High permeance nano porous tubular zeolite membranes for efficient separation of CO_2 and methanol at demanding conditions- HIP NANOMEM

Overview of project participants

Luleå University of Technology

Prof. Jonas Hedlund

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Linda Sandström (PhD student)

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University of Oulu

Professor Juha Tanskanen

Jani Kangas (PhD student)

Oslo University

Professor Karl Petter Lillerud

Bjørn Tore L. Bleken (PhD student)

Zebastian Boström (Post doc)

Project budget, total and with an overview of external funding from other sources

Work package	Budget
1	267 k€ + 70 k€ (faculty funds)
2	325 k€
3	511 k€
4	266 k€ + 100 k€ (faculty funds)
Total	1369 k€ + 170 k€ (faculty funds)

Other funding Project title and sponsor	Budget	Time period
Zeolite membranes for effective production of biofuels, Swedish Foundation for Strategic Research	2400 k€	2009-2014
Bio4Energy - zeolite membrane part, Swedish state	360 k€/year	2010-2014 (at least)
Zeolite membranes for pervaporation, LTU and GSCE	Faculty support for PhD students 2 years (Luleå) + 5 years (Oulu)	2008-2014
Zeolite membranes for CO2 separation, GassMaks	365 k€	2007-2013

Project organisation

Work packages (leader in bold text)

1. **Luleå** will develop ultra thin tubular zeolite Membranes first on alumina tubes and then on zeolite tubes prepared by Fraunhofer IKTS.

2. **Oslo** will develop nanocrystals and ultra thin membranes of a new zeolite structure (SSZ-64) with smaller pores and potentially higher CO_2 selectivity than in current membranes in collaboration with Luleå. Membranes will be modified by Luleå for maximum CO_2 selectivity.

3. **Fraunhofer IKTS** will develop zeolite tubes and Luleå will grow ultra thin films on the tubes when available. This will result in all zeolite membranes with potentially reduced crack formation.

4. The stability and functionality of the membranes prepared by Luleå and Oslo will be evaluated with long-term tests (weeks) by **Oulu**. Fraunhofer IKTS will perform application testing of multi channel tubes. The mass transfer through the membranes, and also the whole gas separation process will be modelled by Oulu.

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Milestones

WP 1: Observed high selectivity for prototype membranes in the applications (for details, see Appendix 1) of:

- natural gas sweetening (application 1) M1.1, after 2 years

- synthesis gas sweetening (application 2), M1.2, after 2.5 years

- alcohol separation from synthesis gas at reaction conditions (application 3), M1.3, after 3 years.

WP 2: Successful preparation of:

- colloidal SSZ-64 crystals with a diameter of 40 nm, M2.1, after 1 year

- continuous ultra thin SSZ-64 films on dense supports, M2.2, after 1.5 years.

- ultra thin crack free SSZ-64 membranes on porous alumina supports with high CO2/CH4 selectivity, M2.3, after 2.5 years

- ultra thin amine grafted MFI zeolite membrane with high CO2/H2 selectivity, M2.4 after 1 year.

Milestones

WP 3: Successful preparation of:

- the first tubular zeolite support with suitable macro and mesopore size for ZM applications, M3.1, after 1.5 years

- the first prototype of high flux ultra thin tubular zeolite supported zeolite membrane, M. 3.2, after 2.5 years.

WP 4:

- Detailed mathematical model of the entire membrane separation process has been developed, M4.2, after 2 years.

- Proven long term stability tests of zeolite membranes during cycling of operating temperature, feed composition, feed pressure etc., M4.1, after 3 years.

- Energy efficiency of the entire membrane process system has been optimized, M4.2, after 3 years.

Project progress and possible deviations

WP 1

- Modest performance of MFI membranes demonstrated for natural gas sweetening. SSZ-64 membranes (that should work better) not yet developed in WP 2. Milestone 1.1 approached.

- World record performance for synthesis gas sweetening (CO_2 separation) with zeolite membranes. Permeance 3 times higher and selectivity 75% of target. The results are published. Milestone 1.2 reached!

