# Perovskites $La_{1-x}M_xNiO_3$ in the Partial Oxidation of Methane

Soraia T. Brandão*, Otanéa B. Oliveira and Paulo Vitor S. Ferreira
*Universidade Federal da Bahia, Salvador, Bahia 40170-290 (Brazil)*
*Catalysis and Polymer Group, Chemistry Institute, Campus de Ondina*
*brandao@ufba.br

## Introduction

The partial oxidation of methane (POM) is an alternative method of obtaining syngas from natural gas which as well as being exothermic, favoring the energy balance, gives synthesis gas at a 2:1 ratio, required in the Fischer-Tropsch process [1, 2].

Catalysts based on noble metals are more active and selective in POM, however, they are expensive. Supported catalyst containing Ni, Co or Fe on the other hand,while active, selective and low-cost, suffer deactivation because of the active phase sintering and the deposition of carbon [3]. One of the alternatives to minimize the deposition of coke is the addition of species with a high ability to "store" oxygen. Thus, promoters such as alkaline earth and $CeO_2$ have been widely studied in the literature [2] in various formulations of catalysts to increase its stability and catalytic performance. According to Bartholomew et al. [4] the formation of coke is low in catalysts with a high dispersion of the metal. The use of catalysts based on mixed oxides such as perovskites presents a promising alternative because this material enables the high dispersion of the metal [4]. In addition high mobility of oxygen species favor the oxidation of the carbon deposited in the form of coke. According to some authors, perovskites doped show the property of accepting electrons and they therefore constitute a promising system in reactions involving oxy-reduction such as the partial oxidation of methane [5] .

This study presents the synthesis, characterization and evaluation of the catalysts $La_{1-x}M_xNiO_3$ (x = 0, 0.02, 0.20 and 0.4) in the partial oxidation of methane.

## Materials and Methods

The perovskites $La_{1-x}M_xNiO_3$ were prepared using the citrate method. In this process nitrates from La, Ni and Sr were dissolved in water. Citric acid was added under constant stirring at a ratio of 1:1.5 metal / citric acid. The solution was heated for 3 h under constant agitation at 70-80°C to form a viscous gel which was then heated to 350ºC for 2 h to produce a dry powder. Then the material was calcined at 800°C for 4 h, under air flow of 50 mL $min^{-1}$. The catalysts obtained were characterized by XRF, XRD, BET, MEV-EDX, TPR, LECO and tested in the partial oxidation of methane by the catalytic test.

## Results and Discussion

DRX analysis indicated that catalyst $LaNiO_3$ was obtained as a single phase but in the other catalysts also NiO phase was detected. In the case of the sample containing x = 0.50, the $CeO_2$ phase was also detected. In the case of Sr perovskites increasing Sr content, a loss of cristalinity and a new phase were observed.

According to the TPR (Fig.1) the catalysts $La_{1-x}Sr_xNiO_3$ presented peaks related to the reduction of the species $Ni^{3+}$ to $Ni^{2+}$. This process is indicative of the mobility of oxygen in the structure of the perovskite favoring the catalytic performance in partial oxidation of methane.

Besides these, for $LaNiO_3$ there was a low $H_2$ consumption at around 200°C. Such a consumption could be due to the reduction of oxygen species adsorbed on the surface [5, 6].

Such evidence added to the results of TPR and BET suggest that there was an effect of the content of Sr and Ce on the temperature of the reduction of the nickel species, decreasing this temperature. Ce addition in the perovskite increased the specific area from 2 to 19 $m^2$/g. Thus Ce may be considered a textural promoter and Sr an electronic promoter as well.

The catalysts $La_{1-x}M_xNiO_3$ were active and selective in the POM and the addition of Sr significantly reduced the amount of coke deposited during the catalytic tests. This can be observed by %C in Table 1.

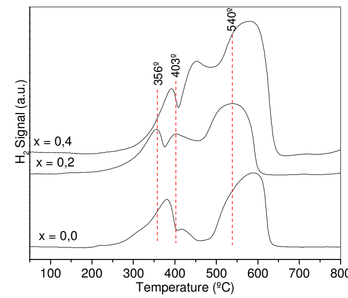


**Figure 1**. TPR of $La_{1-x}Sr_xNiO_3$ catalysts

| Catalysts | C (%) |
|---|---|
| $LaNiO_3$ (after 5 h of test) | 31.3 |
| $La_{0.8}Sr_{0.2}NiO_3$ (after 5h of test) | 0.5 |
| $La_{0.8}Sr_{0.2}NiO_3$ (after 8h of test) | 1.2 |

**Table 1.** Carbon content obtained by LECO

## Significance

The perovskites $La_{1-x}M_xNiO_3$ synthesized are promising catalysts for POM because of their catalytic performance and their resistance to deactivation. The most interesting contribution of this study is the analysis of the effect of Sr and Ce composition in promoting the textural and electronic properties of these catalysts and bringing out a reduction in coke deposition.

## References

1. Albertazzi, S. Arpentinier P., Basile, F. Del Gallo, P., Fornasari, G., Gary, D.,Vaccari, A. *Appl. Catal A:General* 1, 247 (2003).
2. Mattos, L.V., Oliveira, E.R., Resende, P.D., Noronha,F.B, Passos,F.B. *Catal.Today* 77, 245 (2002).
3. Wang, S., *App. Catal. B: Environmental* 19, 267(1998).
4. Bartholomew, C.H., *Catal. Rev.-Sci. Eng.* 24, 67(1982).
5.Valderrama, G., Goldwasser, M.R., Pietri, E., Pérez-Zurita, M.J., Cubeiro, M.L., Navarro, C.U., *Interciencia,* 30, 332 (2005).
6. García de la Cruz, R.M., Falcón, H., Peña, M.A., Fierro, J.L.G. App. Catal.B: *Environmental*, 33, 45(2001).