

# **FINAL SCIENTIFIC REPORT**

**High permeance nano porous tubular zeolite membranes for efficient separation of CO<sub>2</sub> and methanol at demanding conditions (HIP NANOMEM).**

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## **Abstract**

In the present project, the overall focus has been upon the development of high flux and high selectivity zeolite membranes sustainable at process conditions and superior in terms of separation of carbon dioxide from other gases as well as water from ethanol. The project was divided into four related parts; Luleå university of technology focused on the synthesis of thin zeolite films onto zeolite and alumina supports prepared by Fraunhofer IKTS, University of Oulu focused on the evaluation of the stability of the membranes under process conditions and modeling of their function, Fraunhofer IKTS delivered all the necessary tubular and disc-type supports made from zeolite or alpha-alumina, and University of Oslo focused on the synthesis of a new zeolite structure with smaller pores and potentially higher CO<sub>2</sub> selectivity in systems containing methane. The most important results were that very good membrane performance was observed for CO<sub>2</sub> separation from synthesis gas, and that the membranes were surprisingly stable for temperature cycling. The first all zeolite MFI membranes in the world were development and successfully tested in the project. A new method for membrane preparation was developed and a patent application was submitted. Small CHA crystals have been prepared for the first time in the project. The cooperation between the different groups of the project will most likely continue because of the successful outcome of the collaboration.

## **Participants**

### **Luleå University of Technology, Sweden;**

Prof. Jonas Hedlund (project manager); Assoc. prof. Allan Holmgren (researcher); Dr. Linda Sandström (PhD student).

### **University of Oulu, Finland;**

Prof. Juha Tanskanen; Jani Kangas (employed as researcher and doing PhD).

### **Oslo University, Norway;**

Prof. Karl Petter Lillerud; Björn Tore L. Bleken (PhD student); Nelli Pfaff (PhD student for a short time in the project); Dr. Zebastian Boström (Post doc.).

### **Fraunhofer IKTS, Germany;**

Dr. Hannes Richter; Gundula Fischer (Researcher).

**Key words:** Zeolite membranes, tubular supports, high flux, high selectivity, long-term stability, CHA zeolite.

## Executive summary

Zeolite membranes with high flux and high selectivity synthesized on porous tubular supports have potential to become important energy saving components in future separation of gases from various industrial processes, such as the separation of CO<sub>2</sub> from H<sub>2</sub> in e.g. the ammonia synthesis or the production of CO<sub>2</sub>-free natural gas or biogas.

A new membrane preparation method suitable for tubular supports was developed at Luleå University of Technology and a patent application was submitted to PRV (Sweden) and US. It was shown that membranes could be synthesized on tubular supports, by this method, but the examination of their separation behavior had to await the construction of a suitable gas-tight evaluation cell. Membrane discs were however tested very successfully and the results have been published. The zeolite membranes exceeded the targeted permeance by a factor 3 and reached 75% of the high targeted selectivity for synthesis gas sweetening (CO<sub>2</sub> separation). This was world record membrane performance and we consider it as a major breakthrough for zeolite membranes, which may open up for commercial applications of zeolite membranes in the future. Membranes were also evaluated for separation of carbon dioxide from synthesis gas obtained from Chemrec's gasifier in Piteå, Sweden and the results have been published. Preliminary and still unpublished work show that also the targeted selectivity in this separation could be reached easily by reducing the operation temperature of the membrane slightly.

In Hermsdorf, the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>-tubes were prepared and these tubes were subsequently coated with ultra-thin zeolite films using the new membrane preparation technique in Luleå. Also, tubular zeolite supports with suitable pore architecture were successfully developed in Hermsdorf. These membranes were successfully evaluated for ethanol separation from water. However, an unexpected problem was encountered with the tubular zeolite supports. It turned out that it was difficult, or perhaps impossible, to develop a good glazing at the end of the tubular zeolite supports. Such a glazing was necessary to arrive at leak free membrane modules. Although numerous different glazing methods were evaluated, the problem was always the same, i.e. the glazing cracked at some stage in the membrane preparation procedure. In summary, tubular zeolite supports with suitable pore architecture were successfully developed in Hermsdorf, but an unexpected problem, i.e. crack formation in the glazing, reduced the performance of the membranes.

The work in Oslo was delayed due to recruitment problems. After much recruitment efforts, a German PhD student, started to work in April 1 2011, but unfortunately quitted quite soon. Finally, a Swedish post doc student was recruited and he started to work in September 2012. Despite the recruitment problems, small zeolite CHA crystals with a size of 500 nm have been prepared for the first time and films with a thickness of 2.5-5  $\mu$ m have been prepared. Manuscripts describing the results are written, but not yet published. Work is on-going to prepare even smaller crystals and thinner films. These films should give good performance in the separation of carbon dioxide from natural gas due to the small pore size of the CHA crystals. In summary, progress towards the goals was obtained in short time, although the work was delayed due to recruitment problems.

In Oulu, an advanced Maxwell Stefan membrane model has been developed and modelling results have been published. It was shown that the model could accurately predict experimental results obtained using  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supported MFI membrane under high pressure H<sub>2</sub>/CO<sub>2</sub> separation

conditions. Consequently, this model could be used to design a real membrane separation process. Temperature cycling tests with the tubular membranes prepared in Hermsdorf have been performed and it has been shown that alumina supported zeolite membranes are surprisingly stable. This is of course important in commercial applications. In summary, the objectives within this sub-project has been very successful in terms of evaluation of alumina supported zeolite membranes, but we have not been able to evaluate the stability of all-zeolite supported membranes due to glazing problems mentioned above.

Overall, the N-INNER project has been very successful. Excellent (world record by far) separation of CO<sub>2</sub> from hydrogen was demonstrated, using  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> disc supported MFI membranes. Development and successful testing of the first all-zeolite supported tubular membranes in the world was performed separating high concentrated ethanol from low concentrated solution. Membranes on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supports were surprisingly stable during temperature cycling, which is important for future commercial application. Small CHA crystals have been prepared for the first time and even smaller crystals could be very useful for membrane preparation of methane from carbon dioxide. In addition, a new method for membrane preparation was developed and a patent application on the method submitted. Ultra-thin tubular zeolite Membranes were synthesized on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> tubes manufactured by Fraunhofer IKTS, using the new method, but data on these membranes have not been published yet due to the requirements concerning patent applications and initial problems with the fabrication of gas-tight modules for testing membranes on alumina supports.

## **Cooperation/networks**

Contributions from other projects/networks funded by national financial agencies as well as EU are gratefully acknowledged. Among these projects, the projects "Zeolitmembraner för effektiv production av biobränslen"(sponsored by the Swedish Foundation for Strategic Research, SSF), Bio4energy (sponsored by the Swedish Energy agency), Zeolite membranes for pervaporation (sponsored by LTU, and the Finnish GSCE), and Zeolite membranes for CO<sub>2</sub> separation (sponsored by the Norwegian GasMax-program) should be mentioned.

## **Mobility**

The present project has arranged meetings in Luleå, Hermsdorf, Oulu, and Oslo, where the progress of the different sub-projects was discussed and the project has educated three PhD students, one of them defending her doctoral thesis (Linda Sandström, High Flux Zeolite Membranes for Efficient Production of Biofuels) within the project. However, the intended mobility of PhD students between the participants could not be realized because of the recruitment problems mentioned above.

## **Workshops**

A number of workshops were organized in order to communicate the latest research results (progress reports). The workshops were usually two-days meetings with 7 to 9 participants in total with participants from all the sub-projects at each meeting. Luleå University of Technology, Sweden

organized the first meeting on the 23-24 of August, 2010. Fraunhofer IKTS, Germany organized the second one on the 14-15 of June 2011 followed by a workshop at Oulu University, Finland on the 04-05 of June 2012. Finally, Oslo University, Norway organized a 1-day meeting on the 6<sup>th</sup> of February 2013. All meetings were very informative and a valuable contribution to the progress of the on-going research activities within the sub-projects. In addition several telephone conferences were held to discuss progress and issues in the project.

## PhD degrees

PhD student Linda Sandström, at Luleå University of Technology, presented her PhD thesis “High Flux Zeolite Membranes for Efficient Production of Biofuels” on the 16<sup>th</sup> of November 2012. In Norway and Finland, the project also educated PhD students. Jani Kangas in Oulu will defend his doctoral thesis in March 2014 at Oulu University.

