Supporting Information

Ultra-low temperature water-gas shift reaction catalyzed by homogeneous Ru-complexes in a membrane reactor – membrane development and proof of concept

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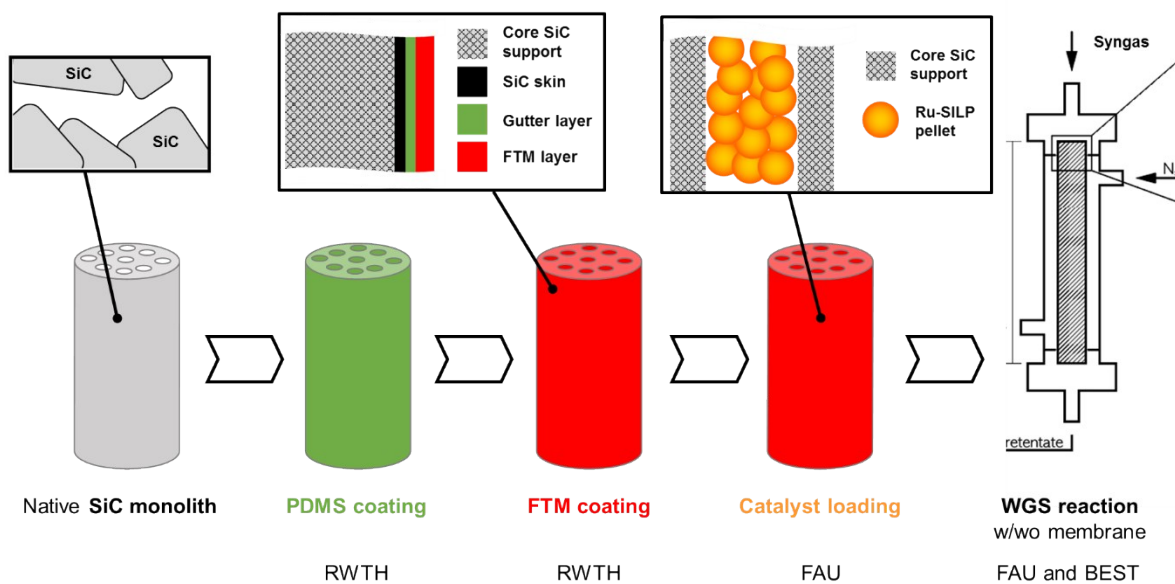
ROMEO project workflow

Figure S1. Schematic description of the workflow within the ROMEO project for the development of Ru-SILP WGS membrane reactors.
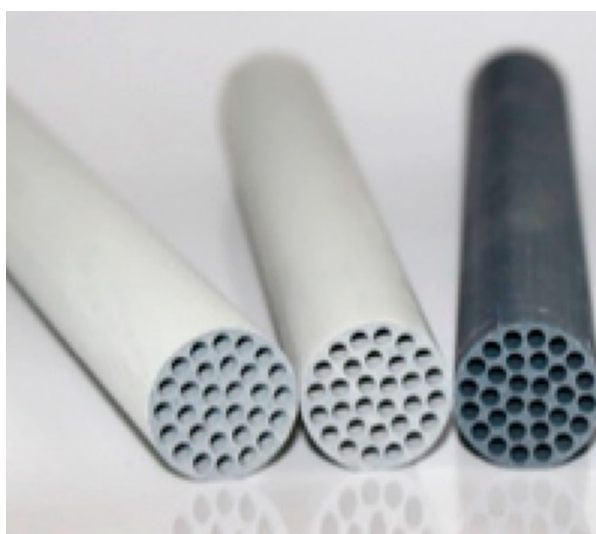
SiC monolith structures

Figure S2. Picture of SiC monolith structures used in the present work.

Dip coating of SiC monoliths

After delivery, the SiC monoliths (LiqTech International A/S, Ballerup, Denmark) were 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).
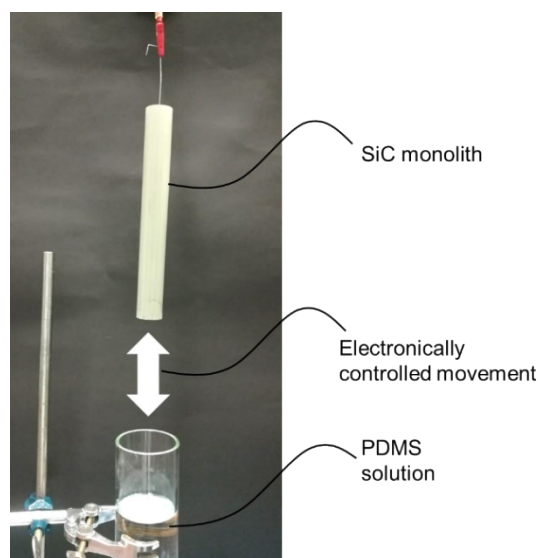

Figure S3. Photograph of the dip-coating process of a SiC monolith.

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 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 S4 shows representative examples of a native SiC monolith and a PDMS coated monolith. The PDMS coating is visible in Figure S4b as a shiny and transparent layer.
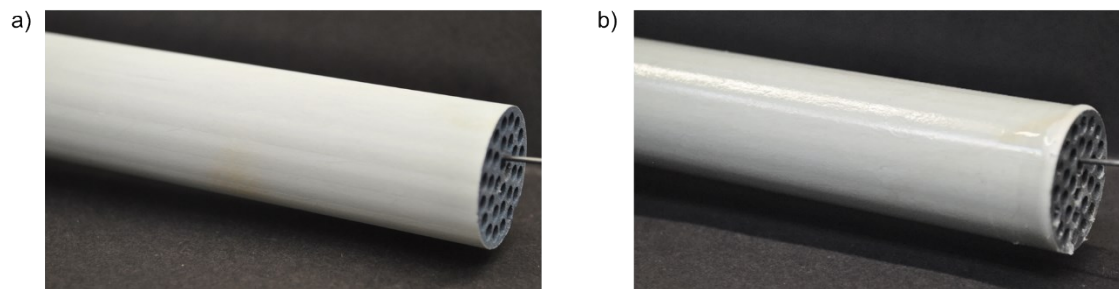
Figure S4. Photographs of a) native SiC monolith and b) SiC monolith with PDMS coating.

