible explanation to this phenomenon is light scattering in thin films since the only compound that can form during the calcination

is CaO, which has a white colour. Single gas permeation data for selected unmodified membranes and modified with one and two steps are given in Table 4.4.

Table 4.4. Single gas permeation data for selected unmodified membranes and after one and two modifications. Data was collected with one pressure difference.

Sample	H_2 Permeance	Permeance ratios		
	/[10^{-7} mol/(s m^2 Pa)]	H_2/ He	CO_2/ H_2	CO_2/N_2
LCV26	229	2.37	0.64	1.56
LCV26[#]	213	2.28	0.7	1.16
LCV26[#*]	176	2.45	0.74	1.19
LCV27	225	2.33	0.66	1.17
LCV27[#]	205	2.3	0.72	1.23
LCV27[#*]	164	2.58	0/78	1.24
LCV28	238	2.29	0.69	1.21
LCV28[*]	217	2.37	0.69	1.21
LCV28[**]	180	2.53	0.72	1.2

According to Table 4.4 a decrease in permeance was observed. This is probably caused by a partial blockage of the pores or pore openings by CaO. From Table 4.4 it can be seen that the CO_2/H_2 permeance ratio for LCV26, LCV27 and LCV28 increases after the spinning modification.

Membranes LCV24 and LCV22 modified with the spinning technique and with the same concentration of $Ca(NO_3)_2 \cdot 4H_2O$ solution (5 wt.%) (see Table 4.5). The number of modification treatments was one.

Table 4.5. Summary Table of modified membranes with the spinning technique applied once. The samples were cooled down to room temperature in a nitrogen atmosphere.

Sample	Modification technique	Concentration of $Ca(NO_3)_2 \cdot 4H_2O$, wt. %	Temperature of modification, ^{0}C
LCV30	unmodified		
LCV22[*+]	spinning	5	25
LCV24[*+]	spinning	5	25

[+]- samples, marked with this sign was cooled in N_2 atmosphere after calcination

Table 4.6 gives single gas permeation data for LCV22 and LCV24. For sample LCV24 all CO_2/gas permeance ratios increased after modification. The CO_2/H_2 ratio was twice as high after the modification. It was found that the CO_2/gas permeance ratios decreased to the levels of the unmodified membranes after storage at 110°C in air. The permeances were lower than for the unmodified membrane. The porosimetry data for LCV24 before and after modification and storage are given in Figure 4.4. As may be seen from the figure, the membrane is still of high quality.
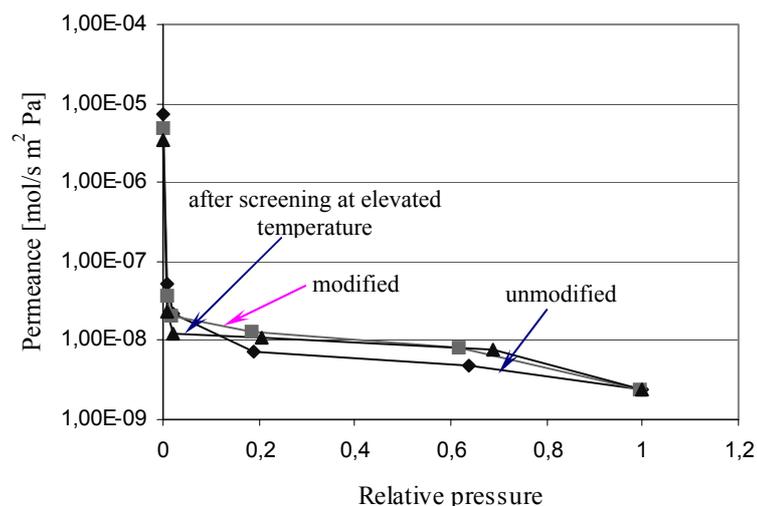
Figure 4.4. n-Hexane porosimetry pattern for LCV24 before and after modification and after testing at elevated temperatures.

