



Modeling spatially resolved data of methane catalytic partial oxidation on Rh foam catalyst at different inlet compositions and flowrates

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ABSTRACT

Spatially resolved species and temperature profiles measured for a wide range of inlet stoichiometries and flowrates are compared with microkinetic numerical simulations to investigate the effect of transport phenomena on the catalytic partial oxidation of methane on Rh foam catalysts. In agreement with the experimental data, the species profiles calculated at different C/O inlet stoichiometries show that both partial oxidation products (H₂, CO) and total oxidation products (H₂O, CO₂) are formed in the presence of oxygen. At the leaner stoichiometries, both oxygen and methane react in the diffusive regime at the catalyst entrance. At the richest methane stoichiometry (high C/O), surface temperatures are lower and methane consumption is only partly determined by transport. For all stoichiometries, a kinetically controlled regime prevails in the downstream reforming zone after O₂ is fully consumed. The effect of increasing the flowrate shifts all species profiles downstream and also slightly modifies the shapes of the axial profiles, due to the different effectiveness of heat and mass transfer. Despite enhanced mass transfer and increased surface temperature, the shortened contact time causes a reduced CH₄ conversion at high flowrates. The effect of flowrate on the dominant regime is investigated, for both reactants, comparing the resistances calculated in the pure transport regime and in the pure kinetic regime. From a chemical point of view, the model allows for the analysis of the reaction path leading to hydrogen. Due to inhibition of H₂O re-adsorption, it can be proven that H₂ can be a primary product even in the presence of gas phase O₂. The analysis of the surface coverages shows analogous effects on the profiles when decreasing C/O or increasing flow, because in both cases the surface temperature is increased. Syngas selectivity was also evaluated, both from measured and calculated profiles. S_{H₂} is well described by the model at each stoichiometry and flowrate, while S_{CO} is underestimated in every case. From this work, it is also indicated that the Rh catalyst works with CO (measured) selectivities higher than equilibrium. Carbon dioxide only forms in the oxidation zone, for C/O = 1 and 1.3, but in the rest of the catalyst zone, there is no further production despite what would be expected from equilibrium. This confirms Rh does not catalyze the water gas shift reaction. On the other hand, at C/O = 0.8, this reaction becomes active, due to the higher temperature, and the CO₂ is also produced in the reforming zone. This suggests that CO₂ will not rise after the oxidation section if the surface temperature is kept sufficiently low. Sensitivity analyses to the active catalytic surface and to the kinetic parameters are provided.

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1. Introduction

Methane catalytic partial oxidation (CPO) to synthesis gas is an alternative to other energy-intensive technologies for industrial exploitation of natural gas. Its optimal utilization requires a deep insight into the underlying chemistry. Even though the reaction

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has been investigated for the past two decades [1–5], there are still open questions and further scientific investigation is required. Methane oxidation kinetics are very complicated, yet they are the simplest among the hydrocarbon oxidation processes. Since both exothermic and endothermic reactions are involved, a temperature variation does not translate directly to a reactant conversion, and energy and mass balances are deeply coupled. Therefore, CPO is a challenging and fascinating application where chemistry and transport phenomena are intrinsically connected with each other, determining the final product distribution. Appropriate modeling is needed to reproduce these complex features and to derive a molecular understanding of the reaction mechanism.

Nomenclature

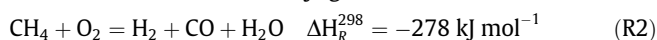
bold	vectors	v	interstitial velocity, m s^{-1}
•	free surface site	W	molar mass, kg kmol_i^{-1}
c_i	concentration, kmol m^{-3}	X_{CH_4}	methane conversion
c_p	bulk gas specific heat, $\text{J kg}^{-1} \text{K}^{-1}$	Y_G	bulk mass fractions, $\text{kg}_i/\text{kg}_{\text{tot}}$
$c_{p,S}$	solid specific heat, $\text{J kg}^{-1} \text{K}^{-1}$	Y_{BL}	BL mass fractions, $\text{kg}_i/\text{kg}_{\text{tot}}$
D_i	species molecular diffusivity, $\text{m}^2 \text{s}^{-1}$	z	axial coordinate, m
dpore	pore diameter, m	Greek letters	
f	tortuosity factor	ε	foam porosity, $V_{\text{void}}/V_{\text{bed}}$
h	species enthalpy, J kmol_i^{-1}	η	viscosity, $\text{kg m}^{-1} \text{s}^{-1}$
ΔH_R	enthalpy of reaction, J kmol^{-1}	λ_G	bulk gas thermal conductivity, $\text{W m}^{-1} \text{K}^{-1}$
K_i^*	pseudo-first-order kinetic constant, m s^{-1}	λ_S	solid thermal conductivity, $\text{W m}^{-1} \text{K}^{-1}$
K	extinction coefficient, m^{-1}	ρ_G	bulk gas density, kg m^{-3}
K_C	mass transfer coefficient, m s^{-1}	ρ_{BL}	boundary layer gas density, kg m^{-3}
K_T	heat transfer coefficient, $\text{W m}^{-2} \text{K}^{-1}$	ρ_S	solid density, kg m^{-3}
L	each monolith length, m	Dimensionless numbers	
Nsp	number of chemical species	Pe_M	Re·Sc
\dot{S}	species production rate by surface reaction, $\text{kmol}_i \text{m}^{-2} \text{s}^{-1}$	Pe_T	Re·Pr
S_V	geometric surface to void volume, $S_V = 4/\text{dpore}$, m^{-1}	Pr	$\frac{\eta \cdot c_p}{\lambda}$
S'_V	geometric surface to bed volume, $S'_V = S_V \varepsilon$, m^{-1}	Re	$\frac{C}{\eta S_V}$
$S_{V,C}$	active catalytic surface to void volume, m^{-1}	Sc	$\frac{\eta}{\rho \cdot D}$
t	time, s		
T_G	bulk gas temperature, K		
T_S	solid temperature, K		

