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

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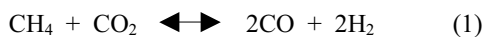
Abstract— The CO_2 reforming of CH_4 was carried out over Ni catalysts supported on γ-Al_2O_3 and CeO_2-promoted γ-Al_2O_3. The catalysts were characterized by means of surface area measurements, TPR, CO_2 and H_2 chemisorption, XRD, SEM, and TEM. The CeO_2 addition promoted an increase of catalytic activity and stability. The improvement in the resistance to carbon deposition is attributed to the highest CO_2 adsorption presented by the CeO_2 addition. The catalytic behavior presented by the samples, with a different CH_4/CO_2 ratio used, points to the CH_4 decomposition reaction as the main source of carbon deposition.

Keywords— Methane; dry reforming; 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 CH_4 as the main component, consists of an interesting 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 CH_4 with 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).

$$CH_4 + CO_2 \longleftrightarrow 2CO + 2H_2 \qquad (1)$$

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 CO_2 reforming of 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 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 CeO_2 application as the metal support in the CO_2 reforming of CH_4 (Wang *et al.*, 2001), due to the low CH_4 conversion observed (Montoya *et al.*, 2000; Wang and Lu, 1998; Noronha *et al.*, 2001). On the other hand, CeO_2 is an effective promoter for the Ni/Al_2O_3 catalysts in the suppression of carbon deposition (Montoya *et al.*, 2000; Wang and Lu, 1998; Xu *et al.*, 1999). The 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 Ce^{4+} and Ce^{3+} (Noronha *et al.*, 2001). The Ce_2O_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 (>800ºC) and at high CO_2/CH_4 ratios (>1) avoid carbon deposition (Reitmeier *et al.*, 1948; Gadalla and Bower, 1988). However, lower temperatures and a CO_2/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 CeO_2-promoted Ni:Al_2O_3 catalysts prepared by the impregnation method. Are investigated the catalytic performance and carbon deposition behavior in the CO_2 reforming of CH_4 under atmospheric pressure and with different CH_4/CO_2 ratios operating at moderate temperature. The sample characterization was performed by

means of X-ray diffraction (XRD), H_2 and CO_2 chemisorption, specific surface area measurement (BET), elemental analysis (CHN) and transmission electron microscopy (TEM).

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_2O_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_2O_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. Nitro-

gen 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_2O_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_2O_3 surface area loss.

Table 1: Chemical analysis and surface properties measured by N_2 physisorption and H_2 chemisorption.

Catalysts	Sg (m^2/g) ‡	Ni (wt%)	H_2 (μmol/g)	
			Tot. #	Ir.*
Ni/Al_2O_3	172	8.6	62.88	42.39
Ni/AlCe-5	149	7.1	72.99	43.24
Ni/AlCe-10	142	8.5	71.09	41.23
Ni/AlCe-15	133	9.2	56.61	37.00
Ni/AlCe-20	125	8.4	69.98	39.50

‡ - 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_2O_3 pores. The profile behaviors observed in Fig. 1 confirm that the pore volume decreasing follows the surface area loss.
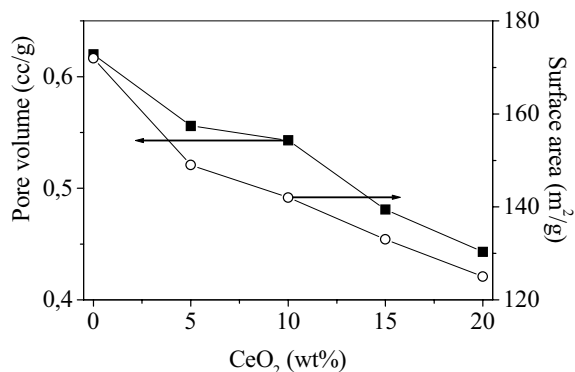

Fig. 1- Pore volume and surface area change promoted by the CeO_2 loading increase.

