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Electronic Supplementary Information

Performance of diffusion-optimised Fischer-Tropsch catalyst layers in microchannel reactors at integral operation

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Film formation

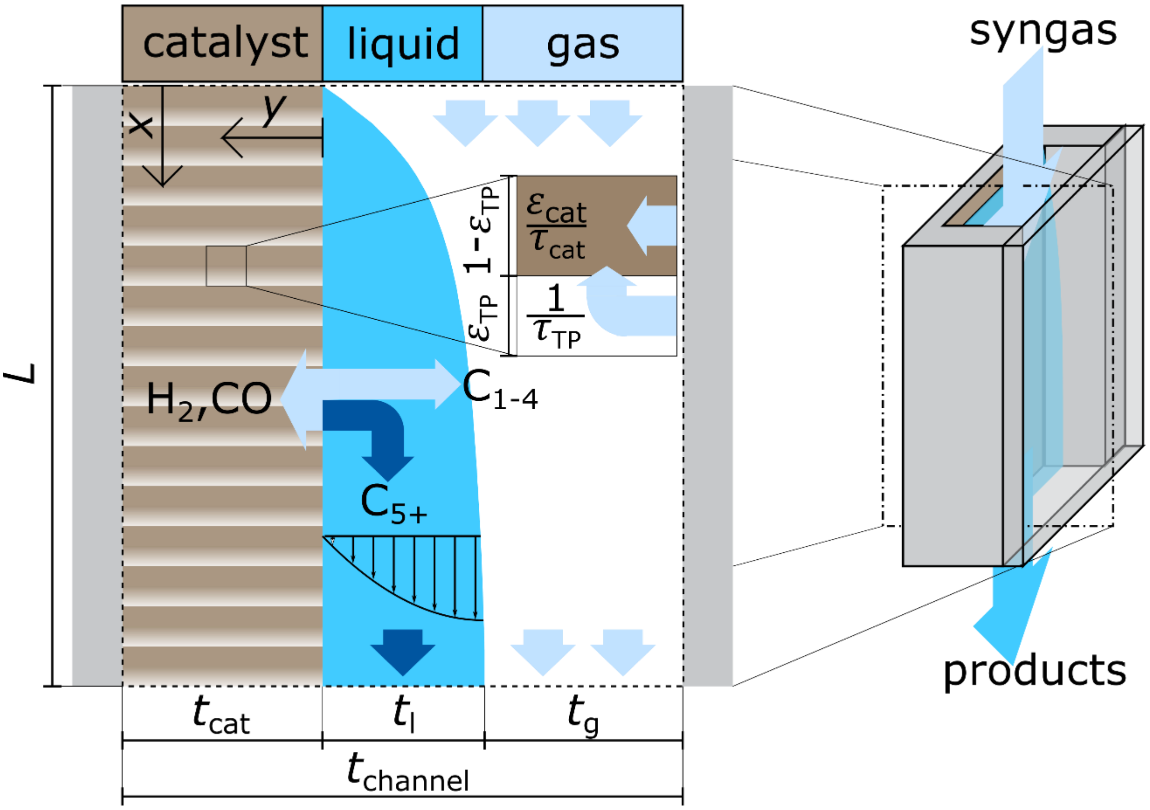

Fig. 1: Schematic of wall coated micro-reactor with catalyst layer, forming liquid film and open gas channel.

The derivation of the liquid film formation is based on the works of Nusselt and adapted for a microchannel reactor with a catalyst layer coated to one wall as depicted in fig. 1. Basis for modelling is a stationary balance of shear stress with gravitational forces, eqn (1).

$$0 = \frac{\partial}{\partial y}(\tau) + (\rho_\mathrm{l} - \rho_\mathrm{g})\, g \qquad (1)$$

Assuming the liquid behaves Newtonian and omitting the buoyancy effect of the gas, eqn (2) and (3) combine to yield eqn (3), which is an ordinary differential equation needing to be solved.

