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; Tomishige et al., 2001; Wang and Ruckenstein, 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).

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 (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 CO₂ application as the main source of carbon deposition (Reitmeier et al., 2000) 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.

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 NiAl₂O₃ 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

CH₄ + CO₂ ⇌ 2CO + 2H₂ (1)

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).
II. MATERIALS AND METHODS

A. Catalyst preparation

The Ce-doping supports were prepared by the impregnation of an aqueous solution of Ce(NO$_3$)$_3$ (Aldrich, 99.99 %) on γ-Al$_2$O$_3$ (AL-3996R, 200 m$^2$/g, Engelhard Exceptional Technologies). The CeO$_2$ content was (0, 5, 10, 15 and 20 wt%). After impregnation the supports were dried for 24 h at 100ºC and calcined at 450ºC during 2h. The supports were denominated AlCe-X (with X = CeO$_2$ wt%). The Ni addition was carried out by impregnation of an aqueous solution of Ni(NO$_3$)$_2$ (Fluka, 98 %) on γ-Al$_2$O$_3$ and on AlCe-X supports. The samples with 10 wt% of Ni were dried for 24h at 100ºC and calcined at 650ºC during 3h.

B. Characterization

The amount of metal (Ni) in the solids was determined by atomic absorption spectrometry, using an HITACHI Z8230 equipment.

The TPR profiles were taken in the Micromeritics TPD/TPR 2900 model equipment, using 10ºC/min of heating rate and monitoring the hydrogen consumption from a 5%H$_2$/N$_2$ mixture at the 50-930ºC temperature range. The surface area and porosity measurements following the nitrogen adsorption method (-196ºC), the metallic accessibility using H$_2$ chemisorption at 27ºC and the CO$_2$ chemisorption at 27 and 625ºC were determined in an Autosorb-1C (Quantachrome Instruments). The amount of irreversible H$_2$ uptake was obtained from the difference between the total adsorption of H$_2$ on the catalyst and a second adsorption series of H$_2$ determined after evacuation of the catalyst sample for 30 minutes at the same temperature.

Elementary chemical analysis was employed to estimate the total coke content after the catalytic reaction (Carlo Erba EA 1110 CHNS-O). The XRD spectra were acquired by the use of a Siemens D-5000 diffractometer with Cu-Kα radiation and a graphite crystal monochromator.

For the microstructure characterization were used the transmission electron microscope CM200 200 kV and the scanning electron microscope DSM940A.

C. Catalytic activity

Reactions were performed in a tubular fixed-bed flow reactor made of a stainless steel tube of 9.5 mm inner diameter. The catalyst (0.050 g) was in situ pretreated in a H$_2$ stream at 650ºC for 1h. The reaction gas was composed of carbon dioxide, methane and nitrogen in the (CO$_2$:CH$_4$:N$_2$) ratios of 1:1:4, 1:2:6 and 2:1:6 with the total flow rate of 35 cm$^3$/min. All catalytic tests were performed at 625ºC under atmospheric pressure. Nitrogen was used as a diluent and an internal standard for the analysis. The reactant and the product gases were analyzed with an on-stream gas chromatograph (GC) SHIMADZU GC 8A, equipped with a thermal conductivity detector (TCD), Porapak-Q and a 5A molecular sieve column (with Ar as the carrier gas). The systematic errors in the conversions are ±1%.

III. RESULTS AND DISCUSSION

The results of chemical analysis, H$_2$ chemisorption and specific surface area for the catalysts are summarized in Table 1.

A gradual surface area decreasing is observed with the CeO$_2$ loading. It is known that low CeO$_2$ loading could stabilize γ-Al$_2$O$_3$ against surface area loss (Piras et al., 2000; Ozawa and Kimura, 1990) when calcined at high temperature (>900ºC). However, in this work the samples have higher then 5 wt% of CeO$_2$ and were heat-treated at 650ºC, a low temperature to promote a γ-Al$_2$O$_3$ surface area loss.

The surface area decreasing promoted by the CeO$_2$ addition points to a partial pore obstruction. In the impregnation process, the Ce is mainly deposited inside the γ-Al$_2$O$_3$ pores. The profile behaviors observed in Fig. 1 confirm that the pore volume decreasing follows the surface area loss.

