Membrane reactor microstructured by filamentous catalyst

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Dedicated to Prof. Wim van Swaaij on the occasion of his 60th birthday

Abstract

A novel design of microstructured membrane reactor with micro-channels formed between closely packed catalytic filaments is reported. The system comprises filaments of 7 μm in diameter and has a laminar flow with a short radial diffusion time. This leads to low pressure drop and to a narrow residence time distribution (RTD) during reactor operation.

The latter device in combination with a membrane permeable to hydrogen is used in non-oxidative propane dehydrogenation. The catalytic filaments of Pt/Sn on alumina were active/selective and sustained periodic regeneration. This innovative micro-reactor system allowed to control the selectivity to propene due to a narrow RTD. At propane conversions exceeding equilibrium, selectivities towards propene up to 97% were attained.
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1. Introduction

Micro-structured reactors are characterized by three-dimensional structures in the sub-millimeter range. Mainly multichannel reactors are currently used with channel diameters between ten and several hundred micrometers. One of the main features of micro-structured reactors is their high surface to volume ratio, being 1–2 orders of magnitudes higher as compared to traditional chemical reactors.

Due to the small reactor dimensions, diffusion times are short and the influence of mass transfer on the rate of reaction is substantially reduced. As heat transfer is greatly improved if compared to conventional systems, higher reaction temperatures are admissible allowing reduced reaction volumes and amount of catalysts (Hardt, Ehrfeld, & Bussche, 2000). Therefore, micro-structured reactors are particularly suitable for fast endo- and exothermic reactions and for the design of autothermal systems. Furthermore, the narrow residence time distribution in microchannel reactors (Ehrfeld, 1995; Ehrfeld, Hessel, & Haverkamp, 1999) allows to optimize the contact time and to suppress formation of by-products in complex reaction.

One of the main problems in using micro-structured reactors for heterogeneously catalyzed reactions is the introduction of a catalytic active phase. The easiest way would be to fill micro-channels by catalyst powder, as proposed by Tonkovich and collaborators for hydrogen generation (Daym et al., 2000; Fitzgerald et al., 2000). The drawback of this method is the high pressure drop. In addition, each channel must be packed identically to avoid maldistribution.

Therefore, research is focused on the development of thin catalytic layers deposited on the reactors' walls within the micro-structure. Hönicke and coworkers (Hönicke & Wiessmeier, 1995; Wiessmeier & Hönicke, 1998) chose aluminium as construction material for micro-channel reactors. The specific surface of the micro-channels was increased by anodic oxidation of the aluminium surface resulting in a thin porous layer of α-Al$_2$O$_3$. The obtained oxide layer had a very regular pore structure oriented perpendicularly to the flow direction. This porous layer served as support for the catalytically active components. The use of aluminium is restricted by temperatures up to $450\,^\circ$C. Therefore, different methods of deposition of active catalytic layers on other materials are under development. Sol–gel methods are commonly proposed to obtain a porous support on the wall of the micro-channels (Wiessmeier, Schubert, & Hönicke, 1997). Catalytically active phase can be deposited on the porous layer by common precipitation or impregnation.

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In the present paper, a novel concept of a micro-reactor system is proposed and tested in the catalytic non-oxidative dehydrogenation of propane. Production of propene via non-oxidative catalytic dehydrogenation of propane has technological constrains due to the high endothermicity ($\Delta_r H = 129$ kJ/mol at 823 K and 0.14 MPa) and the unfavourable thermodynamic equilibrium conversion of 22% under the same conditions. Furthermore, at high temperatures required by the reaction thermodynamics, thermal cracking occurs lowering the selectivity with coke deposition on the catalytic surface. To regenerate the catalyst, the formed coke has to be burned off periodically in oxidative atmosphere.

2. Reactor concept

The micro-structured system reported consists of a two-zone tubular reactor of few millimeters in diameter filled with catalytically active filaments placed parallel to the tube walls. The filaments are introduced in the form of threads. The two zones are separated by a Pd-membrane allowing to eliminate hydrogen from the reaction mixture, thus exceeding equilibrium conversion.

