Supporting Information

Continuous gas-phase hydroformylation of but-1-ene in a membrane reactor by supported liquid-phase (SLP) catalysis

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Workflow

The EU project ROMEO (Reactor Optimization by Membrane Enhanced Operation) developed the monolithic membrane reactor along a process chain with individual tasks assigned for each partner. The workflow is shown in Figure S1 and the sub-chapters are following this workflow.



Figure S1. Workflow of the EU ROMEO project targeting hydroformylation reaction.

Preparation of polydimethylsiloxane (PDMS) coating solution

Dutczak et al. have reported that pre-crosslinking PDMS with multiple solvent dilution steps at a set temperature of 60 °C, aided reaching a final polymeric content of 3.75 wt.% and a viscosity of 100 mPa, which was ideal for membrane formation by dip-coating¹. In other reports, precrosslinked PDMS solutions have been prepared at higher temperatures of 80 °C, which increased the reaction kinetics^{2,3}. However, precise temperature and viscosity control are required, when increasing the temperature above 65 °C. The PDMS solution used within this study was synthesized, according to Dutczak et al., but altered slightly as described in the following.

The PDMS solution was prepared in a four-necked flask placed in a heating mantle for temperature control. In a first step, 20.45 g of the vinyl terminated PDMS pre-polymer RTV 615 A (Technisil) was weighed into the flask and consecutively mixed with 127.5 g of HPLC-grade toluene (Sigma-Aldrich). The solution was then heated to 65 °C under constant stirring (200 rpm), where after 2.05 g of the Pt-catalyzed crosslinker RTV 615 B (Technisil) was added directly to the solution. After 60 to 120 min, the viscosity of the solution increased rapidly and the solution started to wrap around the stirrer. At this point, another 150 g of toluene was added and the stirring rate increased

to 300 rpm, while the solution was concurrent re-heated to 65 °C. After reaching the desired temperature of 65 °C, another 300 g toluene was added and the stirring rate increased to 350 rpm until the solution started to wrap around the stirrer once more (about 30 min). At this point, the flask was placed in an ice bath to quench the reaction immediately.

Coating of SiC monoliths with PDMS membrane

The SiC monoliths (LiqTech International A/S, Ballerup, Denmark) were after delivery washed by multiple submersions in fresh deionized water. Subsequently, they were oven dried at 100 °C overnight and placed under vacuum for more than 4 h prior to PDMS coating.

The PDMS membrane was formed on the outer surface of the SiC monolith via a dip-coating process, where the bore channels of the monolith were sealed to avoid PDMS intrusion into the inner channels (Figure S1).



Figure S1. Photograph of the dip-coating process of a SiC monolith.

The monolith was double-coated in PDMS solution with an insertion speed of 10 mm s⁻¹, a holding time of 60 s in the solution and a retracting speed of 10 mm s⁻¹. Afterwards, the coated monolith

was dried in a fume hood at ambient conditions for 24 h. Following the dip-coating of the monolith, the PDMS layer was thermally crosslinked. Thermal crosslinking of PDMS has been commonly performed in literature and is a process of interconnecting polymer chains to enhance the physical and chemical stability of the polymer by making the matrix more rigid and stiff^{4,5}. However, crosslinking can also deteriorate the membrane permeability⁶. Thermal crosslinking was performed in an oven at 120 °C for 60 min with a heat-up and a cool-down time of 3 h, respectively. Figure S2 shows representative examples of a native SiC monolith and a PDMS coated monolith. The PDMS coating is visible in Figure S2b as a shiny and transparent layer.



Figure S2. Photographs of a) native SiC monolith and b) SiC monolith with PDMS coating.

Gas permeation tests

Gas transport through dense polymer films is based on the solution-diffusion mechanism. The solution-diffusion mechanism consists of three steps, which are the sorption of molecules into the membrane surface at the high-pressure side; molecule diffusion through the membrane; and molecule desorption from the membrane surface at the low-pressure side⁷. These three steps govern the time it takes for a molecule to move from the high-pressure feed side to the low-pressure permeate side and is expressed in the material-specific permeability *P* by Equation (S1), where *S* is the sorption coefficient, and *D* is the diffusion coefficient^{7,8}. The unit of permeability is Barrer (1 Barrer = $1 \cdot 10^{-10}$ cm³(STP) cm cm⁻² s⁻¹ cmHg⁻¹).

$$P = S * D \tag{S1}$$

When *P* is determined experimentally, it is often calculated by Equation (S2), where V(STP) is the flux through the membrane at standard conditions, A_{mem} is the active membrane area, δ_{mem} is the membrane thickness, and Δp is the pressure difference from feed to permeate side.