Table 1: Chemical analysis and surface properties measured by N$_2$ physisorption and H$_2$ chemisorption.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Sg (m$^2$/g) ‡</th>
<th>Ni (wt%)</th>
<th>H$_2$ (μmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/Al$_2$O$_3$</td>
<td>172</td>
<td>8.6</td>
<td>62.88</td>
</tr>
<tr>
<td>Ni/AlCe-5</td>
<td>149</td>
<td>7.1</td>
<td>72.99</td>
</tr>
<tr>
<td>Ni/AlCe-10</td>
<td>142</td>
<td>8.5</td>
<td>71.09</td>
</tr>
<tr>
<td>Ni/AlCe-15</td>
<td>133</td>
<td>9.2</td>
<td>56.61</td>
</tr>
<tr>
<td>Ni/AlCe-20</td>
<td>125</td>
<td>8.4</td>
<td>69.98</td>
</tr>
</tbody>
</table>

‡ - Measured by N$_2$ adsorption at −196ºC; # - Based on total H$_2$ adsorption at 300 K; * - Based on irreversible H$_2$ adsorption at 300 K

The surface area decreasing promoted by the CeO$_2$ addition points to a partial pore obstruction. In the impregnation process, the Ce is mainly deposited inside the γ-Al$_2$O$_3$ pores. The profile behaviors observed in Fig. 1 confirm that the pore volume decreasing follows the surface area loss.
On the other hand, the CeO$_2$ loading promoted an increase in the total H$_2$ chemisorption (Table 1). This points to a higher metal (Ni) dispersion, the best result is observed for the sample with the lowest CeO$_2$ loading (NiAlCe-5). Similar results have been reported (Wang and Lu, 1998; Montoya et al., 2000). It suggests that low CeO$_2$ loading actuates as a textural promoter. In the reduction treatments, the Ni particles can be partially decorated by the CeO$_2$ (Bernal et al., 2003). With this, the metal particles show a better resistance against sintering. However, the occurrence of spillover phenomena should be considered when CeO$_2$ is present (Bernal et al., 2003). The irreversible H$_2$ chemisorption corroborates to that. With the Ni/AlCe-5 sample exception, the CeO$_2$-doping promoted a decreasing in the irreversible H$_2$ adsorption.

Temperature programmed reduction (TPR) profiles for the catalysts are presented in Figure 2. The Ni/Al$_2$O$_3$ exhibited one peak at 600ºC and a second one at 770ºC. The peak at 600ºC is likely due to the more accessible Ni and the peak at 770ºC due to the Ni inside the pore material, what can present a strong support influence on the Ni reduction (Molina and Poncelet, 1998; Chen et al., 1991). It is seen that CeO$_2$ loading shifts the peak around 600ºC to a lower temperature value, pointing to the changes in the catalysts properties promoted by CeO$_2$. The H$_2$ consumption around 900ºC is attributed to the CeAlO$_3$ formation (Piras et al., 2000; Damyanova et al., 2002) what was confirmed by XRD. A broad reduction feature ranging from 270ºC and 400ºC that increases with the CeO$_2$ loading is attributed to the partial CeO$_2$ surface reduction (Trovarcelli, 1996; Damyanova et al., 2002; Perrichon et al., 1994; Fajardie et al., 1998); however, likewise it can be related to the Ni present in CeO$_2$ rich areas (Wang et al., 2001).

Fig. 2 - Temperature programmed reduction (TPR) profiles of Ni/Al$_2$O$_3$ and CeO$_2$ loading catalysts.

By the scanning electron microscopy (SEM) images illustrated in Fig. 3 for NiAlCe-15 and NiAlCe-20 samples, it is possible to see high CeO$_2$ concentration areas on the catalyst surfaces.

In the NiAlCe-20 sample it is possible to see the typical spherical shape of the CeO$_2$ particles.

Fig. 3- Scanning electron microscopy (SEM) images of NiAlCe-15 and NiAlCe-20 samples after activation at 650ºC/1h.

The catalytic performances in the CO$_2$ reforming of CH$_4$ for the catalysts are presented in Fig. 4. With the exception of the Ni/AlCe-5 (5 wt% of CeO$_2$), the catalytic CH$_4$ conversion shows a gradual increase with the CeO$_2$ loading. The particular behavior for the Ni/AlCe-5 sample can be attributed to the higher H$_2$ chemisorption, which points to a higher Ni dispersion (Table 1).