PVA coatings

When cross-linked, polyvinyl alcohol (PVA) serves as a hydrophilic yet stable membrane material. For applications with high water content, like the WGS reaction, PVA is cross-linked to decrease its solubility in water and control the degree of swelling. Several cross-linking agents are known and have been studied, e.g., by Bolto et al.[1] For facilitated transport, cross-linking PVA with aldehydes, such as formaldehyde (FA) and glutaraldehyde (GA), is most common.[2,3] With its low molecular weight of 43.07 g mol-1, for each repeating unit, PVAm is one of the smallest monomers containing amino-groups, which results in the highest charge density known in commercial polymers.[4]

Gas permeation tests

All permeation experiments were conducted in the setup shown in Figure S5.
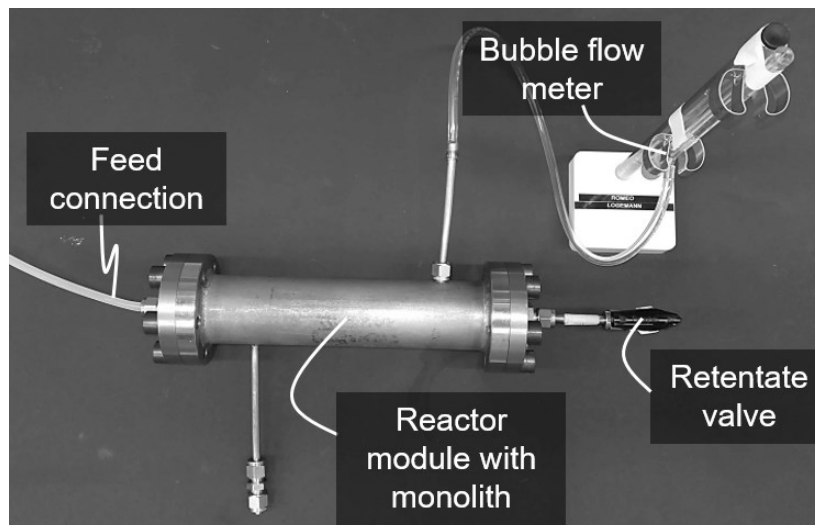

Figure S5. Photograph of the gas permeation setup at RWTH.

Ru-SILP catalyst preparation

The SILP catalysts were prepared using a standard Schlenk flask technique, applying argon atmosphere at ambient pressure and room temperature. The ionic liquid (IL) $[C_4C_1C_1im]Cl$ (Merck KgaA, LOT: 99/818) was dissolved in dichloromethane (DCM; Sigma-Aldrich, LOT: SZBG073AV) and stirred for $10 - 15$ min. Afterward, the Ru-precursor complex $[Ru(CO)_2Cl_3]_2$ (Alfa Aesar, LOT: Q05D029) was added to the mixture and stirred until full dissolution (approx. $10 - 15$ min). Next, gamma-alumina particles with 1.0 mm in size were added to the mixture as support material (1.0 mm, Puralox 1.0/160, Sasol, LOT: TK1480). The suspension was stirred for $2 - 5$ min to avoid mechanical stress of the support material. In a last step, the solvent was removed using a rotary evaporator (step 1: 3 h, 40 °C, 900 mbar; step 2: 1 h, 40 °C, < 3 mbar). Finally, a free-flowing Ru-SILP catalyst was obtained. The Ru-loading of the SILP catalyst was $w_{Ru} = 0.02$

g_{Ru} $g_{support}^{-1}$. The pore filling grade of the support, which describes the IL volume related to the total pore volume of the support material (V_{IL} $V_{support}^{-1}$), was $\alpha_{IL,syn} = 0.34$ vol.-%.
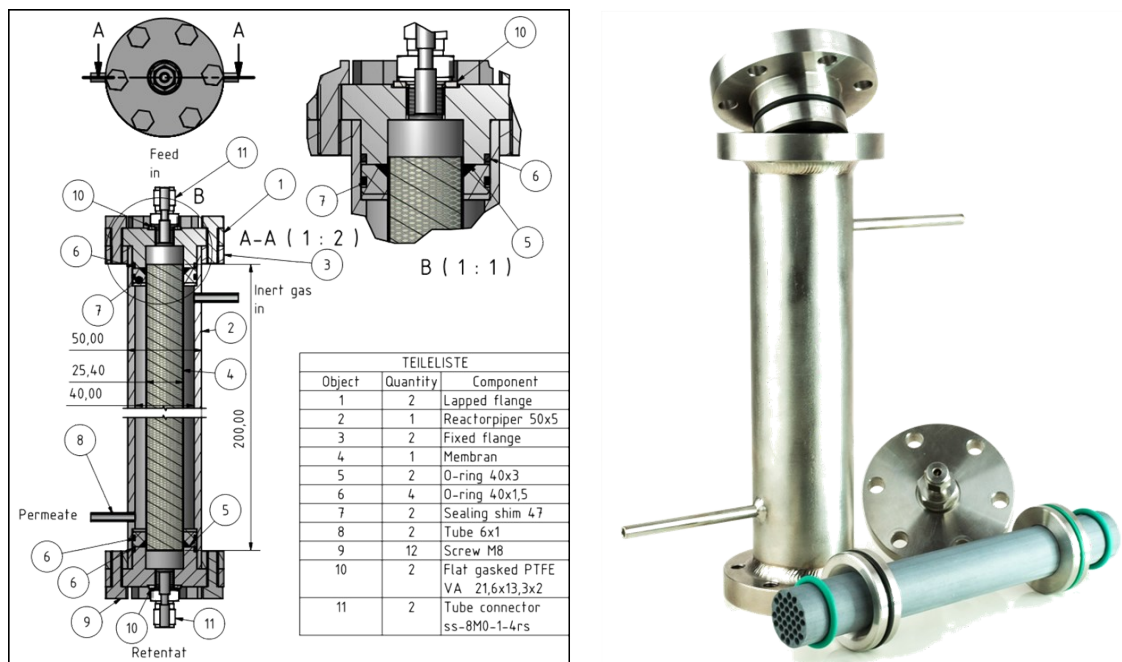
Membrane reactor housing

