

INTERNATIONAL JOURNAL OF CHEMICAL REACTOR ENGINEERING

Volume 9

2011

Article A12

Compatibility of Transport and Reaction in Membrane Reactors Used for the Oxidative Dehydrogenation of Short-Chain Hydrocarbons

Christof Hamel*

Tanya Wolff†

Andreas Seidel-Morgenstern‡

*Otto-von-Guericke University Magdeburg, christof.hamel@ovgu.de

†Max Planck Institute Magdeburg, wolff@mpi-magdeburg.mpg.de

‡Otto-von-Guericke University Magdeburg, anseidel@ovgu.de

ISSN 1542-6580

DOI: 10.1515/1542-6580.2495

Copyright ©2011 De Gruyter. All rights reserved.

Compatibility of Transport and Reaction in Membrane Reactors Used for the Oxidative Dehydrogenation of Short-Chain Hydrocarbons*

Christof Hamel, Tanya Wolff, and Andreas Seidel-Morgenstern

Abstract

The possibility of process intensification by enhancing selectivity and yield in networks of parallel and series reactions was investigated applying asymmetric multilayer ceramic and sintered metal membranes in a dead-end configuration for a controlled distributed reactant feeding. The oxidative dehydrogenation of ethane to ethylene was selected as a model reaction applying three different doped and/or active $\text{VO}_x/\text{-Al}_2\text{O}_3$ catalysts. Experimental investigations were performed in a pilot scale in order to evaluate the potential of a distributed dosing via membranes with respect to operation conditions and compatibility of reaction and membrane properties. It was demonstrated that the rates of reaction and trans-membrane mass transfer have to be compatible for an optimal membrane reactor operation avoiding back diffusion of reactants out of the catalytic zone as well as achieving safety aspects. Therefore, a detailed modeling of the trans-membrane mass transfer under reaction conditions was carried out. As a main result, it was found metal membranes possess a favorable mechanical stability, relatively low costs for production and the possibility to control mass transfer if the rate of reaction and mass transfer in the membrane is compatible which can be adjusted by the trans-membrane pressure and the catalyst activity, respectively.

KEYWORDS: membrane reactors, oxidative dehydrogenation, ceramic membranes, sintered metal membranes, compatibility of transport and reaction in membrane, modeling

*Please send correspondence to Christof Hamel, phone: +49-391-67-12330; fax: +49-391-67-12028; email: christof.hamel@ovgu.de. The financial support of Deutsche Forschungsgemeinschaft (DFG research group "Membranunterstützte Reaktionsführung"), Max-Buchner-Forschungstiftung and "Fonds der Chemischen Industrie" is gratefully acknowledged.

Introduction

Selective oxidations of short-chain hydrocarbons can be described as a network of parallel-series reactions with activated olefins as desired but limited intermediate products whereas carbon dioxide is characterized as the thermodynamically stable final product. The maximal possible yield of desired intermediates is limited by the oxidative reaction itself [Hodnett, 2000, Sheldon und van Santen, 1995]. The olefins belong to the most important and precious base chemicals. Thus, there is a large interest in research and industry to develop new and economically feasible processes for their production. It is well known that the selectivity in specified reaction networks towards a desired product can be enhanced by various concepts. For example a suitable reaction temperature should be adjusted to favor the formation of the desired compounds [Edgar und Himmelblau, 1988]. Second, an active and more selective catalyst should be developed which accelerates specifically the desired reaction [Ertl et al., 2007, Millet et al., 2002]. Last but not least, improvements in the reactor design can offer promising possibilities. Innovative membrane reactors, which are capable to lower the local oxygen partial pressures inside the catalyst bed via distributed oxygen dosing, are promising candidates [Julbe et al., 2001]. Besides direct introduction of reactants into chemical reactors, various possibilities have been suggested to use porous or non-porous membranes in order to arrange different ways of contacting the reactants [Al-Juaied et al., 2001, Alonso et al., 2005, Caro et al., 2007, Coronas et al., 1995, Klose et al., 2003a, Lu et al., 1997b, Seidel-Morgenstern, 2005, Tonkovich et al., 1996]. Although this concept has been identified as interesting and promising, there are still several difficult problems that must be solved prior to an industrial application of membrane reactors of the distributor type. One clear deficit is the availability of suitable membranes. In this work the oxidative dehydrogenation of ethane to ethylene was carried out experimentally applying porous asymmetric ceramic and sintered metal membranes in a pilot-scale membrane reactor. Adjusted dosing profiles were realized by feeding reactants (oxygen diluted with nitrogen) separately through a permeable reactor wall. The investigated concept allows to improve selectivity and yield with respect to the desired intermediate product ethylene. Applying three types of catalysts and two membranes, it will be shown that a compatibility between mass transfer in the membrane itself and reaction rates is essential for successful reactor operation [van de Graaf et al., 1999] - an important aspect investigated in this contribution experimentally and by simulations in detail.

1 Reactor concept and model reaction

Reactant dosing in a membrane reactor - principle and requirements

Figure 1a) demonstrates the feeding concept in a packed-bed membrane reactor (PBMR) applied for a separated and distributed dosing of reactants, e.g. oxygen, through porous reactor walls in comparison to the well-established fixed-bed reactor (FBR).

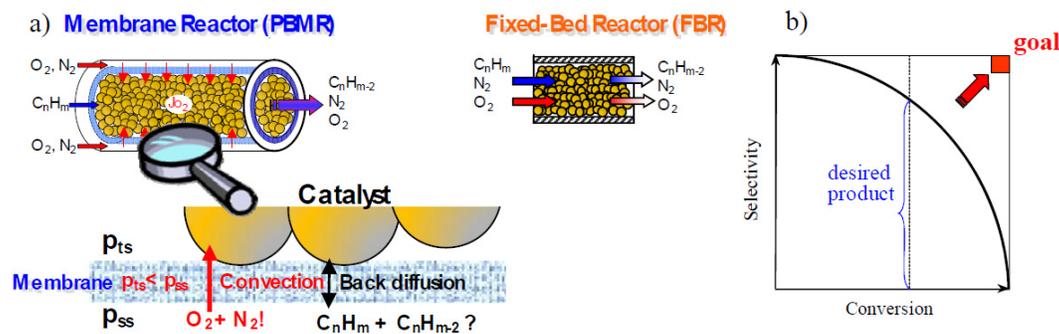


Figure 1: a) Principle of reactant dosing in membrane und fixed-bed reactors and b) illustration of objective for a successful operation.

The simultaneous improvement of conversion and selectivity with respect to desired but kinetically limited intermediates is the general objective of new reactor concepts as illustrated in figure 1b) by the upper right corner of the classical selectivity-conversion diagram.

