

## The effect of CO<sub>2</sub>, H<sub>2</sub>O and metal dispersion on the catalytic partial oxidation of CH<sub>4</sub> over Rh based catalysts

A. Donazzi<sup>1</sup>, M. Maestri<sup>1</sup>, B.C. Michael<sup>2</sup>,

A. Beretta<sup>1\*</sup>, P. Forzatti<sup>1</sup>, G. Groppi<sup>1</sup>, E. Tronconi<sup>1</sup>, L.D. Schmidt<sup>2</sup>, D.G. Vlachos<sup>3</sup>

<sup>1</sup>Laboratory of Catalysis and Catalytic Processes – Dipartimento di Energia, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

<sup>2</sup>Department of Chemical Engineering and Materials Science – University of Minnesota, 421 Washington Avenue SE, Minneapolis, MN 55455, USA

<sup>3</sup>Center for Catalytic Science and Technology – Department of Chemical Engineering, University of Delaware-Newark, DE 19716-3110, USA

\*alessandra.beretta@polimi.it

### Introduction

The Catalytic Partial Oxidation (CPO) of CH<sub>4</sub> has been given increasing attention as a promising alternative technology for the production of synthesis gas at small- to medium-scale. In the field of power generation, novel applications include the conduction of the reaction in catalytic burners under ultra-diluted, O<sub>2</sub>-lean conditions [1]: CH<sub>4</sub> and O<sub>2</sub> react in the presence of large amounts of H<sub>2</sub>O and CO<sub>2</sub> recycled from exhaust streams, consequently avoiding NO<sub>x</sub> production and moderating temperature gradients. Similar recycle may take place in CPO. Rh is commonly recognized as the best performing noble metal, due to its high selectivity to syngas and carbon-free operation [2]. Honeycombs and ceramic foams are the reference supports in structured reactors, as they allow for short contact time operations, with almost no pressure drops, reduced volumes and fast responses to transient load demands. In this work, an extensive investigation of the role of H<sub>2</sub>O and CO<sub>2</sub> in the CPO of CH<sub>4</sub> was carried out over Rh coated foams. Two of the most up-to-date experimental tools proposed in the literature were used in concert: the spatial sampling technique [3] was applied to measure temperature and composition profiles along the axis of the foams; a detailed microkinetic scheme [4] was used for the quantitative analysis of the data.

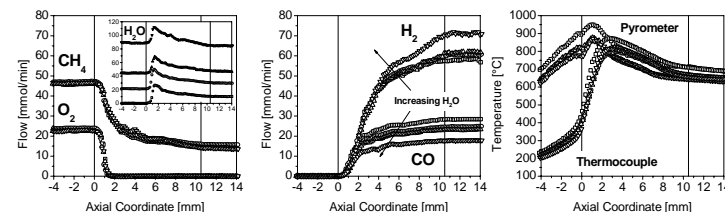
### Materials and Methods

80 ppi  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> reticulated foams were chosen as supports. The monoliths were drilled axially to form a channel. 5 wt% Rh samples and 5 wt% Rh / 2 wt%  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> samples were prepared. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> washcoat (3  $\mu$ m powder) was applied as an aqueous slurry and Rh was deposited using the incipient wetness technique. The reactor consisted of a quartz tube into which the catalytic monolith was placed along with blank monoliths fore and aft, acting as heat shields. A deactivated fused silica capillary was used for sampling the gases through a side orifice (10 ml/min). The sampled gases were analyzed with a quadrupole mass spectrometer (UTI 100C) and a gas chromatograph (HP5890). An optical pyrometer (Mikron MI-GA 5-LO) and a thermocouple (Inconel clad K-type) were used to measure the temperature. The experiments were performed at atmospheric pressure, with 5 slpm flow rate, C/O ratio of 1, and 20% v/v CH<sub>4</sub>. H<sub>2</sub>O-rich tests (10, 20 and 40% v/v) and CO<sub>2</sub>-rich tests (20 and 35% v/v) were carried out. Ar was added to balance. Gases were preheated to 150°C. Characterization of the foam properties was also carried out: metal dispersion was estimated with pulse chemisorption technique, and heat and mass transfer correlations were determined taking into account the geometry of the structure. For the model-based analysis of the data, we have

coupled the previously derived 1D dynamic model of the adiabatic CH<sub>4</sub> CPO reformer [5] with a recently developed microkinetic model for methane activation on Rh [4].

### Results and Discussion

Remarkably, the addition of H<sub>2</sub>O to the feed up to 40% (Figure 1) did not improve the conversion of CH<sub>4</sub>, in line with recent mechanistic findings on the kinetic irrelevance of H<sub>2</sub>O concentration in the rate of SR over noble metals. The products' distribution (the H<sub>2</sub>/CO ratio) changed according to the equilibrium of the WGS reaction. Temperatures decreased, though, because of the increased gas heat capacity; this makes more complex the quantitative interpretation of the results. The addition of CO<sub>2</sub> decreased the conversion of CH<sub>4</sub> and modified the products' distribution according to the stoichiometry of the reverse-WGS reaction. Little sensitivity was found upon adding CO<sub>2</sub>. Between 20 to 35% v/v CO<sub>2</sub> inlet concentration, no differences were observed: CO<sub>2</sub> was only moderately consumed and acted as a thermal diluent. Overall, regardless of the nature and the amount of CH<sub>4</sub> co-reactant, an initial oxidation zone was always present whose length did not change; this shows the primary role of the CH<sub>4</sub>/O<sub>2</sub> surface chemistry in CH<sub>4</sub>/O<sub>2</sub>/H<sub>2</sub>O(or CO<sub>2</sub>) reacting systems and the diffusive control of O<sub>2</sub> consumption. Good match between experimental and simulated curves was found and a detailed microkinetic analysis of the experiments will be presented. An important interplay between mass transfer and surface chemistry emerged and the simulations confirmed that transport phenomena and metal dispersion have a critical role in the reaction. Microkinetic analysis represents the appropriate tool for comprehending the relative affinity of O<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub> to the Rh surface. CPO data collected over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> washcoated samples were also simulated, in order to investigate the effect of Rh dispersion.



**Figure 1:** Effect of H<sub>2</sub>O addition on CH<sub>4</sub> CPO. CH<sub>4</sub> = 20%, H<sub>2</sub>O = 0 – 40%, C/O = 1, 5 slpm.

### Significance

A thorough understanding for the scale-up of CH<sub>4</sub> CPO is presented. The detailed kinetic scheme, the careful characterization of geometrical and transport properties of the foams, and the estimation of metal dispersion proved to be crucial in the description of the experimental behavior of the lab-scale reformer.

### References

1. T. Griffin, D. Winkler, M. Wolf, C. Appel, J. Mantzaras, ASME paper 2004-54101
2. A.P.E. York, T. Xiao and M.L.H. Green, *Top. Catal.* 22 (2003) 345
3. R. Horn, N. J. Degenstein, K. A. Williams, L.D. Schmidt, *Cat. Lett.* 110 (2006) 169
4. M. Maestri, D.G. Vlachos, A. Beretta, G. Groppi, E. Tronconi, *AIChE J.*, doi: AIC11767
5. M. Maestri, A. Beretta, G. Groppi, E. Tronconi, P. Forzatti, *Catal. Today*, 105 (2005) 709