$$P = \frac{V(STP) * \delta_{mem}}{A_{mem} * (\Delta p)}$$
(S2)

If the membrane thickness is unknown, or difficult to determine, the membrane-specific permeance Q can be measured instead of the permeability by Equation (S3).⁹ The unit of permeance is expressed in GPU (1 GPU = 1.10⁻⁶ cm³(STP) cm⁻² s⁻¹ cmHg⁻¹)¹⁰.

$$Q = \frac{P}{\delta_{mem}}$$
(S3)

With the single-gas permeance data of two components, an ideal selectivity for component i and j is calculated with Equation (S4).

$$\alpha_{i,j} = \frac{P_i}{P_j} = \frac{Q_i}{Q_j} \tag{S4}$$

All permeation experiments were conducted in the setup shown in Figure S3.



Figure S3. a) Photograph of the membrane module installed in the gas permeation setup. b) Flow scheme of the gas permeation setup.

Catalyst impregnation into SiC monoliths

All syntheses and impregnation steps were carried out by Schlenk techniques under argon atmosphere (99.999 vol.-%), and all chemicals were used as received. Two different stock solutions were prepared for the catalyst impregnation; One containing Rh precursor, ligand, stabilizer and ionic liquid (catalyst system 1), and one containing all components except the ionic liquid (catalyst system 2).

Catalyst system 1 was prepared by dissolving ligand 6,6'-[(3,3'-di-tert-butyl-5,5'-dimethoxy-1,1'biphenyl-2,2'-diyl)bis(oxy)]bis(di-benzo[d,f][1,3,2]dioxaphosphepin) (biphephos or bpp, Evonik Oxeno GmbH; 3.76 g, 0.00478 mol) and Rh precursor [Rh(acac)(CO)₂] (Sigma-Aldrich, 98 %; 0.309 g, 0.00120 mol) separately in 40 ml anhydrous CH₂Cl₂ (Sigma-Aldrich, ≥99.8 %) during stirring for 15 min, where after the solutions were mixed under consecutive stirring for 60 min. Similarly, stabilizer bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate (sebacate, Evonik Oxeno GmbH; 0.01913 9.20 g, mol) and ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C_2C_1 Im][NTf₂], Sigma-Aldrich, \geq 98.0 %; 18 ml) were dissolved in 60 and 20 ml anhydrous CH₂Cl₂, respectively, during stirring before added to the ligand/Rh precursor solution with an additional 2 ml of anhydrous CH₂Cl₂. The resulting catalyst solution contained a molar bpp-to-Rh ratio of 4 and a molar sebacate-to-Rh ratio of 16, and was stirred for at least 2 h before used for monolith impregnation. Catalyst system 2 was prepared by a similar method as catalyst system 1 without added ionic liquid and by final addition of 40 ml of anhydrous CH₂Cl₂ instead of 2 ml as used for catalyst system 1.

The stock solutions were analyzed via nuclear magnetic resonance (NMR) spectroscopy. Figure S4 depicts the ³¹P NMR spectra (CD₂Cl₂, 25 °C, 400 MHz, Bruker Ascend 400 MHz spectrometer, reference to H₃PO₄) of the bpp ligand (top) and the stock solutions of catalyst system **1** with IL (middle) and catalyst system **2** without IL (bottom). Strong signals from uncoordinated bpp ligand (δ 145.5 ppm) dominated the spectra of both stock solutions, whereas only minor signals from coordinated ligand (δ 150-160 ppm) and bpp oxide (δ 5-10 ppm) were present (species assigned in accordance with literature¹¹). The relative amounts of the oxidized ligand remained essentially unchanged in the stock solutions compared to the parent ligand. Importantly, this left excess ligand available under the hydroformylation reaction conditions for formation of the catalytically active species, which were expected to be identical since the n/iso-selectivities obtained during catalysis for the catalyst systems were similar.



Figure S4. ³¹P NMR of the stock solutions of catalyst system 1, 2 and the bpp ligand as reference.



gure S5. Photograph (a) and schematic flow scheme (b) of the dip-coating procedure used for catalyst impregnation into the monoliths.



Figure S6: Technical drawing of custom-made PTFE tool for catalyst impregnation of membranecoated monoliths. The tool seals the PDMS membrane-coated monolith on top and bottom, enabling impregnation of the monolith with a catalytically active system. The top part allows liquid injection and removal.

| Catalyst | bpp/Rh | sebacate/Rh | Δw | [Rh(acac)(CO) ₂] | Rh | bpp | sebacate | $[C_2C_1Im]NTf_2$ | Rh loading* |
|-------------|-----------|-------------|------------|------------------------------|------|-------|----------|-------------------|-------------|
| system | (mol/mol) | (mol/mol) | (g) | (mg) | (mg) | (g) | (g) | (g) | (wt.%) |
| SLP without | 4 | 16 | 1.29 | 30 | 12 | 0.366 | 0.894 | - | 0.011 |
| PDMS | | | | | | | | | |
| SLP with | 4 | 16 | 1.52 | 35 | 14 | 0.432 | 1.056 | - | 0.013 |
| PDMS | | | | | | | | | |
| SILP | 4 | 16 | 4.31 | 33 | 13 | 0.399 | 0.977 | 2.901 | 0.012 |

Table S1: Composition of the prepared Rh-bpp monolith catalysts.