The goal, high selectivity for a maximal conversion, can be approached in membrane reactors by favorably influencing the local concentrations and residence times of the reactants. Figure 2 illustrates schematically the development of axial reactant concentration profiles and total flow rates in the FBR and PBMR for identical overall inlet flow rates. In the PBMR the reactants are hereby fed separately into the tube side (ts) and the annular shell side (ss) of the membrane. The catalyst is placed in the tube side of the porous membrane as a simple packed bed. A dead-end membrane reactor configuration (shell side closed) is realized in order to feed reactants in well-defined fluxes through the membrane. All reactants, e.g. oxygen, have to permeate through the membrane, which is catalytically inert. This configuration is comparable to that reported in the recent literature, e.g. [Mallada et al., 2000, Ramos et al., 2000, Tonkovich et al., 1996]. However, it differs from suggestions, where the shell side outlet is

open, so that oxidant transfer over the membrane is influenced amongst others by diffusion [Farrusseng et al., 2001, Kölsch et al., 2002, Wang et al., 2009].

The total flow rate in the FBR remains approximately constant along the reactor length if the reaction mixture is diluted and the total number of moles is constant during reaction, respectively. In this simple reactor tube all reactants are fed commonly in a co-feed mode at the reactor inlet and thus have an identical residence time. In contrast, a separated and distributed dosing leads to an increase in the total flow rate along the reactor length based on the axial distributed feeding. Thus, the total flow rate is characterized by the sum of the inlet flow rate on tube side as well as the length-depending dosed amount coming from the shell side. Without chemical reaction the total flow at the reactor outlet is identical for both reactor concepts. The average residence time of the reactants dosed into the PBMR through the membrane is significantly higher compared to the co-feed mode. Therefore, a higher conversion can be expected in a PBMR.

Furthermore, the local concentration of the reactants influences significantly the local reaction rates, consequently conversion and especially selectivity, and thus the overall reactor performance. A mathematical analysis of the differential selectivity is given in the next chapter for concrete model reaction rates.

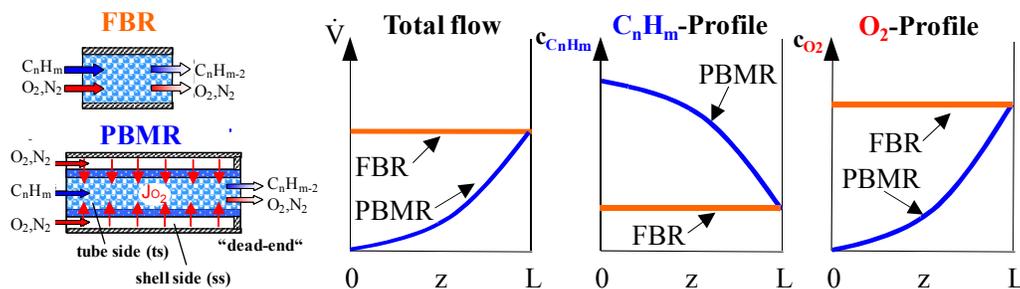


Figure 2: Comparison of axial concentration and total flow profiles in a fixed-bed and in a membrane reactor

To exploit the potential of a PBMR in a distributor as well as dead-end configuration, the total flow rate and the corresponding trans-membrane pressure have to be compatible to the properties of the membrane itself. The mass transfer in porous membranes is governed by convection and diffusion. For a controlled dosing in a dead-end mode it is important to guarantee that convection is dominating. In this way undesired diffusion of reactants from the catalytic zone to the shell side can be avoided.

Reaction network and kinetics

The oxidative dehydrogenation (ODH) of ethane to ethylene on three batches of $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ catalysts with different vanadium content and therefore catalytic activity was chosen as a defined and well-quantified model reaction. A detailed analysis of the reaction network including the five main reactions obtainable is given in [Grabowski, 2006, Klose et al., 2004b]. As illustrated in figure 3 the desired intermediate product ethylene is formed directly by the oxidative dehydrogenation of ethane (r_1). In case of high local concentrations of oxygen the consecutive reaction forming CO (r_3) and the total oxidation product CO_2 (r_4 , r_5) is favored. Furthermore, ethane can be oxidized totally in a direct parallel reaction from ethane (r_2). These unwanted reactions limit the maximal achievable ethylene selectivity to approximately 85% [Klose et al., 2004a].

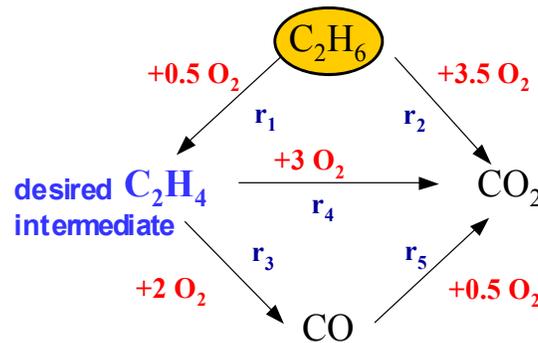


Figure 3: Reaction network of the oxidative dehydrogenation of ethane to ethylene

For the postulated reaction network above, neglecting the undesired reactions r_2 and r_5 , and applying a simple power law kinetic

$$\begin{aligned} r_1 &= k_1 \cdot x_{\text{C}_2\text{H}_6} \cdot x_{\text{O}_2}^{\beta_1} \\ r_3 &= k_3 \cdot x_{\text{C}_2\text{H}_4} \cdot x_{\text{O}_2}^{\beta_3} \\ r_4 &= k_4 \cdot x_{\text{C}_2\text{H}_4} \cdot x_{\text{O}_2}^{\beta_4} \end{aligned} \quad (1-3)$$

the differential selectivity regarding the desired intermediate ethylene is defined as follows:

$$dS_{\text{C}_2\text{H}_4} = \frac{r_1 - r_3 - r_4}{r_1} = 1 - \frac{k_3}{k_1} \cdot \frac{x_{\text{C}_2\text{H}_4}}{x_{\text{C}_2\text{H}_6}} \cdot x_{\text{O}_2}^{\beta_3 - \beta_1} - \frac{k_4}{k_1} \cdot \frac{x_{\text{C}_2\text{H}_4}}{x_{\text{C}_2\text{H}_6}} \cdot x_{\text{O}_2}^{\beta_4 - \beta_1} \quad (4)$$

It is well known that for a successful operation of a PBMR the reaction orders with respect to the dosed component are of essential importance. Typically, for selective oxidation reactions holds that the orders with respect to oxygen are higher in the total oxidation compared to the formation reactions, e.g. β_3 and β_4 in eq. 1-3 are larger than β_1 [Lu et al., 1997a, Lu et al., 1997b]. Based on the local oxygen concentration in the PBMR illustrated in figure 2, a higher selectivity with respect to the intermediate ethylene can be expected.

