

OPTIMAL DESIGN OF SCT-CPO REFORMERS: MODELING ANALYSIS AND EXPERIMENTAL VALIDATION

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Summary

The performance and thermal behavior of SCT-CPO reformers are strongly influenced by heat and mass transfer phenomena in addition to the surface kinetics. In particular, the intensity of the inlet hot-spot (a crucial weakness of the process) is governed by the trade-off between rate of O₂ interphase transport and rate of steam reforming, and is influenced by the solid-phase conduction. Activity profile, geometry and cell density of the structured catalyst supports, reactor aspect ratio are degrees of freedom which can be optimized for lowering the surface temperatures below the threshold for Rh stability. Theoretical analyses and experimental demonstrations are presented.

Keywords: Rational design of catalysts, Hydrogen production, Novel reactor technologies.

Introduction

In a previous work¹, the authors addressed a theoretical and experimental investigation on the behavior of a short contact time CH₄-CPO reformer, operating with Rh-coated honeycomb monoliths. Main results are herein recalled: the measured temperature profiles obtained by sliding thermocouples are qualitatively and quantitatively in line with the calculated temperature profiles of the gas-phase; while gas-phase temperature profiles are characterized by broad maxima, solid-phase profiles present a pronounced hot-spot at the very reactor inlet, and the surface peak temperature can be hundreds of degrees higher than gas temperatures; the shape of the surface temperature profiles is due to the rapid O₂ consumption (fully mass transfer controlled) and heat release which occur at the very reactor inlet, partly balanced by the pyrolytic reactions (and the heat consumption) which are “spread” along the whole monolith length and give rise to syngas formation. Most importantly, the experimental investigation clearly showed that, under severe operating conditions (extremely high flow rates and the presence of preheating can easily increase the hot spot temperature over 1000°C), the CPO reformer shows an unstable thermal behavior, since progressively increasing temperatures are measured in the inlet reactor portion. The modeling analysis showed that the reactor heating can be explained by a loss of catalyst activity, which little affects the conversion of O₂, while strongly influences the more chemically controlled reforming reactions. The most important conclusion is that thermal management is the critical issue for the successful operation of a CH₄-CPO reformer. Guidelines for the optimal reactor design (with

minimum hot-spot temperature) are herein explored in detail and novel experimental solutions are tested.

Figure 1 shows some preliminary but very interesting results. The performances and thermal behavior of two monoliths are compared; black symbols and data refer to an “extra-active” monolith with a Rh content two and half times higher than a standard monolith (red symbols and data). Clearly, axial measurements indicate an effective decrease of temperatures at the inlet and along the whole monolith. Model calculations suggest that the reduction of surface temperature can be successfully achieved even if the extra activity is present at the very reactor inlet, where it is needed for influencing the balance between rate of exothermic and rate of endothermic reactions. The preparation and testing of monolith with such an activity profile is in progress to demonstrate the principle.

Experimental and modeling

Experiments of CH₄ CPO were performed in an adiabatic reformer over a 2 wt% Rh/ α -Al₂O₃ catalyst supported on 400 cpsi honeycomb cordierite monolith. Details of the reactor design are reported elsewhere¹. The reactor is equipped with several sliding thermocouples and a sliding optical fiber connected to an infrared pyrometer that measure the axial temperature profiles.

The CPO reformer was simulated by a dynamic 1D, heterogeneous, single channel model, previously developed and validated¹. In the present form, the model incorporates a C1-microkinetic model² whose adequacy

has been verified against isothermal data of partial oxidation, steam reforming and dry reforming of methane, plus WGS data, and tests of H₂ and CO rich combustion.

Results and discussion

Effect of activity profile – Previous simulations¹ had shown that the catalyst activity can be designed to minimize the hot-spot temperatures. In fact, at increasing intrinsic activity an enhancement of the reforming process is expected, while no effect is expected on the global rate of O₂ consumption due to the prevailing mass transfer limitations.