$$\tau = \eta_l \frac{\partial}{\partial y}(u_l) \qquad (2)$$

$$0 = \eta_l \frac{\partial^2}{\partial y^2}(u_l) + \rho_l\, g \qquad (3)$$

At the liquid-catalyst interface a no-slip condition forces the liquid to a standstill, eqn (4), and at the gas-liquid interface any momentum transfer is neglected, eqn (5).

$$v(y = 0) = 0 \qquad (4)$$

$$\tau(y = t_l) = \frac{\partial}{\partial y}(u_l) = 0 \qquad (5)$$

With the assumptions of the boundary conditions the solution for eqn. (3) is easily found by integration. The obtained eqn. (6) provides the velocity profile of the liquid film.

$$u_l = \frac{\rho_l\, g}{\eta_l}\left(t_l\, y - \frac{1}{2} y^2\right) \qquad (6)$$

Because the reactor model operates only with a simplified bulk flow velocity of the liquid film averaging by integration is done as in eqn. (7). Eqn (8) is the desired relation of the liquid film thickness with the liquid average velocity.

$$\bar{u_l} = \frac{1}{t_l} \int_0^{t_l} \frac{\rho_l\, g}{\eta_l}\left(t_l\, y - \frac{1}{2} y^2\right) dy \qquad (7)$$

$$v_l = \bar{u_l} = \frac{\rho_l\, g\, t_l^2}{3\, \eta_l} \qquad (8)$$

Modified ASF selectivity model

The selectivity model used in this work is based on a variable alpha model, that was further modified according to Förtsch et al.[1] with an additional parameter describing the enhanced formation of methane. A second parameter for the typically low C_2 selectivity was also introduced by Förtsch et al. but not used in this work, as it did not improve the description of the results. Because no general values for the parameters were given in literature, actual values needed to be assigned to the parameters, which are γ, describing the enhanced termination probability for methane, and β, a readsorbtion probability for C_2 species. For evaluation of useful parameter values various data from literature[2–19] for methane, C_{2-4} and C_{5+} selectivity were used. Global parameters for β and γ were tested and a variable α was adjusted for each individual data point to yield best results. When both new parameters are set to zero a conventional ASF distribution is obtained. Fig. 2 shows the parity plots for this case in the left column. With a conventional model only high C_{5+} selectivites are sufficiently described, for lower values for C_{5+} the deviation increases, C_{2-4} is overestimated and methane selectivity is vastly underestimated. The next column in fig. 2 illustrates the results for a given γ value of 0.5 and still no change to the β value. The C_{5+} selectivites are described almost perfectly and the C_{2-4} selectivity is also relatively well matched, disregarding a certain scatter. The methane selectivity is now also much better predicted, values up to 10 % are mostly in line, only for higher values a certain offset still leads to a mild underestimation of the actual value with the model. When both parameters, β and γ, are freely adjusted to produce the best fitting to the experimental data the accuracy for the C_{5+} and the C_{2-4} selectivity barely changes (see. fig. 2, right column). Only for methane the offset at higher values is further reduced. The parameters allowing for this description are with 0.5756 for γ and 0.0 for β only slightly different to the previous case. Interestingly the probability for the readsorption of C_2 species is zero, rendering it unused and justifies the negligence in the main reactor model used for this publication. Additionally, the small difference in the results to the initially guessed value of 0.5 makes the model more conservative. For a full reactor model an increased methane formation rate will also occur when diffusion is taken into consideration. However, this matching of useful parameters cannot and shall not be seen as full validation of a kinetic parameter set. It only acts as a justification for a reasonably working set of parameters that allow for a more realistic description of actual FT cat performance.