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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_2O_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 (Trovarelli, 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).
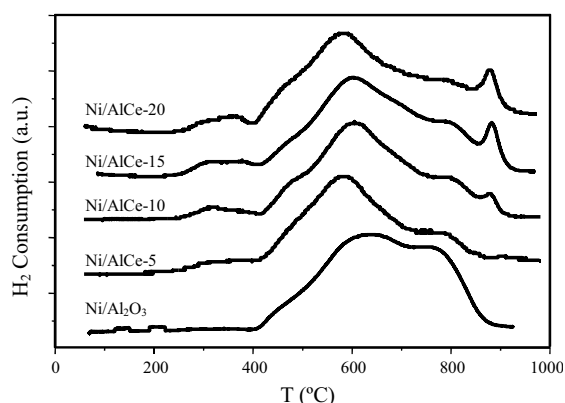

Fig. 2- Temperature programmed reduction (TPR) profiles of Ni/Al_2O_3 and CeO_2 loading catalysts.

By the scanning electron microscopy (SEM) images illustrated in Fig. 3 for Ni/AlCe-15 and Ni/AlCe-20 samples, it is possible to see high CeO_2 concentration areas on the catalyst surfaces.

In the Ni/AlCe-20 sample it is possible to see the typical spherical shape of the CeO_2 particles.
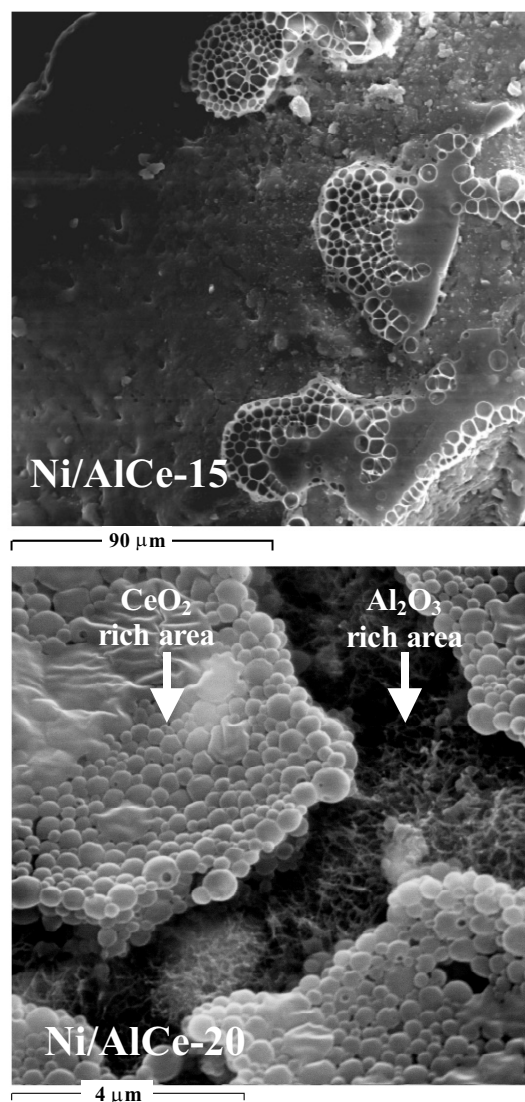

Fig. 3- Scanning electron microscopy (SEM) images of Ni/AlCe-15 and Ni/AlCe-20 samples after activation at 650ºC/1h.

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_2O_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_2O_3 catalytic properties in the CO_2 reforming of CH_4.
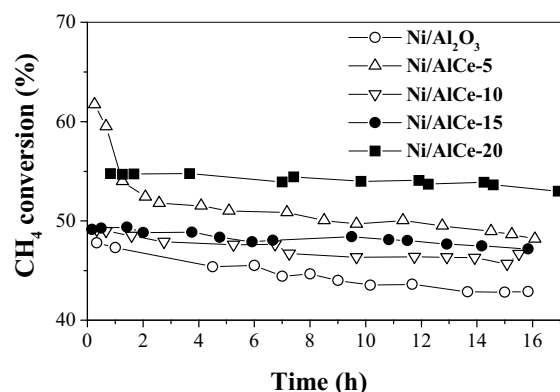
Fig. 4- Profiles of CH_4 conversion with time-on-stream for the catalysts. Activation at 650ºC/1h, 625ºC of reaction temperature, wt = 50 mg