Sample LCV22 was modified in the same way as LCV24 in order to reproduce the obtained results. Single gas permeation data for the unmodified samples LCV22 and LCV24, given in Table 4.6 are similar. The CO_2/gas ratios are also increasing after modification for LCV22[*] as for LCV24[*]. However the increases was not as large as for LCV24.

Table 4.6. Single gas permeation experiments at 1 bar pressure difference LCV22 and LCV24, modified with spinning technique. Measurements for LCV24[*t] were carried out at elevated temperature after its storage.

Sample	H_2 Permeance, /[10-7 mol/(s m^2 Pa)]	Ratios			
		H_2/ He	CO_2/ H_2	CO_2/N_2	CO_2/He
LCV22	643	2,27	0.69	0.69	1.57
LCV22[*]	852	2.42	0.86	0.86	2.08
LCV24	701	2,61	0.66	0.66	1.71
LCV24 (after modification)	1995	3.57	1.36	1.36	4.87
LCV24 (after storage)	717	2.34	0.75	0.75	1.75

The effect of the temperature on the membrane performance was investigated by single gas permeation measurements at varying temperatures. The carbon dioxide permeance as a function of temperature for the modified LCV24 and the unmodified LCV30 is given in Figure 4.5. According to the figure, the permeances decreased with increasing temperature. However, no change in selectivity was observed. A possible explanation for these results is the absence of CO_2 chemisorption in the modified material. The chemisorption is necessary in order to obtain a high selectivity of CO_2 over other gases.
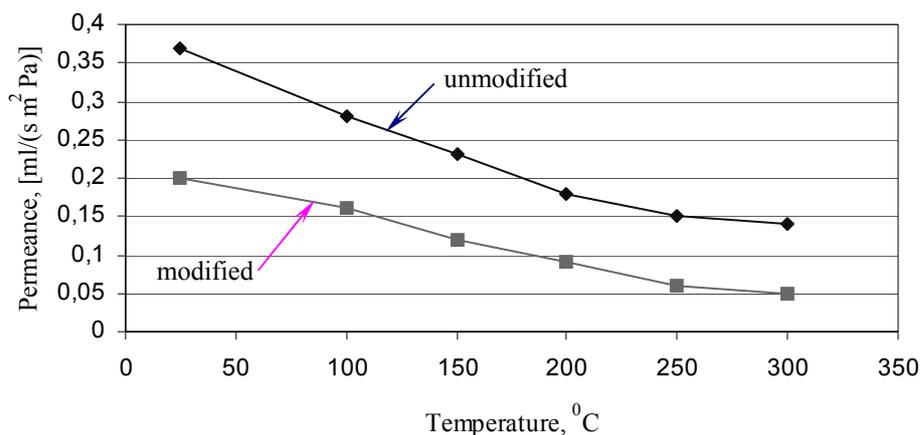
Figure 4.5. CO_2 permeances as a function of temperature for an unmodified (LCV30) and a modified membrane (LCV24).

Scanning electron microscopy (SEM) analysis of the modified membranes showed a smooth silicalite-1 film on the alumina support. Figure 4.6 shows two samples modified with the two techniques: spinning (a) and evacuation (b). According to the figure no pinholes or cracks could be found in the films. No large salt crystals or aggregates could be observed with the SEM. This results is probably due to the low concentration of modifying agent.
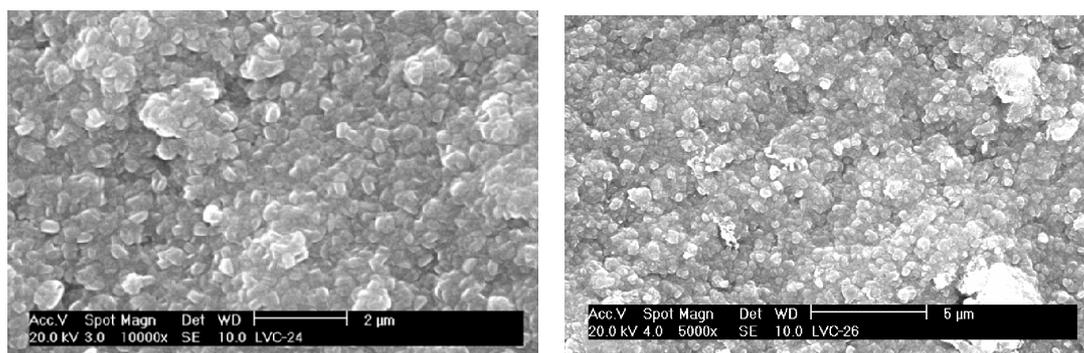
Figure 4.6. SEM images for selected modified membranes (LCV24[*t] and LCV26[*]).