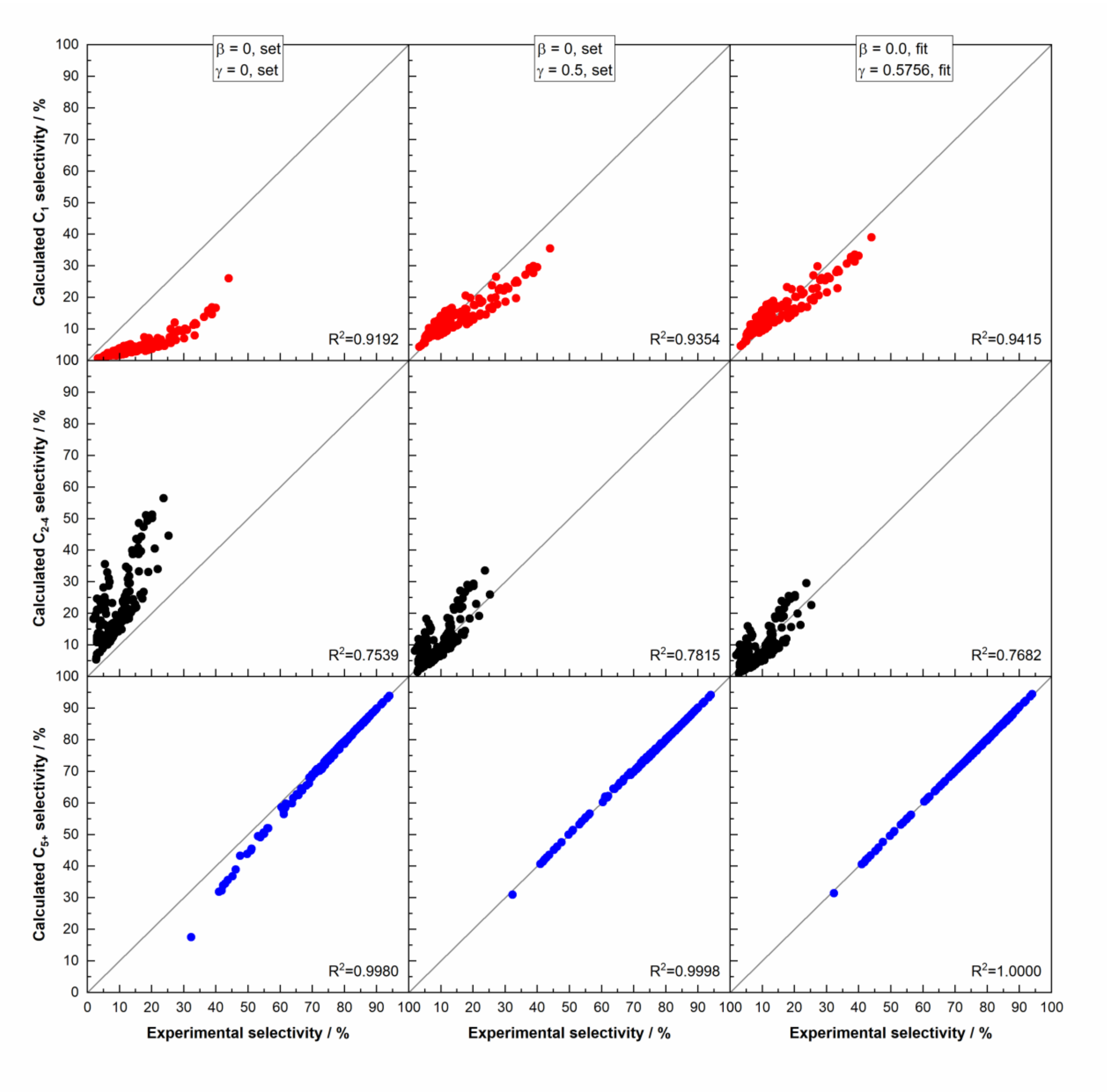

Fig. 2: Parity plots for methane, C_{2-4} and C_{5+} selectivities for three different parameter sets of ASF distribution modifiers; calculation based on formulas by Förtsch et al.[1] and tested against experimental data[2–19] with variable α values for each datum.