- Good alcohol separation from synthesis gas demonstrated at low temperatures, but estimates indicate that it will not work at reaction conditions. Milestone 1.3 given up.

- Draft of patent for new membrane preparation method in progress.

WP 2 (This WP is delayed due to recruitment problems)

- CHA Crystals with a size of about 500 nm has been prepared. Milestone 2.1 has been approached

- 2.5-5.0 µm thick films of CHA have been prepared. Milestone 2.2 approached.

Project progress and possible deviations

WP 3

- Good tubular zeolite support with suitable macro and mesopore size and **end sealing** has been prepared. Milestone 3.1 reached!

- Thin (but not ultrathin) tubular zeolite supported zeolite membranehas been prepared for the first time and the separation performance has been evaluated. Ultrathin zeolite supported membrane **discs** has been prepared and evaluated. Milestone 3.2 has been approached.

WP 4

- Long term stability of zeolite membranes has been proven for temperature cycling. The membranes are surprisingly stable! Milestone 4.1has been reached!

- Mathematical model for synthesis gas sweetening has been developed and the work is published soon. Milestone 4.2 reached!

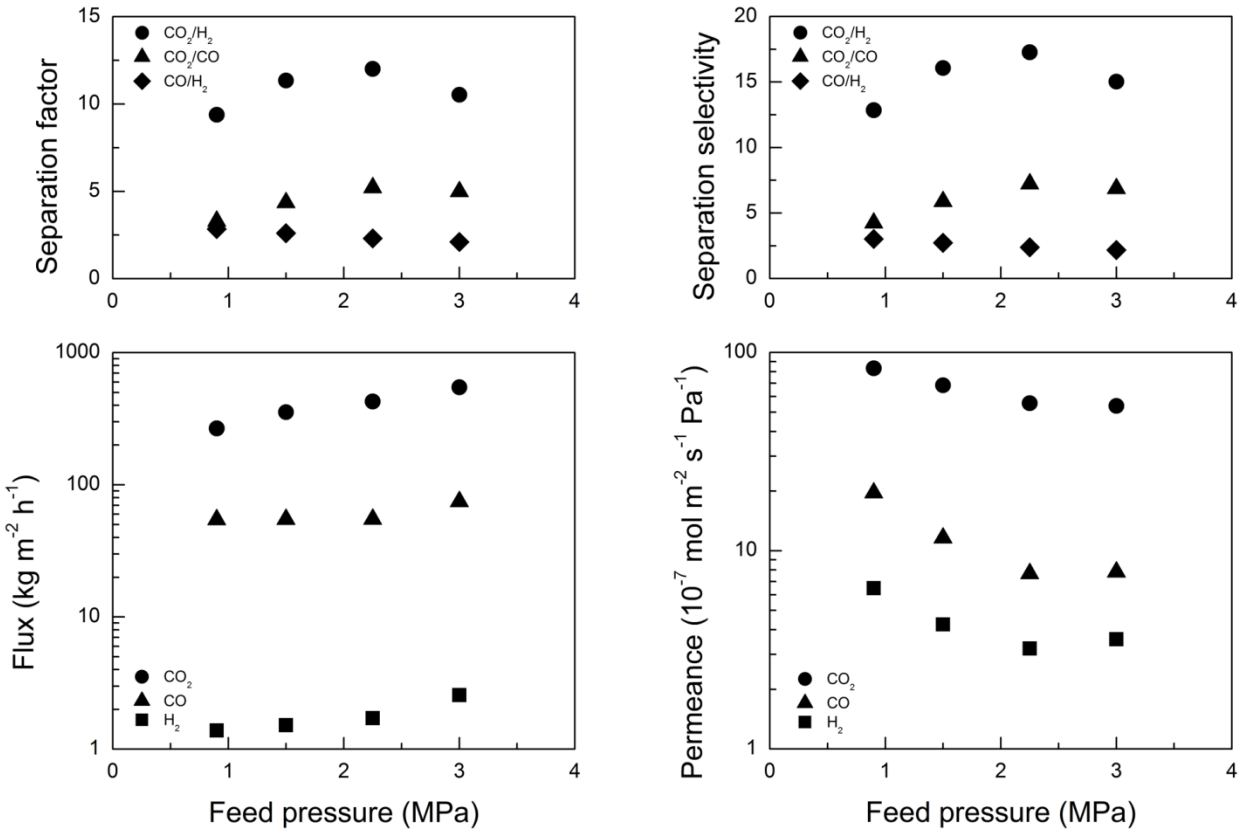
- Energy efficiency **and economy** of the processes under evaluation, and the preliminary results are very promising. Milestone 4.2 has been approached.