In order to confirm the stability increase promoted by the CeO_2 loading, a catalytic test was performed during 50h with a CH_4/CO_2 ratio of 1:1 at 625ºC for the Ni/Al_2O_3 and Ni/AlCe-20 samples. Figure 5 shows that the deactivation rate of Ni/Al_2O_3 is higher than Ni/AlCe-20. The ratios between the CH_4 conversion after 50h and its initial conversion (C_{50}/C_i) are 0.55 and 0.94 for Ni/Al_2O_3 and Ni/AlCe-20, respectively. The CH_4 conversion decreases linearly with time-on-stream for Ni/AlCe-20, however the Ni/Al_2O_3 catalyst showed the same behavior only in the initial test. After 25h of catalytic reaction a non-linear deactivation is considerable for the Ni/Al_2O_3 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
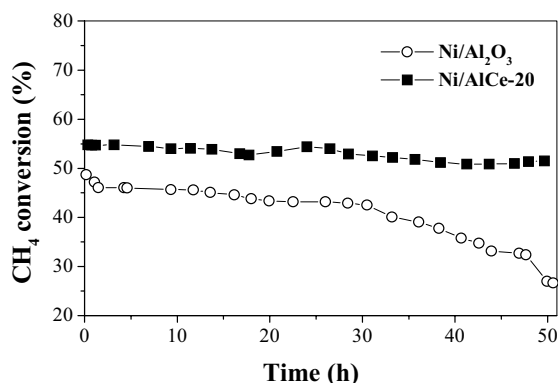

Fig. 5- Profiles of stability performance for the catalysts on CH_4 conversion with time-on-stream. Activation at 650ºC/1h, 625ºC of reaction temperature, wt = 50 mg
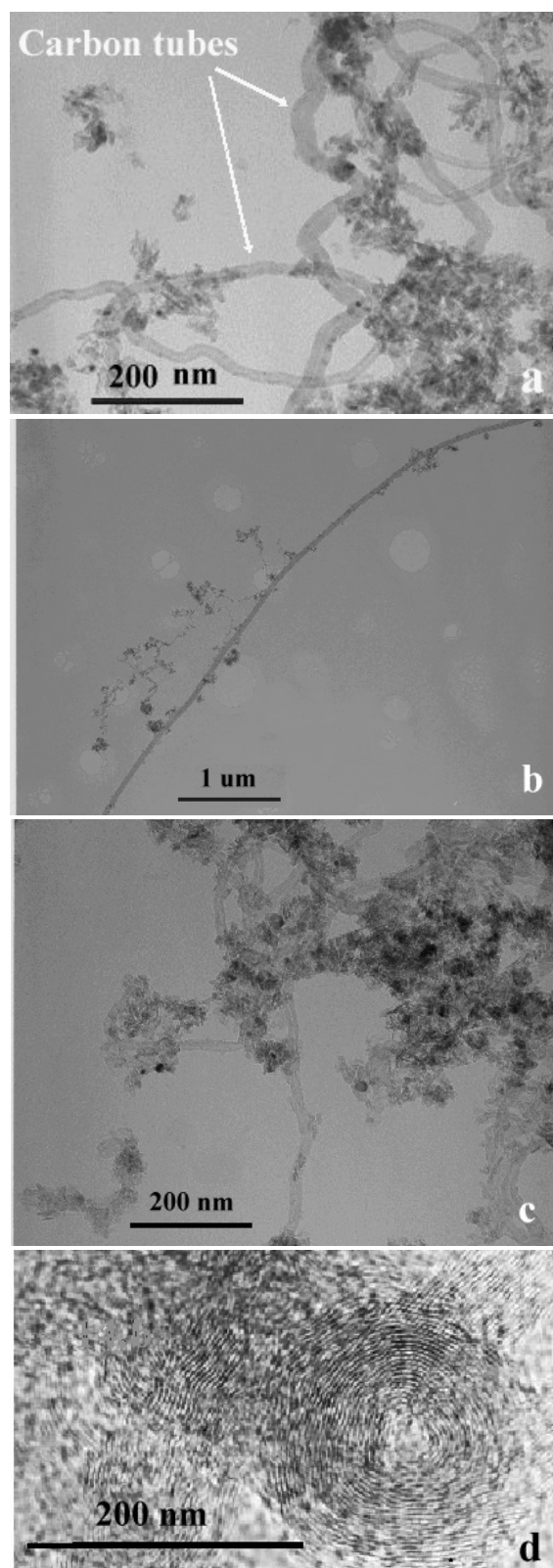

