



Energy research Centre of the Netherlands

Consortium inorganic membrane technology

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31 December 2007

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Acknowledgement/Preface

One of the activities of the group Molecular Separation Technology in the ECN program of the unit Energy Efficiency in Industry is the development of inorganic membrane technology. One source of funding for these activities is the so-called program funding of the Dutch ministry of Economic Affairs. The current “Consortium Anorganische MembraanTechnologie” brings all the relevant expertise, knowledge and experience in this field together. As such, ECN collaborates with the University of Twente, the Technical Universities of Eindhoven and Delft, and TNO. Funding for these partners has been obtained within the SenterNovem program “Energie Onderzoek Subsidie: Lange Termijn (EOS-LT)”. This consortium belongs to category 2 of the research themes as defined in the EOS-LT Leaflet. The ECN-EEI-Multi Year Program is the leading concept for this consortium. This report deals with the outcome obtained during the first 1.5 years of this project (April 2006 - December 2007).

General Project Data

SenterNovem project number:	EOSLT04008
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1. Introduction

The overall goal of the consortium Inorganic Membrane Technology reads *"the realization of more energy efficient industrial processes through the development of inorganic membranes for molecular separations"*. An extensive analysis of the industrial energy consumption has led to a number of priorities:

- Dehydration of organic solvents
- Ammonia separation
- Oxygen production
- Hydrocarbon separation
- Hydrogen separation in a membrane reactor

Furthermore process calculations have shown that inorganic membrane technologies can lead to an estimated energy saving of 25 – 50 % as compared with existing technologies. An extensive description can be found in the original application.

The aim of the current consortium is the development of membranes, systems and processes for energy efficient molecular separations. In accordance with techno-economic constraints, inorganic membranes with the required combination of selectivity, flux, lifetime and cost of production are being developed.

This report describes the results of the research in the field of inorganic membrane technology as obtained during the first 1.5 years of the co-operation within the current consortium, filed under EOSLT04008. The formal starting date of the project was 1 April 2006

The overall research can be divided into three parts: materials development and properties of the selected membranes, design of modules and transport properties, and the design of the membrane based separation processes. Currently, the main emphasis is laid on issues related to the membrane materials. Other aspects, as well as field scale testing, will be addressed in the future.

2. Results

Pervaporation

- Hydrolysis of the polymer phase in the composite membrane is the lifetime limiting property
- A blended polymer composite membrane with a good selectivity has been made.
- High fluxes and selectivities can be achieved with the hybrid membrane system.
- The hybrid membrane system has a high hydrothermal stability.

Ammonia separation

- The substitution of methyl group in the methylated silica membrane by various other terminating organic groups does in general not lead to a measurable change in pore size.
- The affinity of the membrane towards NH_3 can be increased through the incorporation of a small amount of zirconia in the silica structure.
- A design of a pilot-scale membrane unit has been made
- A model that describes the mass (NH_3 , N_2 and H_2) transport through the membrane has been developed.

Production of oxygen

- Porous tubular membranes provided with a dense coated separating layer have been successful up scaled to the desired diameter and elongated lengths after identifying critical parameters during fabrication. Depending on successfully sealing, these membranes now can be tested.
- A seal has been developed that is gastight for non porous perovskite bars up to 950°C . This seal will now be tested for the developed supported tubular membranes.

Separation of hydrocarbons

- The adsorption properties of pure propane and propylene on a specific zeolite are very different which suggest that it can be used effectively for the separation of these two components.
- Stability of silver ions in various supports remains a cause of concern.
- The preparation of defect free layers of any microporous crystalline material shows to be difficult.

Hydrogen separation

- In PdAu alloys, hydrogen occupies preferentially those sites related with the palladium metals.
- At higher degrees of hydrogen loading, hydrogen can equally occupy octahedral and tetrahedral positions. This is confirmed experimentally.
- New ternary alloys have been designed. This has lead to a promising alloy with small volume changes upon hydrogenation and a critical temperature around room temperature.

3. Dissemination

Here, a full list is presented of publications, reports and presentations held in the reporting period.