A CH$_4$ conversion increase promoted by the CeO$_2$ loading is followed by the catalytic stability increase. The stability improvement can be estimated by the ratios between the CH$_4$ conversion after 15h and the CH$_4$ conversion after 2h of time-on-stream (C$_{15}$/C$_2$). The C$_{15}$/C$_2$ ratios were: 0.91, 0.92, 0.95, 0.96 and 0.98 for Ni/Al$_2$O$_3$, Ni/AlCe-5, Ni/AlCe-10, Ni/AlCe-15 and Ni/AlCe-20, respectively. It is shown that the CeO$_2$ addition favors the enhancement of the Ni/Al$_2$O$_3$ catalytic properties in the CO$_2$ reforming of CH$_4$.
In order to confirm the stability increase promoted by the CeO₂ loading, a catalytic test was performed during 50h with a CH₄/CO₂ ratio of 1:1 at 625°C for the Ni/Al₂O₃ and Ni/AlCe-20 samples. Figure 5 shows that the deactivation rate of Ni/Al₂O₃ is higher than Ni/AlCe-20. The ratios between the CH₄ conversion after 50h and its initial conversion (C₅₀/Cᵢ) are 0.55 and 0.94 for Ni/Al₂O₃ and Ni/AlCe-20, respectively. The CH₄ conversion decreases linearly with time-on-stream for Ni/AlCe-20, however the Ni/Al₂O₃ catalyst showed the same behavior only in the initial test. After 25h of catalytic reaction a non-linear deactivation is considerable for the Ni/Al₂O₃ catalyst. This behavior can be related to the coke and carbon filament formation that promotes a blocking of the active surface. This suggests that with the coke and carbon filaments continuous grow with the time-on-stream, the metal particles are encapsulated in the carbon filaments and there is a critical point in the carbon nanotube growth above which the catalyst deactivation is more.
pronounced. The limit of reagent diffusion to the metal particles should be considered, in the case of coke deposition, even with no particle encapsulation.

The condensation of carbon over the Ni crystals exposed on the surface of the catalysts allows the formation of a sheet around the metal particle surface (Hester and Louchev, 2002) with subsequent growth of the carbon nanotubes following the detachment of Ni from the support (Tsang et al., 1995). This leads to the encapsulation of the metal particles that causes the activity loss. Bright-Field (BF) TEM images of Ni/Al2O3 sample after catalytic test (Fig. 6) evidences an abundant carbon nanotube growing out of the Ni particles.

Therefore, there is a close relation between catalytic activity decreasing and the metal particle blocking by the carbon filaments, as illustrated in Fig. 6. Otherwise, the CeO2-doped catalysts do not have the tendency of carbonaceous structure formation. The TEM analysis of Ni/Al2O3 after 50h of catalytic reaction showed a carbon nanotube formation higher than 10 mm, Fig. 6b. On the other hand, the Ni/AlCe-20 presented carbon nanotubes lower than 1 mm. Figure 6d shows the thick carbon tube formation from the carbon deposition on the metal particles. This carbon structure will promote the metal particles disintegration or abstraction from the support.

The ordered carbon structure is detected also by XRD. The powder diffraction patterns of the fresh samples and of the samples after the catalytic reaction are presented in Fig. 7. Both, fresh and spent CeO2-doped catalysts presented a broader and weaker intensity of Ni peaks. This suggests that CeO2 promotes a higher dispersion of Ni or there is an interface region between metal and support, associated to the interaction. This second point is in agreement with Ni dispersion obtained by the irreversible H2 adsorption. Assuming that only Ni0 is responsible for the irreversible H2 adsorption, data from Table 1 points to a decrease in the metal surface area or an increase in the interfacial region, with the CeO2 loading, what is unable to adsorb irreversible H2.

This distinct interfacial region promoted by CeO2 addition may be responsible by the lower carbon deposition, as indicated by the decreasing in the ordered carbon peak in the samples after the catalytic test (Fig. 7b). A decrease in the carbon deposition for all Ni/AlCe samples was confirmed by CHN analysis (Table 2).

CO2 adsorption isotherms uptake were performed at 625°C, the reaction temperature, and at 27°C. The results (Table 2) showed an increase in the CO2 adsorption with CeO2 loading. This suggests that the principal CeO2 contribution is to improve the CO2 adsorption in the interfacial region that leads to a lower carbon deposition, via CH4 decomposition reaction (Eq. 2), as well as via CO disproportionation (Eq. 3), by shifting the equilibrium concentrations (Bradford and Vannice, 1999).

\[
\text{CH}_4 \leftrightarrow \text{C} + 2\text{H}_2 \quad (2)
\]

\[
2\text{CO} \leftrightarrow \text{C} + \text{CO}_2 \quad (3)
\]

Table 2: CO2 chemisorption and elementary chemical analysis of catalysts after CO2 reforming of CH4.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>CO2 (µmol/m²) 27°C</th>
<th>CO2 (µmol/m²) 625°C</th>
<th>Coke deposition (g C/gcat.) 15h</th>
<th>Coke deposition (g C/gcat.) 9h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/Al2O3</td>
<td>2.28</td>
<td>0.08</td>
<td>30.4 (0.2)*</td>
<td>(35.1)*</td>
</tr>
<tr>
<td>Ni/AlCe-5</td>
<td>2.57</td>
<td>0.15</td>
<td>9.5</td>
<td>-</td>
</tr>
<tr>
<td>Ni/AlCe-10</td>
<td>2.81</td>
<td>0.16</td>
<td>9.9</td>
<td>-</td>
</tr>
<tr>
<td>Ni/AlCe-15</td>
<td>2.71</td>
<td>0.27</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni/AlCe-20</td>
<td>3.52</td>
<td>0.24</td>
<td>9.8 (0.1)*</td>
<td>(32.2)*</td>
</tr>
</tbody>
</table>