2 Experimental study

Catalysts and membranes

For the experimental investigation of the ODH of ethane to ethylene and the evaluation of the compatibility of this reaction with the trans-membrane mass transfer for various operation conditions porous membranes were applied in the PBMR. In addition several $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ catalysts were used, prepared by wet impregnation of 1mm $\gamma\text{-Al}_2\text{O}_3$ spheres with vanadyl acetylacetonate in acetone [Klose et al., 2003b]. The vanadium content of the three prepared catalysts was 1.4%, 3.0% and 5.0%. The color of the fresh catalyst was yellow, indicating that vanadium was mainly in the $+5$ oxidation state [Oppermann und Brückner, 1983]. After the measurements the catalyst color had changed to a light blue-green. This can be attributed to a significant reduction of V(V) to V(IV), the species responsible for a high selectivity in the ODH [Oppermann und Brückner, 1983, Zanthoff et al., 1999]. Ceramic and sintered metal membranes for distributing oxygen were investigated experimentally in a pilot-scale apparatus. Precisely, the tubular ceramic composite $\alpha\text{-Al}_2\text{O}_3$ membrane from INOCERMIC (Germany) consists of a mechanically stable support (average pore diameter: 3 μm ; thickness: 5.5 mm) on which two more intermediate layers (pore diameters: 1 μm and 60 nm; thickness 25 μm) and one final layer were deposited (pore diameter: 10 nm; thickness: 2 μm). The ceramic membrane had a length of 350 mm, an inner radius (r_i) of 10.5 mm and an outer radius (r_o) of 16 mm (figure 4). Both ends of the membrane were vitrified (blue color in figure 4), leaving a permeable zone of 104 mm in the center of the membrane. The transport properties of the ceramic membrane were analyzed in [Hussain et al., 2006]. Alternatively, sintered metal membranes were applied for oxygen dosing. These membranes from GKN Sinter Metal (Germany) were made of Inconel 600, and had a similar length as well as inner radius as the ceramic ones (figure 4, right hand side). In contrast, the outer radius was significantly smaller resulting from a different production process and amounted to 12.75 mm (average pore diameter: 1677 nm; thickness: 2.25 mm). The non-permeable zones of the inner tubes were filled with inert $\alpha\text{-}$

Al_2O_3 spheres whereas the porous reaction zones were prepared with the $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ catalyst described above.

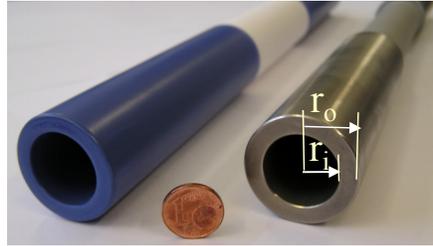


Figure 4: Applied ceramic and sintered metal membranes

Set-up

The applied set-up consisted of a membrane reactor and a fixed-bed reactor, a catalytic afterburner and a gas analysis for reactants and products. Siemens SIMATIC S7 was used as a process control system to run the unit automatically. Feed mixtures and flow configurations were realized using electronic mass flow controllers. All gas samples were analyzed with an Agilent 6890 GC/TCD and 5973 MSD system (AGILENT, Germany).

The housing of the membrane reactor consisted of a stainless steel tube (inner diameter: 38.4 mm) in which the ceramic and sintered metal membrane was implemented, respectively. The reactor was heated by an electric heating sleeve. Ethane, for safety reasons diluted 1:10 in nitrogen, was fed into the tube side of the membrane. As described above, air was pressed from the shell side through the porous membrane into the catalyst bed. Dosing all air over the membrane in a dead-end configuration has the advantage of an easy control of the amount of oxygen fed. Eight thermocouples were placed on shell and tube side. Gas samples were taken at the tube side inlet, directly after the reactor outlet and on the shell side, analyzing back diffusion of components through the membrane experimentally. Both membrane sides were sealed gas-proof by graphite seals during the assembling. The seals had a distance of 125 mm from the hot reaction zone to avoid temperatures above 550 °C at the seals, which are critical for the sealing material. Applying the realized reactor construction, it was possible to operate the reactor at catalyst temperatures up to 650 °C without any damage of the seals or the membrane. Performing experiments in a fixed-bed reactor, operating in a co-feed mode, the same reactor equipment was used. In contrast to the PBMR operation a completely vitrified alumina membrane with the same geometry was installed in the membrane reactor housing. The application of a vitrified membrane allows to avoid wall reactions, compared to a simple

laboratory fixed-bed reactor made from stainless steel only, and to perform experiments under comparable heat transfer conditions as in the PBMR.

Experimental procedure

The experimental studies were carried out in a temperature range between 500-630 °C. The molar $O_2/C_2H_6^{in}$ feed ratio was chosen as 1 which was found suitable for the model reaction selected in preliminary studies, e.g. [Seidel-Morgenstern 2010]. For the investigations carried out in a pilot-scale, relatively high flow rates were applied, approaching requirements set by industry. The W/F ratio (catalyst mass/total volumetric flow rate) was varied between 100-400 kg/s/m³ for all dosing strategies considered. In all measurements performed in the membrane reactor the shell side/tube side feed ratio was adjusted at 8, i.e. 88% of the total feed flow was introduced over the membrane. Reproducibility of the results was checked by conducting every product stream analysis three times for every set of experimental conditions and additionally by twice repeating every complete run.

3 Results and discussion of the experiments

Comparison between PBMR and FBR using ceramic membranes

In Figure 5 the performance of the membrane reactor applying ceramic membranes and the conventional FBR is compared in a wide temperature range. As illustrated in figure 5a) the selectivity of the desired intermediate product ethylene could be significantly increased in the PBMR for temperatures higher than 550 °C. Thus, the concept of decreasing the local oxygen concentration by a distributed dosing of oxygen to avoid undesired series reactions forming CO and CO₂ works successfully.

Furthermore, the ethylene selectivity can be significantly enhanced using the PBMR with ceramic membranes at similar levels of ethane conversion compared to the FBR (Figure 5b). A higher ethane conversion can be expected in the membrane reactor as long as the oxygen availability does not become rate determining. This is due to the prolonged contact time of ethane over the catalyst bed compared to the conventional co-feed mode (see figure 2). Thus, a benefit regarding the ethylene yield is given by the application of ceramic membranes. The trans-membrane pressure drop measured for the used asymmetric $\alpha-Al_2O_3$ membranes is depicted in figure 6a). For the experimental results given in figure 5 and obtained for $W/F = 400$ kgs/m³ the corresponding total shell side pressure was around 1.6 bar. No ethane or ethylene could be detected by random sampling on the shell side. Thus, the effect of back diffusion of reactants or products could be excluded for the applied ceramic membranes. However, this type of ceramic

membrane is expensive and sensitive with respect to thermal as well as mechanical stress.