Parallel filaments of few micro-meters in diameter (3–10 µm) (Wolfrath, Kiwi-Minsker, & Renken, 2000) form micro-channels with flow hydrodynamics similar to multi-channel micro-reactors. The equivalent diameter (d_{eq}) of the channels for gas flow between the filaments (see Fig. 1) depend on the diameter of the filaments (d_f) and their geometric arrangement (Fig. 2). As the equivalent diameter is defined as

$$d_{eq} = 4\frac{A}{b} \tag{1}$$

with A the cross section, b the circumference,

$$d_{eq}^{(1)} = \left(\frac{2\sqrt{3}}{\pi} - 1\right) d_f \cong 0.103\ d_f \text{ (Fig. 2a)}, \tag{2a}$$

$$d_{eq}^{(2)} = \left(\frac{4}{\pi} - 1\right) d_f \cong 0.273\ d_f \text{ (Fig. 2b)}. \tag{2b}$$

The flow system described has a hydraulic diameter in the range of a few microns ensuring laminar flow. At first glance, the parabolic laminar flow profile should result in a vast residence time distribution. But Tayler and Aris showed that radial diffusion can compensate the broadening effect of the parabolic flow profile (Baerns, Hofmann, & Renken, 1999). For circular tubes, the axial dispersion coefficient, D_{ax}, is given by

$$D_{ax} = D + \frac{u^2 d_t^2}{192\,D}, \tag{3}$$

where D is the molecular diffusion coefficient, u the average linear velocity, d_t the tube diameter.

Due to the small tube diameters of micro-channels, the radial diffusion time of gases is in the order of milliseconds
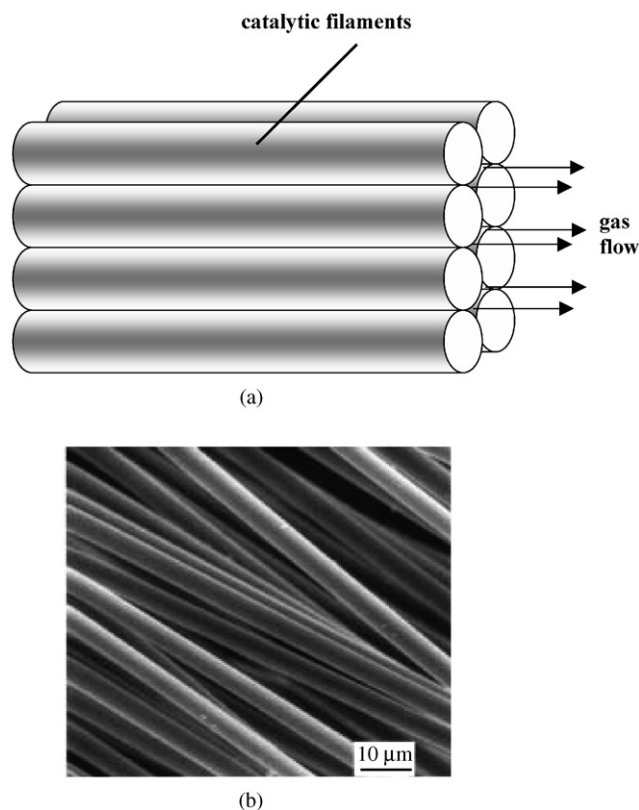

Fig. 1. (a) Schematic presentation of axial flow of gases between catalytic filaments. (b) SEM of catalytic filaments in a thread.
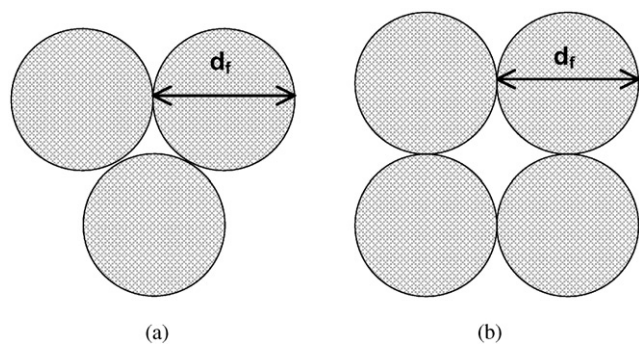

Fig. 2. Geometrical arrangement of filaments in a structured catalytic packing.

and the axial dispersion can be efficiently suppressed, as shown by theoretical and experimental studies (Commenge, Rouge, Renken, Corriou, & Matlosz, 2001; Rouge, Spoetzl, Gebauer, Schenk, & Renken, 2001).

