Optimal Design of CH_4 Catalytic Partial Oxidation Reformers on Rh-Based Catalysts for Small-Scale Syngas Production

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Introduction

The possibility to produce H_2/CO mixtures without external energy input in small reactors with reduced heat capacity makes the catalytic partial oxidation (CPO) of methane and higher hydrocarbons a promising solution for small-scale syngas production (e.g., [1, 2]). The severe operating conditions pose a challenge [3] for process stability requiring a suitable trade-off between low hot spot temperature and high syngas productivity and, in this respect, a comprehensive physically sound mathematical model would be a valuable tool both for gaining insights into the complexity of the process and for enabling rational design and optimisation of the reactor. In this work, we have coupled the previously derived 1D dynamic model of the adiabatic CH_4 CPO reformer [4] with our recently developed microkinetic model for CH_4 activation on Rh based catalysts [5] for the model-based analysis of spatially resolved CH_4 CPO experimental data on foams under adiabatic conditions [6]. This improved model allows us to analyse in detail the behaviour of the reactor including transport phenomena at the macroscale and surface chemistry at the microscale.

Results and Discussion

Figure 1 compares spatially resolved experimental data [6] and model predictions for a typical CPO experiment on foam. The value of Rh specific surface used for this simulation is in close agreement with the value inferred from CO chemisorption experiments on the catalyst. Overall, there is a good agreement between the model predictions and the experiments, both for species concentrations and for temperatures (not shown). Along the entire reactor, the most abundant reactive intermediates (MARI) are CO* and H* and the surface turns out to be reasonably clean. Under those conditions of surface coverages, methane consumption occurs via pyrolysis followed by oxidation of C* species by OH* and O_2 consumption is always mass transfer controlled. In line with previous results [4], this is confirmed by the analysis of the species concentration at the catalyst interface, that points out that O_2 concentration at the surface interface is nearly zero. Consequently, the heat release on the catalyst surface is strictly governed by mass transfer. On the other hand, methane consumption is controlled by a mixed chemical-mass transfer regime and consequently the catalyst loading and distribution along the reactor affect the rates of the endothermic reactions. Overall, it turns out that the final temperature profile is determined by the combination of several physical phenomena in addition to the chemical reactions (including quenching effect of the feed cold gas, rate of O_2 mass transfer, axial thermal dispersion). As an example, we investigated (Figure 2) the effect of varying transport properties of the bed by decreasing the pore foam cell density, while keeping constant the Rh load: the resulting increase in interphase mass transfer resistances results in a more gradual dosing of O_2 along the axial coordinate and consequently in a reduction of the hot-spot temperature (from 1080°C for a 100 ppi foam to 950°C for a 40 ppi foam). As a whole, the great sensitivity of the reactor behaviour upon those characteristics offers a large number of degrees of freedom for reactor design and optimization, by proper tailoring of the type, the geometry and the material of the catalyst support with a twofold purpose: reduction in hot spot temperature and enhanced production of syngas. Variation of other parameters leading to reactor optimization will also be discussed. Experimental validation is currently on-going.

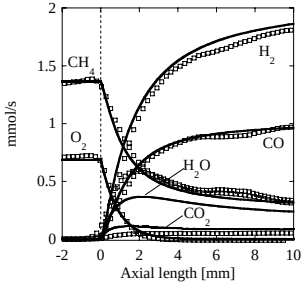

Figure 1. Species along the axial length. Solid lines: model predictions – Square symbols: experimental data [6].

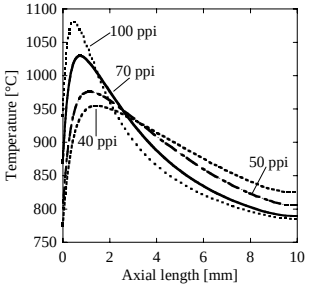

Figure 2. Effect on catalyst temperature profiles changing the pore density of the foam.

Significance

A fundamental and multiscale analysis of CPO experimental data is shown, using a an adiabatic heterogeneous reactor model with a detailed microkinetic scheme, that unravels for the first time the mechanisms. Results inferred from the analysis are then employed to propose a rational optimization of the reactor, in terms of reduction in hot-spot temperature and enhanced production of syngas.

References

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