Electronic Supporting Information for:

Total oxidation of methane over Pd/Al_2O_3 at pressures from 1 to 10 atm

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Reactor model

The model considers a two-dimensional (2D) monolith reactor model with axial and radial gradients. The monolith is simulated as a single-channel reactor model and the channel is discretised into 10 tanks-in-series, while the washcoated porous catalyst is divided into 12 layers to consider for internal mass and heat transport. The discretised tank length and the layer thickness increases successively with 30% from the inlet and 50% from the catalyst surface, respectively, to obtain a finer resolution where the gradients are steeper. The chosen numbers of tanks and layers are sufficient to achieve satisfactory accuracy within a reasonable amount of computational time. The density of the active sites is calculated in each tank and layer, while maintaining the total palladium loading, to obtain an even distribution of active sites in the coated monolith.

The Weisz-Prater method

The Weisz-Prater method is used to estimate the influence of internal mass transport at 1 atm and 350 $^{\circ}\mathrm{C}$

$$\Phi = \frac{r_v r_p^2}{C_{CH_4}^b D_{eff}} \tag{1}$$

where $\Phi < 1$ implies that the washcoat is free from internal concentration gradients. Due to the low GHSV used during the experiments (3500 h⁻¹), it is reasonable to assume that there are no external concentration gradients. Further, a conservative estimate of Φ is made, by assuming full conversion and a washcoat thickness of 50 μ m. The Weisz-Prater method can be rewritten as

$$\Phi = \frac{r_{obs}\rho_{cat}L_{wc}^2}{C_{CH_4}^b D_{eff}} \tag{2}$$

where $r_{obs}=1.05 \cdot 10^{-3} \text{ mol s}^{-1} \text{ kg}_{cat}^{-1}$ (calculated from reported catalyst properties and assuming full conversion), $\rho_{cat} = 1500 \text{ kg m}^{-3}$, $L_{wc} = 50 \ \mu\text{m}$, $C_{CH_4}^b = 19.56 \cdot 10^{-3} \text{ mol m}^{-3}$ and $D_{eff} = 3.8*10-7 \text{ m}^2 \text{ s}$. Inserting the values into Eq. 1, results in $\Phi=0.53$ at 1 atm and 350 °C. Hence the internal mass transport can be assumed to not affect the reaction rate of methane oxidation under these conditions. Performing the same calculations, but for a total pressure of 10 atm and temperature of 350 °C, results in the same value ($\Phi=0.53$) since the reaction rate, at full conversion, and concentration both increases by an order of magnitude. Assuming full conversion of methane, an inlet flow rate of 100 mL/min, a catalyst density of 1500 kg/m³ and an effective diffusivity of $3.8*10^{-7}$ m²/s yields a washcoat thickness of 70 micron at which internal mass transport can be expected to influence the reaction rate.

Simulations at isothermal reactor conditions



Figure SI.1: Simulations of methane conversion at isothermal reactor conditions for 1 (blue), 2 (red) 4 (yellow) and 10 (black) atm with experimental lightoff profiles.

Coverages in monolith

Figure SI.2 shows the coverage of the most abundant surface species under the present reaction conditions; hydroxyl species, water and hydrogen at 350, 400 and 450 °C for varying total pressures. Re-adsorption of produced carbon dioxide is not included since the coverage is low (<0.03) at all examined reaction conditions. If carbon dioxide would be included in the feed gas at realistic concentrations, its negative effect would be seen as a surface bicarbonate specie, which has been shown earlier [1, 2]. At 350 °C, the kinetic model shows that the coverage of hydroxyl and water species increases inside the monolith. At elevated total pressures steeper gradients are seen since the adsorption events become more frequent. The



Figure SI.2: Coverage of hydroxyl (OH), water (H₂O) and hydrogen (H) in the monolith at 350 (left column), 400 (middle column) and 450 °C (right column) and 1 (blue), 2 (red), 3 (purple), 4 (yellow) and 10 (black) atm. All reported surface species, except hydrogen, are adsorbed on the palladium atom (S₁(Pd)) while hydrogen is adsorbed on the oxygen atom (S₂(O)).

increasing coverages in the monolith are probably not the sole reason for underestimating the activity at low temperatures and it should again be stated that the kinetic model lacks transient effects on the palladium oxide site and support effects. At 400 and 450 °C a lower coverage of hydroxyl and water species is displayed since desorption events are more frequent. The coverage of hydroxyl species are in fact slightly higher or not affected at 400 compared to 350 °C. The explanation is found in how hydroxyl species are formed. Hydroxyl has two major formation channels, one from dissociation of water onto the S₂(O) site and a second through surface reaction where CH_X (X=1-3) releases a hydrogen to the S₂(O) site. The surface hydrogen is formed when CH_X (X=1-4) adsorbs on the S₁(Pd) site and splits into CH_{X-1} with hydrogen dissociating into the S₂(O) site.



Activation energy

Figure SI.3: Arrhenius plots with corresponding linear regression lines over 0.15 wt.-% Pd/Al₂O₃ monolith for a gas composition of 1000 vol.-ppm CH₄ and 2 vol% O₂ at 1 (blue), 2 (red), 4 (yellow) and 10 (black) atm.

Optical microscopy of washcoat thickness



Figure SI.4: Picture of washcoat distribution in the middle (L/2) of the monolith using optical microscopy at 100x.



Figure SI.5: Picture of washcoat distribution in the middle (L/2) of the monolith using optical microscopy at 100x.



Figure SI.6: Picture of washcoat distribution in the middle (L/2) of the monolith using optical microscopy at 100x.



Figure SI.7: Picture of washcoat distribution in the middle (L/2) of the monolith using optical microscopy at 100x.



Figure SI.8: Picture of washcoat distribution in the middle (L/2) of the monolith using optical microscopy at 100x.



Figure SI.9: Picture of washcoat distribution in the middle (L/2) of the monolith using optical microscopy at 100x.



Figure SI.10: Picture of washcoat distribution in the middle (L/2) of the monolith using optical microscopy at 100x.



Figure SI.11: Picture of washcoat distribution at the end of the monolith using optical microscopy at 100x.



Figure SI.12: Picture of washcoat distribution at the end of the monolith using optical microscopy at 100x.



Figure SI.13: Picture of washcoat distribution at the end of the monolith using optical microscopy at 100x.



Figure SI.14: Picture of washcoat distribution at the end of the monolith using optical microscopy at 100x.



Figure SI.15: Optical microscopy at 100x of the monolith sample to estimate a washcoat thickness for mass transport calculations.



Figure SI.16: Picture of washcoat distribution at the end of the monolith using optical microscopy at 100x.



Figure SI.17: Picture of washcoat distribution at the end of the monolith using optical microscopy at 100x.

References

- Carl-Robert Florén, Per-Anders Carlsson, Derek Creaser, Henrik Grönbeck, and Magnus Skoglundh. Multiscale reactor modelling of total pressure effects on complete methane oxidation over pd/al2o3. *Catal. Sci. Technol.*, 9:3055–3065, 2019.
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