The micro-structured membrane reactor with filamentous catalyst was used in the continuous production of propene from propane via non-oxidative dehydrogenation. A Pd/Ag membrane, permeable to hydrogen, separates two concentric zones of the tubular reactor shown schematically in Fig. 3. On one side of the membrane (zone I), the dehydrogenation takes place with simultaneous coke formation on the catalyst surface and diffusion of hydrogen to zone II. On the other side of the membrane
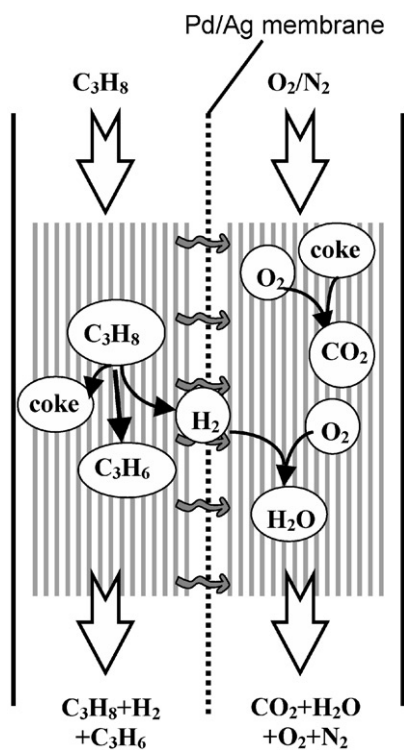
Fig. 3. Scheme of the two-zone microstructured membrane reactor.

(zone II), hydrogen is oxidized by air, thus generating heat for the endothermic dehydrogenation in zone I. Moreover, due to the permanent oxidation of hydrogen, a high radial concentration gradient of hydrogen is obtained. This allows an efficient removal of hydrogen from the reaction zone and consequently to exceed reaction equilibrium. Simultaneously with the hydrogen oxidation, the deactivated catalyst is regenerated by burning off coke from the catalyst surface. The feeds of air and propane are switched periodically between the two zones to produce propene continuously.

3. Experimental

Aluminoborosilicate glass fibres in woven form (Vetrotex France SA) with a specific surface area of SSA = 2 m² g⁻¹ were used as starting material for the catalyst preparation. First, the fabrics were treated at 90°C in 1.0 N aqueous solutions of HCl to leach out the non-silica components of the glass, then the material was rinsed in distilled water and dried in air at 50°C overnight (Kiwi-Minsker, Youranov, Slavinskaia, Zaikovskii, & Renken, 2000). By this procedure the specific surface area is increased up to 290 m² g⁻¹ indicating that porous filaments were obtained. The filament's surfaces were then covered by γ-alumina via deposition/precipitation of aluminium hydroxide from aqueous solution of a suitable salt followed by drying and calcinations in air at 650°C during 3 h. The resulting support material— alumina/silica filaments (ASF)—is stable up to 800°C, and

has a SSA in the range of 100–230 m² g⁻¹. The specific surface area was determined by the BET method.

The active metals (Pt and Sn) were deposited via two-steps impregnation from aqueous ammonia solutions (pH = 10). $SnCl_2$ and hexachloroplatinic acid (H_2PtCl_6) (purum, Fluka Chemie AG, Buchs, Switzerland) were used as precursors. Impregnation was followed by drying at 50°C overnight and calcination at 450°C in air for 1 h. The concentrations of the solutions were adjusted to obtain a catalyst formulation of 0.5%Pt–1%Sn on ASF. This composition was reported to be selective towards propene and to have acceptable long-term stability (Yarusov, Zatolokina, Shitova, Belyi, & Ostrovskii, 1992).

