

Spatially Resolved Species and Temperature Determination during Methane and Propane Partial Oxidation over a Rh-Coated Monolith

Jae-Soon Choi^{1*}, William P. Partridge¹, Galen B. Fisher², Eric C. Tan³, Jeffrey G. Weissman⁴,
John E. Kirwan², and L. Curt Maxey¹

¹Oak Ridge National Laboratory, Oak Ridge, TN 37831-6472 (USA)

²Delphi Corp., Shelby Twp, MI 48315; ³Delphi Catalysts, Tulsa, OK 74158 (U.S.A.)

⁴Delphi Corp., Rochester, NY 14602 (USA)

*choijs@ornl.gov

Introduction

Fuel reformers, which convert a broad array of hydrocarbons into hydrogen-rich gas streams, can enable various advanced power generation technologies such as fuel cell-based auxiliary power units and reformate-assisted high efficiency clean combustion [1]. While monolith catalyst designs have shown potential for small-scale fuel reforming [2,3], significant technological improvements are needed for their wide commercial implementation. In this respect, it is important to further our understanding, which has been hampered by the fact that intrinsically non-isothermal and gradient-rich reformer operation is very difficult to analyze via temporally and spatially integrated conventional reactor-outlet measurements. Detailed in-situ, intra-reactor measurements are therefore critical to understanding the detailed interplay of various reactions and their influence on reformer design, efficiency, and robustness. Indeed, a currently emerging spatially resolved intra-catalyst measurement approach has shown the potential for elucidating the chemistry related to methane reforming over rhodium-coated foam catalysts [4] and in automotive emission control catalysts [5].

In this work, we have measured for the first time local species and temperature profiles along a honeycomb monolith catalyst during methane and propane partial oxidation (POx) and validated a microkinetics-based reactor model using the obtained data. Combined experimental and computational results have been used to elucidate underlying mechanisms.

Materials and Methods

Partial oxidation experiments were performed over a Rh-containing washcoated monolith (62 cells per cm²; 2-cm diameter; 2.54-cm length) in a horizontal quartz reactor heated by an electric furnace. Spatially Resolved Capillary Inlet Mass Spectrometer (SpaciMS) [5] was used for species measurements and fiber-optic thermometry and K-type thermocouples were used for temperature measurements. Both species and temperature probes are minimally invasive both in terms of physical size and sample flow rate (see Fig. 1).

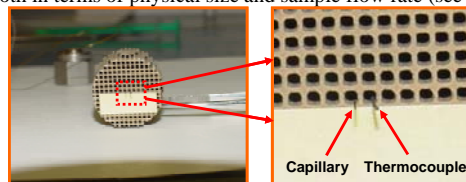


Figure 1. Rh-coated reformer catalyst with species and temperature probes inside channels.

The kinetic calculations were performed using both the gas-phase kinetic (325 reactions) and surface kinetic (56 reactions) models with the Plug Flow Reactor (PFR) driver program in the CHEMKIN Collection v. 4.1 suite programs.

Results and Discussion

The employed approach provided useful information under realistic reformer conditions. In particular, the combined intra-channel species and temperature measurements gave a clear picture of how POx processes evolve axially along the catalyst (see Fig. 2). At the front portion of the monolith, a fraction of the CH₄ undergoes total oxidation consuming the available oxygen and producing mainly CO₂, H₂O and a significant exotherm. Some H₂ and CO were also observed in this “combustion” zone. Further downstream, endothermic reforming of the remaining CH₄ became predominant, consuming H₂O and CO₂ with the released heat, resulting in major H₂ and CO formation (“reforming zone”) and a gradual observed temperature drop. In this presentation, we will discuss space velocity effects on axial species profiles and temperature distributions, thermodynamic and kinetic aspects, and methane vs. propane POx. The experimental data will be compared with modeling results (see Fig. 2). Moreover, we will describe in detail the SpaciMS and thermometry that appear, as a result of this study, to be valuable tools for reformer research, design, and modeling.

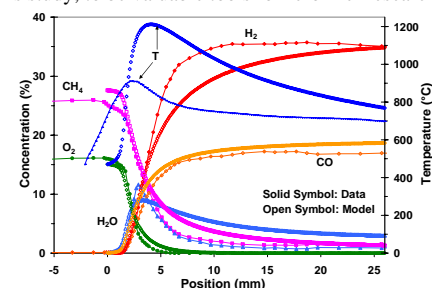


Figure 2. Experimental and calculated species and temperature profiles for methane partial oxidation. 27.6% CH₄, 15.1% O₂, Ar balance; 47000 h⁻¹ space velocity; no external heating.

Significance

The understanding generated in this study will provide significant information valuable for reformer design. Detailed understanding of spatial evolution of the thermal environment and reaction chemistry will enable tailoring of catalyst materials and formulations both for solid oxide fuel cell and vehicle powertrain applications.

References

1. Kirwan, J.E., Quader, A.A., and Grieve, M.J., *SAE Technical Paper* 2002-01-1011 (2002).
2. Giroux, T., Hwang, S., Liu, Y., Ruettinger, W., and Shore, L., *Appl. Catal. B* 56, 95 (2005).
3. Hickman, D.A., and Schmidt, L.D., *Science* 259, 343 (1993).
4. Horn, R., Williams, K.A., Degenstein, N.J., and Schmidt, L.D., *J. Catal.* 242, 92 (2006).
5. Choi, J.-S., Partridge, W.P., and Daw, C.S., *Appl. Catal. A* 239, 24 (2005).