Figure S6. Assembly list for the membrane reactor housing (left) and picture of the individual parts together with SiC monolith.
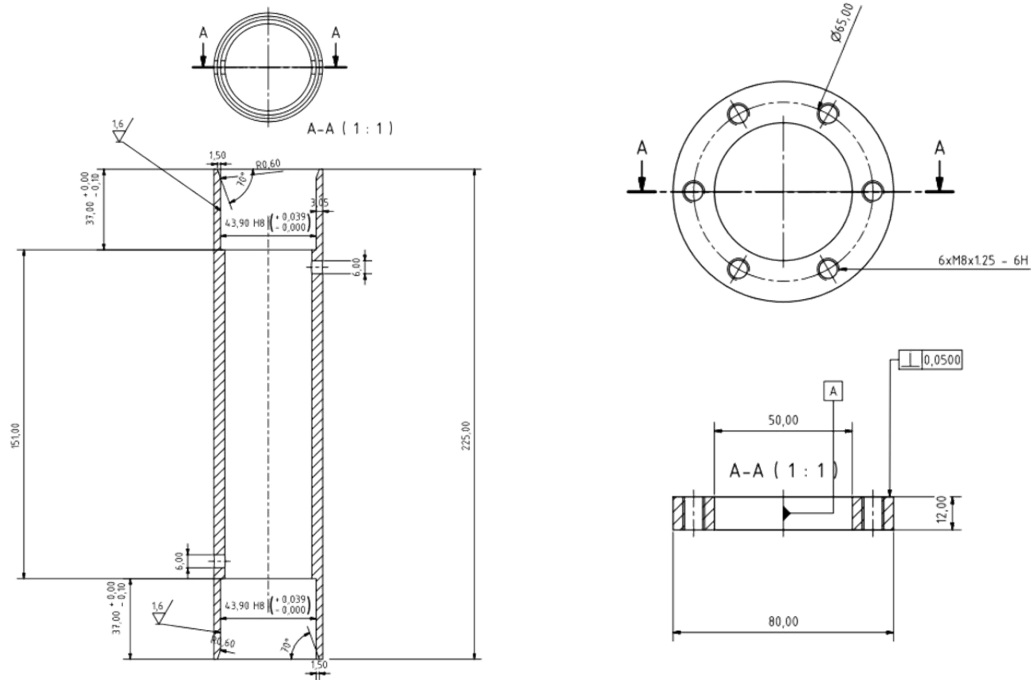
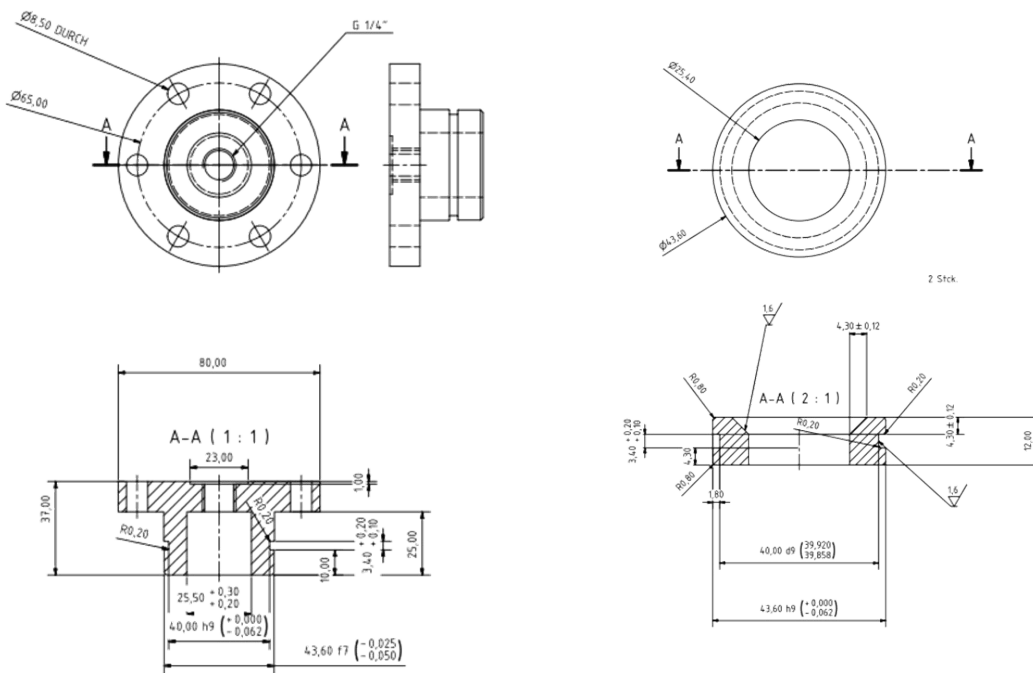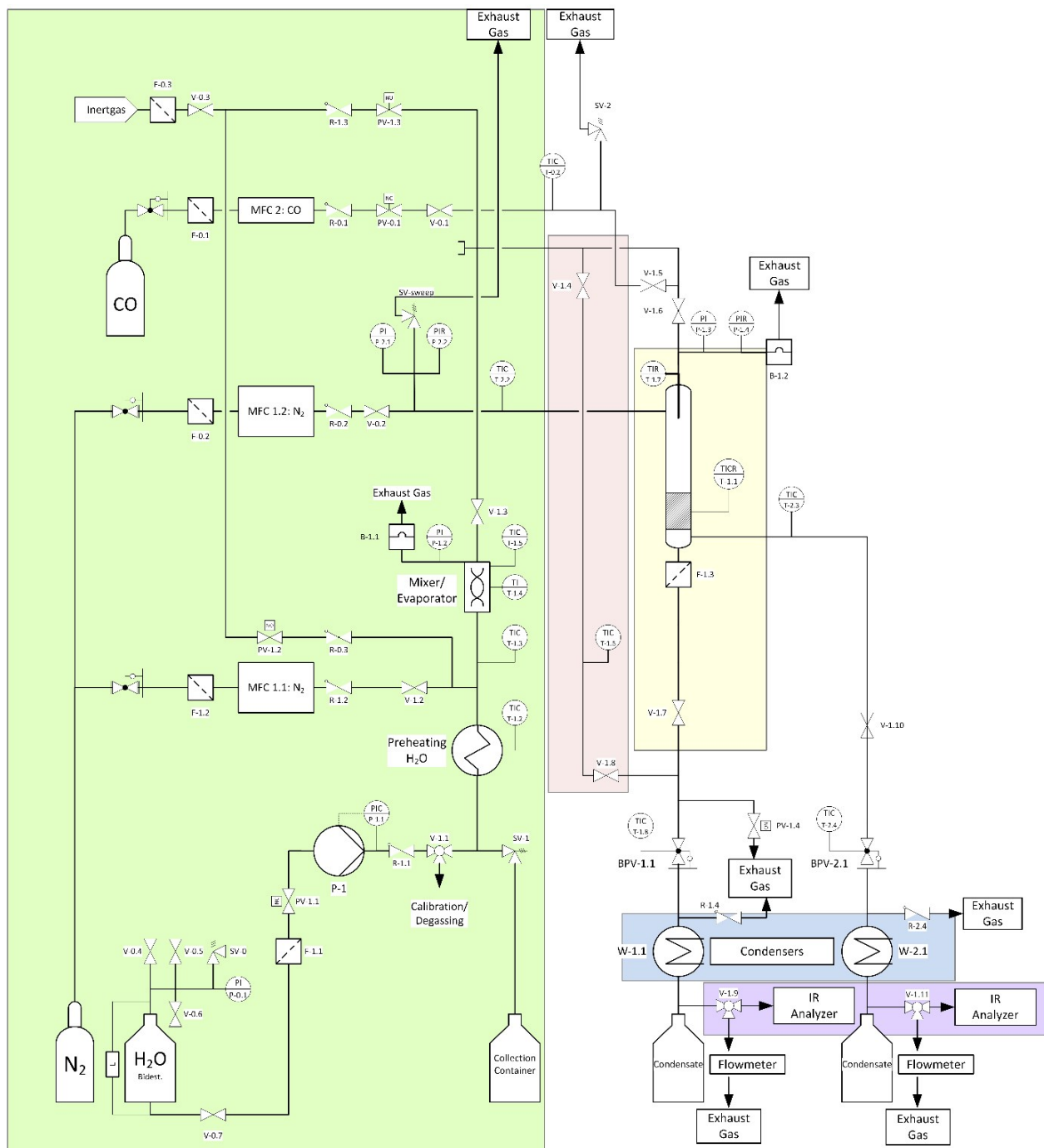Figure S7. Technical dimensions for the housing plus fixed flanges.