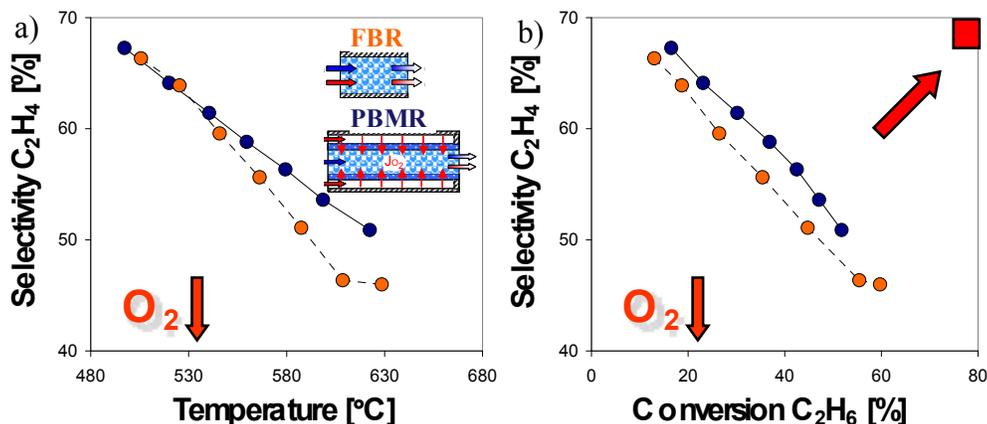


Figure 5: Ethylene selectivity vs. temperature (a) and vs. ethane conversion (b); $x_{C_2H_6}^{ts} = 1.5\%$, $x_{O_2}^{ss} = 1.5\%$, $W/F = 400 \text{ kg/m}^3$, 1.4%V catalyst, ceramic membrane (pore diameter: 10 nm)

Comparison between ceramic and sintered metal membranes

In spite of the performance improvement achieved by membrane assisted oxidant dosing, the drawback of a higher construction effort has to be addressed. Further, safe and cost-effective solutions for a temperature-resistant sealing of the membranes have to be found. In this study graphite was used for sealing the ceramic membrane. An alternative can be the use of sintered metal membranes as specified in chapter 2. Unfortunately, sintered metal membranes are currently available only with larger pores than ceramic ones (1677 vs. 10 nm). Thus, the trans-membrane pressure drop can be expected to be much lower than for mesoporous ceramic membranes as illustrated in figure 6a), too. When the trans-membrane pressure drop in a PBMR is of the same order of magnitude as the pressure drop over the catalyst bed, the distribution of the reactants along the length is not uniform anymore. This aspect can significantly affect the reactor performance. Furthermore, according to the theoretical analysis shown in chapter 4, it seems to be impossible to compensate the driving force for diffusion by convection for such sintered metal membranes. Only at higher feed flow rates coming from the shell side or with significantly thicker membranes, where higher pressure gradients are established, the application of sintered metal membranes appears to be attractive.

The sintered metal membranes were investigated by selected experiments under the same conditions as applied for the ceramic composite membranes, too. A comparison of the main results is given in figure 6. It has to be noted that the pressure drop over the metal membrane is approximately only one third compared to the ceramic membrane (see figure 6a). For this reason, the focus of the analysis carried out was set on those experiments with varying contact times because they demonstrate most sensitively the impact of the trans-membrane pressure drop on reactor performance.

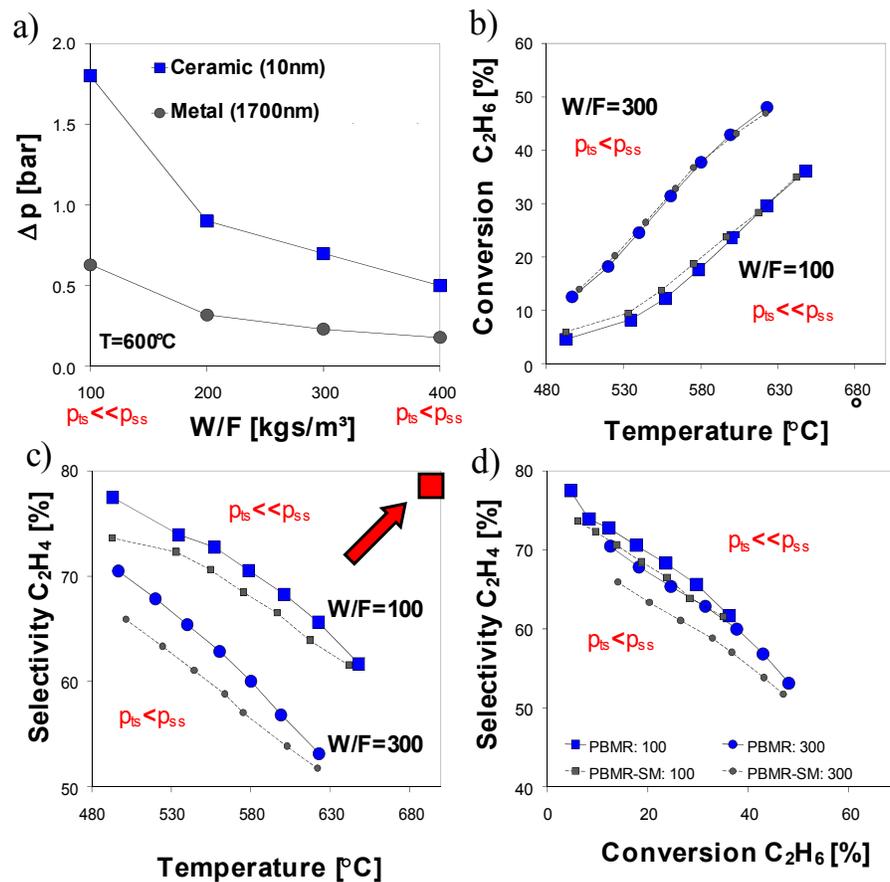


Figure 6: a) Trans-membrane pressure drop b) ethane conversion c-d) ethylene selectivity using ceramic membranes (Ceramic) and sintered metal membranes (Metal); $x_{\text{C}_2\text{H}_6}^{\text{ts}} = 1.5\%$, $x_{\text{O}_2}^{\text{ss}} = 1.5\%$, $W/F=100$ and 300kgs/m^3 , $W=17\text{g}$, $1.4\%V$ catalyst, $p^{\text{ts}}=1\text{bar}$

In comparison to the PBMR experiments with the ceramic membrane for short contact times, i.e. for high feed flow rates ($W/F = 100 \text{ kgs/m}^3$) corresponding to a high shell side pressure ($p_{ts} \ll p_{ss}$, figure 6a), the performance and especially the ethylene selectivity of the PBMR with the sintered metal membrane is lower (see figure 6b-c). Plotting the ethylene selectivity vs. ethane conversion also for higher contact times ($W/F = 300 \text{ kgs/m}^3$), corresponding to a negligible trans-membrane pressure drop ($p_{ts} \sim p_{ss}$), the performance of the PBMR applying a sintered metal membrane is significantly lower, as illustrated in figure 6d). For these conditions ethane was found in random samples on the shell side. This indicates that, due to the lower trans-membrane pressure drop for the reaction conditions applied with the metal membrane, back diffusion occurred. Due to these results the aspect of back diffusion was investigated by a more detailed modeling study of the porous sintered metal and ceramic membranes.

