Partial Oxidation of Methane using Mo₂C/CeO₂ as Catalyst

Karine A. Cortez¹, Adriana M. Silva, Fabio B. Noronha² and Victor Teixeira da Silva³*
¹CENPES, Petrobras,Ilha do Fundão, Rio de Janeiro, RJ 21941-915 (Brazil)
² LACAT, Instituto Nacional de Tecnologia, Rio de Janeiro, RJ (Brazil)
³NUCAT, 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 it 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% MoO₃/CeO₂ and 5 wt% MoO₃/Al₂O₃) were prepared using the incipient wetness methodology. The carbides were synthesized by a temperature-program which consisted in flowing a 20%/v/v CH₄/H₂ gas mixture (100 ml min⁻¹) from room temperature up to 800°C at a heating rate of 10 °C min⁻¹ 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 1 atm using a CH₄/O₂ = 2. The reverse water-gas shift was tested at the same temperature and pressure conditions. For comparative purposes physical mixtures of MoO₃/CeO₂ 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 MoO₃/CeO₂, XRD diffratograms of 5, 10 and 15 wt% MoO₃/CeO₂ samples did not exhibit the lines characteristic of CeO₂ 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% MoO₃/CeO₂ physical mixture was done and it was found, as can been seen in Figure 1, that the increase of temperature led to a decrease in intensity of the MoO₃ diffractions, implying that a solid-state reaction between MoO₃ and CeO₂ was taking place during the heating. In fact, XPS data support this assumption because a γ-Ce₂Mo₃O₁₃ was found to be present in the surface of the x wt% MoO₃/CeO₂ (x = 5, 10, 15) calcined samples.

References