Reactor performance parameters

For evaluation of reactor performance different parameters are required to describe the impact of diffusion resistances and integral operation on the observed reaction rate (catalyst efficiency, η) product distribution (selectivities, S_{C1} and $S_{\text{C5+}}$) and productivity (areal time yield, *ATY*). To distinguish further between the effects of diffusion on a local level and the total integral operation of the reactor a differentiation between "local" and "total" quantities is made. "Local" measures are just a result of an integral over the lateral domain, thus they represent the effective performance of a slice of the catalyst layer at a given axial position. "Total" quantities on the other hand describe the effective performance of the entire layer in the reactor by being the result of integration over both domains, axial and lateral. For differential reactors there are no differences between both types, as there are no axial gradients in that case.

The formulas for the local catalyst efficiency, η, the local methane selectivity, S_{C1}, the local C_{5+} selectivity, $S_{\text{C5+}}$, and the local productivity, *ATY*, are shown in eqn (9) to (12).

$$\eta(x) = \frac{\left|j_{\text{gl,CO}}(x)\right|}{t_{\text{cat}} \cdot r(x, \text{y} = 0) \cdot (1 - \varepsilon_{\text{TP}})} = \frac{\left|(1 - \varepsilon_{\text{TP}}) \int_0^{t_{\text{cat}}} r(x, y) \cdot \nu_{\text{CO}}(\text{x}, \text{y})\, dy\right|}{t_{\text{cat}} \cdot r(x, \text{y} = 0)) \cdot (1 - \varepsilon_{\text{TP}})} \tag{9}$$

$$S_{\text{C1}} = \frac{j_{\text{gl,C1}}(x)}{\left|j_{\text{gl,CO}}(x)\right|} = \frac{\int_0^{t_{\text{cat}}} r(x, y) \cdot \nu_{\text{C1}}(x, y)\, dy}{\int_0^{t_{\text{cat}}} r(x, y) \cdot \nu_{\text{CO}}(\text{x}, \text{y})\, dy} \tag{10}$$

$$\begin{aligned} S_{\text{C5+}}(x) &= 1 - S_{\text{C1-4}}(x) = 1 - \frac{j_{\text{gl,C1}}(x) + j_{\text{gl,C2}}(x) \cdot 2 + j_{\text{gl,C3}}(x) \cdot 3 + j_{\text{gl,C4}}(x) \cdot 4}{\left|j_{\text{gl,CO}}(x)\right|} \\ &= 1 - \frac{\int_0^{t_{\text{cat}}} r(x, y) \cdot [\nu_{\text{C1}}(x, y) + \nu_{\text{C2}}(x, y) \cdot 2 + \nu_{\text{C3}}(x, y) \cdot 3 + \nu_{\text{C4}}(x, y) \cdot 4]\, dy}{\int_0^{t_{\text{cat}}} r(x, y) \cdot \nu_{\text{CO}}(\text{x}, \text{y})\, dy} \end{aligned} \tag{11}$$

$$\begin{aligned} ATY(x) &= \left|j_{\text{gl,CO}}(x)\right| - j_{\text{gl,C1}}(x) - j_{\text{gl,C2}}(x) \cdot 2 - j_{\text{gl,C3}}(x) \cdot 3 - j_{\text{gl,C4}}(x) \cdot 4 \\ &= \int_0^{t_{\text{cat}}} r(x, y) \cdot [\left|\nu_{\text{CO}}(\text{x}, \text{y})\right| - \nu_{\text{C1}}(x, y) - \nu_{\text{C2}}(x, y) \cdot 2 - \nu_{\text{C3}}(x, y) \cdot 3 - \nu_{\text{C4}}(x, y) \cdot 4]\, dy \end{aligned} \tag{12}$$

The catalyst efficiency, as defined by eqn (9), is the true efficiency of the catalyst without being affected by the diluting effect of the transport pore phase. This efficiency is only used as a local variable, because any use for the integral reactor in total could lead to ambiguity. The ambiguity stems from the fact that the efficiency requires a reference for the reaction rate in the denominator of eqn (9). As reference either the reaction at the layer surface ($y = 0$) at the reactor inlet ($x = 0$) can be used or the rate at the catalyst surface ($y = 0$) along the axial domain for each individual point of the integration can be used. Neither case was deemed useful for evaluation and thus omitted. For the C_{5+} selectivity and for the *ATY* no neat equation was found to produce the value as function of α and γ. Instead the values were calculated as the difference of the production of C_1 to C_4 and the consumption of CO.