## Sub-projects

The project was divided into four related sub-projects: Luleå university of technology focused on the synthesis of thin zeolite films onto zeolite and alumina supports prepared by Fraunhofer IKTS (sub-project 1). University of Oslo focused on the synthesis of a new CHA zeolite structure with smaller pores and potentially higher CO<sub>2</sub> selectivity in systems containing methane (sub-project 2). Fraunhofer IKTS developed and delivered all the necessary tubular and disc-type supports made from all-zeolite or alpha-alumina (sub-project 3). Finally, the University of Oulu focused on the stability of the membranes under process conditions and modelling of their function (sub-project 4). In the following, the main results and conclusions from these sub-projects are described in brief. All the results are published unless for a few exceptions, and then it is stated that the results are not published yet.

## Results and conclusions

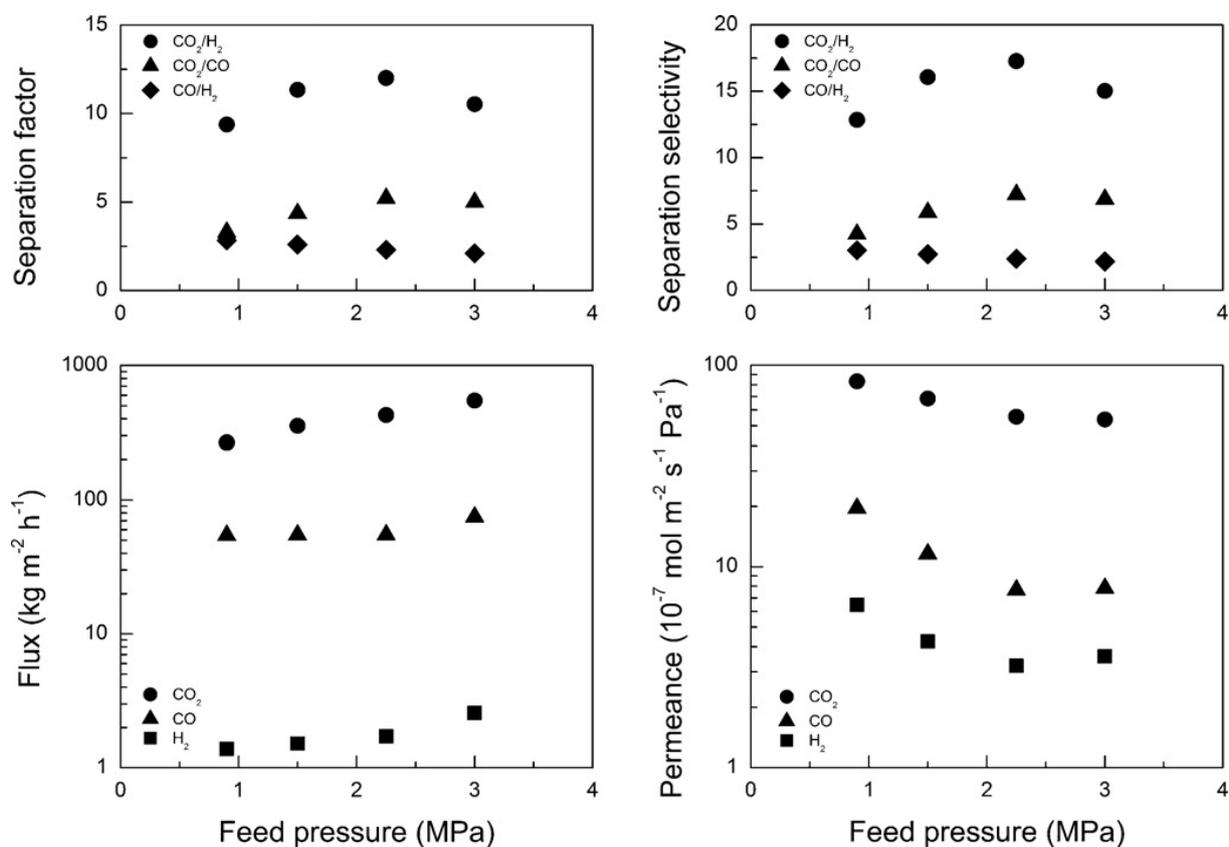
### *1. Very high flux MFI membrane for CO<sub>2</sub> separation*

Synthesis gas is a mixture of mainly CO, CO<sub>2</sub>, H<sub>2</sub> and H<sub>2</sub>O, but the proportions of the components may vary substantially. Biomass derived synthesis gas is an environmentally friendly feed stock that may be used for production of a wide range of products, such as hydrogen, methanol and Fischer Tropsch Diesel via established processes. Natural gas is a mixture of mainly CH<sub>4</sub> and CO<sub>2</sub>. It is often necessary to remove some or all CO<sub>2</sub> from synthesis gas or natural gas, which can be achieved by e.g., water scrubbing, alkanolamine absorption, pressure swing adsorption, cryogenic separation or membrane separation [1].

In this project, it was found that membrane separation of CO<sub>2</sub> from synthesis gas, natural gas or biogas may be a simple and energy efficient alternative to other separation techniques. In this work, membranes comprised an about 0.7 μm thick MFI film on a graded alumina support was used to separate mixtures of CO<sub>2</sub>/H<sub>2</sub>, CO<sub>2</sub>/CO/H<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> gas at high pressure. The membranes were prepared on masked supports. The single gas permeance of H<sub>2</sub> was larger than that of CO<sub>2</sub>, but for a

binary CO<sub>2</sub>/H<sub>2</sub> mixture, the H<sub>2</sub> permeability was blocked and the membrane was CO<sub>2</sub> selective. A CO<sub>2</sub> flux as high as 657 kg m<sup>-2</sup> h<sup>-1</sup> was observed at room temperature, 3000 kPa feed pressure and 600 kPa permeate pressure. Under these conditions, the CO<sub>2</sub>/H<sub>2</sub> separation factor was 16.2. The maximum CO<sub>2</sub>/H<sub>2</sub> separation factor was 32.1, and was observed at 1000 kPa feed pressure, a permeate pressure of 200 kPa and a temperature of 275 K. Under these conditions, the CO<sub>2</sub> flux was still as high as 332 kg m<sup>-2</sup> h<sup>-1</sup>. The highest measured CO<sub>2</sub> permeance for the binary CO<sub>2</sub>/H<sub>2</sub> mixture was 93 × 10<sup>-7</sup> mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup>. The membrane was also CO<sub>2</sub> selective for a CO<sub>2</sub>/CO/H<sub>2</sub> mixture. However, both the CO<sub>2</sub> flux and the CO<sub>2</sub>/H<sub>2</sub> separation factor were reduced slightly in the presence of CO, probably as a result of competing adsorption between CO and CO<sub>2</sub>. The CO<sub>2</sub>/CH<sub>4</sub> separation factor was much lower than the CO<sub>2</sub>/H<sub>2</sub> separation factor, probably because of competing adsorption between CO<sub>2</sub> and CH<sub>4</sub> in the first case. The highest measured CO<sub>2</sub>/CH<sub>4</sub> separation factor was 4.5. The results show that MFI membranes are promising candidates for separation of CO<sub>2</sub> from synthesis gas, natural gas or biogas. The very high CO<sub>2</sub> fluxes likely result from a combination of several factors such as: low film thickness, a fully open graded support, high CO<sub>2</sub> pressure in the feed resulting in saturation of the zeolite at the feed side, relatively high CO<sub>2</sub> diffusivity in MFI pores, relatively high molecular weight, and high pressure drop. Efficient blocking of H<sub>2</sub> transport by CO<sub>2</sub> adsorption likely causes the separation.

In figure 1, fluxes, permeances, separation factors and separation selectivities for an equimolar CO<sub>2</sub>/H<sub>2</sub> feed at 296 K and 275 K are shown. The ratio between feed pressure and permeate pressure was 7.5.



**Fig. 1.** Fluxes, permeances, separation factors and separation selectivities for an equimolar CO<sub>2</sub>/CO/H<sub>2</sub> feed at 296 K. The pressure ratio was 7.5.

