

# A catalytic membrane micro-reactor for the direct synthesis of propene oxide

**Citation for published version (APA):**

Kertalli, E., Schouten, J. C., & Nijhuis, T. A. (2012). A catalytic membrane micro-reactor for the direct synthesis of propene oxide. In *Proceedings of the 22nd International Symposium on Chemical Reaction and Engineering (ISCRE 2012)*, 2-5 September 2012, Maastricht, The Netherlands

**Document status and date:**

Published: 01/01/2012

**Document Version:**

Accepted manuscript including changes made at the peer-review stage

**Please check the document version of this publication:**

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

**General rights**

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

[www.tue.nl/taverne](http://www.tue.nl/taverne)

**Take down policy**

If you believe that this document breaches copyright please contact us at:

[openaccess@tue.nl](mailto:openaccess@tue.nl)

providing details and we will investigate your claim.

# A CATALYTIC MEMBRANE MICRO-REACTOR FOR THE DIRECT SYNTHESIS OF PROPENE OXIDE

E. Kertalli, J.C. Schouten, T.A. Nijhuis

Eindhoven University of Technology, Laboratory for Chemical Reactor Engineering  
Eindhoven, The Netherlands

## Summary

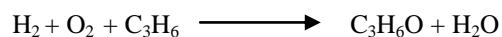
In this work, a catalytic membrane reactor for the direct epoxidation of propene oxide is developed. The titania and silica membranes synthesis method from an alcoxide precursor, TiO<sub>2</sub> nano-particle powder and SiO<sub>2</sub> colloidal solution is described. Stainless steel is used as a support for the intermediate ceramic layers. In order to obtain thin and crack-free membranes different parameters were optimized, such as drying conditions, calcination temperature, precursor concentration and viscosity of solution. The as-developed membranes were tested in a Wicke-Kallenbach cell under different operating conditions (temperature and pressure).

## Keywords

Membranes, coating, permeation tests.

## Introduction

Propylene oxide is an important intermediate in the chemical industry which is used for the realisation of different kind of products such as polyether polyols, propene glycol, butanediol etc. However, the main processes used for PO production are nowadays considered environmentally unfriendly, complex or lead to different and large amounts of undesired co-products with an important loss of the main component. The realisation of a sustainable and eco-friendly chemistry in accordance with the competitiveness of the industry's policy is one of the most important challenges to be afforded by the scientific community. The first effort to address these problems was made by developing a single stage reaction for the direct synthesis of propylene oxide starting from hydrogen, oxygen and propene<sup>1</sup>.



This reaction was first performed on highly dispersed gold nano-particles on titania catalysts. Higher selectivity to PO is achieved by using titanium silicalite -1 (TS-1) as a support<sup>2</sup>.

However, the application of this reaction is limited to too low yields. In fact, for avoiding the formation of explosive mixtures, it is necessary to use diluted reactants that allow working in safe conditions. These problems can be resolved by introducing and connecting different important and innovative concepts in the realisation of one single engineering element for the direct synthesis of Propene Oxide (PO): *catalytic membrane micro-reactor*. The presence of the catalytic membrane

enables the optimisation of the first step of the total reaction by feeding separately and in a controlled way hydrogen and oxygen gas. This avoids the formation of explosive regimes and contemporary the attainment of high concentrated gas mixtures<sup>3</sup>. The catalytic membrane also gives the possibility to control the consecutive reactions that can occur with the consequence of increasing selectivity and final production of PO.

Even more, all the benefits represented by the catalytic membrane are improved by connecting this technology with the micro-reactor concepts that allows working in an explosive regime without risks and to control possible runaway reaction effects.

## Experimental

The experimental part of the work was divided in two separated steps.

The first part focused on the synthesis of titania and silica membranes by testing several preparation methods like sol-gel technique, layers from powders and colloidal solutions. A titanium alcoxide was used as precursor and mixed with a solvent (alcohol), nitric acid and distilled water under controlled condition in order to obtain a sol solution. A dip-coating and a spin coating method were used for the preparation of the samples. The titania nano-particle powder was mixed with distilled water, plasticizer and film forming agent in order to obtain an homogeneous solution and scrape it on the stainless steel support. Silica coating layers were obtained, initially from a colloidal (30%v silica in water) and then from a gel-solution solution obtained from the mixing of

colloidal silica with fumed silica obtaining gel-solution.