Article in journals with peer review:

- ‘*Microporous structure and enhanced hydrophobicity in methylated SiO₂ for molecular separation*’, Hessel L. Castricum, Ashima Sah, Marjo C. Mittelmeijer-Hazeleger, Cindy Huiskes and Johan E. ten Elshof, *J. Mater. Chem.* **17** (2007) 1509 – 1518
- ‘*Hybrid ceramic nanosieves: stabilizing nanopores with organic links*’, Hessel L. Castricum, Ashima Sah, Robert Kreiter, Dave H.A. Blank, Jaap F. Vente and Johan E. ten Elshof, *Chem.Comm*, 2008, 1103-1105
- *Journal of Alloys and Compounds* 446–447 (2007) 571–574; *Phase stabilities of Pd-based alloys for membranes for hydrogen gas separation: A statistical thermodynamics approach* D.E. Nanu, A.J. Böttger

Oral presentations:

- ‘*Hybrid organic-inorganic membranes with long-term stability for pervaporation*’, Hessel L. Castricum, Ashima Sah, Jaap F. Vente, and Johan E. ten Elshof, NCCC 8, Noordwijkerhout, 6-3-2007
- ‘*Durable molecular sieve membranes from hybrid organosilica for pervaporation*’, Hessel Castricum, Ashima Sah, Rob Kreiter, Dave Blank, Jaap Vente and Andre ten Elshof, annual scientific meeting of CW study groups, Lunteren, 19-3-2007
- ‘*Durable molecular sieve membranes from hybrid organosilica for pervaporation*’, Hessel Castricum, Ashima Sah, Rob Kreiter, Dave Blank, Jaap Vente and Andre ten Elshof, Materials Research Society spring meeting, San Francisco, US, 11-4-2007
- Gascon, J.; Miltenburg, A.van; Zhu, W.; Kapteijn, F.; Moulijn, J.A. “Separation of propylene/propane mixtures over microporous materials”. Abstract Oral communication, NCCC VIII. Noordwijkerhout, The Netherlands, March 2007. CDROM.
- D. Nanu, KNCV- Inorganic Materials & Devices for Sustainable Energy Technologies symposium, 19-04-2007 Ede; “*Membrane Technology for Hydrogen Gas Separation: Towards Designing Metal Membranes*”
- A. Böttger, NVK symposium - Energieke kristallen 19-11-2007 ECN-Petten; *Designing Membranes for Hydrogen Gas Separation: A Study of H-induced Structural Changes in Metal Membranes*”
- D. Nanu, A.Böttger, CALPHAD XXXV Conference, May 7 - 12, 2006 Haifa, Israel; “*Exploring Phase Stabilities in FCC Ternary Interstitial Alloys using the Cube Approximation of CVM*”,

Posters:

- Gascon, J.; Miltenburg, A.van; Zhu, W.; Kapteijn, F.; Moulijn, J.A. Separation of propylene/propane mixtures over microporous materials. Poster presentation, at the 2nd International School & Workshop INSIDE PORES. Thessaloniki, Greece, February 2007. Book of abstracts, P-1, pp 33.
- Miltenburg A. van, Gascon J., Zhu W., Kapteijn F., Moulijn J. “Ligth oleffin/paraffin mixtures adsorption on FAU sorbents”. Poster communication, Fundamentals on adsorption 9, (FOA 9). Sicily, May 2007.
- Vehring M, Gascon J, Kapteijn F, Dubbeldam D, Snurr RQ, Stallmach F. “Intracrystalline Self-Diffusion of propane and propylene in metal organic framework Cu-BTC”. Poster communication. 19th German Zeolite Conference. poster P74, Book of Abstracts 202-203.

- Gascon, J; Miltenburg, A. van; Zhu, W.; Kapteijn, F.; Moulijn, J.A Propylene/propane mixture adsorption on Faujasite. Poster presentation at NPS6, Veldhoven, The Netherlands, 24-25 October 2006. Book of abstracts, P-94.
- Gascon, J. Propane/Propene separation using inorganic membranes, in OSPT Process Technology PhD projects Miniposter book 2006, ISBN 90-365-2422-9, p.63.
- Diana E. Nanu, Amarante J. Böttger, Wim G. Haije, Jaap F. Vente, Bas B. van Aken, Matt G. Tucker, International Symposium on Materials Issues in a Hydrogen Economy November 12-15, 2007 in Richmond, Virginia USA; “*H-induced Structural Changes in Metal Membranes for Hydrogen Purification: Model Predictions vs Neutron Diffraction*”