From all findings in this work, the conclusion was that an MFI membrane comprised of an approximately 0.7  $\mu\text{m}$  film on a fully open and graded porous alumina support was able to separate  $\text{CO}_2/\text{H}_2$ ,  $\text{CO}_2/\text{CO}/\text{H}_2$  and  $\text{CO}_2/\text{CH}_4$  mixtures at high pressures. The  $\text{CO}_2$  permeance and flux were very high; fluxes up to  $657 \text{ kg m}^{-2} \text{ h}^{-1}$  were observed, which is many times larger than previously reported for any zeolite membrane. The very high flux was a result of a thin film, open support, high pressure, relatively high diffusivity, molecular weight and pressure drop (all the latter of  $\text{CO}_2$ ). The membrane was also selective and the selectivity was controlled by  $\text{CO}_2$  adsorption. The highest observed  $\text{CO}_2/\text{H}_2$  separation factor was 32 for a binary feed mixture. Likely due to competitive adsorption of  $\text{CO}_2$  and  $\text{CH}_4$ , the maximum observed  $\text{CO}_2/\text{CH}_4$  separation factor was, however, lower. For a  $\text{CO}_2/\text{CO}/\text{H}_2$  feed mixture, the membrane was also  $\text{CO}_2$  selective. The presence of  $\text{CO}$  only had a small effect on the  $\text{CO}_2$  and  $\text{H}_2$  permeances, and a  $\text{CO}_2/\text{H}_2$  separation factor of 23 was observed for the ternary feed mixture. The results show that MFI membranes are promising candidates for membrane separation of  $\text{CO}_2$  from synthesis gas, natural gas or biogas at high pressures.

## ***II. Separation of $\text{CO}_2$ from black liquor derived syngas using an MFI membrane***

Black liquor is the spent cooking liquor from the Kraft process when digesting pulpwood into paper pulp removing lignin, hemicelluloses and other extractives from the wood to free the cellulose fibers. The development plant gasifier in Piteå, Sweden, consists of an entrained flow reactor where the black liquor is partially oxidized at  $1000 \text{ }^\circ\text{C}$  and 3 MPa. The valuable cooking chemicals are separated from the gas and recycled to the pulp mill. Impurities and particles are removed from the synthesis gas in a counter current condenser. Production of dimethylether via methanol synthesis has recently been demonstrated from the gas on pilot scale. The ideal synthesis gas composition for methanol synthesis can be represented by the stoichiometric number,  $\text{SN} = (\text{H}_2 - \text{CO}_2)/(\text{CO} + \text{CO}_2)$ , which should be equal to or slightly above 2 [2]. Synthesis gas produced via gasification of biomass, e.g. black liquor, is usually too rich in  $\text{CO}_2$  [3]. The synthesis gas produced by the DP-1 gasifier contains ( $\text{N}_2$  and  $\text{H}_2\text{O}$  free basis) 34.8%  $\text{H}_2$ , 33.6%  $\text{CO}_2$ , 28.5%  $\text{CO}$ , 1.7%  $\text{H}_2\text{S}$ , and 1.4%  $\text{CH}_4$  [4, 5], which corresponds to a stoichiometric number of 0.02. The composition of the gas must therefore be substantially modified prior to methanol synthesis. One possibility is to remove  $\text{CO}_2$  from the gas and to carry out the water gas shift reaction in order to increase the stoichiometric number and the challenge in this project was to accomplish this separation using a zeolite membrane.

Membrane separation of  $\text{CO}_2$  from synthesis gas could be an energy efficient and simple alternative to other separation techniques. In this work, a membrane comprised of an about 0.7  $\mu\text{m}$  thick MFI film on a graded alumina support was used to separate  $\text{CO}_2$  from synthesis gas produced by pilot scale gasification of black liquor. The separation of  $\text{CO}$  from the synthesis gas was carried out at a feed pressure of 2.25 MPa, a permeate pressure of 0.3 MPa and room temperature. In the beginning of the experiment, when the  $\text{H}_2\text{S}$  concentration in the feed was 0.5 % and the concentration of water in the feed was 0.07 %, a  $\text{CO}_2/\text{H}_2$  separation factor of 10.4 and a  $\text{CO}_2$  flux of  $67.0 \text{ kgm}^{-2} \text{ h}^{-1}$  were observed. However, as the  $\text{H}_2\text{S}$  concentration in the feed to the membrane increased to 1.7 %, the  $\text{CO}_2/\text{H}_2$  separation factor and the  $\text{CO}_2$  flux decreased to 5 and  $61.4 \text{ kgm}^{-2} \text{ h}^{-1}$ , respectively. The results suggest that MFI membranes are promising candidates for the separation of  $\text{CO}_2$  from synthesis gas. The figure below shows separation factors for the various systems as a function of time.

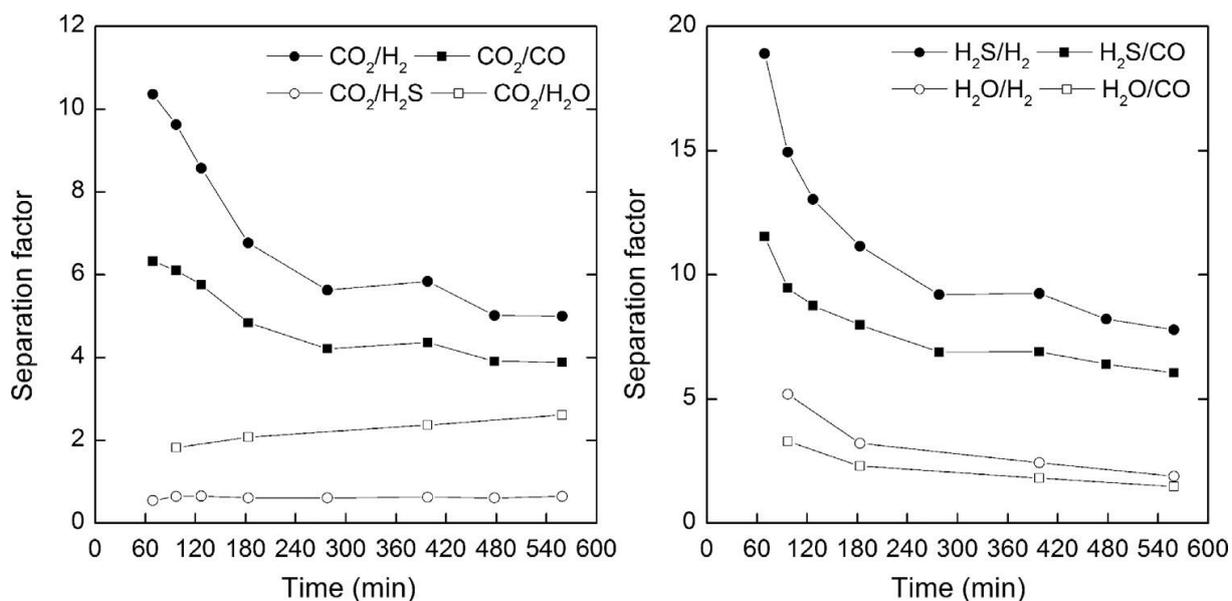


Fig. 2. Separation factors as a function of time. Points represent experimental data, and lines are a guide for the eye.

This was the first time an MFI membrane was used to separate CO<sub>2</sub> from a synthesis gas produced by a pilot scale black liquor gasifier. The membrane could successfully separate CO<sub>2</sub> and H<sub>2</sub>S from the synthesis gas at a feed pressure of 2.25 MPa, a permeate pressure of 0.3 MPa and room temperature. The CO<sub>2</sub> separation performance was the highest in the beginning of the experiment, when the H<sub>2</sub>S concentration in the membrane feed was low.