The catalytic filaments were introduced into the tubular reactor in the form of threads. Each thread with a diameter of about 0.5 mm consists of a bundle of ∼ 100 filaments, Fig. 1b), with a diameter of ∼ 7 μm. The catalytic threads were placed in parallel into the tube to form a cylindrical catalytic bed of different lengths in the range of 10–200 mm. The catalytic bed arranged in this manner has about 300 threads per cm² within the tube cross-section. The porosity of the filamentous packed bed is $\varepsilon \cong 0.8$. The specific surface per volume is in the order of 108 m² m⁻³ and thus, about 50 times higher compared to washcoated tubes of the same inner diameter (Hatzlantonlou, Andersson, & Schöön, 1986).

The membrane used in this study consists of a Pd/Ag (23 wt%) alloy in the form of a tube of 6 mm internal diameter with a wall thickness of 70 μm (Johnson Matthey and Brandenberger SA, Zürich, Switzerland). The length of the structured catalytic bed is $L_{cat} = 130$ mm, corresponding to 1.54 g catalyst in each zone. It is inserted in a quartz tube of 8.6 mm inner diameter (Fig. 4). The tube and shell volumes are equal to 4.0 ml.

The reaction was carried out at a temperature of $T = 823$ K and a pressure of 0.14 MPa. Before reaction, the catalyst was heated under nitrogen flow at 10 K min⁻¹ up to the reaction temperature. After 15 min of temperature stabilization, nitrogen was replaced by a flow of pure propane and the reaction products were monitored.

The reaction mixture was analyzed by gas chromatography (Hewlett Packard, HP 6890, capillary column: Sulpeco Carboxen 1010).

Conversion of propane was calculated according to Eq. (4). The calculation does not consider the conversion of propane to coke as its instantaneous formation is time dependent and difficult to estimate. Therefore, the calculation is based on propane conversion to propene, ethane, ethene and methane. The relative error is estimated to be in the order of 2–4%

$$X_{C_3H_8} = \frac{y_{C_3H_6} + \frac{2}{3}y_{C_2H_6} + \frac{2}{3}y_{C_2H_4} + \frac{1}{3}y_{CH_4}}{y_{C_3H_8} + y_{C_3H_6} + \frac{2}{3}y_{C_2H_6} + \frac{2}{3}y_{C_2H_4} + \frac{1}{3}y_{CH_4}}, \quad (4)$$

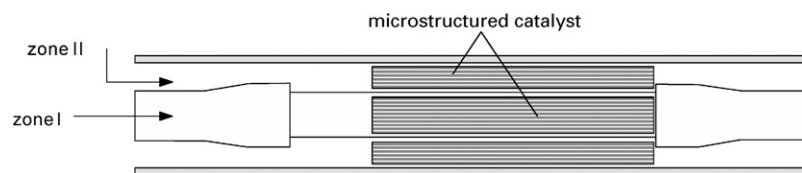$$S_i = \frac{(c_i/3)y_i}{y_{C_3H_6} + \frac{2}{3}y_{C_2H_6} + \frac{2}{3}y_{C_2H_4} + \frac{1}{3}y_{CH_4}}, \quad (5)$$

Fig. 4. Set-up of the membranereactor with two concentric zones.

