IMPROVED ACTIVITY AND STABILITY OF Ce-PROMOTED Ni/γ-Al2O3 CATALYSTS FOR CARBON DIOXIDE REFORMING OF METHANE

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Abstract — The CO2 reforming of CH4 was carried out over Ni catalysts supported on γ-Al2O3 and CeO2-promoted γ-Al2O3. The catalysts were characterized by means of surface area measurements, TPR, CO2 and H2 chemisorption, XRD, SEM, and TEM. The CeO2 addition promoted an increase of catalytic activity and stability. The improvement in the resistance to carbon deposition is attributed to the highest CO2 adsorption presented by the CeO2 addition. The catalytic behavior presented by the samples, with a different CH4/CO2 ratio used, points to the CH4 decomposition reaction as the main source of carbon deposition.

Keywords — Methane; dry reforming; CeO2; 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 CH4 as the main component, consists of an interesting H2 and synthesis gas source (Hu and Ruckenstein, 2002). This can furnish a fraction of the energetic and chemical products demands through the Fischer-Tropsch process (Hu and Ruckenstein, 2002; Rostrup-Nielsen, 2000).

The catalytic reforming of CH4 with CO2 (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).

\[ \text{CH}_4 + \text{CO}_2 \leftrightarrow 2\text{CO} + 2\text{H}_2 \]  

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 CO2 reforming of CH4 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 CeO2 application and properties (Trovaergili, 1996; Probst and Valentini, 2001; Piras et al., 2000; Rossignol and Kappenstepen, 2001). But there is only a limited amount of work devoted to study the CeO2 application as the metal support in the CO2 reforming of CH4 (Wang et al., 2001), due to the low CH4 conversion observed (Montoya et al., 2000; Wang and Lu, 1998; Noronha et al., 2001). On the other hand, CeO2 is an effective promoter for the Ni/Al2O3 catalysts in the suppression of carbon deposition (Montoya et al., 2000; Wang and Lu, 1998; Xu et al., 1999). The CeO2 enhancement in the catalytic properties like stability against coke deposition is attributed to the ability of Ce to reversibly change oxidation states between Ce4+ and Ce3+ (Noronha et al., 2001). The CeO2 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°C) and at high CO2/CH4 ratios (>1) avoid carbon deposition (Reitmeier et al., 1948; Gadalla and Bower, 1988). However, lower temperatures and a CO2/CH4 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 CeO2-promoted Ni/Al2O3 catalysts prepared by the impregnation method. Are investigated the catalytic performance and carbon deposition behavior in the CO2 reforming of CH4 under atmospheric pressure and with different CH4/CO2 ratios operating at moderate temperature. The sample characterization was performed by