Figure S8. Technical dimensions for the lose flanges.

Continuous gas-phase setup (FAU)

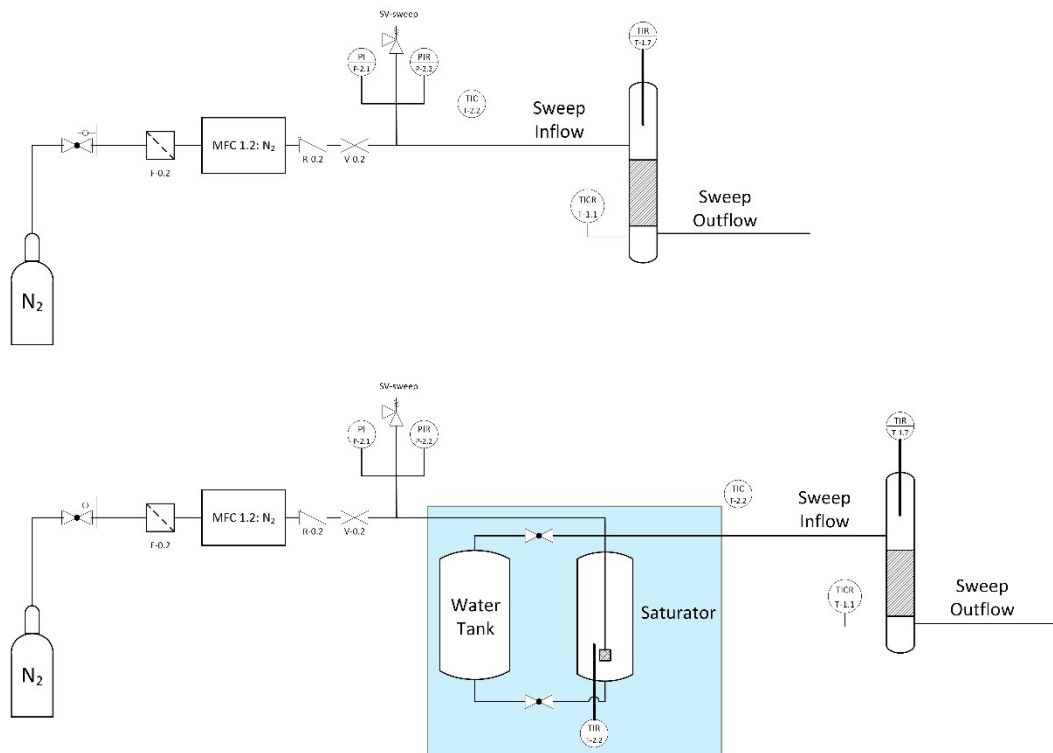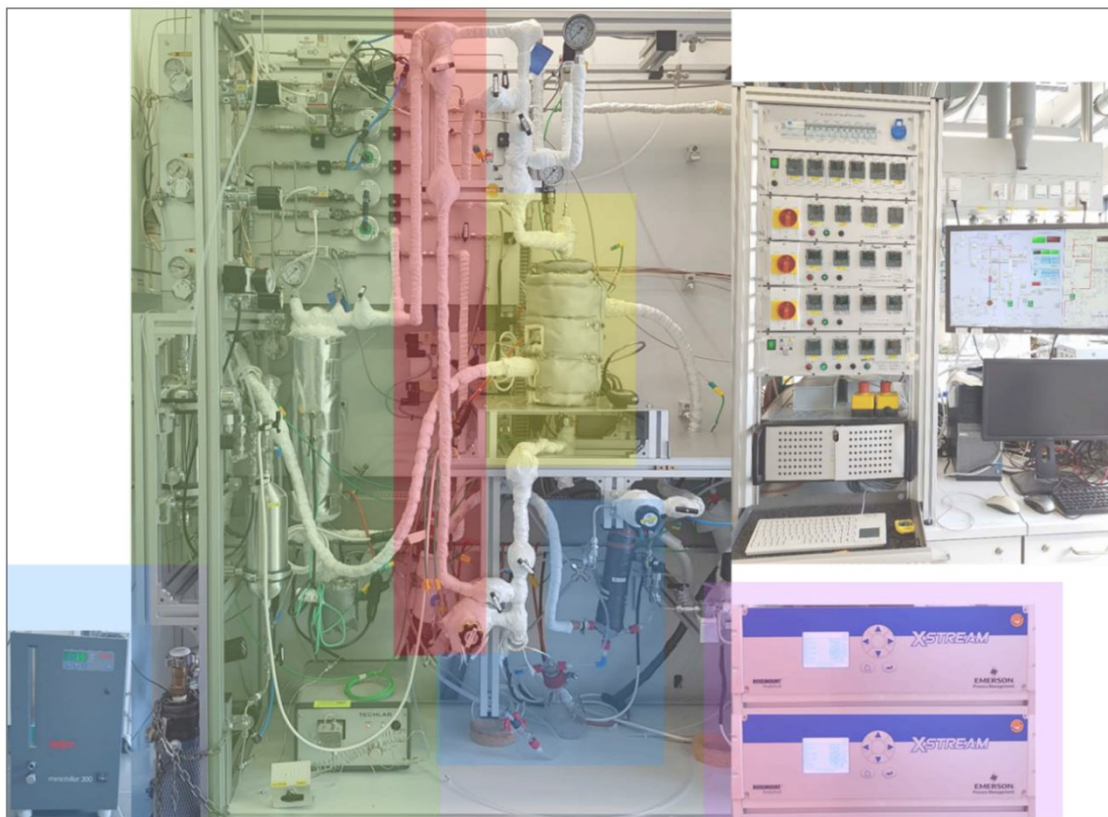Figures S9. Flow scheme of the setup for the Ru-SILP WGS membrane reactor.