The remaining parameters for the total performance of the reactor, S_{C1}, S_{C5+} and *ATY*, are shown in eqn (13) to (15). They are merely the result of averaging the local parameters over the axial domain via integration.

$$S_{\mathrm{C1}} = \frac{\int_0^{\mathrm{L}} j_{\mathrm{gl,C1}}(x)dx}{\int_0^{\mathrm{L}} \left|j_{\mathrm{gl,CO}}(x)\right|dx} \tag{13}$$

$$S_{\mathrm{C5+}} = 1 - \frac{\int_0^{\mathrm{L}} \left(j_{\mathrm{gl,C1}}(x) + j_{\mathrm{gl,C2}}(x)\cdot 2 + j_{\mathrm{gl,C3}}(x)\cdot 3 + j_{\mathrm{gl,C4}}(x)\cdot 4\right)dx}{\int_0^{\mathrm{L}} \left|j_{\mathrm{gl,CO}}(x)\right|dx} \tag{14}$$

$$ATY = \frac{\int_0^{\mathrm{L}} \left|j_{\mathrm{gl,CO}}(x)\right|dx}{L} - \frac{\int_0^{\mathrm{L}} \left(j_{\mathrm{gl,C1}}(x) + j_{\mathrm{gl,C2}}(x)\cdot 2 + j_{\mathrm{gl,C3}}(x)\cdot 3 + j_{\mathrm{gl,C4}}(x)\cdot 4\right)dx}{L} \tag{15}$$

Convective transport in liquid vs. gas phase

The used model neglects the axial transport in the liquid phase. To have an impact, that justifies inclusion in the model, the amount of reactants transported in the liquid phase, as described by eqn. (16), needs to be of similar magnitude than the amount transported in the gas phase, eqn. (17). Hence a high velocity and film thickness of the liquid and a high concentration of the reactants in the liquid phase, which is limited by their solubility, would increase the amount of reactants being transported in the liquid phase.

$$j_{\mathrm{liq}}(x)\cdot t_{\mathrm{liq}}(x) = u_{\mathrm{liq}}(x)\cdot t_{\mathrm{liq}}(x)\cdot c_{\mathrm{liq}}(x) \tag{16}$$

$$j_{\mathrm{gas}}(x)\cdot t_{\mathrm{gas}}(x) = u_{\mathrm{gas}}(x)\cdot t_{\mathrm{gas}}(x)\cdot c_{\mathrm{gas}}(x) \tag{17}$$

For all tested scenarios the reactor with highest activity factor of 10, the longest channel length of 1 m, and ideal transport pore fraction and optimal catalyst layer thickness (42.3%, 114.7µm) led to the highest liquid film thickness. Additionally, a high CO conversion of 80% results in a low gas velocity. All this pronounces the role of the convective transport in the liquid film over the convective transport in the gas phase. Yet, the axial profiles of thickness, velocity and concentration indicate a vastly more effective transport in the gas phase, that is more than three magnitudes larger than in the liquid phase, fig. 3. This result warrants to neglect the convective transport in the liquid phase as done for the main reactor model.