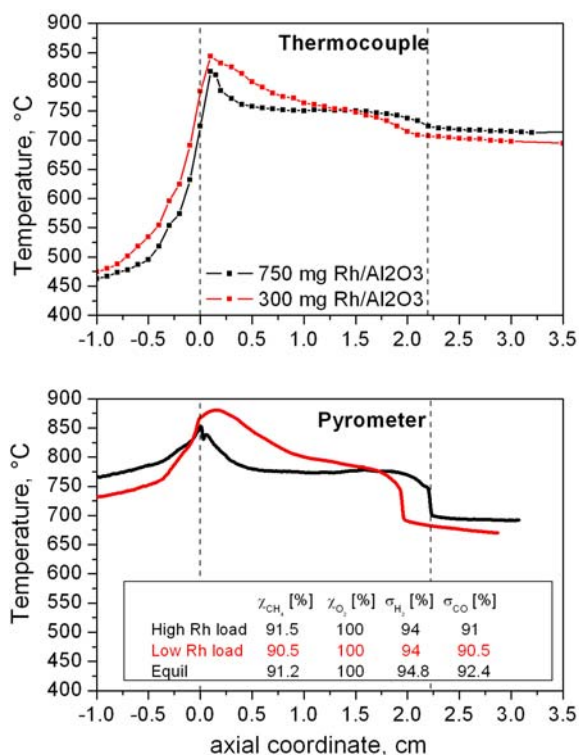


Figure 1 – Effect of Rh-load on the thermal behavior of a CH₄-CPO honeycomb monolith. Flow rate (air + CH₄)= 10 NI/min; O₂/C=0.56.

Effect of channel opening – Figure 2 shows the calculated effect of the channel size in an honeycomb monolith at fixed catalyst load. At increasing channel opening, the rate of O₂ interphase transfer slows down progressively and the surface hot-spot temperature decreases accordingly. Of course, the decrease of heat and mass transfer rate lowers the overall efficiency of the reformer and longer monoliths are needed at increasing channel size to keep CH₄ conversion high. However, the lengthening of the monolith could in principle be avoided by adopting a graded-monolith configuration wherein the inlet portion is characterized by larger channels (to effectively decrease the hot spot temperatures). Figure 3 shows experimental results obtained by graded cell density configuration, obtained by adopting a 5 mm long monolith with 3 mm channel opening in front of a standard 400 cpsi monolith.

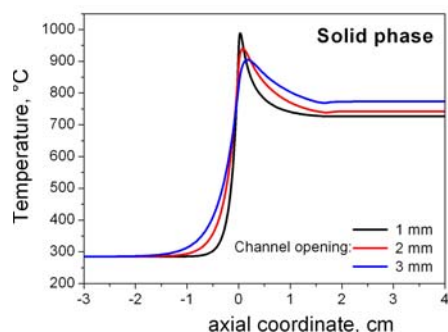


Figure 2 – Calculated effect of channel size. Conditions as Fig 1

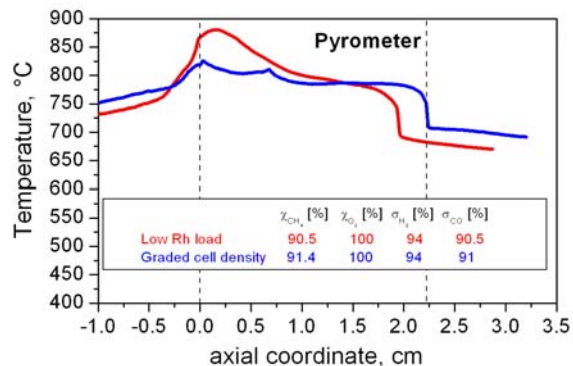


Figure 3 – Performances of a graded-cell density configurations.

Effect of aspect ratio – Also the geometry of the reactor can greatly affect the thermal behavior. It was shown¹ that at increasing diameter/length ratio, the decrease of the linear velocity tends to favor the heat back conduction with a beneficial effect on the surface temperatures. The on-going experimental investigation clearly shows the key role of the thermal conductivity of monolith and front shield.

Conclusions

The minimization of the surface hot-spot temperature is the primary goal of reactor design, since thermal stability is the true weakness of noble metal based SCT-CPO reformers. In this work we show that the catalyst activity, the cell density and nature of the structured support and the geometry of the reactor offer room for an effective optimization; solutions are offered by the correct rationalization of the complex physical and chemical phenomena which govern the reactor behaviour. Experimental demonstrations are promising and application to C₂+fuels is of great interest.

References

- (1) Beretta A.; Groppi G.; Lualdi M.; Tavazzi I.; Forzatti P.; Experimental and Modeling Analysis of Methane Partial Oxidation: Transient and Steady-State Behavior of Rh-Coated Honeycomb Monoliths, IECRes., **2009**, *48*, 3825.
- (2) Maestri M.; Vlachos D.G.; Beretta A.; Groppi G.; Tronconi E.; A C-1 Microkinetic Model for Methane

Conversion to Syngas on Rh/Al₂O₃, *AIChE J.*, **2009**, 55, 993.