Scientific findings and uniqueness of the project

Summary of unique findings

- Excellent (world record by far) separation of CO_2 demonstrated
- Development and successful testing of the first tubular all zeolite membranes in the world
- The membranes are surprisingly stable for temperature cycling
- New method for membrane preparation developed (patent draft)
- Small CHA crystals have been prepared for the first time (useful for membrane preparation)

WP 1 best results: CO_2/H_2 separation using non-modified MFI membranes



CO_2 permeance: 60 x 10^{-7} mol/(m^2·s·Pa), i.e. **4 times above target**
CO_2/H_2 selectivity: 15, i.e. **30% below target**

Very high flux MFI membrane for CO_2 separation. Linda Sandström, Erik Sjöberg, Jonas Hedlund, Journal of Membrane Science, Volume 380, Issues 1-2, ***15 September*** *2011, Pages 232-240*

Results **WP 2A** CHA SSZ-13 Particle size (UiO /SMN, Oslo)

- We are currently able to prepare CHA SSZ-13 zeolite with a particle size of **500** nm.
- Standard CHA SSZ-13 preparation procedures results in approximate particle sizes of more than **2000** nm.
- Patent literature (U.S. Patent, 6,709,644 B2, 2001) describes how to prepare **0.5-1.0 µm** SSZ-62 at a Si/Al 25-40.

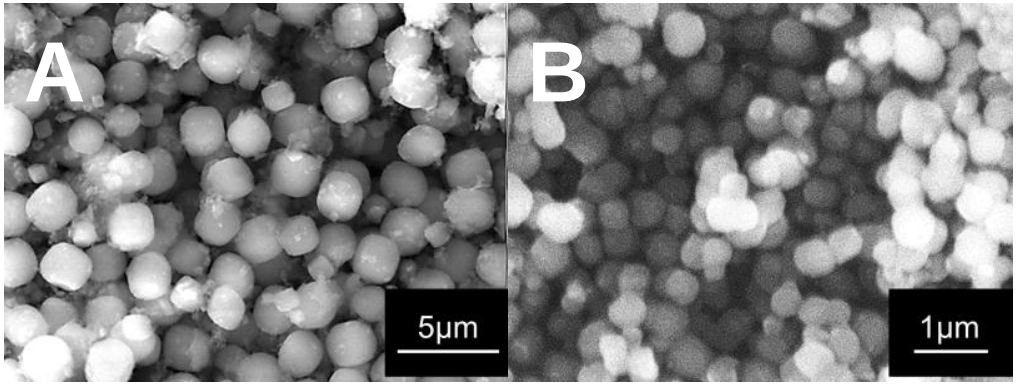


Figure WP2-1. SEM images showing CHA SSZ-13 particles prepared at (A) standard conditions and (B) optimized conditions for obtaining small particle size distributions.

Project goal

CHA SSZ-13 with a particle size of 40 nm at a Si/Al ratio of 100.

Results **WP 2B** CHA SSZ-64 zeolite films (UiO /SMN, Oslo)

- We are currently able to prepare dense CHA SSZ-64 zeolite films with a film thickness ranging from **2.5-5.0 µm**.
- We are currently using crushed CHA SSZ-64 zeolites with a particle size of **about 300 nm**.