4. Modelling of porous membranes

The trans-membrane mass transfer in the used porous materials is characterized by viscous flux, molecular diffusion and Knudsen diffusion. In this contribution the Dusty Gas Model (DGM) suggested by [Mason und Malinauskas, 1983] was applied for the description of the internal transport effects. The following equation of the DGM is frequently used to quantify the mass transfer of N species in porous media e.g. [Edreva et al., 2009, Thomas et al., 2001, Zivkovic et al., 2004].

$$\sum_{j=1; j \neq i}^N \frac{x_i \cdot J_j - x_j \cdot J_i}{D_{ij}^e} - \frac{J_i}{D_{K,i}^e} = \frac{p}{R \cdot T} \nabla x_i + \frac{x_i}{R \cdot T} \cdot \left(1 + \frac{B_0^e \cdot p}{\eta \cdot D_{K,i}^e} \right) \cdot \nabla p \quad i=1, N \quad (5)$$

The two terms on the left hand side describe the influence of molecular diffusion and Knudsen diffusion [Taylor und Krishna, 1993]. The effective binary diffusion coefficient, D_{ij}^e , can be calculated by means of the ratio of porosity to tortuosity, ψ/τ , and the binary diffusion coefficient, D_{ij} . The latter is proportional to $T^{3/2}$ and $1/p$ [Cussler, 1999]. The effective Knudsen diffusion coefficient for an ideal, cylindric pore can be calculated using eq. 7 [Kärger und Ruthven, 1992]. $D_{K,i}^e$ is proportional to $T^{1/2}$ and does not depend on the total pressure.

$$D_{ij}^e = \frac{\psi}{\tau} \cdot D_{ij} \quad (6) \quad D_{K,i}^e = \frac{1}{3} \cdot \frac{\psi}{\tau} \cdot d_{Pore} \cdot \sqrt{\frac{8 \cdot R \cdot T}{\pi \cdot M_i}} \quad (7)$$

The second term on the right hand side of eq. 5 characterizes the contribution of convection through the membrane, which is a function of the trans-membrane pressure gradient. A high pressure gradient is necessary if convection should dominate in porous membranes in order to avoid an uncontrolled diffusion of

reactants in the applied membrane distributor in a dead-end configuration. B_0^e is the permeability constant which depends on the membrane material ($\psi; \tau$). For a cylindrical pore of diameter d_{pore} holds:

$$B_0^e = \frac{\psi}{\tau} \cdot \frac{d_{\text{pore}}^2}{32} \quad (8)$$

To apply the model introduced above the following parameters have to be known: $D_{K,i}^e$, B_0^e and ψ/τ . They can be estimated using specific measurement techniques [Hussain et al., 2006, Thomas et al., 2001]. For the two different types of investigated porous membranes the mass transfer parameters were estimated in previous works and are available elsewhere for the asymmetric ceramic membranes [Hussain et al., 2006, Thomas et al., 2001] and for the sintered metal membranes [Edreva et al., 2009].

Preliminary simulation study

First of all without chemical reaction and based on the geometry discussed in chapter 2 as well as the derived mass transfer parameters for the ceramic membranes and the sintered metal ones ($D_{K,i}^e$, B_0^e and ψ/τ), internal molar fraction profiles of ethane were calculated for three different trans-membrane pressures as illustrated in figure 7. It can be concluded that with increasing trans-membrane pressure the influence of convection depending directly on the total pressure gradient increases. Hence, the molar fraction of ethane in the membrane can be reduced and undesired back diffusion of ethane out of the reaction zone (to shell side) can be avoided. For the trans-membrane pressures covered in the simulations an accumulation of ethane could be suppressed only by applying the ceramic membrane and a pressure gradient of at least 1 bar. But the trans-membrane pressure is directly correlated with the flux through the membrane as well as the residence time of the reactants to obtain sufficient conversions of ethane. In contrast, for applying metal membranes, pressure gradients higher than 1 bar are needed to suppress the influence of back diffusion in this material as well. Thus, the compatibility between the rates of mass transfer and the rates of reaction have to be adjusted which is discussed in the following chapter.

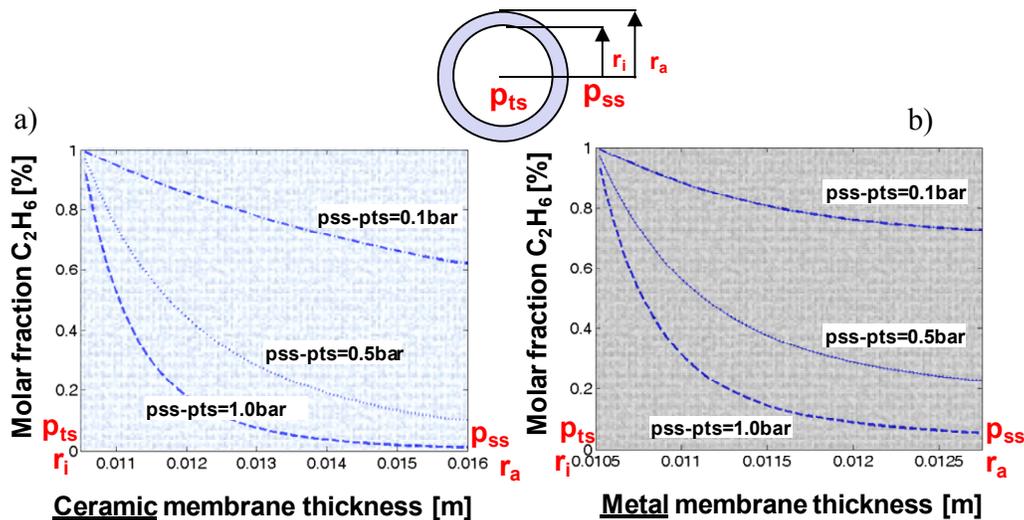


Figure 7: Molar fraction of ethane versus membrane thickness of a) ceramic and b) metal (2.25 mm) membranes for different trans-membrane pressures; $T=500^{\circ}C$, tube side in: $x_{C_2H_6}^{ts}=1.0\%$, $p_{ts}=1\text{bar}$, $x_{N_2}^{ts}=99\%$; shell side in: $x_{N_2}^{ss}=100\%$