During the second step permeability tests on the prepared titania-silica and  $\alpha$ -alumina provided membranes were carried out in a Wicke-Kallenbach cell. The membranes were evaluated for several gases at different temperatures, pressures and gas flow rates. The outlet stream, swept with argon and analyzed by a GC, allowed the net molar diffusion flux through the membrane to be calculated.

## Results

In order to obtain homogeneous crack free intermediate layers, several parameters were changed and optimized during the experimental part. The most important factors that were considered for improving the quality of the membranes were the concentration of the starting titania precursor, an accurate dip coating system and applying several coating intermediate layers (for the sol gel technique).

The addition of other components such as plasticizer and dispersant (to the powder-solution), the control of the drying and calcination method and the activation of the stainless steel support before utilization shows an improvement of the membrane characteristics. Figure 1 and Figure 2 show a picture of a titania-stainless steel used membrane and an alumina provided one.

The as-synthesized samples were tested in the W-K cell in order to calculate transport parameters for the diffused gas (oxygen). The permeation of the gas was correlated to the influence of the temperature and pressure.

The repetition of the experiments systematically increasing the temperature from room temperature to 250 °C allows finding out an optimal gas permeation value.

At the same time it was also possible to investigate the influence of the partial pressure on the oxygen diffusion through the membrane. The partial pressure of the inlet gas was changed by mixing the oxygen with another gas such as nitrogen.

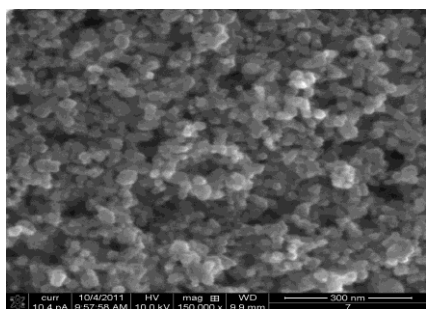


Figure 1. SEM of  $\text{TiO}_2$  layer on Stainless Steel.

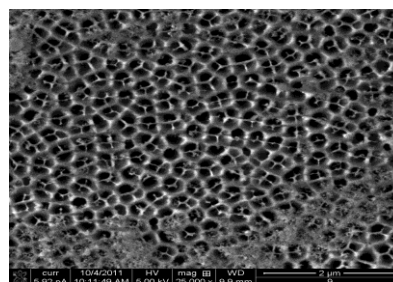


Figure 2. SEM of  $\alpha\text{-Al}_2\text{O}_3$  disc membrane.

## Conclusions

In conclusion, this work allows to observe that using a very simple method it was possible to obtain porous silica and titania membranes on stainless steel support. Better results were obtained from titania powder and colloidal silica compared to the sol gel technique.

The so prepared membranes were successfully tested under different oxygen flow rates temperature and pressure.

## Acknowledgements

The research leading to these results has received funding from the European Community's Seventh Framework Programme through the Collaborative Project INCAS, under agreement n° 245988.

## References

- [1] T. Hayashi, K. Tanaka, M. Haruta, Selective Vapor-Phase Epoxidation of Propylene over Au/TiO<sub>2</sub> Catalysts in the Presence of Oxygen and Hydrogen, *J. Catal.* 178 (1998) 566-575.
- [2] T. Alexander Nijhuis, Bart J. Huizinga, Michiel Makkee, Jacob A. Moulijn, Direct Epoxidation of Propene Using Gold Dispersed on TS-1 and Other Titanium-Containing Supports, *Ind. Eng. Chem. Res.* 38 (1999) 884-891.
- [3] S. T. Oyama, X. Zhang, J. Lu, Y. Gu, T. Fujitani, Epoxidation of propylene with H<sub>2</sub> and O<sub>2</sub> in the explosive regime in a packed-bed catalytic membrane reactor, *J. Catal.* 257 (2008) 1-4.