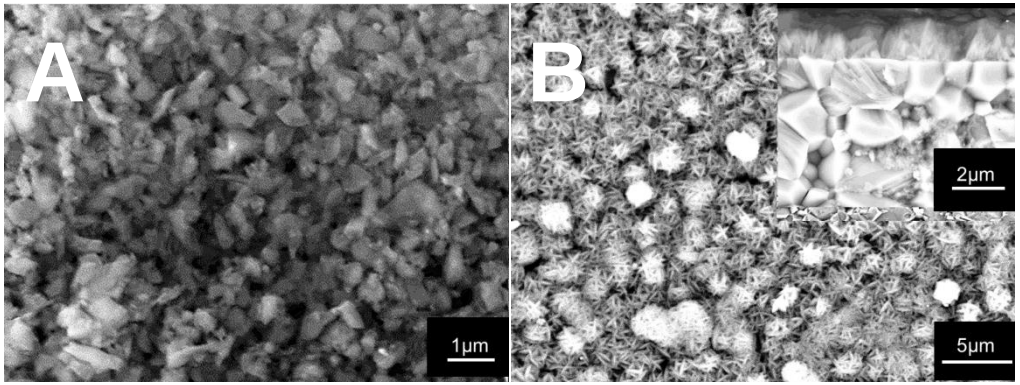
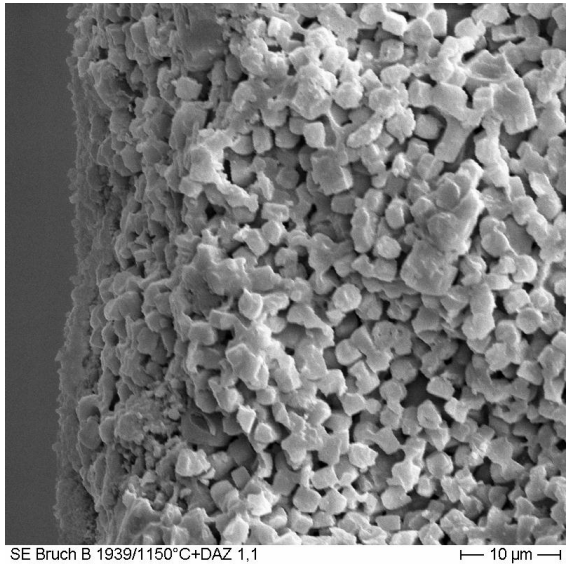


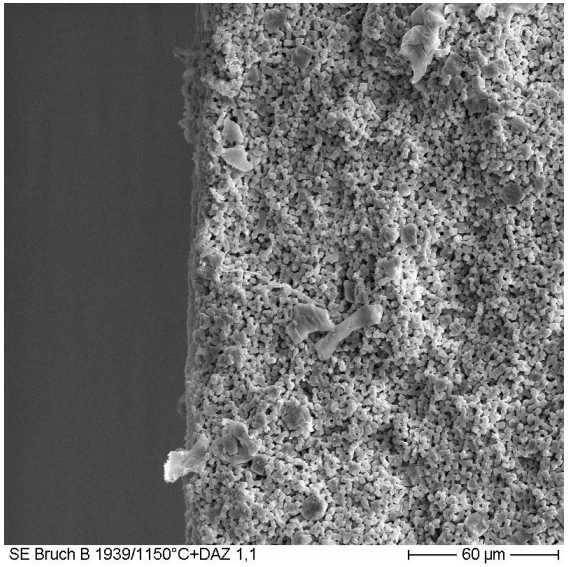
Figure WP2-2. SEM images of (A) crushed CHA SSZ-64 particles used as seeds and (B) prepared CHA SSZ-64 zeolite film.

Project goal

CHA SSZ-64 films with a thickness of 0.5 µm.