Figure S10. Extension of the sweep gas piping with a saturation unit. Comparative presentation of the setup with (lower part) and without (upper part) saturation unit.

Figures S11. Picture of the setup for the Ru-SILP WGS membrane reactor. Color coding according to Figure S9.
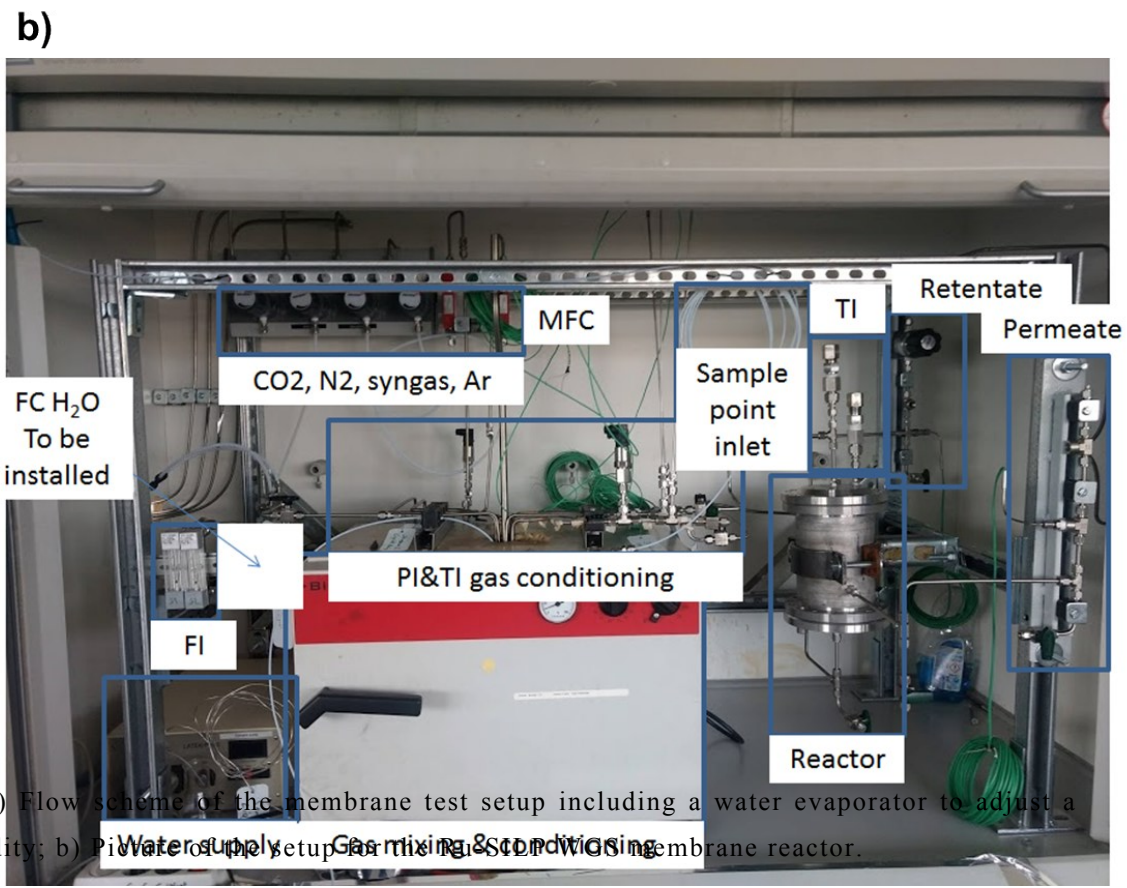
Continuou a)

b)
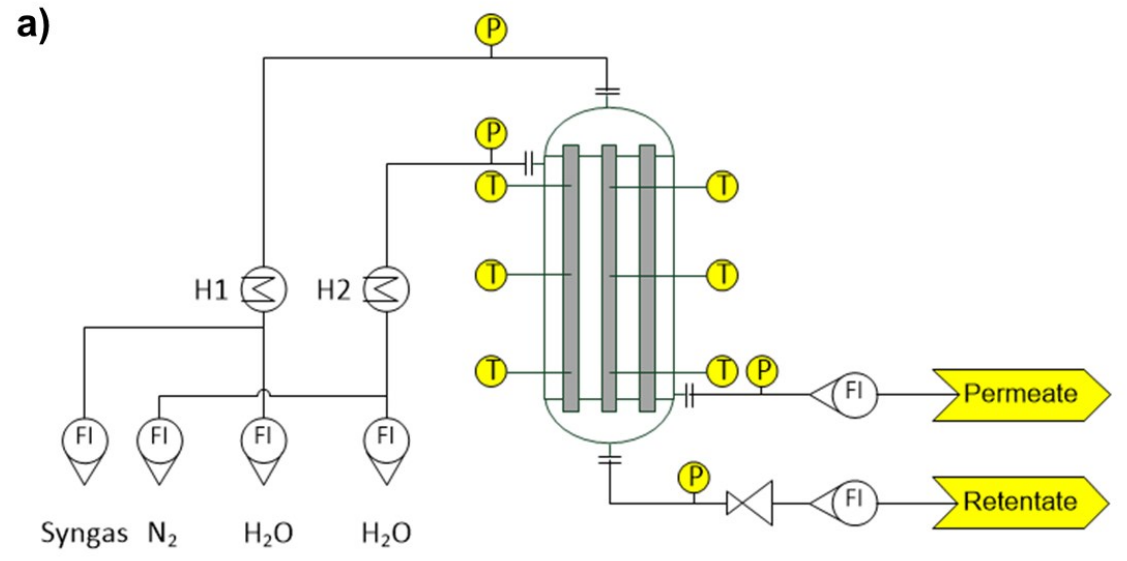

Figure S12. a) Flow scheme of the membrane test setup including a water evaporator to adjust a defined humidity; b) Picture of the setup for the RuSCu WGS membrane reactor.