*Mass fraction of rhodium over neat monolith.

Electron microscopy

High-resolution images of monoliths were taken using a tabletop microscope (TM3030plus, Hitachi) and two scanning electron microscopes (S-3000 and S-4800, Hitachi). A high vacuum sputter coater (EM ACE600, Leica) was used, to sputter the scanning microscope samples with an approximately 3 nm thick gold layer. For sample preparation, all samples were placed in liquid nitrogen for 2 min. Mechanical stress was applied to break the samples immediately after removing them from the liquid nitrogen bath.

Membrane reactor design

The housing system of the membrane reactor was custom-built in stainless steel (1.4571) and consisted of a pipe sealed via a flange system to both sides with a fixed flange welded to the pipe and the counterpart attached with 6 screws. To connect the reactor to the peripheral structures of a test rig, tube connectors were used on top of both loose flanges ensuring fast assembling and disassembling of the whole reactor within the rig. Inside the housing, the membrane module was stabilized via a removable disc located on top of a phase inside the tube. To the side of the tube additional bores with smaller tubes were installed opposite to each other, forming the back-flushing

gas system by which the permeated product can be removed from the system. Figure S7 depicts an explosion diagram of the reactor system.



Figure S7. Explosion diagram of the high-pressure membrane housing including the membrane module (left). Three stage sealing system indicated by blue, green and orange arrows of the membrane housing (right).

The sealing of the membrane reactor was realized in three different stages using O-sealing rings of FFKM to be compatible with aldehydes. The first sealing stage (depicted by the orange arrow) ensured sealing of the permeate section against the inlet/outlet of the membrane module. The blue arrow indicates the location of the second sealing stage, which was realized by an O-ring around the removable disk. This O-ring ensured sealing of the permeate section against the reactor wall itself. The final and third sealing stage (green arrow) was implemented by an O-ring surrounding the outer loose flange keeping all the reactants inside the reactor housing. The sealing system was tested under elevated pressure and revealed to be pressure resistant up to 20 bars (referring to the sealing system).

In order to heat the reactor system evenly, an aluminum shuttering was constructed to compensate the difference in diameter between the flanges and the pipe itself. With an even diameter of the construction, a ceramic heating jacket could be used providing efficient heat supply to the system and easy handling. To minimize the heat loss of the system, an insulating jacket was applied around the whole system allowing to keep a temperature difference over the length of the reactor to less than 5 °C with a temperature offset as low as 2 °C. All described parts of the heating system are depicted in Figure S8.



Figure S8. Ceramic heating jacket with notches for back-flushing gas system (left), heating jacket closed via clip-locks for fast assembly and disassembly (middle), insulating jacket to minimize heat loss (right).

Continuous gas-phase hydroformylation

The catalytic testing of the monoliths (with and without PDMS membrane layer) for hydroformylation of but-1-ene was carried out at 100 °C and 11 bar feed pressure using the reactor setup shown in Figures S9 and S10. The reactor was assembled inside a glovebox to prevent possible air contamination. To keep the monolith inert, an inert gas stream of helium was applied to the feed inlet when installing the reactor module in the set-up.



Figure S9. Photograph of the continuous gas-phase hydroformylation reactor setup.

A detailed flowsheet of the reactor setup is shown in Figure S10. All gases were purchased from Linde Gas and individually regulated by mass flow controllers (Bronkhorst AG), while but-1-ene was dosed using an HPLC Smartline pump 100 (Knauer) equipped with a 10 ml pump head. The feed stream contained 2.20 mmol min⁻¹ of helium (purity 99.97 vol.-%), 4.58 mmol min⁻¹ of hydrogen (purity 99.999 vol.-%), 4.13 mmol min⁻¹ of carbon monoxide (purity 99.97 vol.-%) and 1.59 mmol min⁻¹ of but-1-ene (purity 99.5 vol.-%).



Figure S10. Flow scheme of the continuous gas-phase hydroformylation reactor setup.