Fig. 6- BF-TEM images of the catalysts. Images of the Ni/Al_2O_3, (a) 15h of time-on-stream and (b) 50h of time-on-stream. Ni/AlCe-20, (c) 50h of time-on-stream, (d) transversal image of a carbon tube formation with a metal particle in the center.

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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 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/Al_2O_3 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 CeO_2-doped catalysts do not have the tendency of carbonaceous structure formation. The TEM analysis of Ni/Al_2O_3 after 50h of catalytic reaction showed a carbon tube formation higher than 10 mm, Fig. 6b. On the other hand, the Ni/AlCe-20 presented carbon tubes 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 CeO_2-doped catalysts presented a broader and weaker intensity of Ni peaks. This suggests that CeO_2 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 H_2 adsorption. Assuming that only Ni^0 is responsible for the irreversible H_2 adsorption, data from Table 1 points to a decrease in the metal surface area or an increase in the interfacial
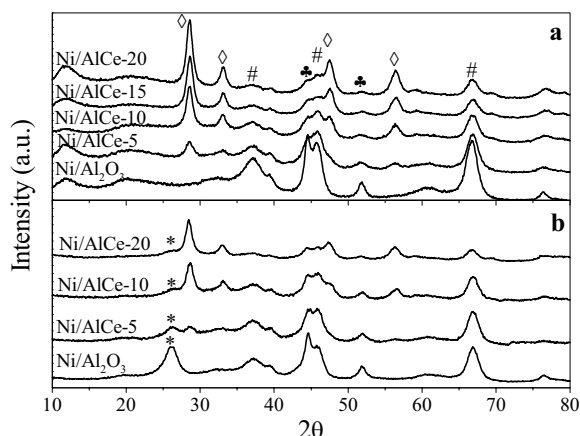
region, with the CeO_2 loading, what is unable to adsorb irreversible H_2.

This distinct interfacial region promoted by CeO_2 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).

CO_2 adsorption isotherms uptake were performed at 625ºC, the reaction temperature, and at 27ºC. The results (Table 2) showed an increase in the CO_2 adsorption with CeO_2 loading. This suggests that the principal CeO_2 contribution is to improve the CO_2 adsorption in the interfacial region that leads to a lower carbon deposition, via CH_4 decomposition reaction (Eq. 2), as well as via CO disproportionation (Eq. 3), by shifting the equilibrium concentrations (Bradford and Vannice, 1999).
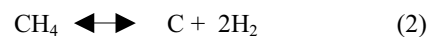
$$CH_4 \longleftrightarrow C + 2H_2 \qquad (2)$$

$$2CO \longleftrightarrow C + CO_2 \qquad (3)$$

Table 2: CO_2 chemisorption and elementary chemical analysis of catalysts after CO_2 reforming of CH_4.

Catalysts	CO_2 ($\mu mol/m^2$)		Coke deposition (g C/$g_{cat.}$)	
	27ºC	625ºC	15h	9h
Ni/Al_2O_3	2.28	0.08	30.4	(0.2)[*], (35.1)[♦]
Ni/AlCe-5	2.57	0.15	9.5	-
Ni/AlCe-10	2.81	0.16	9.9	-
Ni/AlCe -15	2.71	0.27	-	-
Ni/AlCe -20	3.52	0.24	9.8	(0.1)[*], (32.2)[♦]

[*] - CH_4/CO_2 = 0.5; [♦] - CH_4/CO_2 = 2.0;

In order to support this conclusion, the Ni/Al_2O_3 and Ni/AlCe-20 catalysts were tested with different gas compositions, CH_4/CO_2 = 0.5 and 2.0. The CH_4 conversions for these new CH_4/CO_2 ratios are plotted in Fig. 8.