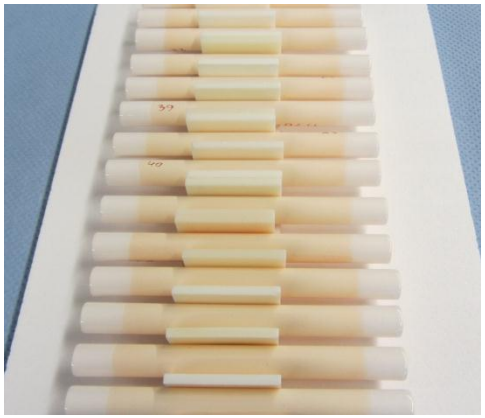
WP 3: Tubular all zeolite membranes



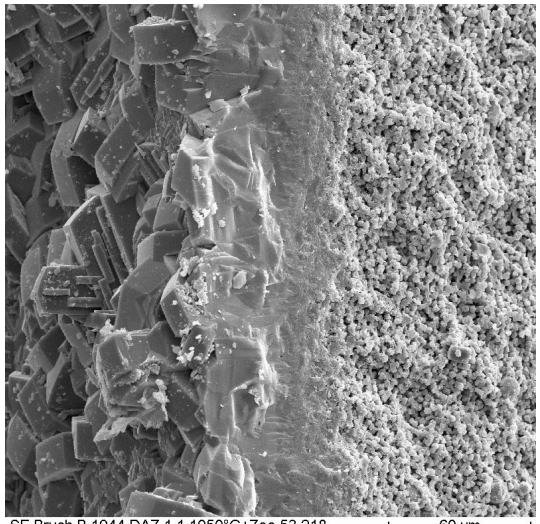


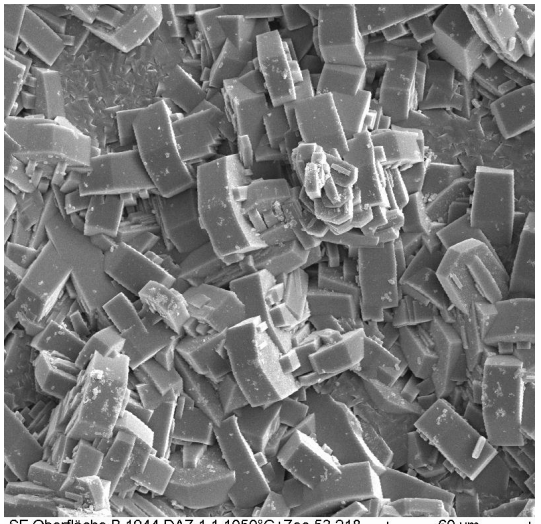
All zeolite MFI tube with zeolite intermediate layer (1µm thickness).

Zeolite MFI membrane inside of all zeolite MFI tube.



All zeolite MFI tubes with glass sealing.





