Separation and isomerization of xylenes using stainless-steel supported MFI zeolite membranes

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Objectives

The research aims at the investigation of permeation and isomerization of xylenes in different types of MFI zeolite membrane reactors. MFI zeolites are able to separate the para-xylene isomer from meta- end ortho-xylene based on the different size of the molecules as compared to the pore size of the zeolite framework. In addition, zeolites containing alumina (e.g. H-ZSM-5) are active for xylene isomerization.

The zeolite membranes are prepared by our project partner at the University of Erlangen (group of Prof. Schwieger) on stainless steel supports.

The membranes are characterised in terms of permeation behaviour and catalytic activity for isomerization. Moreover, a detailed simulation model is being developed which allows to treat the following three different configurations of membrane reactors.

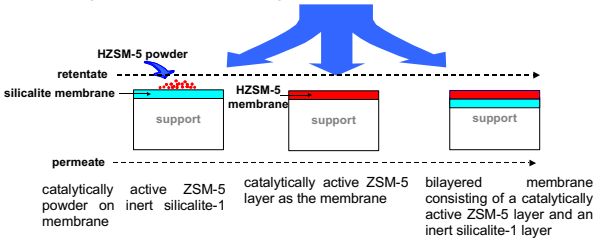

Fig. 1: Configurations of membrane reactors

Experimental setup and procedure

Setup:

- Membranes: stainless steel supported zeolite membranes with a diameter of 18 mm
- Range: permeation and reaction experiments at temperatures up to 500°C and pressures up to 5bar
- Sealing: copper ring pressed between membrane and holder (gas tight up to 600°C)

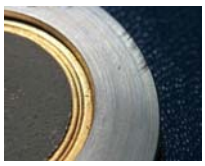

Fig. 2: membrane in holder sealed in holder before synthesizing the zeolite layer

Procedure:

- measurements of the fluxes of pure components, single xylene isomers in nitrogen, and xylene isomers mixtures in nitrogen
- single component measurement: a fixed amount of xylene vapour is fed to the closed retentate side; the pressure difference between permeate and retentate side is measured
- mixture experiments: nitrogen is used a diluent gas in retentate and permeate side
- the permeated amount of xylene is adsorbed on activated carbon and quantified by weighing and GC analysis

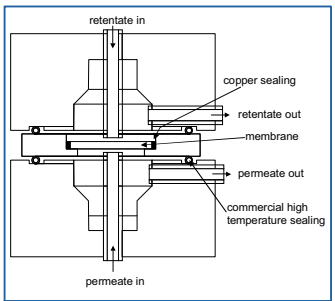

Fig. 3: Permeation cell

Modelling

The permeation through the membrane is modelled by a combination of the dusty-gas model (support), activated Knudsen diffusion model (transport through defects), and generalized Maxwell-Stefan model for surface diffusion (zeolite pores) [1] (network of independent transport pathways [2]).

$$-S_V c_{i,Sat}\frac{\Theta_i}{R\cdot T}\nabla\mu_i=\sum_{\substack{j=1\\ j\neq i}}^{n}\left(\frac{c_{jS}N_{iS}-c_{iS}N_{jS}}{c_{j,sat}\cdot Đ_{ijS}}\right)+\frac{N_{iS}}{Đ_{iS}}$$

Besides structural parameters describing the transport resistance of the support, the model requires the single-component Maxwell-Stefan-surface-diffusivities and their dependency on occupation as well as the individual component isotherms (IAS, NIAS [3, 4]).

$$c_{jS}\cdot Đ_{ijS}=\left(c_{jS}\cdot Đ_{iiS}\right)^{\frac{\Theta_i}{\Theta_i+\Theta_j}}\cdot\left(c_{iS}\cdot Đ_{ijS}\right)^{\frac{\Theta_i}{\Theta_i+\Theta_j}}$$

$$Đ_{iiS}=\frac{\Theta_i}{\frac{1}{D_{self,iS}}-\frac{1}{Đ_{iS}}}\qquad D_{self,iS}\text{ and }Đ_{iS}\text{ : determinated from experiments}$$

Moreover an empirical parameter describing the defect density of the membrane has to be determined by regression.

[1] R. Dittmeyer; G. Emig. in G. Ertl; et al. (Eds.): Handbook of Heterogeneous Catalysis. Vol. 8, 1727-1784, 2nd Ed., 2008, Wiley-VCH Verlag, Weinheim
[2] M. Hanebuth; et al. Catalysis Today 104 (2005), 352-359
[3] A.L. Myers. AIChE J. 48 (2002), 145-160
[4] F.R. Siperstein; A.L. Myers. AIChE J. 47 (2001), 1141-1159

Experimental and simulation Results

Fig. 4 and 5: Single component permeance of the three xylene isomers through a silicalite-1 membrane as a function of temperature and pressure. These measurements were used to determine the Maxwell-Stefan surface diffusivities for the permeation through the zeolite pores by numerical regression.

Fig. 4: - linear dependence of the permeance on the pressure
- this is typical for viscous, pressure driven flow
- conclusion: the permeation behaviour observed in these experiments (with high absolute pressure difference) depends mainly on the flow through the defects

In this case, the surface diffusion parameters calculated from these experimental results are inadequate and the model description of the flow through the zeolite pores is false.

Fig. 5: - permeance decreases with increasing temperature
- permeances of different xylene isomers are nearly the same
- the model can qualitative describe these behaviour

To determine the surface diffusion parameters from the experiments made in Erlangen additional work must be done. These experiments - carried out by zero pressure difference absolute - should focus more on the flow through the zeolite pores.

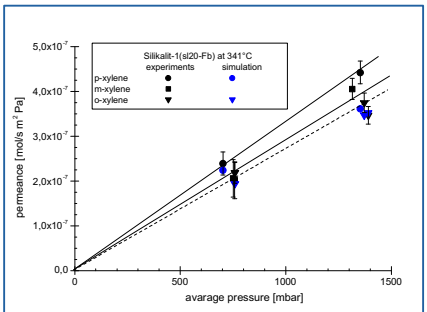

Fig. 4: Permeation results in dependence on the absolute pressure

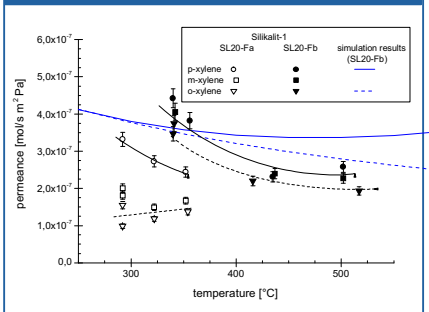

Fig. 5: Permeation results in dependence on the temperature

Conclusions

- Sealing with copper ring allows reliable measurements up to 600°C. The zeolite film must be deposited after pressing the support into the holder.
- The permeation through the membranes examined by the KWI is mainly defined by defect pores.
- A permeation model for the composite membrane, based on a network of independent pathways was created. It describes our permeation experiments.
- Diffusion parameters (determined from a singe component permeation experiments, with its high absolute pressure difference) cannot describe the permeation through the zeolite pores. We hope to obtain this parameters from the experiments made in Erlangen.