

## Partial Oxidation of Methane on Rh/CeZrO<sub>2</sub> Catalysts

Raquel Lima Oliveira<sup>1</sup> and Fabio B. Passos<sup>1\*</sup>

<sup>1</sup>Departamento de Engenharia Química e de Petróleo – Universidade Federal Fluminense  
Niterói, RJ, 2420-240, (Brazil)

\*fbpassos@vm.uff.br

### Introduction

Besides the interest of producing synthesis gas efficiently for use in GTL plants, there has been a lot of interest in developing compact reformers, able to produce a H<sub>2</sub> rich stream [1] from a hydrocarbon feedstock. Rh catalysts are well known catalysts for the partial oxidation of methane and the use of CeZrO<sub>2</sub> as support proved to be beneficial for this reaction for Pt supported catalyst [2]. In this work, we investigate the use of CeZrO<sub>2</sub> as supports for Rh catalysts used in the partial oxidation of methane.

### Materials and Methods

The catalysts were prepared by incipient wetness using Rh(NO<sub>3</sub>)<sub>3</sub> (final Rh content equal to 1.5%) as precursor.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and CeO<sub>2</sub> supports were calcined at 800°C for 1 hour. The CeZrO<sub>2</sub> support was obtained by a co-precipitation method. An aqueous solution of cerium (IV) ammonium nitrate and zirconium nitrate was prepared in order to obtain the desired amounts of CeO<sub>2</sub> and ZrO<sub>2</sub>. Then, the ceria and zirconium hydroxides were co-precipitated by the addition of an excess of ammonium hydroxide. Finally, the precipitate was washed with distilled water and calcined at 800°C for 1h. The prepared catalysts were characterized by temperature programmed reduction (TPR) and the number of active sites was estimated by using the cyclohexane reaction at 270 °C a structure insensitive reaction. [2]. The reaction mechanism was investigated using temperature programmed surface reaction (TPSR) experiments using a mixture of 5% O<sub>2</sub>/He and 20% CH<sub>4</sub>/He with flow rates of 40 mL/min and 20 mL/min, resulting in CH<sub>4</sub>:O<sub>2</sub>:He ratio of 2:1:27

### Results and Discussion

TPR profile for the 1.5%Rh/Al<sub>2</sub>O<sub>3</sub> catalyst presented a peak at 156°C, which may be attributed to the reduction of Rh<sub>2</sub>O<sub>3</sub> [3], while the 1.5%Rh/CeO<sub>2</sub> catalyst showed peaks at 97°C, 225°C e 975°C which may be attributed to the reduction of Rh<sub>2</sub>O<sub>3</sub>, surface ceria and to bulk ceria, respectively. For 1.5%Rh/ZrO<sub>2</sub>, there was a peak at 207°C corresponding to Rh<sub>2</sub>O<sub>3</sub> reduction (4). TPR of Rh/CeZrO<sub>2</sub> catalysts indicated an increase in ceria reduction due to the presence of rhodium

The cyclohexane reaction rate can be interpreted as a measure of the amount of surface active sites. When we compare the reaction rates for the studied catalyst, the following order of apparent dispersion was obtained Rh/Ce<sub>75</sub>Zr<sub>25</sub>O<sub>2</sub>>Rh/Ce<sub>50</sub>Zr<sub>50</sub>O<sub>2</sub>≈1.5%Rh/Ce<sub>25</sub>Zr<sub>75</sub>O<sub>2</sub>≈ Rh/CeO<sub>2</sub>>Rh/ZrO<sub>2</sub>≈Rh/Al<sub>2</sub>O<sub>3</sub>.

The TPSR results for Rh/Al<sub>2</sub>O<sub>3</sub> were consistent to a indirect mechanism for the partial oxidation of methane. In the beginning of the reaction, rhodium particles are covered by oxygen making the catalyst active for methane combustion. Then, there is the formation of CO and H<sub>2</sub> by CO<sub>2</sub> and H<sub>2</sub>O reforming of methane. On the other hand, Rh/CeO<sub>2</sub> and Rh/ZrO<sub>2</sub> and

Rh/CeZrO<sub>2</sub>. presented similar TPSR profiles which indicated a direct mechanism for the formation of synthesis gas.

### Significance

For Rh/Al<sub>2</sub>O<sub>3</sub> catalyst, temperature programmed surface reaction (TPSR) analysis showed the partial oxidation of methane occurs in two steps: combustion of methane followed by H<sub>2</sub>O and CO<sub>2</sub> reforming of unreacted methane, while Rh/CeO<sub>2</sub> and Rh/ZrO<sub>2</sub> and Rh/CeZrO<sub>2</sub>.a direct mechanism was observed. The difference in the mechanisms was explained by different surface oxygen species concentration in these catalytic systems. This difference may also be responsible for enhanced stability in the reaction for long time runs.

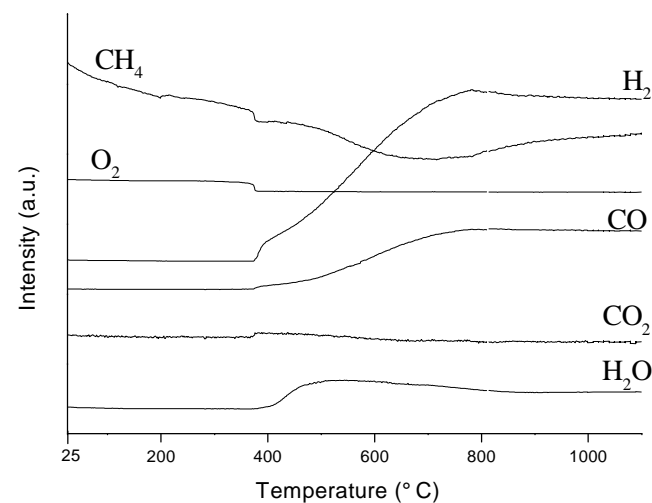


Figure 1. 1,5%Rh/CeO<sub>2</sub>-TPSR spectra in flowing He, CH<sub>4</sub> and O<sub>2</sub>.

### References

1. Z. Tian, O. Dewaele, G.B. Marin. Catal. Lett. 1999, 57, 9.
2. L.V. Mattos, E.R. de Oliveira, P.D. Resende, F.B. Noronha, and F.B. Passos, Catal. Today Catal. Today, 77 (2002) 245.
3. H.C. Yao, M. Sieg, H.K. Plummer. J. Catal., 1979, 59, 365.
4. J.A Wang,, T. Lopes, X. Bokhimi, O. Novaro., Journal of Molecular Catalysis, 2005, 239-256