When carrying out experiments with membrane-coated monoliths, a flow of 2.93 mmol min⁻¹ of nitrogen (purity 99.999 vol.-%) was applied as a sweep stream with a TMP of 3 bar. The retentate and permeate stream were analyzed alternatingly using an on-line gas chromatograph (Bruker 450-GC) equipped with two FID detectors (CP-Wax 52CB, 25 m length, 0.53 mm inner diameter, 2 μ m coating for C5-C10 separation; CP-Porabond Q, 25 m length, 0.53 mm inner diameter for C4 separation) and one TCD detector (Shincarbon column for permanent gases).

For analysis, the permanent gases hydrogen, helium, nitrogen and carbon monoxide were calibrated by a dilution series on the TCD, while but-1-ene was calibrated on the FID. The resulting calibration lines are given in graph S11.



Figure S11. Calibration lines of permanent gases helium (green), hydrogen (orange), nitrogen (blue) and carbon monoxide (grey) on TCD (bottom graph) and but-1-ene (red) on FID (upper graph).

The calibration of the remaining hydrocarbons was done according to Scanlon *et al.* using relative response factors according to the concept of the effective carbon number.¹³

Kinetic evaluation of catalytic experiments

The turnover frequency (TOF) of but-1-ene was used to express the activity of the system and calculated according to Equation (S5), where the molar flows of but-1-ene ($\dot{n}_{but-1-ene}$) are related to the moles of Rh applied in the SLP catalyst.

$$TOF = \frac{\dot{n}_{but-1-ene, in} - \dot{n}_{but-1-ene, out}}{n_{catalyst}}$$
(S5)

The chemoselectivity of the reaction was calculated taking into account that several by-products including iso-pentanal, cis-but-2-ene, trans-but-2-ene, butane, n-pentanol, iso-pentanol as well as the aldol products 3-hydroxy-2-propylheptanal and 2-propylhept-2-enal were formed besides the desired aldehyde product n-pentanal. To compare the different monolithic systems (with and without ionic liquid, with and without PDMS membrane layer), the resulting permeate and retentate streams of the experiment with membrane were added up. By doing so, the activity and chemoselectivity could be calculated similarly to systems without membrane. The reaction selectivities for all products were calculated using Equation S6.

$$S_{product} = \frac{\dot{n}_{product, out}}{\dot{n}_{but - 1 - ene, in} - \dot{n}_{but - 1 - ene, out}} * \frac{v_{but - 1 - ene}}{v_{product}}$$
(S6)

In addition to the product selectivity of the pure component, the n/iso-selectivity is generally used as a characterization value for the catalyst performance. It represents the percentage of formed desired n-product compared to all formed aldehydes, as described by Equation S7.

$$S_{n/iso} = \frac{\dot{n}_{n-pentanal,out}}{\dot{n}_{n-pentanal,out} + \dot{n}_{iso-pentanal,out}}$$
(S7)

To evaluate the membrane functionality, it is common to calculate the membrane selectivity¹² but due to the simultaneous consumption, formation and permeation of the respective components the average partial pressures are unknown. Hence, a membrane selectivity cannot be determined but instead an enrichment factor is defined according to Equation S8. This factor represents the enrichment of the n-pentanal over but-1-ene ratio in the permeate stream compared to the same ratio in the retentate stream.

Enrichment factor =
$$\frac{\left(\frac{\dot{n}_{n-pentanal,out}}{\dot{n}_{but-1-ene,out}}\right)_{permeate}}{\left(\frac{\dot{n}_{n-pentanal,out}}{\dot{n}_{but-1-ene,out}}\right)_{retentate}}$$
(S8)

Catalyst stability

The SLP catalyst was tested for long time stability under standard reaction conditions. Over 300 h time on stream no sign of deactivation of change in selectivity pattern was observed. We attribute this to the high stability of the Rh-SLP system inside the SiC monolith.



Figure S12. Hydroformylation of but-1-ene using Rh-bpp catalyst dissolved in sebacate 3 impregnated on SiC monolith without PDMS membrane coating applied. Conversion of but-1-ene (\mathbf{O}) and resulting TOF (\Box) are shown in the top graphs, while selectivities toward n-pentanal (*),

isomerization products (\Box), aldol products (ϖ) and n/iso ratio (\bullet) are shown in the bottom graphs. Reaction conditions: T = 100 °C, p_{feed} = 11 bar(abs), $\dot{n}_{\text{He,feed}}$ = 2.2 mmol min⁻¹, $\dot{n}_{\text{H2,feed}}$ = 4.6 mmol min⁻¹, $\dot{n}_{\text{CO,feed}}$ = 4.1 mmol min⁻¹, $\dot{n}_{\text{but-1-ene,feed}}$ = 1.6 mmol min⁻¹, bpp-to-Rh ratio = 4, Rh-loading a) = 13.0 mg, Rh-loading b) = 12.0 mg.

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