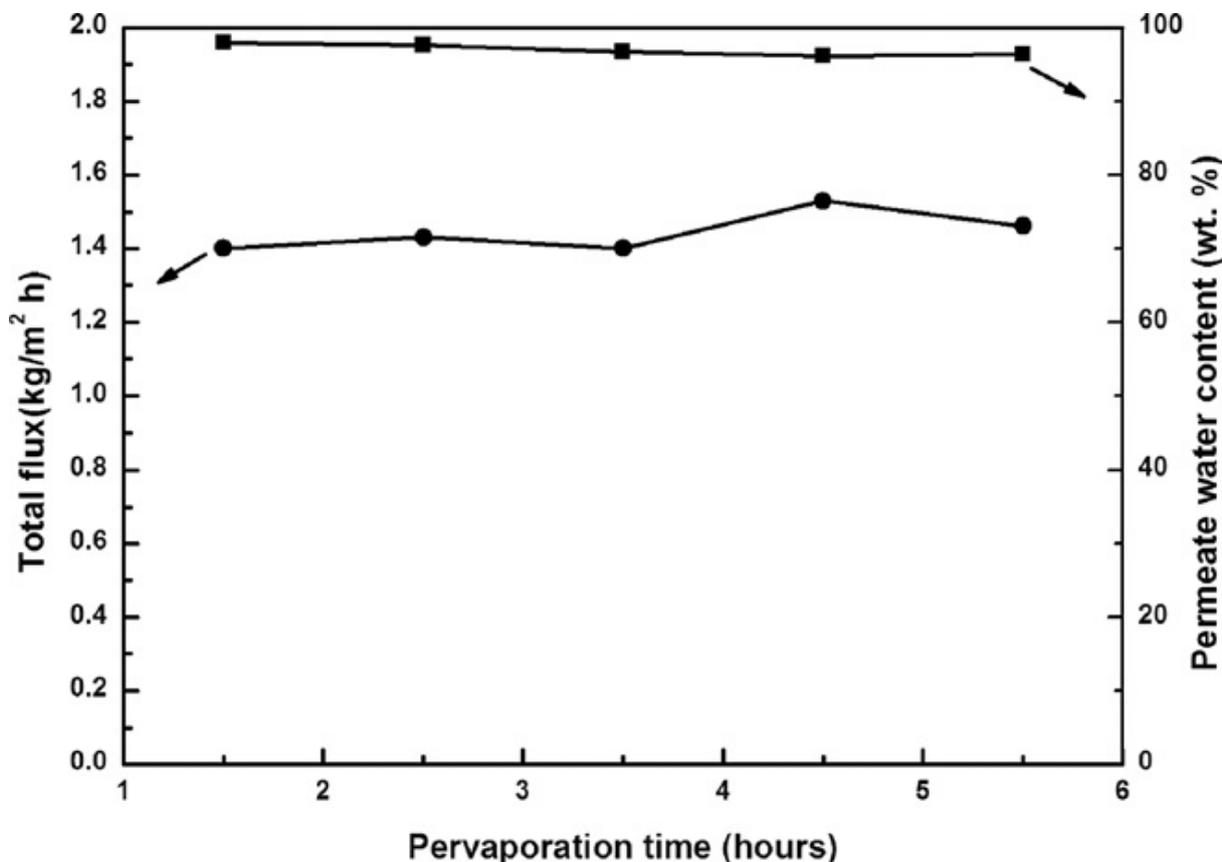
### III. Ultrathin zeolite X membranes for pervaporation dehydration of ethanol

Among the renewable biofuels, ethanol produced by fermentation is of major interest. Distillation is still the dominating method for enriching ethanol from fermentation broths. However, distillation processes are very energy-demanding and standard distillation can only reach the concentration of the ethanol–water azeotrope (about 4 wt.% water). Pervaporation (PV) is a process in which a liquid mixture is fed to a membrane and one or several of the mixture components are selectively transported through the membrane and evaporated on the other side of the membrane. PV can potentially be an energy efficient separation method, and continuously separate azeotropes, close-boiling mixtures and concentrate species with a low concentration at much lower temperature than distillation, without regenerating sorbent or removing entrainers [6–10]. Therefore, to enrich ethanol from fermentation broths, PV can be an environmentally friendly alternative to distillation. Compared with the commercially available polymer membranes, zeolite membranes have uniform micropores, high chemical and thermal stability, with no or negligible expansion in organic liquids. Therefore, the application of zeolite membranes in PV is of great interest in the academic and industrial sectors [11–18].

In this study, discrete Faujasite zeolite nanocrystals with an average size of about 60 nm were attached as a well-defined monolayer on the surface of porous graded alumina supports. Ultrathin zeolite X films with a total thickness of about 1  $\mu\text{m}$  were grown from the seed monolayers by hydrothermal treatment in clear synthesis solutions. One of the membranes showed a total flux of  $3.37 \pm 0.08 \text{ kg m}^{-2} \text{ h}^{-1}$  and a separation factor of  $296 \pm 4$  for dehydration of a 90/10 wt.%

ethanol/water mixture by pervaporation at 65 °C. Moreover, the membranes displayed stable

performance during pervaporation for 5.5 h operation. Figure 3 shows the PV performance of a zeolite X membrane.



**Fig. 3.** The PV performance of the zeolite X membrane for 90/10 wt. % ethanol–water mixture at 50 °C.

A mathematical model indicated that the flux and selectivity of the membranes were limited by pressure drop in the supports. Therefore, in order to obtain higher flux, the permeability of the support must be improved.

However, to our knowledge, this is the first report describing preparation and evaluation of an ultra-thin FAU membrane (thickness of 1  $\mu\text{m}$  or less) with high flux and selectivity for the PV dehydration of ethanol. The membranes showed good separation performance for the PV dehydration of ethanol. However, mass transfer resistance in the support limited the water flux and selectivity.

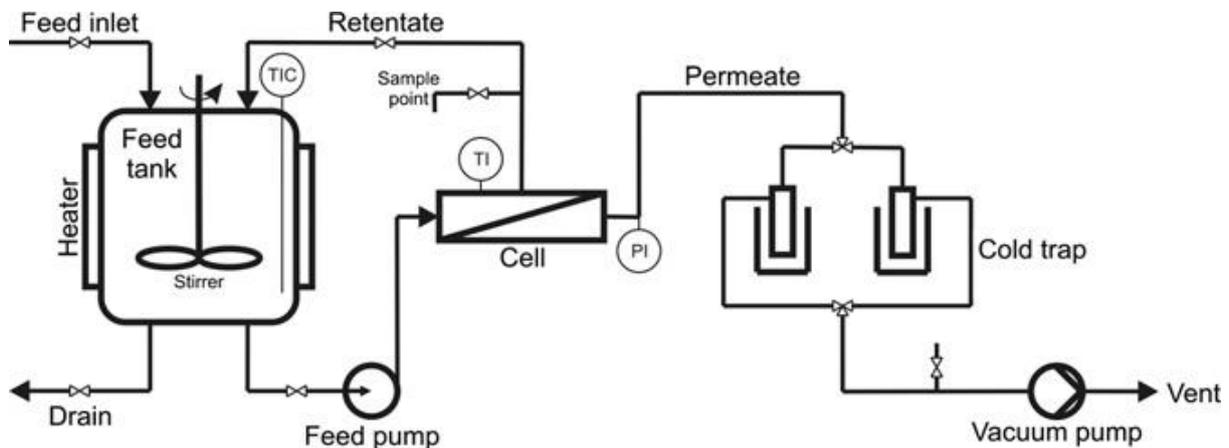
#### ***IV. MFI membranes for pervaporation***

##### **Ultra-thin MFI membranes on alumina discs**

By altering the silicon-to-aluminum (Si/Al) ratio of the zeolite, the polarity of a membrane can be controlled. The lower the Si/Al ratio, the more hydrophilic is the membrane and the higher is the membrane affinity for water. For instance, rather hydrophilic LTA zeolite membranes prepared by Morigami et al. [19], was shown to be effective for ethanol dehydration in terms of both flux and selectivity. These membranes have been evaluated in a large scale separation process. On the other hand, the least hydrophilic zeolite membranes are selective towards alcohols rather than water and