O$_2$-plasma treatment
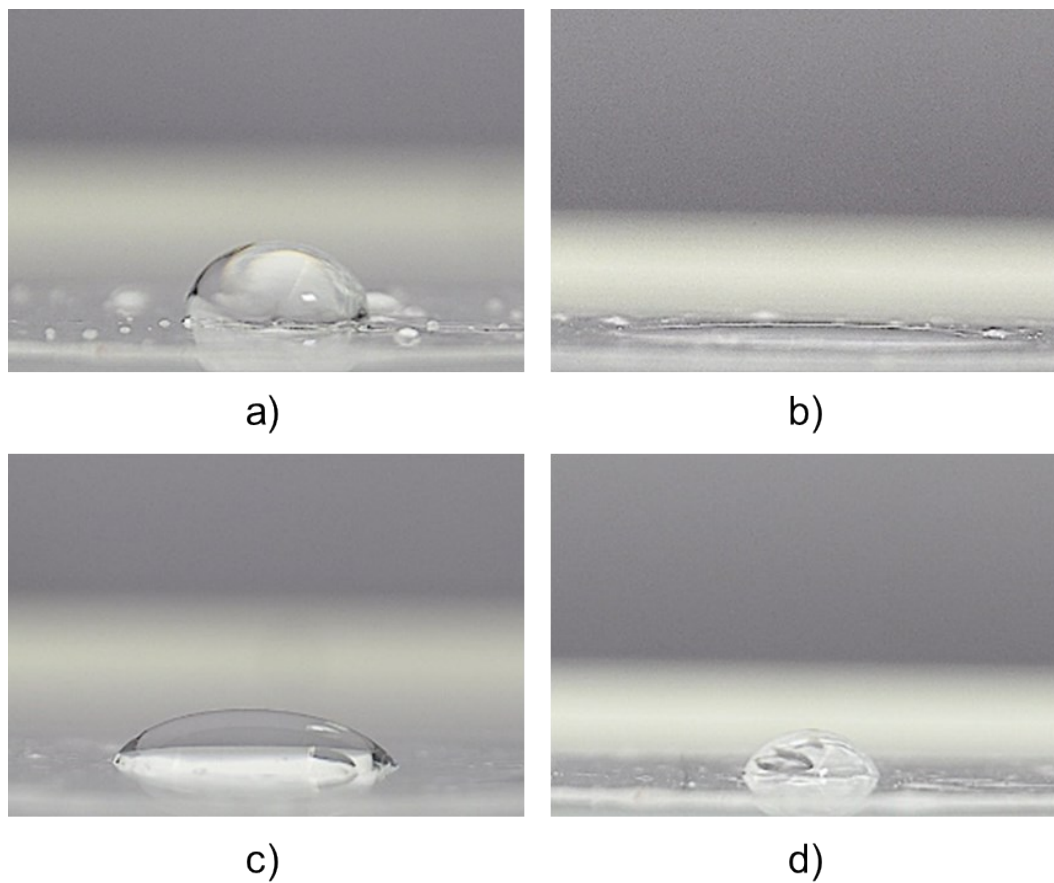
Figure S13. Contact angle observation of a) untreated PDMS and O$_2$-plasma-treated PDMS after b) 5 minutes, c) 2.5 hours and d) 18 hours.
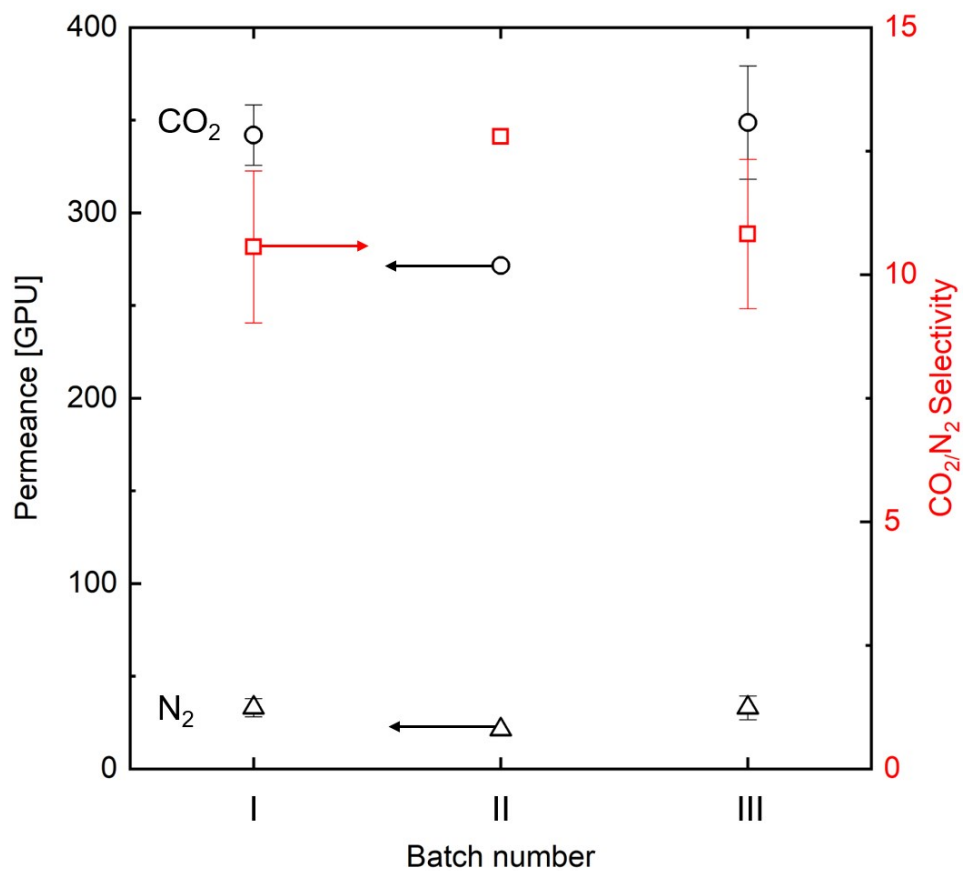
Gas permeability tests