5. Adjustable compatibility between reaction and membrane

Membrane modifications for a given catalyst

For a mathematical quantification of the phenomenon back diffusion, observed in the experiments by means of sintered metal membranes, eqs. 5-8 were applied again to simulate the mass transfer in the membrane texture for the experimental conditions applied, now including chemical reaction. Figure 8 shows the radial molar fractions of the reactant ethane in the ceramic and metal membrane for W/F ratios of 100 and 300 kgs/m^3 investigated in the experiments, too. In the applied ceramic membrane convection should be the dominating mass transfer contribution. Thus, a high trans-membrane pressure could be recognized and no ethane could be analyzed during the experiments or calculated in the annulus, too. In contrast to the results obtained for the ceramic membranes, the sintered metal ones reveal different mass transfer behavior. For $W/F = 300 \text{ kgs/m}^3$ and the corresponding shell side pressure of 1.2 bar (trans-membrane pressure 0.2 bar) diffusion is the dominating process in the metal membrane resulting in high ethane concentrations in the membrane itself and consequently on the shell side, where an undesired total oxidation reaction with the stainless steel housing takes place. Thus, lower ethylene selectivity for comparable conversions was found in the experiments as illustrated in figure 6. With an increasing total flux corresponding with a higher shell side pressure the convective part of mass

transfer in the used sintered metal membrane is more pronounced and the effect of diffusion can be repressed more efficiently.

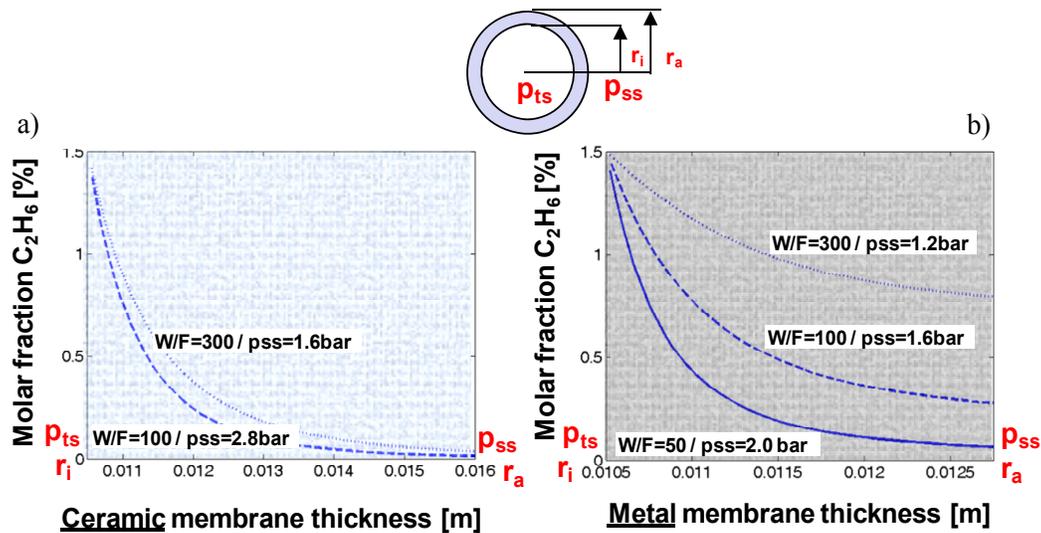


Figure 8: Molar fraction of ethane versus membrane thickness using a) ceramic and b) sintered metal membranes for flow rates investigated experimentally; $x_{C_2H_6}^{ts}=1.5\%$, $p_{ts}=1\text{bar}$, $T=550^\circ\text{C}$, $W=17\text{g}$

This is almost the case for $W/F > 50\text{ kg/m}^3$. But the increase of the total volumetric flow rate coming from the shell side is not independent from the chemical reaction. To realize acceptable conversions, suitable residence times as well as flow rates have to be adjusted. A more practical way to increase the trans-membrane pressure drop and, consequently, to enhance the part of convection is to manufacture the metal membranes with a wall thickness 3 or 4 times higher compared to the used tube thickness (2.25 mm), this the calculations revealed. If the membrane properties are fixed or the technical production procedure is limited with respect to such a kind of modifications discussed before, the catalyst should be adjusted as discussed in the following chapter.

Catalyst modifications for a given membrane

A second possibility, other than modifying the membrane geometry, is to enhance the reaction rates by influencing the catalyst activity. In Figure 9 the experimental results of ethane conversion and ethylene selectivity for three Vanadium catalysts with different Vanadium content (1.4%, 3.0% and 5.0% V) and therefore activity are illustrated. Beyond, a high trans-membrane flux ($W/F = 100\text{ kg/m}^3$) was

considered. The plots for 3.0% V reveal that with increasing catalyst activity the performance of sintered metal and ceramic membranes are more and more similar. Hence, a higher reaction rate of r_1 and r_2 can be expected consuming the reactant ethane significantly faster. Thus, the back diffusion of ethane can be suppressed by the chemistry itself using a more active catalyst, too. However, the influence of the undesired series reactions $r_2 - r_5$, reducing the desired intermediate product ethylene, is enhanced as well. That means, for a maximum ethylene yield the higher conversion based on a higher catalyst activity has to compensate the corresponding decrease in ethylene selectivity, which is evidently not the case for a Vanadium loading of 5.0%. Thus, no additional measurements for 5.0% V were performed with sintered metal membranes. The loss in the ethylene selectivity is dominating. In this case a lower catalyst activity should be chosen in combination with a thicker membrane discussed before.

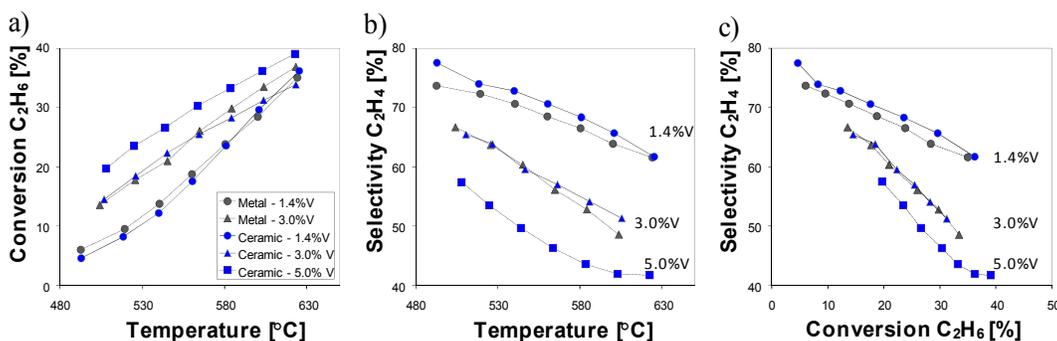


Figure 9: a) Ethane conversion and b) ethylene selectivity vs. temperature using ceramic membranes (Ceramic) and sintered metal membranes (Metal); $x_{C_2H_6}^{in}=1.5\%$, $x_{O_2}^{ss}=1.5\%$, $W/F=100\text{kg}/\text{m}^3$, $W=17\text{g}$, 1.4%, 3.0%, 5.0% V catalyst

However, despite this limitation, the application of metal membranes with their better characteristics regarding construction and mechanical stability can be attractive. Sintered metal membranes could be an alternative to overcome several disadvantages of ceramic membranes. Therefore back diffusion has to be suppressed by a dominating convection part in mass transfer which can be realized by a sufficient level of the trans-membrane pressure drop.