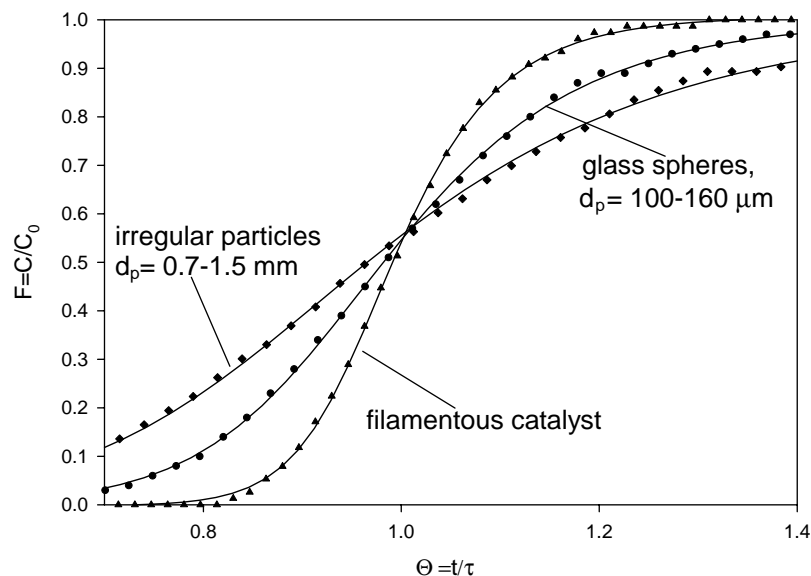Fig. 5. Step response curves for differently packed bed reactors ($Q = 30$ cm^3 min^{-1} (STP), tracer: 10 vol % Ar in $N_2 \Rightarrow N_2$).

where y_i is the molar fraction of compound i (propene, ethane, ethene, methane), and c_i is the number of carbon atoms in this compound.

Residence time distribution in different catalytic beds was determined by measuring the response on a step function (10% Ar in N_2) via a quadrupole mass spectrometer (TSU 260D, Balzers, Balzers, Liechtenstein) in a larger tubular reactor: $L = 230$ mm, ID $= 15$ mm, OD $= 18$ mm. The residence time distribution (RTD) was measured in a tube packed with the filamentous catalyst and with particles of silica and γ-alumina of different shapes and sizes.

4. Results and discussion

4.1. Residence time distribution

Hydrodynamics of gas flow through the micro-structured filamentous catalytic bed was studied and compared to different conventional packings. Experimental results are presented in Fig. 5. Under identical experimental conditions, randomly packed beds showed significantly broader RTD as compared to the structured filamentous packing.

The RTD is characterized by the mean residence time, $\bar{t}$, and the variance around the mean value, σ^2. Based on the

step response curves, the two parameters can be calculated as follows (Baerns et al., 1999):

$$\bar{t} = \int_0^1 t \, \mathrm{d}F = \int_0^\infty (1 - F) \, \mathrm{d}t, \tag{6}$$

$$\sigma^2 = \int_0^1 (t - \bar{t}) \, \mathrm{d}F = 2 \int_0^\infty t(1 - F) \, \mathrm{d}t - \bar{t}^2. \tag{7}$$

In dimensionless form

$$\sigma_\theta^2 = \sigma^2 / \bar{t}^2. \tag{8}$$

For the dispersion model, the Bodenstein number, $Bo = uL/D_{\mathrm{ax}}$, characterizes the spreading of the residence times in a tubular reactor. D_{ax} is the axial dispersion coefficient, representing the spreading process (Baerns et al., 1999; Levenspiel, 1999).

For the three packings shown in Fig. 5, the numerical results are shown in Table 1.

Besides the significantly narrower RTD in structured filamentous packed reactors as compared to randomly packed beds, the pressure drop is also considerably lower. For the same volumetric gas flow of 30 cm^3 min^{-1} (STP), the pressure drop through the filamentous packing was found to be $\Delta P \cong 7$ hPa. This values is roughly 5 times lower compared to the fixed bed packed with spheres of 100–160 μm