Figure S14: Permeances (left) and selectivity (right) results of 10 coated monoliths from PDMS batch I, 1 coated monolith from batch II, and 8 coated monoliths from batch III. All CO_2 and N_2 tests were conducted at 2 bar transmembrane pressure with at 20 °C.
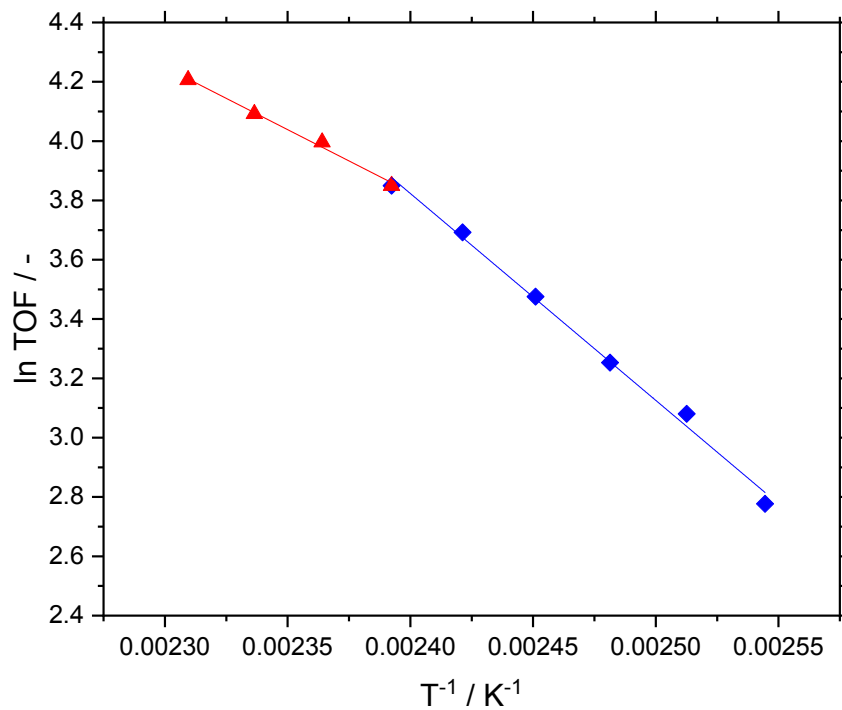
Ru-SILP WGS catalysis – effective activation energy

Figure S15. Arrhenius plot for effective activity (expressed as TOF). The effective activation energy was calculated from the slope of the linear fit for two temperature regimes: between 120 and 145 °C (blue line, slope = 6975.5, R2 = 0.9945) and between 145 and 160 °C (red line, slope 4218.5, R2 = 0.9938).

Ru-SILP catalyst arrangement inside SiC monolith
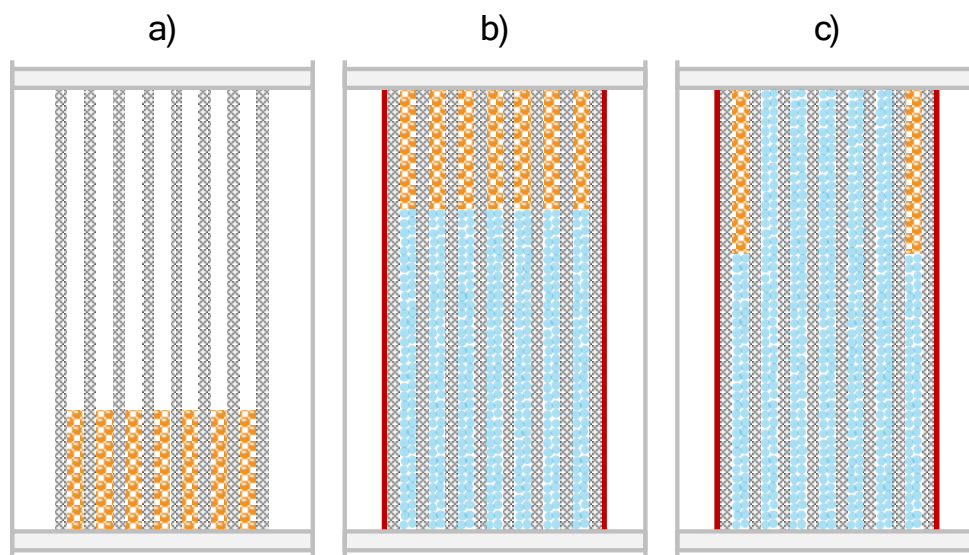
Figure S16. Different possibilities to locate the catalyst in the monolithic structures following approach B. a) simple multiple fixed bed at the bottom of the monolith (no membrane added), b) evenly distribution of the SILP particles onto a bed of glass beads, c) location of the SILP particles in the outer channels of the monolith to minimize the diffusion length to the membrane (glass beads arbitrary depending on the amount of catalyst).
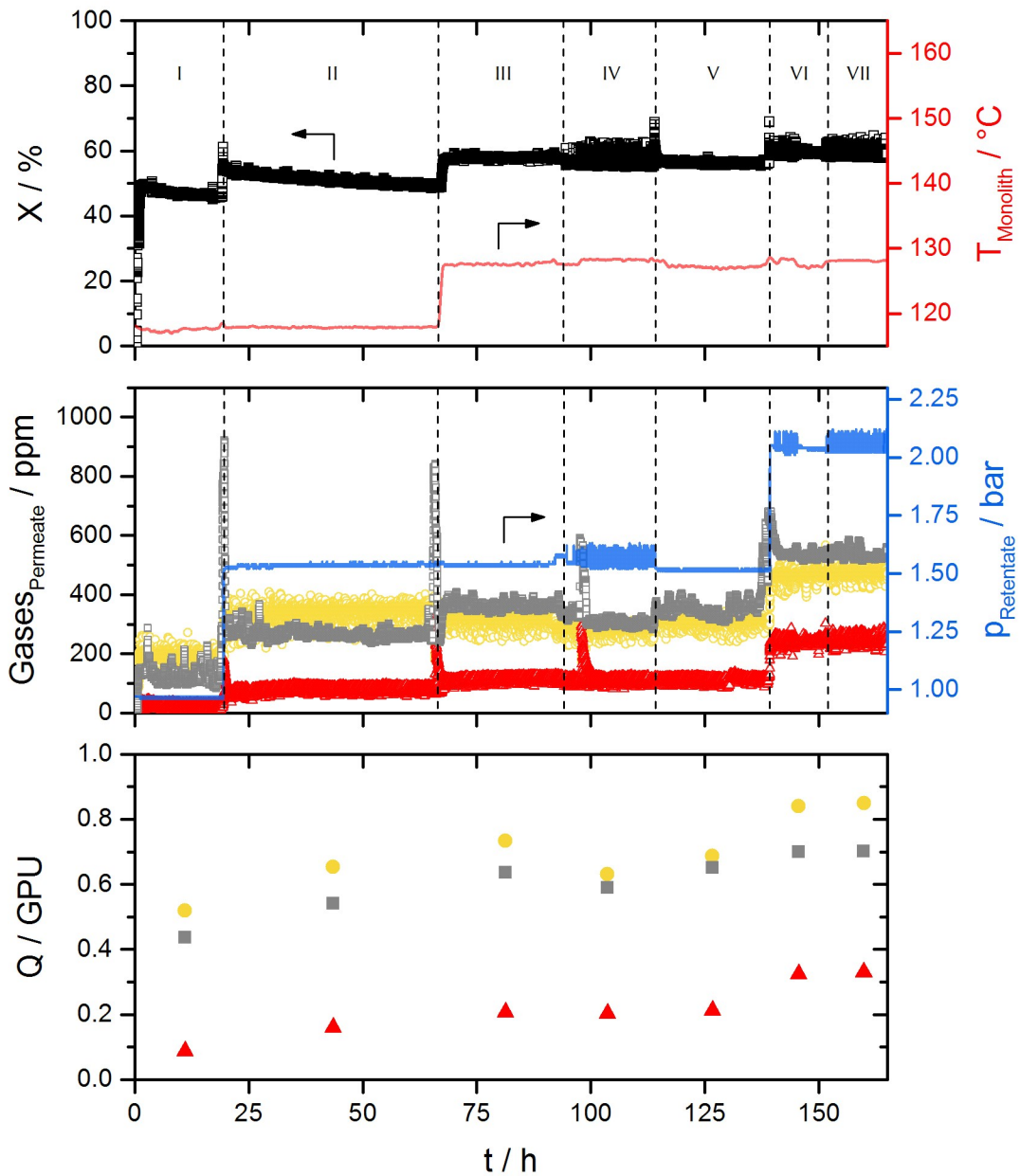
Single monolith membrane reactor (FAU)

