

# Catalytic Partial Oxidation of Hydrocarbons: a comparison between CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub> reactivity over Rh-based catalysts

A. Donazzi, A. Beretta, G. Groppi\* and P. Forzatti

Nemas – Centro di Eccellenza per l'Ingegneria dei Materiali e delle Superfici Nanostrutturate,  
Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Politecnico di  
Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

\*gianpiero.groppi@polimi.it

## Introduction

Short contact time catalytic partial oxidation of hydrocarbons have recently received growing attention especially for energy related applications, for example the integration of catalytic CH<sub>4</sub> combustors in advanced GT, feeding of SOFC for on-board APU units or on-site H<sub>2</sub> production for metallurgical treatments. Compared to the conventional homogeneous process, the use of a catalyst allows to reduce the reactor temperatures, thus enabling the feed of air instead of pure O<sub>2</sub>, to decrease the volumes and to shorten the dynamic response to transient load demands. Rh is generally regarded as the best performing catalyst in CPO because of its high selectivity towards syngas, low carbon formation attitude and thermal stability [1,2]. A comparative study of CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub> reactivity over a 2.7 wt Rh/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst was performed with a short contact time annular reactor, specifically designed for testing very fast and exothermic reactions [3]. The effect of several variables, i.e. O<sub>2</sub>/C ratio, GHSV and temperature, was investigated.

## Materials and Methods

A 2.7 wt Rh/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by dry impregnation of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support (5 m<sup>2</sup>/g) with a commercial Rh(NO<sub>3</sub>)<sub>3</sub> solution (14.68 wt % Rh, Chempur). The catalytic powders were deposited in the form of a thin layer (20  $\mu$ m) on an alumina tube by a dip coating procedure. The catalyst coated tube was assembled in a short contact time annular reactor. The reactor was externally heated by a three zone Carbolite oven; a micro-GC (3000 A, Agilent Technologies) was used to analyze the inlet and outlet gas compositions.

The catalyst was conditioned *in situ* with a standard reaction mixture (CH<sub>4</sub> = 4%, O<sub>2</sub>/C = 0.56, N<sub>2</sub> to balance) at 8.0\*10<sup>5</sup> Ncc/g<sub>cat</sub>/h by successive heating ramps till reaching the final stable state. Then, activity tests were performed feeding either CH<sub>4</sub> or C<sub>3</sub>H<sub>8</sub>, at fixed O<sub>2</sub> concentration (1.7%). For each activity test, the pressure was atmospheric and the temperature was increased from 350°C to 850°C (50°C step). For each fuel, O<sub>2</sub>/C ratio (0.56 – 1.3) and GHSV (2\*10<sup>6</sup> – 4\*10<sup>6</sup> Ncc/g<sub>cat</sub>/h) were varied. Nearly isothermal conditions ( $\Delta T < 20^\circ\text{C}$ ) were maintained by means of the high dilution of the reactants and the effective dissipation of reaction heat by radiation. A quantitative analysis of the experimental data was performed through simulations with a 1D heterogeneous model of the reactor, accounting for gas-solid internal and external mass transfer limitations [3].

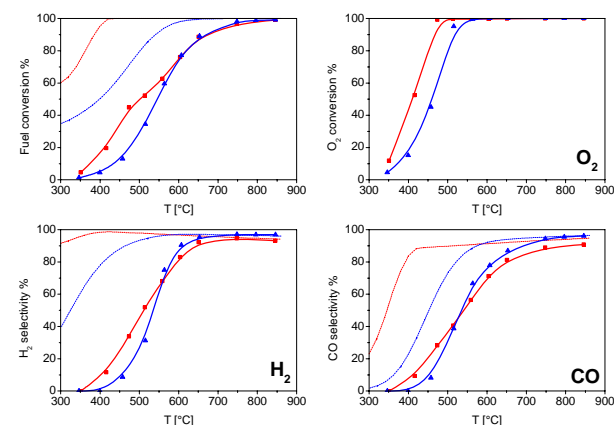
## Results and Discussion

The results of C<sub>3</sub>H<sub>8</sub> partial oxidation tests evidenced that a consecutive indirect kinetic scheme, previously developed for CH<sub>4</sub> [2], which consists of combustion followed by reforming reactions, shift equilibration and post combustion of H<sub>2</sub> and CO, can be extended to

C<sub>3</sub>H<sub>8</sub>. At lower temperatures deep oxidation prevails, while at higher temperatures secondary dry and steam reforming results in high selectivity to syngas.

Comparing the results of C<sub>3</sub>H<sub>8</sub> and CH<sub>4</sub> tests (Figure 1), it is apparent that at lower temperature the oxidation activity of C<sub>3</sub>H<sub>8</sub> is markedly superior than that of CH<sub>4</sub>, while at higher temperature the reforming activity is the same for both the fuels as evidenced by overlapping of the conversion curves. This suggests that at lower temperatures the different energy barrier for activation of the first C-H bond is responsible for the higher reactivity of C<sub>3</sub>H<sub>8</sub> [4], while at higher temperatures the surface reaction of a common intermediate species (e.g. adsorbed CH<sub>x</sub>) could be the rate controlling step for both C<sub>3</sub>H<sub>8</sub> and CH<sub>4</sub>.

**Figure 1.** Temperature effect on fuel conversion and product selectivity; C<sub>3</sub>H<sub>8</sub> (■) CH<sub>4</sub> (▲), dashed lines = equilibrium, O<sub>2</sub>/C = 0.56, O<sub>2</sub> = 1.7%, N<sub>2</sub> to balance, GHSV = 2\*10<sup>6</sup> Ncc/m<sup>3</sup>/g<sub>cat</sub>/h, P = 1 atm.



## Significance

In this work, the partial oxidation reactivities of CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub> over a 3 wt% Rh/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst were compared by kinetic tests under well controlled conditions. The data showed that the reforming reactivity is equal for both the fuels while the oxidation reactivity of C<sub>3</sub>H<sub>8</sub> is higher than that of CH<sub>4</sub>. For the reforming reactions, RDS is proposed to be the surface reaction of a common intermediate species, while the oxidation reactivity is controlled by activation of the first C-H bond.

## References

1. D.A. Hickman, L.D. Schmidt, *Science*, 259 (1993) 343
2. A.P.E. York, T. Xiao and M.L.H. Green, *Top. Catal.* 22 (2003) 345
3. I. Tavazzi, A. Beretta, G. Groppi, P. Forzatti, *J. Catal.* 241 (2006) 1
4. R. Burch, M.J. Hayes, *J. Mol. Catal. A: Chemical*, 100 (1995) 13