Table 1
Variance of the residence time distribution curves

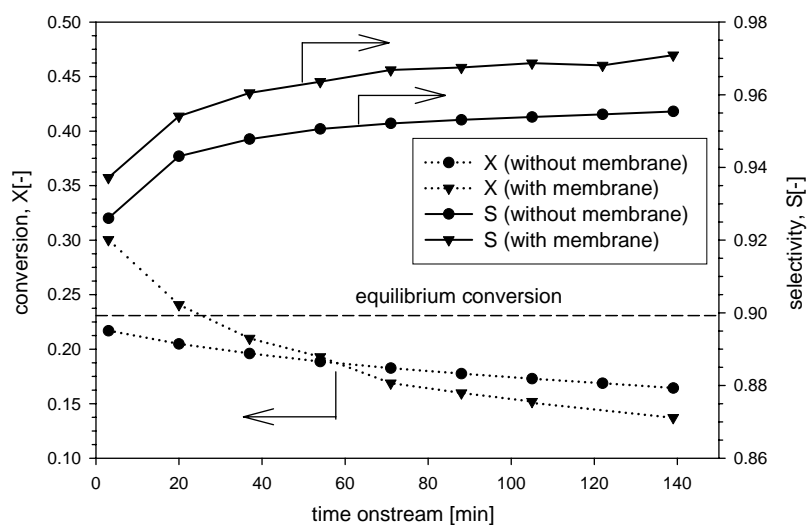|	Variance	Bodenstein no.
Randomly packed bed		
Irregular particles (0.7–1.5 mm)	$\sigma_\theta^2 = 75 \times 10^{-3}$	$Bo = 30$
Randomly packed bed		
Glass spheres (0.10–0.16 mm)	$\sigma_\theta^2 = 32 \times 10^{-3}$	$Bo = 66$
Structured bed		
filamentous catalyst	$\sigma_\theta^2 = 8.7 \times 10^{-3}$	$Bo = 234$

Fig. 6. Propane conversion and selectivity towards propene in microstructured reactors with and without membrane ($T = 823$ K, $P = 0.14$ MPa, GHSV $= 189$ h^{-1}, $\tau = 19$ s.

diameter with the same volume and 3.5 times lower if compared with reactors with the same mass of catalyst.

The pressure drop measured under laminar flow for the structured reactor can be used to estimate the equivalent diameter of the channels based on the well-known relationship of Hagen–Poisieulle.

Thus, the catalytic bed of 15 mm inner diameter consisting of about 46,000 filaments is equivalent to $N = 38,000$ cylindrical microchannels of 70 μm diameter.

The estimated hydraulic diameter of 70 μm is in the same order of magnitude as for conventional multichannel micro-reactors.

4.2. Catalyst testing and reactor operation

The propane dehydrogenation was first performed in a quartz tube reactor of 6 mm internal diameter. At 823 K and 0.14 MPa, propane conversion of 22% corresponding to thermodynamic equilibrium is reached. Observed by-products are methane, ethane and ethene. Under identical reaction conditions, the conversion was found to be similar on powdered and on filamentous catalyst (Wolfrath, Kiwi-Minsker, & Renken, 2001). Deactivation due to coke formation is slow in both cases. But the selectivity towards

propene is higher over the filamentous catalyst: a maximum of 95.5% is reached, instead of 88%, over the powdered catalyst. This is explained by the narrower RTD obtained in the structured bed, thus suppressing undesired consecutive reactions.

The reaction was then carried out in the membrane reactor with micro-structured catalytic bed installed in zones I and II (Fig. 4). The residence time was increased to 15 s to maximize propane conversion. At the same temperature and pressure, the initial conversion in the membrane reactor reached 30% thus exceeding significantly the equilibrium conversion of 22% (Fig. 6). Due to coke formation, the catalytic activity decreases with time on stream. According to the coke formation scheme proposed by Larsson et al. (Larsson, Henriksson, & Andersson, 1997), the equilibrium between propene and coke precursors is shifted to the latter due to hydrogen removal from the catalytic bed. This explains the faster deactivation of the catalyst in the membrane reactor as seen from Fig. 6.

