

## Partial Oxidation of Methane using Mo<sub>2</sub>C/CeO<sub>2</sub> as Catalyst

Karine A. Cortez<sup>1</sup>, Adriana M. Silva, Fabio B. Noronha<sup>2</sup> and Victor Teixeira da Silva<sup>3\*</sup>

<sup>1</sup>CENPES, Petrobras, Ilha do Fundão, Rio de Janeiro, RJ 21941-915 (Brazil)

<sup>2</sup>LACAT, Instituto Nacional de Tecnologia, Rio de Janeiro, RJ (Brazil)

<sup>3</sup>NUCAT, PEQ, COPPE, Universidade Federal do Rio de Janeiro, Rio de Janeiro, RJ (Brazil)

\*victor.teixeira@peq.coppe.ufrj.br

### Introduction

The global warming's effect over the planet climate has triggered an intense search for new sources of energy aiming oil substitution in the world energy matrix. Natural gas has been mainly used to heat and power generation, but its importance is growing since is being pointed as the transient step to implement the economy based on hydrogen as the main source of energy in the near future.

There are several technologies to produce hydrogen from natural gas such as steam reforming, partial oxidation and autothermal reforming. All these technologies make use of metal catalysts which besides expensive are sensitive to the sulfur present in natural gas and lead to their deactivation. Due to catalyst contamination by sulfur, it is imperative to pre-treat natural gas before its use in the reforming reaction, leading to an increase in cost and size of fuel processor.

Because of its tolerance to sulfur, the main objective of this work was to use molybdenum carbide supported on ceria as catalyst in the partial oxidation of methane (POM) in substitution of noble metals.

### Materials and Methods

Precursors of the catalysts (5, 10 and 15 wt% MoO<sub>3</sub>/CeO<sub>2</sub> and 5 wt% MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>) were prepared using the incipient wetness methodology. The carbides were synthesized by a temperature-program which consisted in flowing a 20%(v/v) CH<sub>4</sub>/H<sub>2</sub> gas mixture (100 mL min<sup>-1</sup>) from room temperature up to 800°C at a heating rate of 10 °C min<sup>-1</sup> and holding the final temperature for 1 hour. Once the carburization step was over, the samples were evaluated for the methane partial oxidation at 800°C and 1atm using a CH<sub>4</sub>/O<sub>2</sub> = 2. The reverse water-gas shift was tested at the same temperature and pressure conditions. For comparative purposes physical mixtures of MoO<sub>3</sub>-CeO<sub>2</sub> with the same contents of supported catalysts were prepared and carburized. The samples were characterized by several techniques such as X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF) and X-Ray Photoelectron Spectroscopy (XPS).

### Results and Discussion

Contrarily to the X-ray diffraction patterns of the physical mixtures MoO<sub>3</sub>/CeO<sub>2</sub>, XRD diffratograms of 5, 10 and 15 wt% MoO<sub>3</sub>/CeO<sub>2</sub> samples did not exhibit the lines characteristic of CeO<sub>2</sub> thus suggesting that during the calcining step some molybdenum oxide could have been lost due to volatilization. However, molybdenum and cerium oxides contents obtained by XRF were in accordance with the theoretical ones, indicating that such phenomenon did not occur. In order to investigate the absence of the molybdenum oxide diffractions, an *in situ* calcining experiment of the 10 wt% MoO<sub>3</sub>-CeO<sub>2</sub> physical mixture was done and it was found, as can be seen in Figure 1, that the increase of temperature led to a

decrease in intensity of the MoO<sub>3</sub> diffractions, implying that a solid-state reaction between MoO<sub>3</sub> and CeO<sub>2</sub> was taking place during the heating. In fact, XPS data support this assumption because a  $\gamma$ -Ce<sub>2</sub>Mo<sub>3</sub>O<sub>13</sub> was found to be present in the surface of the x wt% MoO<sub>3</sub>/CeO<sub>2</sub> (x = 5, 10, 15) calcined samples.

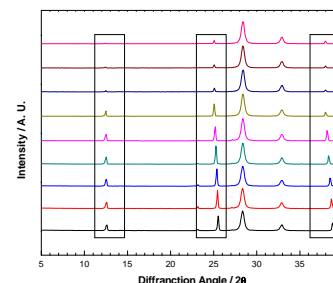


Figure 1. X-Ray Diffraction Patterns for the *in situ* calcining of the 10 wt% MoO<sub>3</sub>-CeO<sub>2</sub> physical mixture (Temperature increases from bottom to top. MoO<sub>3</sub> diffractions are shown inside the boxes).

The activity of the carburized samples was evaluated on the methane partial oxidation and compared to a 1,5 wt% Pt/Al<sub>2</sub>O<sub>3</sub> reference. While the noble metal catalyst deactivated during the course of the reaction probably due to coke formation (initial and final methane conversions were 60 and 18%, respectively), the carburized samples presented a constant conversion of 35%. The stability presented by the carbides can be explained taking into account that in parallel to the main reactions there is a cyclic process of carbide oxidation and recarburation as proposed in the literature [1]. In addition, a Ce<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> sample was synthesized [2], carburized following the same temperature-program and evaluated at the same conditions as the supported samples, presenting exactly the same conversion. This result indicates that a carburized molybdenum-cerium mixed oxide ( $\gamma$ -Ce<sub>2</sub>Mo<sub>3</sub>O<sub>13</sub>) is likely the active site for the POM.

In spite of the fact that the carburized samples did not exhibit deactivation which would be an advantage when compared to noble metal based catalysts, their H<sub>2</sub>/CO ratio was quite low (H<sub>2</sub>/CO = 0.5) than that obtained for the platinum catalyst indicating that other reactions than those associated with methane partial oxidation were taking place, in particular the reverse water gas-shift as proved in additional experiments.

### Significance

Carburized molybdenum supported on ceria is a potential catalyst to perform the partial oxidation of methane either untreated or under high sulfur levels.

### References

1. York, A. P. E., Xiao, T., and Green, M. L. H. *Topics in Catalysis* 22, 345 (2003).
2. Kuang, W., Fan, Y. and Chen, Y. *Catalysis Letters* 50, 31 (1998)