Electronic Supplementary Information for:

Multiscale reactor modelling of total pressure effects for complete methane oxidation over Pd/Al$_2$O$_3$

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Complete methane conversion with Knudsen diffusion

The effect of Knudsen diffusion on complete methane conversion is evaluated for a pore size 10 nm. Knudsen diffusion is accounted for by

$$D_{k,i} = \frac{d_p}{3} \sqrt{\frac{8R_g T_s}{M_i \pi}} \tag{1}$$

The effective diffusivity is, instead of Eq. 10 in the article, estimated by the Bosanquet correlation

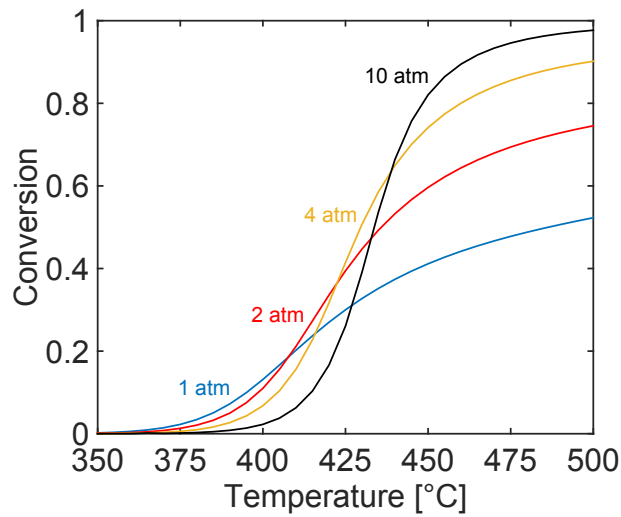$$D_{eff,i} = \frac{f_D}{\frac{1}{D_i} + \frac{1}{D_{k,i}}} \tag{2}$$

Figure ESI.1: Knudsen diffusion affected conversions for a pore size of 10 mn at varying temperatures and total pressures of 1 atm (blue), 2 atm (red), 4 atm (yellow) and 10 atm (black).

Mass and heat transport effects for examined gas conditions in multiscale reactor model

To evaluate whether mass transport affects the conversion of methane in the two dimensional multiscale model without Knudsen diffusion resistance, the external (td),

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internal (twc) and reaction (tr) time constants were calculated in each tank for all temperatures and total pressures. The significance of external and internal transport is determined as the ratio td/tr and twc/tr, respectively. The significances are here taken as the weighted average over all the tanks in the monolith to make a crude analysis of at which experimental conditions the reaction rate is affected by mass transport. It should, however, be noted that the axial variations are small and not affecting the outcome. Further, the method does not offer a sharp criterion for determining the reaction rate controlling phenomenon but gives an insight in the relative time scales between mass tranport and reaction. The external and internal mass transport significances are displayed in Figure ESI.2. The internal mass transport in Figure ESI.2b displays a similar trend to the external significance since the lumped mass transport coefficient, Γ, is calculated as the effective diffusivity multiplied by a structure independent factor in each tank and catalyst layer (see Eq. 11-12). The internal mass transport is shown to possess a higher significance than the external mass transport. In Figure ESI.2 the internal and external mass transport significance increases with temperature due to an increased reaction rate (decreased reaction time constant, tr). Increasing the total pressure has a negative effect on diffusion (increased external, td, and internal, twc, time constant) due to the inverse proportionality of total pressure on the diffusivity in Eq. 9. Therefore, increasing the total pressure always contributes to a slower diffusion. However, the effect of total pressure on diffusion is low when compared to its effect on surface kinetics, where the latter is also strongly temperature dependent. It is seen that below 450 °C the significance of mass transport is decreasing while increasing them at higher temperatures. The difference illustrates the interplay between the relative speed of reaction to diffusion. Below 450 °C, increasing the total pressure has a strong negative effect on surface kinetics due to the increasing amounts of bicarbonates, hydroxyl species and adsorbed water. This result is a significantly increased reaction time constant, tr, which obscures the negative effect that total pressure exerts on diffusion, twc and td. The net contribution is a decreaseing significance for increasing total pressures below 450 °C. However, at higher temperatures the significance increases with total pressure. While the reaction time constant still increases with increasing total pressures, due to a slightly decreasing availability of free PdO site pairs, the effect is low compared to what is observed at temperatures below 450 °C. For example, at 500 °C the reaction time constant increases marginally when the total pressure is increased from 1 to 10 atm. Thus, the increased external and internal time constants are here of relatively greater significance compared to the reaction time constant. Hence, the increasing significance of mass transport resistance for increasing total pressures, is attributed to the increasing external and internal time constants. The internal mass tranport limits the reaction rate at temperatures above 465 and 475 °C for total pressures of 10 and 4 atm, respectively. Figure ESI.2a shows that the external mass transport significance is below unity, i.e. external mass transport does not limit the reaction rate at all simulated temperatures and total pressures. At temperatures below 430 °C the external mass transport
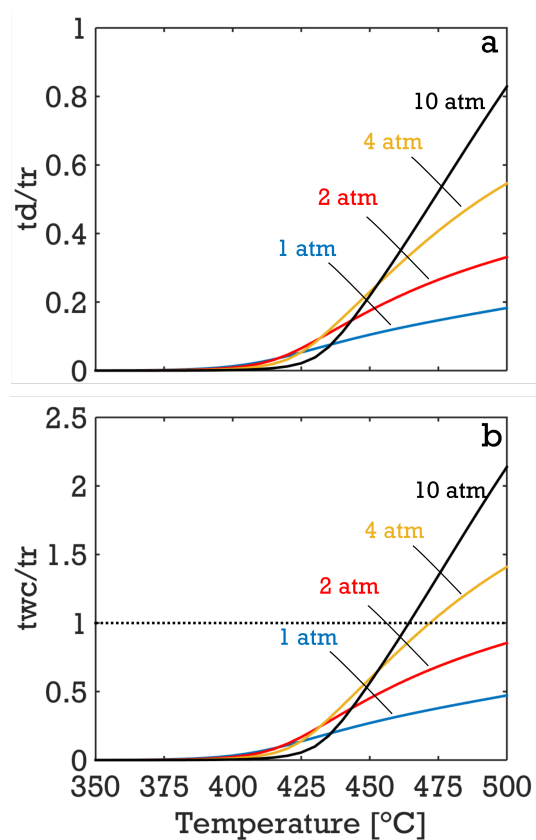
Figure ESI.2: The external (a) and internal (b) mass transport significance, here taken as the weighted average over all tanks, at total pressures of 1 (blue), 2 (red), 4 (yellow) and 10 (black) atm and varying temperatures.

significance is less than 0.1 at all examined total pressures and thus has an insignificant effect on the reaction rate. The significance increases with increasing temperature and it is observed that at high temperatures and total pressures the time constants of external mass transport and surface reaction are comparable. To determine whether external, internal or kinetics are controlling the observed reaction rate a criterion must be defined where one of the three time constants must be at least a predetermined factor larger than the other two. Thus, external mass transport cannot be said to be completely controlling the observed reaction rate. The internal mass transport is shown to exceed unity for total pressures of 4 and 10 atm. The highest value for internal mass transport significance is 2.14 for 500 °C and 10 atm. This value indicates that internal mass transport resistance is influencing the observed reaction rate, but not completely controlling. A significance exceeding 10 could be considered a stronger indication of controlling behavior.