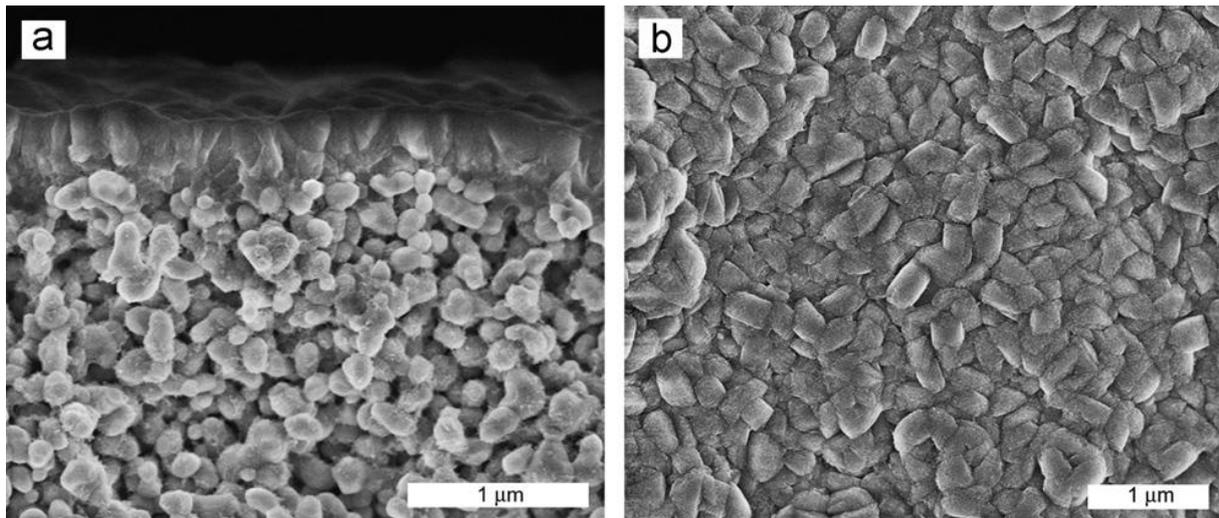
may potentially be used for concentration of lean alcohol solutions (5 to 10 wt.%) such as bioethanol [6] by pervaporation. Besides bioethanol production, acetone–butanol–ethanol (ABE) fermentation is a potential process to produce liquid fuels from biomass. Butanol inhibition is a severe problem in the ABE fermentation. However, butanol concentration by distillation would require more energy than the energy content in butanol itself. In order to make the process energetically and economically attractive, pervaporation is considered one of the most promising alternatives. Zeolite membranes have an advantage in terms of flux and stability and, therefore, have a great potential for butanol separation by pervaporation. Nevertheless, publications in scientific journals on the use of zeolite membranes for this application are scarce and generally show a low flux through the membrane although the separation factor may be high. The scope of the present work was for the first time to investigate the performance of high flux MFI membranes [20] for the separation of n-butanol and ethanol from the respective aqueous solutions by pervaporation.

Separation of homogeneous aqueous solutions of n-butanol and ethanol by pervaporation was carried out using a set-up illustrated in Fig. 4.



**Fig. 4.** Pervaporation set-up.

MFI membranes with a thickness of 0.5 mm were prepared on a graded  $\alpha$ -alumina support and evaluated for separation of feed mixtures of 3 wt.% n-butanol/water and 10 wt.% ethanol/water by pervaporation. Fig. 5 shows top-view and cross-sectional SEM images of an as synthesized MFI membrane. The zeolite film appears to be continuous and rather even with a thickness of about 0.5  $\mu\text{m}$ , see Fig. 5a.



**Fig. 5.** Cross-section (a) and top view (b) of SEM images of an as-synthesized MFI membrane.

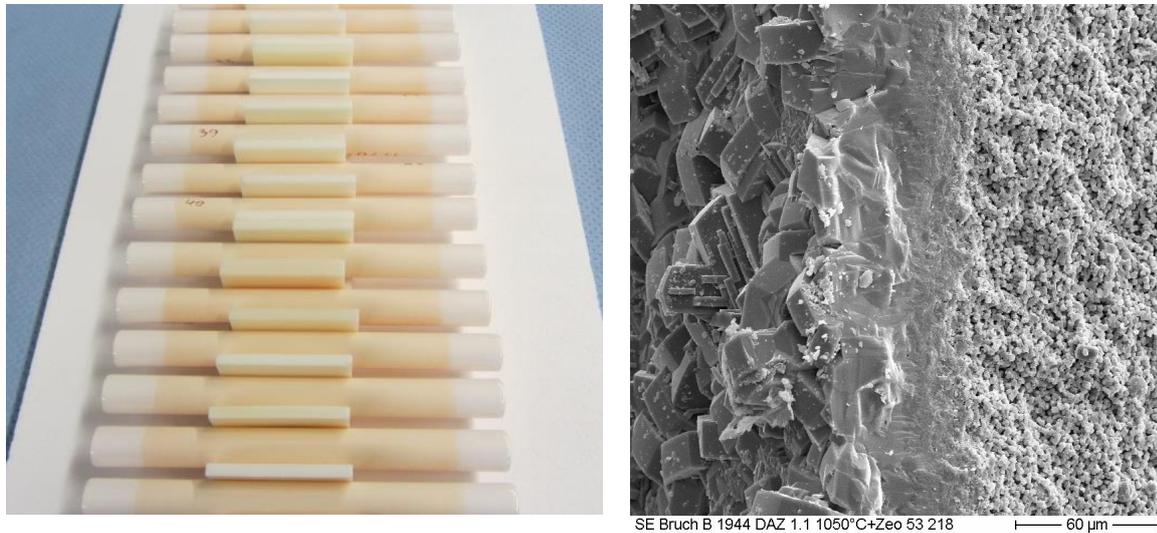
The film is composed of well intergrown crystals with a length of up to 400 nm. No defects in the form of cracks or pinholes larger than 5 nm were observed.

The membranes were selective to both n-butanol and ethanol and the flux observed was about 100 times higher than that previously reported for n-butanol/water separation by pervaporation and about 5 times higher than that for ethanol/water separation by pervaporation. At 60 °C, the observed n-butanol/water flux was about 4 kg m<sup>-2</sup> h<sup>-1</sup> and the n-butanol/water separation factor was about 10 for the best membrane. At the same temperature, the membrane displayed an ethanol/water flux of ca. 9 kg m<sup>-2</sup> h<sup>-1</sup> and an ethanol/water separation factor of ca. 5.

The membranes exhibited the highest ever reported flux for pervaporation of 3 wt.% n-butanol/water and 10 wt.% ethanol/water mixtures. The n-butanol/water separation factor increased from ca. 5 to ca. 10 with increasing temperature from 30 to 60 °C, whereas the ethanol/water separation factor remained nearly constant at about five. Modeling results indicated that there was a significant pressure drop across the support, which reduced the flux and membrane selectivity, whereas heat transfer limitations were found to be negligible at the conditions studied.

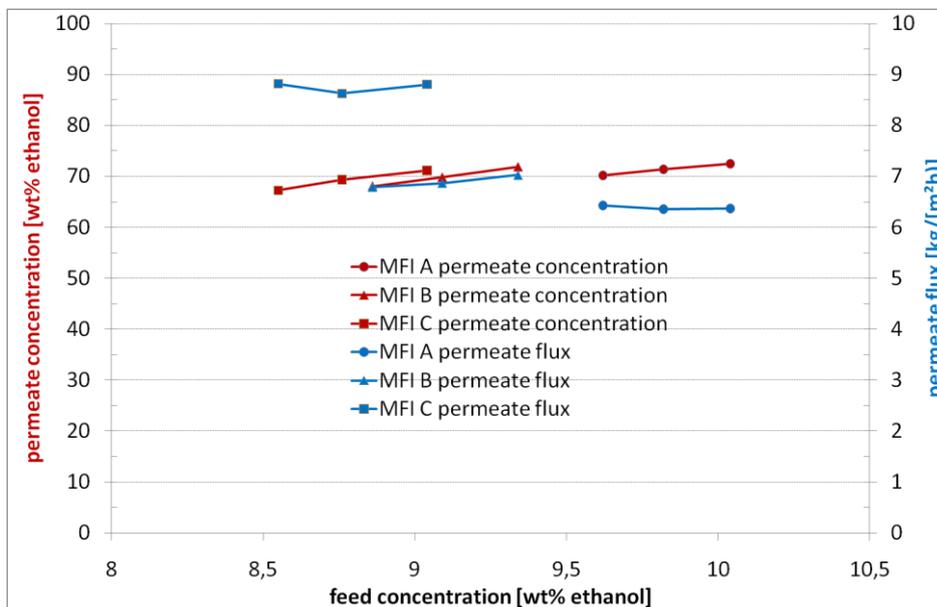
### Preparation the first all zeolite MFI membranes on zeolite tubes (still unpublished results)

All-zeolite tubular supports with glass sealing and an inner layer of MFI membranes were prepared at IKTS, see Figure 6. The membranes were used to separate ethanol from water.