6 Summary

Based on a separated and distributed reactant feeding characteristic concentration and residence time effects result and thus a different reactor performance of

packed-bed membrane reactors and conventional fixed-bed reactors operating in a co-feed mode can be expected.

An experimental study of both reactor concepts was carried out applying ceramic and sintered metal membranes in a pilot-scale. As a model reaction the oxidative dehydrogenation of ethane to the desired but due to series and parallel reactions limited intermediate product ethylene was selected. The experiments using asymmetric ceramic membranes (pore diameter of the final layer: 10 nm; thickness: 5.5 mm) revealed for low concentrations of oxygen that the selectivity of the desired product ethylene could be increased significantly for simultaneously high ethane conversions compared to the well-established fixed-bed reactor.

In further experiments applying sintered metal membranes (average pore diameter: 1677 nm; thickness: 2.25 mm) a nearly comparable performance for short residence times corresponding with a high volumetric flow rate as well as high trans-membrane pressure gradients was recognizable, due to conditions where convection was found to be the domination part in the trans-membrane mass transfer.

However, due to back diffusion of reactants, the more promising operation region of the membrane reactor, at higher contact times and lean oxygen conditions, could not be covered with the applied metal membranes. Furthermore, the safety aspect of a separated feeding of hydrocarbons and oxygen is not guaranteed if back diffusion of reactants can occur and all the reactants are in contact on both sides of the membrane.

In a performed simulation study with respect to mass transfer in the membranes itself operation parameters were appreciated to adjust the compatibility of trans-membrane mass transfer in ceramic as well as sintered metal membranes and reaction rates avoiding back diffusion of reactants out of the reaction zone. Therefore the mass transfer rates in the membrane and the rates of the chemical reaction have to be compatible. To improve the compatibility between sintered metal membrane and reaction, two possibilities are thinkable regarding the used experimental equipment and materials. The first one is a modification of the membrane. Thicker membranes are suitable to enhance the trans-membrane pressure and correspondingly the part of convection. Thus, the molar fraction of ethane in the membrane could be reduced under comparable reaction conditions, as the performed simulation studies revealed. The second possibility is to realize higher reaction rates by a more active catalyst using the given membrane geometry as well as high trans-membrane fluxes. Nevertheless, for a maximum ethylene yield the higher conversion based on a more active catalyst has to compensate the corresponding decrease in ethylene selectivity.

However, potential is also seen in particular for the application of sintered metal membranes because of efforts regarding construction and mechanical stability. If the state of development of sintered metal membranes had reached the

one of ceramic membranes, the establishment of membrane reactors in industry would be a little bit more conceivable.

Notation

B_0^e	[m ²]	permeability constant
d_{Pore}	[m]	pore diameter
$dS_{\text{C}_2\text{H}_4}$	[-]	differential selectivity of ethylene
D_{ij}	[m ² /s]	binary diffusion coefficient
D_{ij}^e	[m ² /s]	effective diffusion coefficient
$D_{K,i}^e$	[m ² /s]	effective Knudsen diffusion coefficient
J_i	[mol/(s*m ²)]	flux of component i through reactor wall
k	[mol/(s*kg)]	reaction rate constant
M_i	[g/mol]	molar mass of component i
p	[Pa]	pressure
r	[mol((s*kg)]	reaction rate
r_i	[m]	reaction rate
r_o	[m]	reaction rate
R	[J/(mol*K)]	universal gas constant
T	[K]	temperature
x_i	[-]	molar fraction of component i

Greek

β_j		reaction orders of oxygen
η	[Pas]	dynamic viscosity
τ	[-]	tortuosity
ψ	[-]	porosity

Subscripts

i	component index
j	component index
ss	shell side
ts	tube side

Abbreviations

DGM	Dusty Gas Model
FBR	Fixed-bed reactor
ODH	Oxidative dehydrogenation
PBMR	Packed-bed membrane reactor

References

- [Al-Juaied et al., 2001] M.A. Al-Juaied, D. Lafarga, A. Varma, Ethylene epoxidation in a catalytic packed-bed membrane reactor: experiments and model, *Chemical Engineering Science*, 56, 2001
- [Alonso et al., 2005] M. Alonso, M.J. Lorences, G.S. Patience, A.B. Vega, F.V. Díez, S. Dahl, Membrane pilot reactor applied to selective oxidation reactions, *Catalysis Today*, 104, 2005
- [Caro et al., 2007] J. Caro, K.J. Caspary, C. Hamel, B. Hoting, P. Kölsch, B. Langanke, K. Nassauer, T. Schiestel, A. Schmidt, R. Schomäcker, A. Seidel-Morgenstern, E. Tsotsas, I. Voigt, H. Wang, R. Warsitz, S. Werth, A. Wolf, Catalytic Membrane Reactors for Partial Oxidation Using Perovskite Hollow Fiber Membranes and for Partial Hydrogenation Using a Catalytic Membrane Contactor, *Industrial & Engineering Chemistry Research*, 46, 2007
- [Coronas et al., 1995] J. Coronas, M. Menendez, J. Santamaria, Use of a ceramic membrane reactor for the oxidative dehydrogenation of ethane to ethylene and higher hydrocarbons, *Industrial & Engineering Chemistry Research*, 34, 1995
- [Cussler, 1999] E.L. Cussler, Diffusion mass transfer in fluid systems, Cambridge University Press, Cambridge, ISBN: 0-521-56477-8, 1999
- [Edgar and Himmelblau, 1988] T.F. Edgar, D.M. Himmelblau, Optimization of Chemical Processes, McGraw-Hill Education, ISBN: 0070189927, 1988
- [Edreva et al., 2009] V. Edreva, F. Zhang, M. Mangold, E. Tsotsas, Mass Transport in Multilayer Porous Metallic Membranes - Diagnosis, Identification and Validation, *Chemical Engineering & Technology*, 32, 4, 2009
- [Ertl et al., 2007] G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp, Handbook of Heterogeneous Catalysis, Wiley VCH, Weinheim, ISBN: 3527312412, 1-8, 2007
- [Farrusseng et al., 2001] D. Farrusseng, A. Julbe, C. Guizard, Evaluation of porous ceramic membranes as O₂ distributors for the partial oxidation of alkanes in inert membrane reactors, *Separation and Purification Technology*, 25, 2001
- [Grabowski, 2006] R. Grabowski, Kinetics of oxidative dehydrogenation of C₂-C₃ alkanes on oxide catalysts, *Catalysis Reviews*, 48, 2006
- [Hodnett, 2000] B.K. Hodnett, Heterogeneous catalytic oxidation : fundamental and technological aspects of the selective and total oxidation of organic compounds, John Wiley and Sons, LTD, ISBN: 0-471-48994-8, 2000.