EDS analysis on sample LCV24 after modification, given on Figure 4.7 indicated that a low amount of Ca has been deposited. The concentration of Ca varied depending on position in the sample. It was also found that the calcium was not present as aggregates at specific positions. This result is probably caused by the preparation procedure that might not spread the solution homogeneously. A more controlled modification procedure may provide a better distribution of Ca and probably a higher CO_2 selectivity.
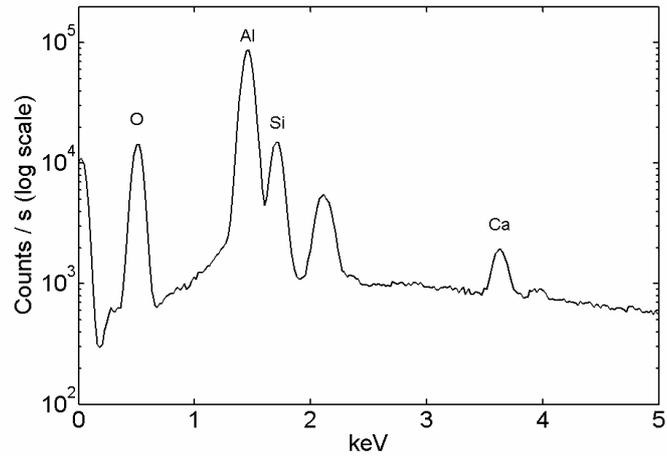
Figure 4.7. EDS data for LCV24[*] with the elements oxygen, aluminium, silicon and calcium indicated

5. CONCLUSIONS

Thin silicalite-1 films were synthesised on alumina supports using the seed film method. The films were modified with $Ca(NO_3)_2$ dissolved in water to obtain a preferential chemisorption of CO_2 on CaO active sites within the zeolite pores. The CaO sites was obtained by calcination of the $Ca(NO_3)_2$. The chemisorption of CO_2 would enhance the CO_2 selectivity over the other gases such as hydrogen.

Single gas permeation measurements were carried out before and after the modification procedure. Permeances of CO_2, H_2, N_2, He, were also measured at various temperatures in order to investigate the transport properties. All unmodified samples had a uniform permeation characteristics and a good quality according to porosimetry.

Two different modification methods of zeolite films were used in the present work: the evacuation technique and spinning technique. No significant change in permeation characteristics between unmodified and modified membranes was found for the two methods. Only a slight increase of CO_2/gas ratios was observed after the modifications.

It was found that the spinning technique was better for modifying the zeolite film compared with the evacuation technique. However more work should be carried out in order to find more suitable modification conditions.

According to porosimetry patterns, no significant changes in the defect distribution of the zeolite film were observed before and after modification. That is the modification techniques are not damaging the membranes unless the concentrations of the modifying species are too high.

A negative effect was observed for one membrane that was stored in air at 110°C. The permeance ratios were similar for the sample that was stored compared with the unmodified membrane It was also found that the permeances were lower than for the unmodified sample and higher directly after modification.

EDS analysis showed that the zeolite film contained Ca. Consequently, the modification techniques described and used in the present work, are useful to impregnate a Ca-containing solution into a zeolite film. However, further work is necessary in order to obtain a high quality carbon dioxide selective membrane.

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