* - CH4/CO2 = 0.5; * - CH4/CO2 = 2.0;

In order to support this conclusion, the Ni/Al2O3 and Ni/AlCe-20 catalysts were tested with different gas compositions, CH4/CO2 = 0.5 and 2.0. The CH4 conversions for these new CH4/CO2 ratios are plotted in Fig. 8.

A higher CH4 conversion is observed with the increase in the CO2 concentration as a consequence of the equilibrium shifting (Eq. 1). In this condition (CH4/CO2 = 0.5) the Ni/Al2O3 sample presented better initial catalytic performance with higher CH4 conversion (Fig. 8a). However, with the CH4 concentration increase (CH4/CO2 ratio of 2:1), the better catalytic performance, CH4 conversion and stability, is presented by the Ni/AlCe-20 sample (Fig. 8b).

With the CH4/CO2 ratio of 2:1, the catalysts showed a high initial deactivation rate and an apparent stabilization after 3h of time-on-stream. This behavior is attributed to the coke deposition as a consequence of the favorable coking reaction condition, low temperature and high CH4/CO2 ratio (Gadalla and Bower, 1988;
Bradford and Vannice, 1999). With a high CH₄ concentration, the metal particles that have a higher tendency to promote the carbon deposition via CH₄ decomposition are deactivated faster.

In spite of the higher initial CH₄ conversion for Ni/Al₂O₃ with CH₄/CO₂ ratio of 1:2, it is seen that Ni/AlCe-20 has a superior performance on the catalytic stability in all reaction composition.

The results presented in Fig. 8 show that an increase in the CO₂ adsorption promoted by the CeO₂ loading is very important to improve the catalytic performance.

On the other hand, increases in the CO₂ concentration promote a lower H₂/CO ratio, mainly through the reverse water gas shift (RWGS) reaction (Eq 4), that leads to the H₂ consumption and CO production.

\[
\text{H}_2 + \text{CO}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O} \quad (4)
\]

The H₂/CO ratios presented in Fig. 9 are in agreement with this, in spite of the higher CH₄ conversion.

Experimental observations reported in the literature (Richardson and Paripatayadar, 1990) showed that the main contributor to carbon deposition is the CO disproportionation. A low CO₂ concentration (CH₄:CO₂ ratio higher than unity) favors the Boudouard reaction (Eq. 3), in agreement with thermodynamic calculations (Reitmeier et al., 1948; Gadalla and Bower, 1988).

The profile of H₂/CO ratio presented in the CH₄/CO₂ ratio of 2:1 (Fig. 9b) suggests that the carbon deposition is promoted mainly by the CH₄ decomposition reaction (Eq. 2). It is observed a high H₂/CO ratio (>1.0) in the initial reaction. These behaviors suggest a fast deactivation of the main active sites that promotes the CH₄ decomposition. This signs that after 3h of time-on-stream only the active sites with lower deactivation affinity, or coke generation, are actives. It is known that CH₄ decomposition is a structure sensitive reaction (Beebe et al., 1987), therefore this site deactivation promotes a decrease in the CH₄ conversion. With decreasing of the CH₄ decomposition, the H₂ production drastically diminished, the same is not observed for the CO formation.

\[
\text{CO}_2 + \text{C} \leftrightarrow 2\text{CO} \quad (5)
\]

The reactions of Eq. 2 and Eq. 5 are endothermic and the equilibrium constants increase with the increase of the temperature, promoting the CH₄ decomposition and the CO₂ reaction with the deposited carbon (Eq. 5). This is in agreement with thermodynamic calculations (Reitmeier et al., 1948; Gadalla and Bower, 1988) that point to a lower carbon deposition with high reaction temperature and high CO₂/CH₄ ratio.

In addition, the CH₄ decomposition reaction (without CO₂) carried out for the Ni/Al₂O₃ and Ni/AlCe-20 samples, presented a CH₄ conversion of 25 and 16% at 2min of reaction time, respectively, and at 7min the CH₄ conversion was near 1%.

**IV. CONCLUSIONS**

The activity and stability of Ni/Al₂O₃ catalysts are improved by CeO₂ addition. The catalyst deactivation is promoted by carbon deposition, which is mainly due to the CH₄ decomposition reaction.

The main CeO₂ contribution is on the CO₂ adsorption increase, which plays an important role on the coke elimination.
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