

## IMPROVED ACTIVITY AND STABILITY OF Ce-PROMOTED Ni/ $\gamma$ - $\text{Al}_2\text{O}_3$ CATALYSTS FOR CARBON DIOXIDE REFORMING OF METHANE

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**Abstract**— The  $\text{CO}_2$  reforming of  $\text{CH}_4$  was carried out over Ni catalysts supported on  $\gamma\text{-Al}_2\text{O}_3$  and  $\text{CeO}_2$ -promoted  $\gamma\text{-Al}_2\text{O}_3$ . The catalysts were characterized by means of surface area measurements, TPR,  $\text{CO}_2$  and  $\text{H}_2$  chemisorption, XRD, SEM, and TEM. The  $\text{CeO}_2$  addition promoted an increase of catalytic activity and stability. The improvement in the resistance to carbon deposition is attributed to the highest  $\text{CO}_2$  adsorption presented by the  $\text{CeO}_2$  addition. The catalytic behavior presented by the samples, with a different  $\text{CH}_4/\text{CO}_2$  ratio used, points to the  $\text{CH}_4$  decomposition reaction as the main source of carbon deposition.

**Keywords**— Methane; dry reforming;  $\text{CeO}_2$ ; carbon formation; syngas.

### I. INTRODUCTION

Oil is the main source of chemical products and fuels. In spite of this, the natural gas explored in many countries is a good alternative (Dry, 2002). The natural gas abundance, with  $\text{CH}_4$  as the main component, consists of an interesting  $\text{H}_2$  and synthesis gas source (Hu and Ruckenstein, 2002). This can furnish a fraction of the energetic and chemical products demands through the Fisher-Tropsch process (Hu and Ruckenstein, 2002; Rostrup-Nielsen, 2000).

The catalytic reforming of  $\text{CH}_4$  with  $\text{CO}_2$  (Eq. 1) for the production of synthesis gas is an interesting process. Besides the production of high-value compounds it is followed by the consumption of greenhouse gases (Tang *et al.*, 1995; Kroll *et al.*, 1996; Nichio, 2000).



Numerous authors (Nichio, 2000; Tomishige *et al.*, 2000; Tomishige *et al.*, 2001; Wang and Ruckenstein, 2001; Takeguchi *et al.*, 2001; Frusteri *et al.*, 2001; Xu *et al.*, 2001) have carried out the  $\text{CO}_2$  reforming of  $\text{CH}_4$  on different catalysts, and the major problem is the catalyst deactivation, induced by carbon deposition (Hu and Ruckenstein, 2002; Kroll *et al.*, 1996). Noble metal catalysts supported on different carriers exhibit better activity and high stability (Zhu and Stephanopoulos, 2001), but they are expensive. In spite of the carbon

deposition, the Ni-based catalysts have high activity, stability and selectivity and are cheap. Therefore, the development of such catalysts is an attractive challenge (Crisafulli *et al.*, 2002).

Several processes have been used for reducing the coke deposition on the catalysts. Recently, Leite *et al.* (2002) described a route to synthesize nanometric Ni particles embedded in a mesoporous silica material. This method showed promising results in the catalytic carbon dioxide reforming of methane, with low coke deposition (Probst *et al.*, 2002).

There are several publications reporting the  $\text{CeO}_2$  application and properties (Trovarelli, 1996; Probst and Valentini, 2001; Piras *et al.*, 2000; Rossignol and Kappenstein, 2001). But there is only a limited amount of work devoted to study the  $\text{CeO}_2$  application as the metal support in the  $\text{CO}_2$  reforming of  $\text{CH}_4$  (Wang *et al.*, 2001), due to the low  $\text{CH}_4$  conversion observed (Montoya *et al.*, 2000; Wang and Lu, 1998; Noronha *et al.*, 2001). On the other hand,  $\text{CeO}_2$  is an effective promoter for the Ni/ $\text{Al}_2\text{O}_3$  catalysts in the suppression of carbon deposition (Montoya *et al.*, 2000; Wang and Lu, 1998; Xu *et al.*, 1999). The  $\text{CeO}_2$  enhancement in the catalytic properties like stability against coke deposition is attributed to the ability of Ce to reversibly change oxidation states between  $\text{Ce}^{4+}$  and  $\text{Ce}^{3+}$  (Noronha *et al.*, 2001). The  $\text{Ce}_2\text{O}_3$  oxide present on the catalyst surface promotes the process of transferring oxygen (Xu *et al.*, 1999).

It is known that the coke deposition during dry reforming is a function of operating conditions. Operations at high temperature ( $>800^\circ\text{C}$ ) and at high  $\text{CO}_2/\text{CH}_4$  ratios ( $>1$ ) avoid carbon deposition (Reitmeier *et al.*, 1948; Gadalla and Bower, 1988). However, lower temperatures and a  $\text{CO}_2/\text{CH}_4$  ratio near unity are more interesting.

The aim of the present study is to obtain a better understanding of the nature of the carbon deposition on  $\text{CeO}_2$ -promoted Ni: $\text{Al}_2\text{O}_3$  catalysts prepared by the impregnation method. Are investigated the catalytic performance and carbon deposition behavior in the  $\text{CO}_2$  reforming of  $\text{CH}_4$  under atmospheric pressure and with different  $\text{CH}_4/\text{CO}_2$  ratios operating at moderate temperature. The sample characterization was performed by