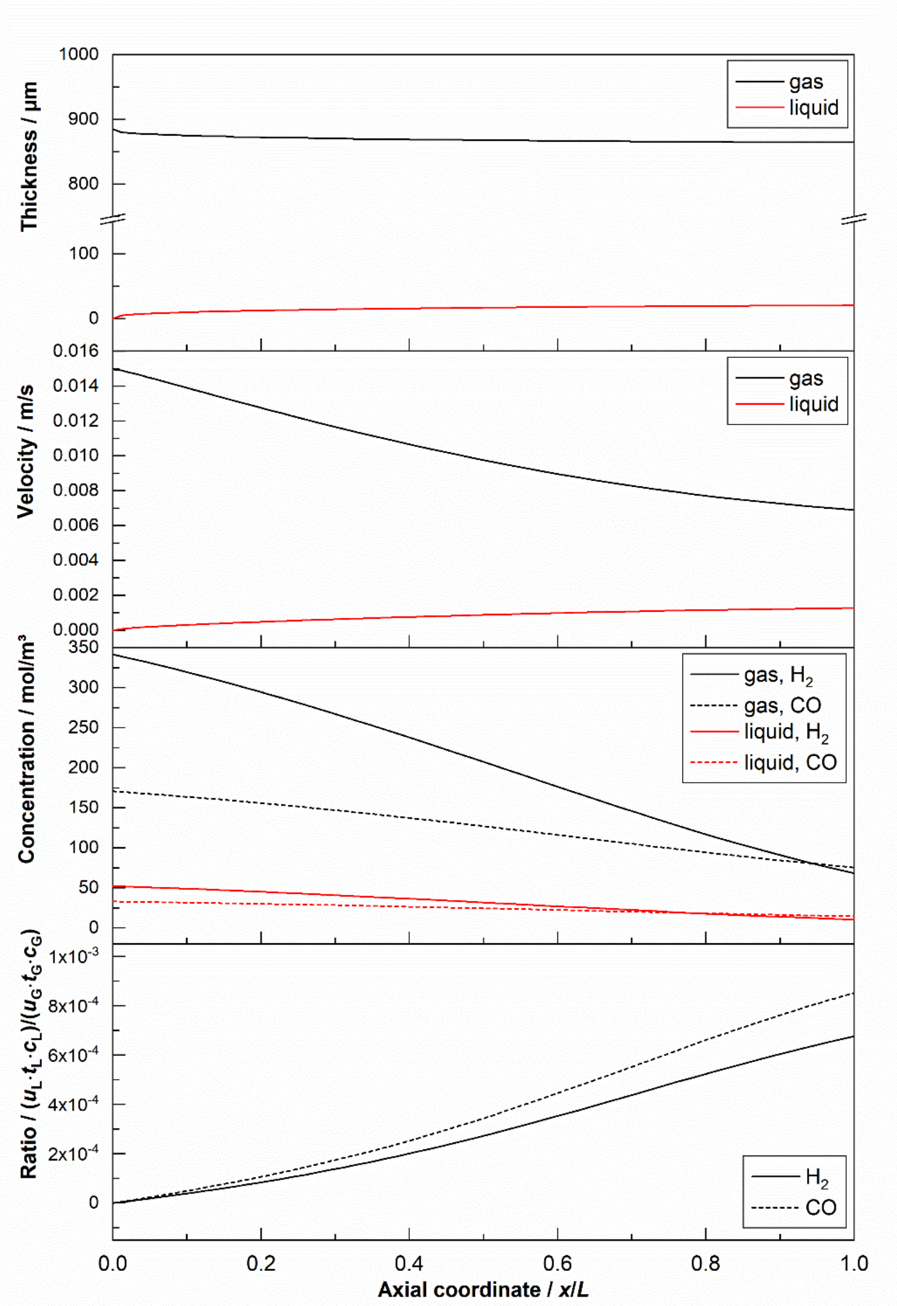

Fig. 3: Axial profiles of thickness, velocity and concentration of reactants for the gas phase and the liquid phase. 80% CO conversion, t_{cat} = 114.7 µm, ε_{TP} = 0.423, F = 10.