**Fig. 6.** All zeolite MFI tubes with glass sealing (left). Cracks are observed after a closer inspection of the glass sealing (not shown here) and cross section of zeolite membrane (right)

The permeate concentration and the permeate flux of these membranes are shown in figure 7.



**Fig. 7.** The figure shows the results from separation of high concentrated ethanol from low concentrated solution using a Zeolite MFI membrane inside an all- zeolite MFI tube.

The figure illustrates that a feed concentration of 9 wt.% ethanol gives a flux of about 8.7 kg/m<sup>2</sup>h and a permeate concentration of about 70% for the best membrane. These results are comparable with the ones discussed above for the ultra-thin membrane. However, here it is probably problems with the end sealing that limits the selectivity.

## ***V. Utilization of $P_i^{sat}$ temperature-dependency in modelling adsorption on zeolites***

The adsorption of gases and vapours by zeolites is important in the field of gas separation, purification and the removal of environmentally harmful components from waste streams. The adsorption characteristics of zeolites are largely based on their aluminosilicate framework based structure, where  $[\text{SiO}_4]^{4-}$  and  $[\text{AlO}_4]^{5-}$  tetrahedral are linked to each other by sharing the oxygen atoms at the corners. Adsorption on zeolites is mainly physical in nature. The characteristics of physisorption are affected by adsorbent porosity, size and geometry of the pores, defects in the adsorbent structure and interactions between adsorbent–adsorbate and adsorbate–adsorbate couples, among other factors.

Due to the wide spectrum of adsorption characteristics aimed to be modelled, a number of isotherm formulations have been proposed in the literature for gaseous component adsorption on porous adsorbents. The isotherm models are functions of either  $P$  or  $P$  and  $P_i^{sat}$ , and the adsorbed amount depends on the temperature with two or three adjustable parameters, which are determined on the basis of equilibrium measurements or data acquired from molecular dynamics simulation. The notations  $P$  and  $P_i^{sat}$  are the actual gas pressure and the saturated vapor pressure of component,  $i$ , respectively.

Using data from various publications, it was observed in this work that when the adsorbed amount on zeolites is presented as a function of  $P/P_i^{sat}$ , the experimental adsorption data derived at different temperatures overlap extraordinarily well. It was thus proposed that the temperature dependency of physical adsorption on zeolites can be described by using only the temperature dependency of the pure component saturated vapour pressure  $P_i^{sat}$ , in contrast to the existing adsorption isotherm formulations. The approach proposed is more flexible and not specifically bound to any particular isotherm model. However, the approach proposed in this paper can be used in context with existing adsorption models having a predetermined functional form with respect to pressure  $P$ , by replacing the  $P$  term with  $P/P_i^{sat}$ .

A lot of time was saved by using only  $P_i^{sat}$  to describe the temperature dependency of the amount adsorbed. In the case of water adsorption on zeolites, when the experimentally adsorbed amount at equilibrium is plotted versus  $P/P_i^{sat}$ , the data points at various temperatures clearly overlap. This phenomenon is observed regardless of the hydrophilic or hydrophobic character of the zeolite. On closer observation, there is some deviation in adsorption behavior in the low-pressure region. However, this deviation is not large. Thus, it is possible to describe the temperature dependency of water adsorption on zeolites solely by  $P_i^{sat}$ .

However, the temperature dependency of aromatics adsorption cannot be described with  $P_i^{sat}$  alone. There are several studies stating that aromatic compounds bond first with extra framework cations forming strong cation–aromatic complexes, followed by more loosely held species at high coverages [22,23]. This type of complexation means that chemisorption is also present. Chemisorption is always exothermic, except for a few special cases [24]. The aromatics adsorption data considered in this study is on zeolites that are more hydrophobic in nature, but not totally aluminium free, which means that extra framework cations are also present. Thus, it is reasonable to state that due to the temperature dependency of complexation,  $P_i^{sat}$  cannot solely describe the temperature dependency of adsorption since chemisorption is also clearly present. The proposed method for utilizing the

temperature dependency of  $P_i^{\text{sat}}$  to describe adsorption seems to work best for systems where the adsorption is mainly physical in character.

In this work it was proposed that the temperature dependency of physical adsorption on zeolites can be described with a timesaving and thus engineering-friendly manner by covering the temperature dependency with pure component saturated vapour pressure  $P_i^{\text{sat}}$ . Thus, it is possible to predict the adsorption on zeolites at several temperatures based on adsorption equilibrium data at only one temperature. The proposed approach can be used in the modelling and design of industrial processes exploiting adsorption, such as in zeolite membrane systems, where separation is based on both adsorption and diffusion phenomena. Application of the proposed approach using  $P_i^{\text{sat}}$  temperature dependency is flexible since it is not bound to any particular isotherm formulation. However, in the context of traditionally utilized isotherms that have some predetermined functional form with respect to pressure, the  $P$  term can be replaced with  $P/P_i^{\text{sat}}$  representation. Based on our examination it has been concluded that  $P_i^{\text{sat}}$  is able to describe the temperature dependency of adsorption especially for water adsorption on both hydrophilic and hydrophobic zeolites. The method works relatively well also for alcohol adsorption on zeolites. For systems where the role of chemisorption is significant, such as aromatics adsorption on zeolites, the  $P_i^{\text{sat}}$  alone is not capable of representing the temperature dependency of adsorption with sufficient accuracy. It is also concluded that the traditional routine of fitting the parameters in the adsorption isotherm separately at different temperatures is questionable. This kind of individual fitting usually results in a decline in the saturation loading with increasing temperature. However, the decline may be a result of the lack of adsorption data over a sufficiently extensive pressure range. This can be observed clearly when presenting the data as a function of  $P_i^{\text{sat}}$ . In order to be able to define the  $q_i^{\text{sat}}$  value that represents the actual saturation loading reliably, the experimental adsorption data should cover pressures close to the saturated vapour pressure  $P_i^{\text{sat}}$ . Based on the observations made in this work, the maximum adsorption loading  $q_i^{\text{sat}}$  of components on zeolite is practically independent of temperature. The conclusion is reasonable given the rigid structure of zeolites. Therefore, when using the proposed approach of utilizing  $P_i^{\text{sat}}$  temperature dependency in adsorption models, it is justifiable to keep the saturation loading  $q_i^{\text{sat}}$  constant, and thus independent of temperature.

#### ***VI. Mixture adsorption on zeolites applying the $P_i^{\text{sat}}$ temperature-dependency approach***

Adsorption equilibrium data are typically reported for single components, as pure component adsorption measurements are the most reliable and easiest to perform. On the other hand, applications of adsorption usually involve mixtures. Mixture adsorption equilibrium measurements, however, are considerably more complicated, tedious and error-prone than single component measurements [25]. Nevertheless, multi-component adsorption data is crucial, but it is challenging to cover experimental mixture adsorption data for a wide range of temperature, pressure and composition conditions [26]. In practice, typically only single component isotherms are determined experimentally, and mixture adsorption is then predicted by adsorption models. Models developed for the purpose include e.g., ideal adsorbed solution theory, real adsorbed solution theory, and extended Langmuir-type models. The models are often sufficiently accurate to be used for engineering purposes such as process design and modelling.

In this work it was studied whether the  $P_i^{\text{sat}}$  temperature-dependency approach describing pure component adsorption on zeolites presented in Leppäjärvi et al. [27] can be applied in the prediction

of binary mixture adsorption on zeolites as well. The feasibility of the  $P_i^{\text{sat}}$  temperature-dependency approach was studied through example cases. Mixture adsorption was predicted with the typical methods of ideal adsorbed solution theory, real adsorbed solution theory or extended Langmuir by applying the  $P_i^{\text{sat}}$  temperature dependency. The binary mixture adsorption loadings were predicted with sufficient accuracy in various temperature, pressure and composition conditions based on pure component adsorption data at only one temperature. The approach is not restricted to the vapour phase as it is also applicable for adsorption modelling of liquid phase mixtures. This is advantageous as many industrial adsorption processes are performed in the liquid phase. The emphasis of the approach is on the applicability perspective. The  $P_i^{\text{sat}}$  temperature-dependency approach can be a convenient engineering tool, especially in cases where there is a lack of adsorption data. One possible application is zeolite membrane modelling where the role of adsorption is significant.