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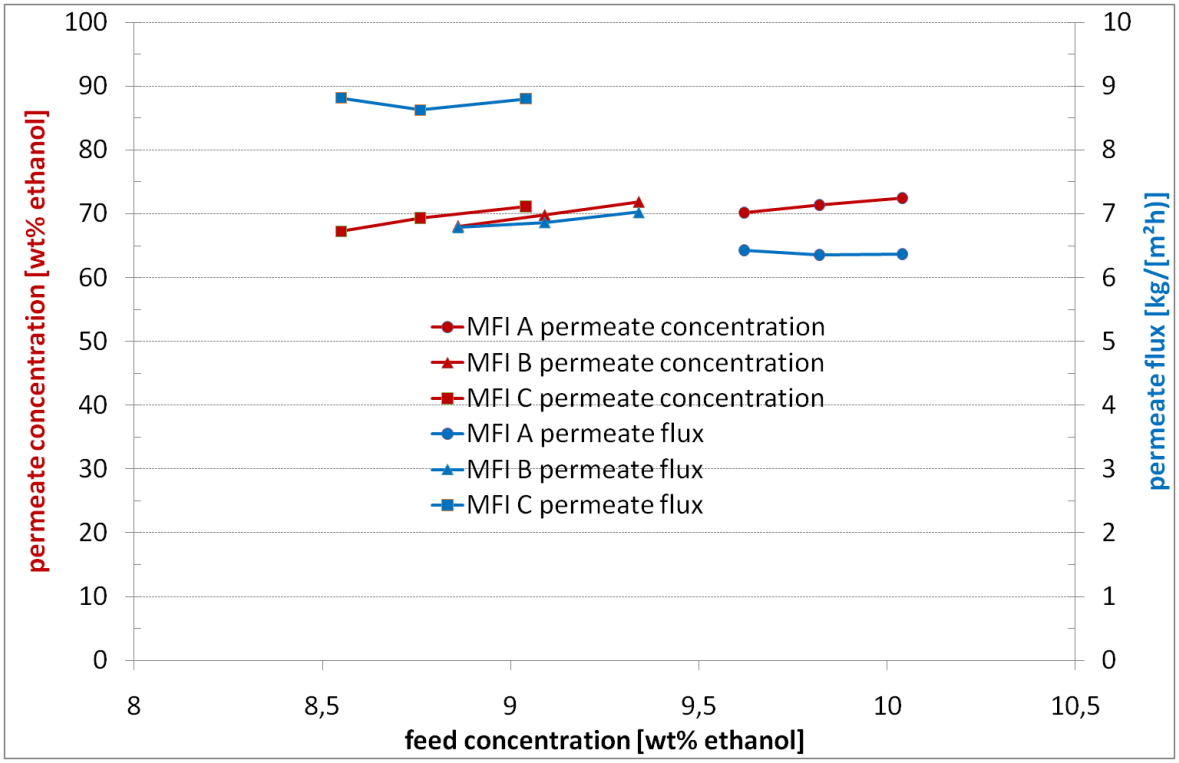
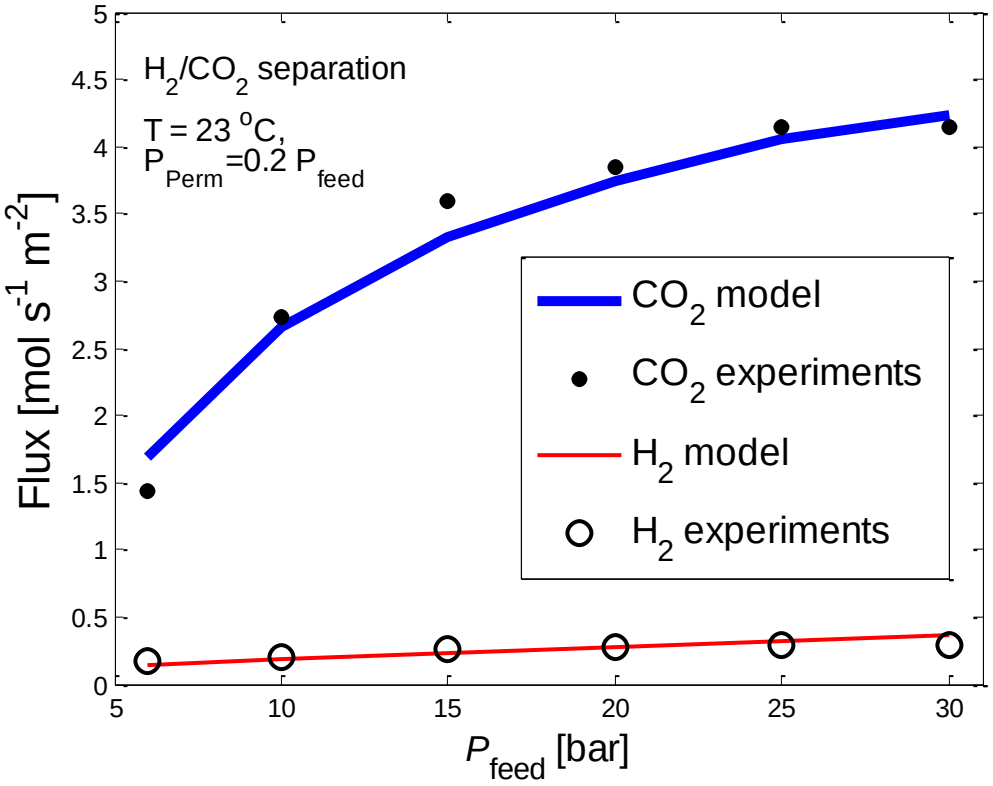
WP 3: Tubular all zeolite membranes

Zeolite MFI membrane inside of full zeolite MFI tube separating high concentrated ethanol from low concentrated solution.