Figure S17. FTM plus catalyst for a TOS of 165 h. Upper diagram: conversion (black) and monolith temperature (red), middle graph: gas composition of the permeate stream (CO_2: red triangles, CO: yellow circles, H_2: grey squares) and retentate pressure (blue), lower graph: calculated permeability values for the different gases (CO_2: red triangles, CO: yellow circles, H_2: grey squares).). Retentate: T = 120 – 130 °C, p = 1 – 2 bar, precursor: $[Ru(CO)_3(Cl)_2]_2$, $w_{Ru} = 0{,}02\ g_{Ru}\ g_{Support}^{-1}$, IL: $[C_4C_1C_1Im]Cl$, $\alpha = 0{,}34$, $m_{cat} = 10{,}56$ g, $p_{H2O} : p_{CO} = 2 – 3 : 1$, $V_{total} = 187\ mL\ min^{-1}$, permeate: $p_{H2O} = 0{,}7 – 0{,}85$ bar, $V_{Sweep} = 95\ mL\ min^{-1}$

Multi monolith membrane reactor (BEST)

Table S1. Adjusted gas composition, steam to CO ratio, relative humidity, space velocity, temperature and transmembrane pressure during the experiment.

Parameter	Value
H_2	17.93 v%
CO	8.73 v%
N_2	73.34 v%
H_2O/CO ratio	2.85
Rel. humidity feed / partial pressure	15 % / 0.22 bar
Rel. humidity sweep / partial pressure	30 % / 0.72 bar
Space velocity	144 h^{-1}
Steady state temperature	139.60 °C
Transmembrane pressure	0.94 ± 0.04 bar

Procedure for X and TOF calculation

The conversion was calculated according to:

$$X_{CO} = \frac{\dot{n}_{CO,0} - \dot{n}_{CO}}{\dot{n}_{CO,0}}$$

(S1)

The incoming mass flow of CO can be determined by means of bypass measurement before each experiment. Since the reaction is operated under ambient pressure and no volume change takes place, the mass flow rates can be calculated by changing the ideal gas law:

$$\dot{n}_{CO,i} = \frac{p_{CO,i} \cdot \dot{V}_{total}}{RT}$$

(S2)

Since the gas constant is a fixed quantity and the temperature in the gas analyzer is constant, these two quantities are not included in the calculation of conversion. In addition, the product of total volume flow and partial pressure can be simplified to the individual volume flow of the component under consideration.

$$X_{CO} = \frac{\dot{V}_{CO,0} - \dot{V}_{CO}}{\dot{V}_{CO,0}}$$

(S3)

Equation S3 can be extended with the total volume flow without changing the total value:

$$X_{CO} = \frac{\dfrac{\dot{V}_{CO,0}}{\dot{V}_{total}} - \dfrac{\dot{V}_{CO}}{\dot{V}_{total}}}{\dfrac{\dot{V}_{CO,0}}{\dot{V}_{total}}}$$

(S4)

With the definition of the volume fraction xi the Equation S4 simplifies to:

$$X_{CO} = \frac{x_{CO,0} - x_{CO}}{x_{CO,0}}$$

(S5)

Hence, the volume shares measured by the IR gas analyzer can be used directly for the calculation of conversion.

However, since conversion depends on the quantity of catalyst used, another activity variable must be defined which takes into account the mass of the catalyst - more precisely its molar quantity. For this purpose, the turn over frequency (TOF) is introduced, which makes different catalyst systems directly comparable with each other in terms of their activity:

$$TOF = \frac{\dot{n}_{CO}}{n_{Ru}}$$
(S6)

Due to the fact that the molar flow of CO after the reaction cannot be precisely measured, the equation must be modified using the previously derived conversion:

$$TOF = \frac{X_{CO} \cdot \dot{n}_{CO,0}}{n_{Ru}}$$
(S7)

References

[1]   B. Bolto, T. Tran, M. Hoang, Z. Xie, *Prog. Polym. Sci*. **2009**, *34*, 969–981.

[2]   S. Rafiq, L. Deng, M.-B. Hägg, *ChemBioEng Rev*. **2016**, *3*, 68-85.

[3]   Z. Tong, W.S.W. Ho, *Sep. Sci. Technol*. **2017**, *52*, 156-167.

[4]   A. Schmalen, *Post Polymerization Modification of Poly(vinyl amine) with Functional Epoxides: Multifunctional, Antimicrobial, Protein-like Polymers*, Dissertation, RWTH Aachen University, **2014**.