Propene selectivity is enhanced in the membrane reactor: the amount of by-products is twice lower and propene selectivity reaches 97%. This increase can be explained by the lower concentration of hydrogen in the gas phase, suppressing hydroisomerization and hydrogenolysis reactions (Matsuda, Koike, Kubo, & Kikuchi, 1993).
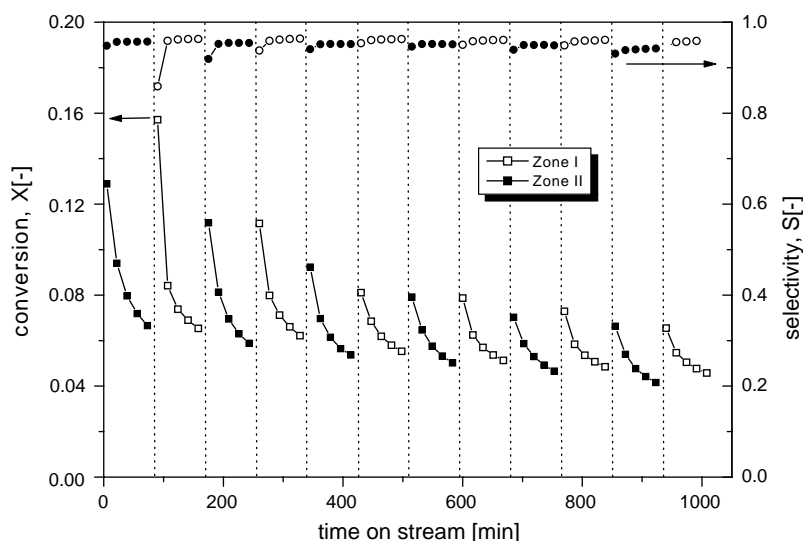
Fig. 7. Propane conversion and propene selectivity in a periodically operated two-zone microstructured membrane reactor (T=823 K, P=0.14 MPa, τ=17 s, hydrogen and coke oxidation in air).

Finally, the two zone micro-structured membrane reactor was tested in a long-term reaction run. Temperature and pressure were held constant at 823 K and 0.14 MPa, respectively. Pure propane was fed in one zone, whereas hydrogen was continuously oxidized by air under the same conditions in the second zone together with the catalyst regeneration by burning off the coke. Every 85 min, the feeds were switched between the two zones. The experimental results are shown on Fig. 7. Within the first cycle, the conversion drops in both zones from about 16 to 7%. After the oxidation period, the initial conversion increases, but the activity observed in the first cycle over fresh catalyst cannot be reached. After 4 reaction/regeneration periods, the conversion profiles become reproducible in both zones. The propane conversion varies regularly between 7% and 5%.

Compared to industrial processes with selectivities in the range of 80–90% (Eisele & Killpack, 2000), the observed propene selectivity of 95–97% is relatively high. Furthermore, the selectivity is not effected by the catalyst deactivation being independent on time-on-stream and the different reactor zones.

5. Conclusions

A novel micro-structured catalytic bed was reported, which is made of long threads consisting of fine filaments of 7 μm in diameter. In this micro-structured packing, gas flow through micro-channels formed between the filaments. The advantages of the microstructure with estimated hydraulic channel diameters of $\cong$ 70 μm, namely laminar flow, low pressure drop and narrow residence time distribution is confirmed.

Applied to non-oxidative propane dehydrogenation, it allowed a better control of reaction time due to the narrower residence time distribution leading to increased propene selectivity from 88% to 95%.

In a reactor with a hydrogen permeable membrane, the propene selectivity was increased up to 97% due to the removal of H_2 suppressing hydroisomerization and hydrogenolysis reactions. As the hydrogen is oxidised in a second compartment integrated in the system, autothermal reactor behavior can be realized. In long-term runs, stable activity and high selectivity could be achieved in periodic operation.

The presented micro-structured packings gives new opportunities for the design of heterogeneous catalytic reactors.

Notation

A	cross section, m^2
ASF	Alumina silica filament
b	circumference, m
Bo	Bodenstein number ($=uL/D_{ax}$) dimensionless
d_{eq}	equivalent diameter, m
d_f	diameter of filaments, m
D	diffusion coefficient, m^2 s^{-1}
D_{ax}	axial dispersion coefficient, m^2 s^{-1}
GHSV	gas hourly space velocity, h^{-1}
ID, OD	internal and outer diameter, m
L	Length, m
P	pressure, Pa
Q	volumetric flowrate, m^3 s^{-1}
RTD	residence time distribution
SSA	specific surface area, m^2 g^{-1}
$\bar{t}$	mean residence time, s
X, S	Conversion and selectivity, dimensionless

Greek letters

μ	viscosity, Pa s
σ^2	variance of the RTD, s^2
τ	space time, s

Acknowledgements

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