- [Hussain et al., 2006] A. Hussain, A. Seidel-Morgenstern, E. Tsotsas, Heat and mass transfer in tubular ceramic membranes for membrane reactors, *International Journal of Heat and Mass Transfer*, 49, 2006
- [Julbe et al., 2001] A. Julbe, D. Farrusseng, C. Guizard, Porous ceramic membranes for catalytic reactors — overview and new ideas, *Journal of Membrane Science*, 181, 2001
- [Kärger and Ruthven, 1992] J. Kärger, D.M. Ruthven, Diffusion in zeolites and other microporous materials, John Wiley & Sons, New York, ISBN: 0-471-50907-8, 1992
- [Klose et al., 2003a] F. Klose, Hamel, M. Joshi, A. Tota, A. Seidel-Morgenstern, Optimized oxidant dosing in packed-bed membrane reactors for the catalytic oxidation of hydrocarbons, *International Conference on Chemical Reactors*, Berlin, 01.-05.12.2003a
- [Klose et al., 2004a] F. Klose, M. Joshi, C. Hamel, A. Seidel-Morgenstern, Selective oxidation of ethane over a VO_x/Al₂O₃ catalyst – investigation of the reaction network, *Applied Catalysis A: General*, 260, 2004a
- [Klose et al., 2003b] F. Klose, T. Wolff, M. Alandjiyska, M. Joshi, H. Weiß, A. Seidel-Morgenstern, Partial oxidation of ethane - the potential of membrane reactors, *J. Univ. Chem. Technol. Metall.*, 38, 2003b.
- [Kölsch et al., 2002] P. Kölsch, M. Noack, R. Schäfer, G. Georgi, R. Omorjan, J. Caro, Development of a membrane reactor for the partial oxidation of hydrocarbons: direct oxidation of propane to acrolein, *Journal of Membrane Science*, 198, 2002
- [Lu et al., 1997a] Y.P. Lu, A.G. Dixon, W.R. Moser, Y.H. Ma, Analysis and optimization of cross-flow reactors for oxidative coupling of methane, *Industrial & Engineering Chemistry Research*, 36, 3, 1997a
- [Lu et al., 1997b] Y.P. Lu, A.G. Dixon, W.R. Moser, Y.H. Ma, Analysis and optimization of cross-flow reactors with distributed reactant feed and product removal, *Catalysis Today*, 35, 4, 1997b
- [Mallada et al., 2000] R. Mallada, M. Menéndez, J. Santamaría, Use of membrane reactors for the oxidation of butane to maleic anhydride under high butane concentrations, *Catalysis Today*, 56, 2000
- [Mason and Malinauskas, 1983] E.A. Mason, A.P. Malinauskas, Gas transport in porous media: The Dusty-Gas Model, Elsevier, Amsterdam, ISBN: 0-444-42190-4, 1983
- [Millet et al., 2002] J.M.M. Millet, H. Roussel, A. Pigamo, J.L. Dubois, J.C. Jumas, Characterization of tellurium in MoVTeNbO catalysts for propane oxidation or ammoxidation, *Applied Catalysis a-General*, 232, 1-2, 2002
- [Oppermann and Brückner, 1983] H. Oppermann, W. Brückner, Vanadiumoxide, Akademie-Verlag, Berlin 1983

- [Ramos et al., 2000] R. Ramos, M. Menéndez, J. Santamaría, Oxidative dehydrogenation of propane in an inert membrane reactor, *Catalysis Today*, 56, 2000
- [Seidel-Morgenstern, 2005] A. Seidel-Morgenstern, Analysis and experimental investigation of catalytic membrane reactors, in *Integrated chemical processes : synthesis, operation, analysis, and control*, Wiley-VCH, Weinheim, ISBN: 3-527-30831-8, 2005.
- [Seidel-Morgenstern, 2010] A. Seidel-Morgenstern, *Membrane Reactors: Distributing reactants to Improve Selectivity and Yield*, Wiley-VCH, Weinheim, ISBN: 978-3-527-32039-3, 2010
- [Sheldon and van Santen, 1995] R.A. Sheldon, R.A. van Santen, *Catalytic Oxidation: Principles and Applications -A course of the Netherlands Institute for Catalysis Research*, World Scientific Publishing, 1995
- [Taylor and Krishna, 1993] R. Taylor, R. Krishna, *Multicomponent mass transfer*, John Wiley & Sons, New York, ISBN: 0-471-57417-1, 1993
- [Thomas et al., 2001] S. Thomas, R. Schäfer, J. Caro, A. Seidel-Morgenstern, Investigation of mass transfer through inorganic membranes with several layers, *Catalysis Today*, 67, 2001
- [Tonkovich et al., 1996] A.L.Y. Tonkovich, J.L. Zilka, D.M. Jimenez, G.L. Roberts, J.L. Cox, Experimental investigations of inorganic membrane reactors: A distributed feed approach for partial oxidation reactions, *Chemical Engineering Science*, 51, 1996
- [van de Graaf et al., 1999] J.M. van de Graaf, M. Zwiép, F. Kapteijn, J.A. Moulijn, Application of a silicalite-1 membrane reactor in metathesis reactions, *Applied Catalysis A: General*, 178, 1999
- [Wang et al., 2009] H. Wang, A. Feldhoff, J. Caro, T. Schiestel, S. Werth, Oxygen selective ceramic hollow fiber membranes for partial oxidation of methane, *AIChE Journal*, 55, 10, 2009
- [Zanthoff et al., 1999] H.W. Zanthoff, S.A. Buchholz, A. Pantazidis, C. Mirodatos, *Chemical Engineering Science*, 54, 1999
- [Zivkovic et al., 2004] T. Zivkovic, N.E. Benes, H.J.M. Bouwmeester, Gas transport efficiency of ceramic membranes: comparison of different geometries, *Journal of Membrane Science*, 236, 2004