Effects of conversion on selectivity

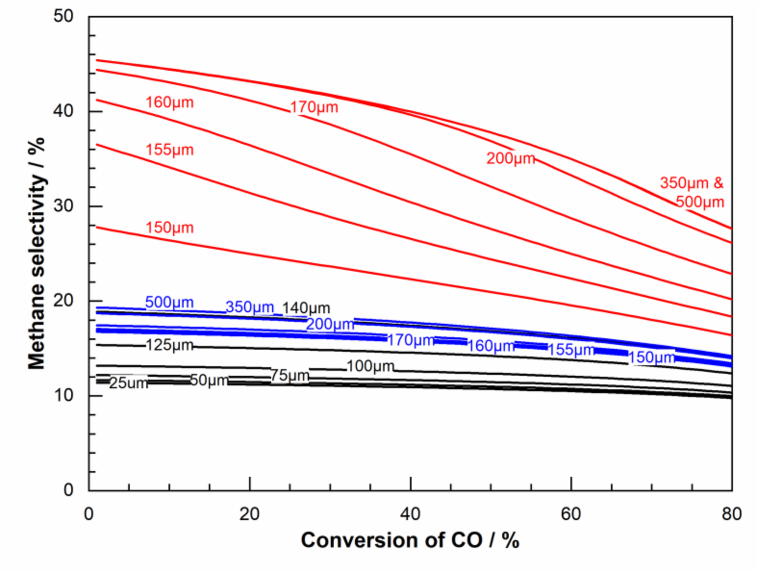

Fig. 4: Effect of CO conversion on total methane selectivity of layers of different thickness and kind; thin layers with minor diffusion effects (black); thick layers with significant mass transport restrictions (blue); thick layers with added, ideal fraction of transport pores (red).

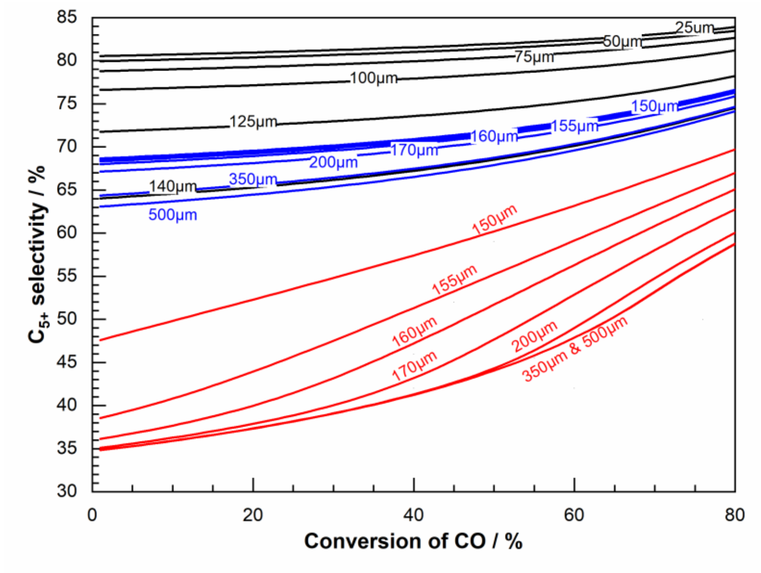

Fig. 5: Effect of conversion on total C_{5+} selectivity of layers of different thickness and kind; thin layers with minor diffusion effects (black); thick layers with significant mass transport restrictions (blue); thick layers with added, ideal fraction of transport pores (red).

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Additional values for effect of conversion

Table 1: Effect of conversion on required optimal thickness and resulting total ATY.

	"dense", ε_{TP} =0		"ideal", ε_{TP}= 0.42	
CO Conversion	thickness	*ATY*	thickness	*ATY*
%	µm	mol/(m² h)	µm	mol/(m² h)
1	140.2	1.249	357.1	1.837
5	140.5	1.247	358.2	1.834
10	140.7	1.244	358.6	1.830
15	140.8	1.241	359.0	1.825
20	141.0	1.237	359.6	1.820
25	141.3	1.234	360.1	1.814
30	141.5	1.229	360.8	1.808
35	141.8	1.225	361.5	1.801
40	142.1	1.219	362.3	1.793
45	142.5	1.213	363.2	1.784
50	142.8	1.206	364.2	1.773
55	143.2	1.196	365.1	1.759
60	143.5	1.196	365.9	1.742
65	143.7	1.168	366.4	1.718
70	143.7	1.145	366.4	1.684
75	143.3	1.111	365.4	1.634
80	142.2	1.059	362.6	1.558

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