WP 4: Membrane separation modelling

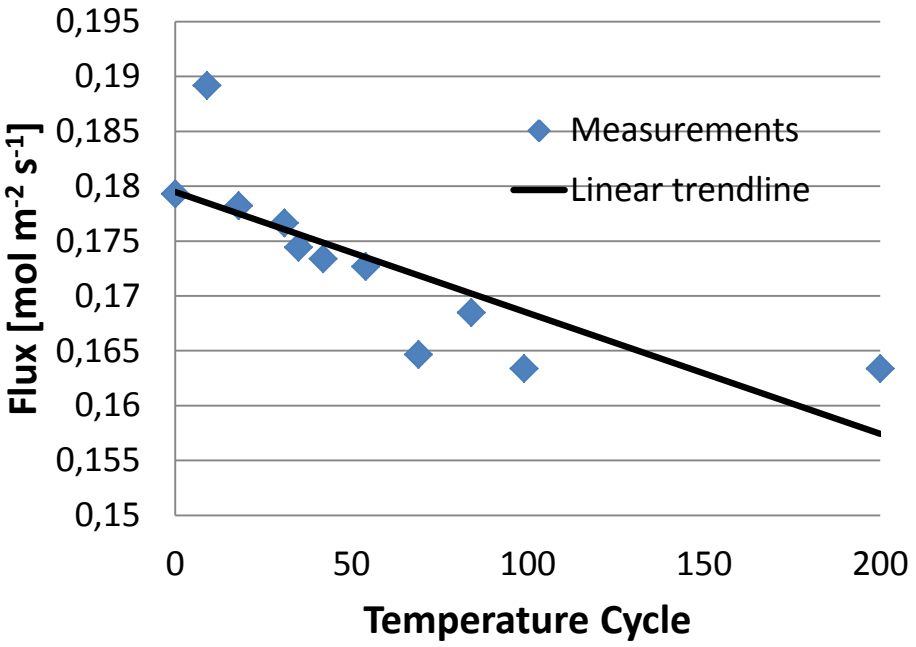
Occupancy dependence of CO_2 Maxwell-Stefan diffusivity was applied successfully first time on a real MFI membrane modelling at high pressure H_2/CO_2 separation conditions

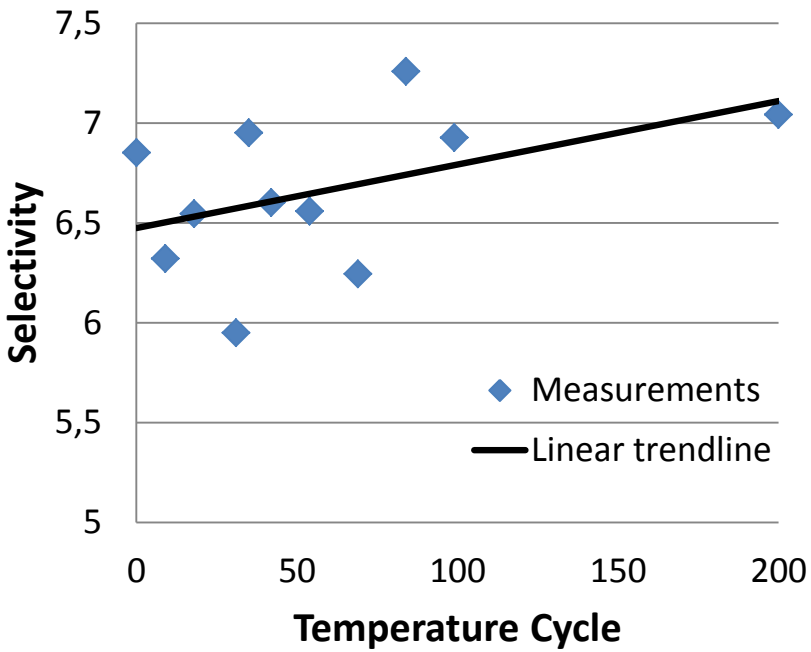


Reference: J. Kangas, L. Sandström, I. Malinen, J. Hedlund, J. Tanskanen "Maxwell-Stefan modeling of the separation of H_2 and CO_2 at high pressure in an MFI membrane", Submitted to Journal of Membrane Science

WP 4: Long-term stability tests with tubular membranes

Asymmetric tubular MFI membrane prepared at IKTS
Temperature cycling effects





Measurement conditions: P^{feed} =15 bar, P^{perm} = 1.5 bar, T = 30°C
Feed composition: 52.5% CO_2 and 47.5% H_2
Feed flow = 11 nl/min

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Networks, co-operations, seminars and mobility. Has the project cooperated with other projects, has it arranged summer schools or international conferences and has there been mobility within the project?