### ***VII. Maxwell–Stefan modelling of the separation of H<sub>2</sub> and CO<sub>2</sub> at high pressure in an MFI membrane***

Separation of CO<sub>2</sub> from gaseous mixtures has become an important application in environmental engineering, especially due to climate change reasons. In addition, removal of CO<sub>2</sub> has attracted attention in the purification of natural gas and collection of methane from landfill gas [28]. Further to the environmental considerations, separating CO<sub>2</sub> with a zeolite membrane could enhance e.g., the properties of synthesis gas as a feed gas for methanol synthesis [29]. In natural gas treatment applications, the feed gas is usually obtained directly from gas wells with in a wide range of pressures (normally 20–70 bar) and compositions (5–50% CO<sub>2</sub>) [30]. Similarly, methanol synthesis is performed at high pressure. Therefore a membrane with good pressure endurance is a basic requirement. Zeolite membranes, like MFI, offer high endurance to high pressure and temperature. However, the H<sub>2</sub>/CO<sub>2</sub> flux ratio increased at high temperature [31]. Yet, at low temperature and high pressure, MFI membranes have shown both a high selectivity to CO<sub>2</sub> and high flux of CO<sub>2</sub> [31]. In this study, a Maxwell–Stefan based model was built on pure component experimental data with the aim of predicting binary separation data. The main membrane-related factors limiting flux and separation selectivity are:

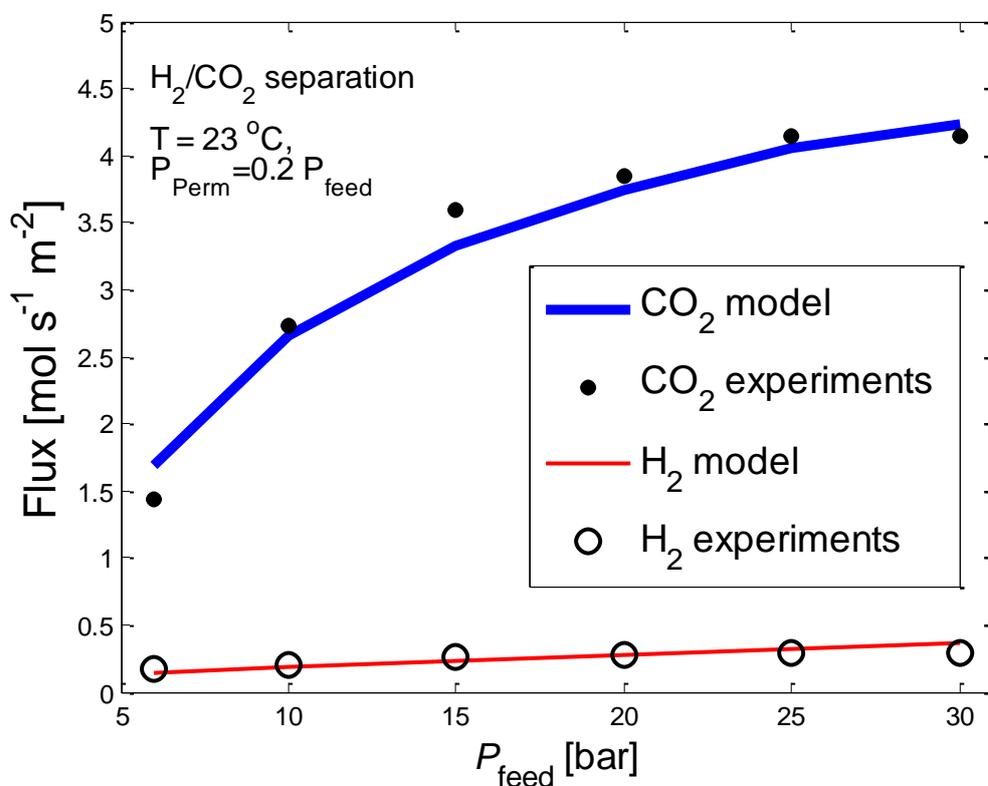
- the zeolite film adsorption behaviour,
- the zeolite film diffusivity characteristics,
- the film thickness,
- the defects in the zeolite film, and
- the support layer properties.

The extent of the factors above was investigated here by comparing the model predictions to the experimental binary data.

A Maxwell–Stefan based model was developed for the separation of CO<sub>2</sub> from H<sub>2</sub> at high pressure in an MFI membrane. The usage of the Vignes interpolation formula for mixture surface diffusivities together with the ideal adsorbed solution theory using bulk gas phase fugacities for mixture adsorption proved to be a feasible combination for this case. Both the effects of defects in the zeolite film and the mass transfer resistance caused by the support layers were studied and included in the model. Only pure component experimental data was used in the model building to predict the gas mixture permeation. The fitted diffusion parameters were in line with the literature values. The

occupancy fraction dependence of CO<sub>2</sub> surface diffusivity was utilized for the first time in the prediction of binary separation of H<sub>2</sub>/CO<sub>2</sub> at high pressure on a real MFI membrane. Usage of an occupancy fraction dependence for CO<sub>2</sub> surface diffusivity improved the model predictions. The adsorption parameter fitting for hydrogen based on the permeation measurements resulted in a feasible adsorption model, but should be used with caution. The model predicts binary separation measurement results relatively well. Both defects and support have a noticeable impact on the overall performance of the membrane.

As shown in Fig. 8, the model with the occupancy dependence predicts the fluxes for both components well and the difference between the model and the experimental results is smaller than it was without consideration of the occupancy dependence.

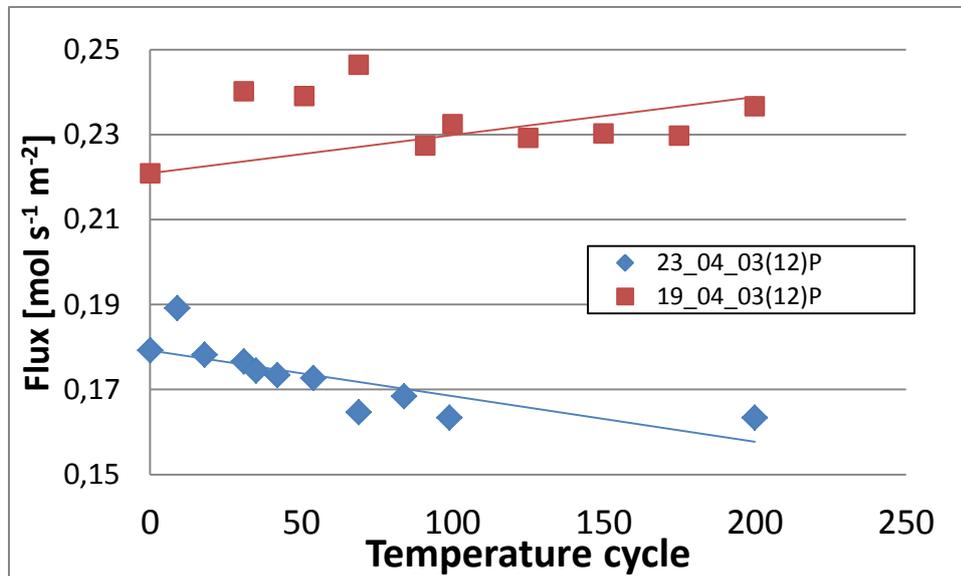


**Fig. 8.** Model predictions and experimental fluxes of H<sub>2</sub> and CO<sub>2</sub> as a function of feed pressure. The MFI membrane used was 710 nm thick.

The membrane studied had a relatively small proportion of defects. Thus, the effect of the defects was around 10 % of the total hydrogen flux in binary H<sub>2</sub>/CO<sub>2</sub> separation conditions. The support pressure drop was at maximum 20 % of the total pressure drop in mixture separation conditions. In addition to experiments related to support parameters, further studies should include the rigorous application of the occupancy fraction dependence of surface diffusion to verify its general applicability in conjunction with experimental data. In combination with this, the adsorption model/data should be selected with care because of the linkage of surface diffusivity and adsorption phenomenon.