Although there are many possible elementary reactions in the methane CPO system, the number of global reactions which may take place is not that high because the system is constrained to give only six products: CH₄, CO₂, CO, H₂, H₂O and O₂ (higher hydrocarbons are commonly not detected). Some of the possible exothermic oxidation reactions ranging from total oxidation to partial oxidation are listed below.

Total Oxidation: $\text{CH}_4 + 2\text{O}_2 = 2\text{H}_2\text{O} + \text{CO}_2$

$$\Delta H_R^{298} = -803 \text{ kJ mol}^{-1} \quad (\text{R1})$$

Partial Oxidation to H₂O and syngas:



Partial Oxidation to Syngas: $\text{CH}_4 + 1/2\text{O}_2 = 2\text{H}_2 + \text{CO}$

$$\Delta H_R^{298} = -36 \text{ kJ mol}^{-1} \quad (\text{R3})$$

After oxygen is consumed, there are only three global reactions which can take place (only two of them independent): steam reforming (SR), water gas shift (WGS) and dry reforming (DR), even if there is experimental evidence that DR does not occur on Rh and is a result of the combination of SR and WGS [6–9].

Steam Reforming: $\text{CH}_4 + \text{H}_2\text{O} = 3\text{H}_2 + \text{CO}$

$$\Delta H_R^{298} = +206 \text{ kJ mol}^{-1} \quad (\text{R4})$$

Water Gas Shift: $\text{H}_2\text{O} + \text{CO} = \text{H}_2 + \text{CO}_2$

$$\Delta H_R^{298} = -41 \text{ kJ mol}^{-1} \quad (\text{R5})$$

Dry Reforming: $\text{CH}_4 + \text{CO}_2 = 2\text{H}_2 + 2\text{CO}$

$$\Delta H_R^{298} = +247 \text{ kJ mol}^{-1} \quad (\text{R6})$$

The interplay between chemical and physical processes has been acknowledged to be a fundamental issue in the modeling [10,11] of fast, exothermic reactions. Plug flow reactor (PFR) mod-

els are unsatisfactory for catalytic combustion applications because of the excessive simplifications in heat and mass transport; full computational fluid dynamics (CFD) models or at least lumped models accounting for transport phenomena [12–14] are required.

The reaction rate of species involved in very fast reactions will be dominated by the system's mass transfer characteristics. However, for the other slower reactions, a good kinetic model and accurate assumption for active surface area are required. It is obvious that for an optimal kinetic study, all the species should be in kinetic control and also a safe determination of the reaction (surface) temperature is necessary. Only if the temperature is well captured by the model is a proper kinetic study possible. The dominant regime is investigated for oxygen and methane, at every flowrate, comparing the mass transfer coefficient and the kinetic constant of the pseudo-first-order reaction, i.e. the consumption rate divided by the concentration.

The reaction path influences and is in turn influenced by the temperature profile. This means that even if chemical kinetics are accurately described, incorrect species profiles will result unless a suitable temperature profile is used. However, the latter is not easy to model, because it is affected simultaneously by several physical transport processes. Heat released by the reaction [15] is transported by gas convection and conduction (minor gas phase influence of radiation) and solid conduction and radiation. Given the exponential temperature dependence of the kinetics on the one hand and the complexity of the phenomena contributing to the heat balance on the other hand, the kinetics will be more influenced by the temperature profile than vice versa. Therefore, a model capable of reproducing the temperature profile will reasonably predict species profiles, in particular far from the catalyst entrance.

At relatively long residence times, the kinetics slow down and the exit composition approaches equilibrium, which depends only on temperature. The authors showed [14] that also the PFR model correctly describes the exit composition, with the correct exit temperature, even if the onset of the calculated profiles diverges greatly from the experimental data at the inlet of the catalyst.

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