- 2 day (lunch to lunch) face to face project meetings
  - in Luleå August 2010
  - in Hermsdorf June 2011
  - in Oulu June 2012
  - in Oslo 2013 (this evening and tomorrow)
- Telephone meetings

  -One in 2010 and 2 in 2012
- Frequent communication on telephone and e-mail during the work with joint manuscripts (3 so far).
- Frequent exchange of samples/materials within the project.
- Post doc from Oslo planning to work with membrane testing in Luleå.
- Cooperation + mobility (Oulu-Luleå + Oslo-Luleå) between with the N-INNER project and the four projects mentioned on slide 3.

Results: Phd degrees and academic publications.

PhD degree: Linda Sandström, 2012-11-16, Thesis entitled High Flux Zeolite Membranes for Efficient Production of Biofuels

Publications in peer review international scientific Journals

2011

- L. Sandström, E. Sjöberg, J. Hedlund: “Very high flux MFI membrane for CO2 separation” Journal of membrane Science (380) 232-240

2012

- T. Leppäjärvi, I. Malinen, J. Kangas, J. Tanskanen: “Utilization of P_i^{sat} temperature dependency in modelling adsorption on zeolites” Chemical Engineering Science, (69) 503-513
- T. Leppäjärvi, J. Kangas, I. Malinen, J. Tanskanen: ” Mixture adsorption on zeolites applying the P_i^{sat} temperature-dependency approach” Chemical Engineering Science (89) 89-101
- H. Zhou, D. Korelskiy, T. Leppäjärvi, M. Grahn, J. Tanskanen, J. Hedlund: “Ultrathin zeolite X membranes for pervaporation dehydration of ethanol” Journal of Membrane Science, (399–400) 106–111.

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2013

- D. Korelskiy, T. Leppäjärvi, H. Zhou, M. Grahn, J. Tanskanen, J. Hedlund: “High flux MFI membranes for pervaporation” Journal of membrane Science (427) 381-389

Submitted

- E. Sjöberg, L. Sandström, Jonas Hedlund: “Separation of CO2 and H2S from black liquor derived syngas using an MFI membrane”, Submitted to Journal of membrane Science
- J. Kangas, L. Sandström, I. Malinen, J. Hedlund, J. Tanskanen “Maxwell-Stefan modeling of the separation of H_2 and CO_2 at high pressure in an MFI membrane, accepted for publication in Journal of membrane Science

Conference 2011

- H. Richter, G. Fischer, “Full zeolite bodies for zeolite membranes and adsorption applications” 12th International Conference and Exhibition of the European Ceramic Society, June 19-23, 2011, Stockholm/Sweden

Other publications / information activities (web, social media, television, daily press et cetera)

Web links to the project

http://www.ltu.se/research/subjects/Kemisk-teknologi/Research-projects/HIP-NANOMEM-1.53806

http://www.zeomem.se/index.php?option=com_content&view=article&id=5&Itemid=9

Patents

Draft of patent application (in collaboration with patent bureau)
New method for production of zeolite membranes

What did the n-inner call do for the initiation of collaboration, research area and network, how will it move forward

1. It boosted and prolonged already existing collaborations (Oulu-Luleå, Oslo-Luleå)
2. It initiated new collaborations between Hermsdorf and the 3 Nordic groups.
3. All zeolite membrane tubes were developed, which is an important contribution to the research area
4. Excellent CO_2 separation was demonstrated and modeled, which is an important contribution to the research area
5. The membranes were shown to be stable, which is an important contribution to the research area
6. The research network will most likely continue its collaborative work and move forwards towards preparation of larger membranes, which are more close to commercial applications.