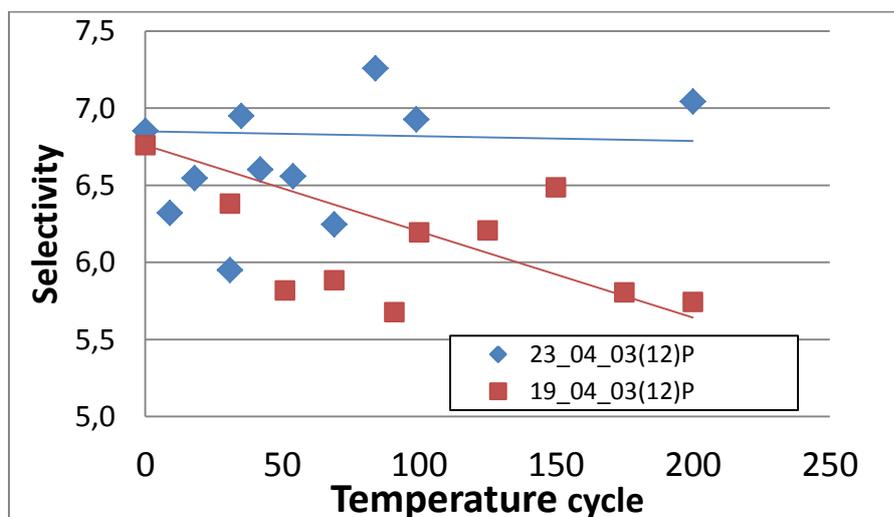
### VIII. Membrane stability during temperature cycling (these results are not yet published)

Zeolite MFI membranes prepared at IKTS inside tubular substrates were found to be surprisingly stable during temperature cycling in Oulu, as shown in figure 9.



**Fig. 9.** The figure shows the flux vs. temperature cycles for two different tubular membranes. The measurement conditions were:  $P^{\text{feed}} = 15$  bar,  $P^{\text{perm}} = 1.5$  bar,  $T = 30$  °C, feed flow = 11 nL/min, and the composition of the feed was 52.5 % CO<sub>2</sub> and 47.5 % H<sub>2</sub>.

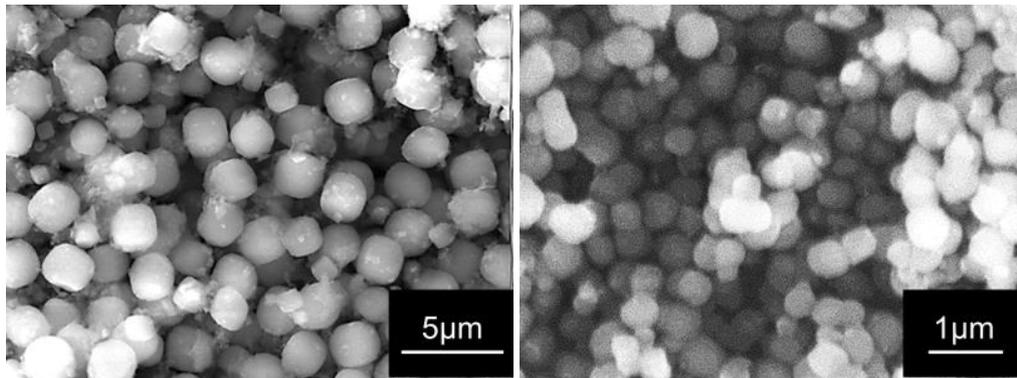
The figure shows that only very small changes in the flux occurred during 200 temperature cycles. Temperature cycles from 1 to 100: 30°C->160°C with max gradient  $dT/dt=5.5$ °C/min, cycles from 101 to 200: 30°C->125°C with max gradient  $dT/dt=6.5$ °C/min. In between the measurements, a small nitrogen feed of 0.07 nL/min was flowing with a pressure of approximately 1.2 bar. The total operating time with a single membrane was 48 days. The selectivity of the two membranes was also measured and the results are shown in figure 10. Again, very small changes are observed, and it can thereby be concluded that the membranes are surprisingly stable for temperature cycles.



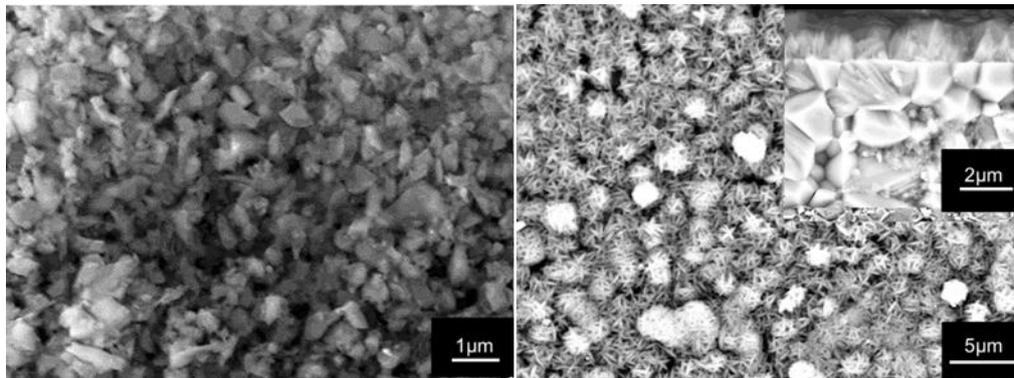
**Fig. 10.** The selectivity vs. temperature.

### ***IX Preparation of small CHA crystals and thin CHA films (these results are not yet published)***

Small zeolite CHA crystals with a size of 500 nm were prepared for the first time and films with a thickness of 2.5-5  $\mu\text{m}$  have been prepared. Work is on-going to prepare even smaller crystals and thinner films. These films should give good performance in the separation of carbon dioxide from natural gas due to the small pore size of the CHA SSZ-13 crystals. The crystals obtained by a standard method and an optimized method to get small crystals are shown in figure 12. Films grown from crushed crystals are shown in Figure 13.



**Fig. 12.** SEM images showing CHA SSZ-13 particles prepared at (left) standard conditions and (right) optimized conditions for obtaining small particle size distributions.



**Fig. 13.** SEM images of (left) crushed CHA SSZ-64 particles used as seeds and (right) prepared CHA SSZ-64 zeolite film.

### **Publications generated partially or completely within the project**

High Flux Zeolite Membranes for Efficient Production of Biofuels. PhD Thesis by Linda Sandström 2012-11-16. ISBN 978-91-7439-494-8, Luleå University of Technology 2012.

Very high flux MFI membrane for CO<sub>2</sub> separation, L. Sandström, E. Sjöberg, J. Hedlund. Journal of Membrane Science, 2011, (380) 232-240.

Utilization of  $P_i^{\text{sat}}$  temperature-dependency in modelling adsorption on zeolites, T. Leppäjärvi, J. Kangas, I. Malinen, J. Tanskanen, Chemical Engineering Science, 2012, (69) 503-513.

Ultrathin zeolite X membranes for pervaporation dehydration of ethanol, H. Zhou, D. Korelskiy, T. Leppäjärvi, M. Grahn, J. Tanskanen, J. Hedlund. *Journal of Membrane Science*, 2012 (399-400), 106-111.

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Separation of CO<sub>2</sub> from black liquor derived syngas using an MFI membrane, Sjöberg, Erik; Sandstrom, Linda; Ohrman, Olov G. W. *Journal of Membrane Science*, 2013, (443) 131-137.

Mixture adsorption on zeolites applying the  $P_i^{sat}$  temperature-dependency approach, T. Leppäjärvi, J. Kangas, I. Malinen, J. Tanskanen. *Chemical Engineering Science*, 2013, (89) 89-101.

Maxwell-Stefan modeling of the separation of H<sub>2</sub> and CO<sub>2</sub> at high pressure in an MFI membrane, Kangas, Jani; Sandström, Linda; Malinen, Ilkka, Hedlund, Jonas, Tanskanen, Juha, *Journal of Membrane Science*, 2013, (435) 186-206.

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