A higher CH_4 conversion is observed with the increase in the CO_2 concentration as a consequence of the equilibrium shifting (Eq. 1). In this condition (CH_4/CO_2 = 0.5) the Ni/Al_2O_3 sample presented better initial catalytic performance with higher CH_4 conversion (Fig. 8a). However, with the CH_4 concentration increase (CH_4/CO_2 ratio of 2:1), the better catalytic performance, CH_4 conversion and stability, is presented by the Ni/AlCe-20 sample (Fig. 8b).

With the CH_4/CO_2 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 CH_4/CO_2 ratio (Gadalla and Bower, 1988;
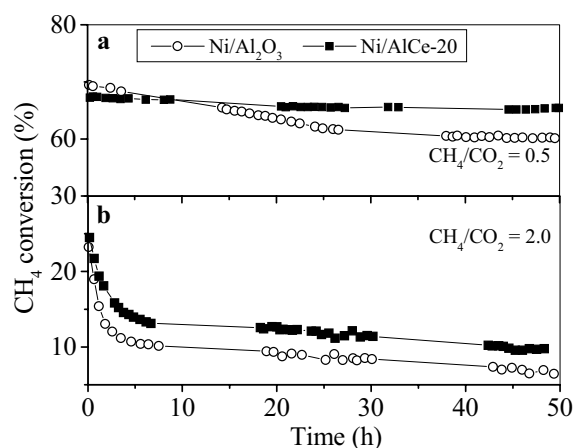

Fig. 7- X-ray diffraction patterns of the samples (a) activated at 650 ºC for 1 h in H_2 flow, (b) after catalytic reaction at 625 ºC for 15h. ◊ = CeO_2; # = Al_2O_3; ♣ = Ni; * = coke deposition.

Fig. 8- Profile performance for the catalysts on CH_4 conversion with time-on-stream at different CH_4/CO_2 ratios. Activation at 650ºC/1h, 625ºC of reaction temperature, wt = 50 mg

Bradford and Vannice, 1999). With a high CH_4 concentration, the metal particles that have a higher tendency to promote the carbon deposition via CH_4 decomposition are deactivated faster.

In spite of the higher initial CH_4 conversion for Ni/Al_2O_3 with CH_4/CO_2 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 CO_2 adsorption promoted by the CeO_2 loading is very important to improve the catalytic performance.

On the other hand, increases in the CO_2 concentration promote a lower H_2/CO ratio, mainly through the reverse water gas shift (RWGS) reaction (Eq 4), that leads to the H_2 consumption and CO production.

$$H_2 + CO_2 \longleftrightarrow CO + H_2O \qquad (4)$$

The H_2/CO ratios presented in Fig. 9 are in agreement with this, in spite of the higher CH_4 conversion.

Experimental observations reported in the literature (Richardson and Paripatyadar, 1990) showed that the main contributor to carbon deposition is the CO disproportionation. A low CO_2 concentration ($CH_4:CO_2$ 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 H_2/CO ratio presented in the CH_4/CO_2 ratio of 2:1 (Fig. 9b) suggests that the carbon deposition is promoted mainly by the CH_4 decomposition reaction (Eq. 2). It is observed a high H_2/CO ratio (>1.0) in the initial reaction. These behaviors suggest a fast deactivation of the main active sites that promotes the CH_4 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 CH_4 decomposition is a structure sensitive reaction (Beebe *et al.*, 1987), therefore this site deactivation promotes a

decrease in the CH_4 conversion. With decreasing of the CH_4 decomposition, the H_2 production drastically diminished, the same is not observed for the CO formation.
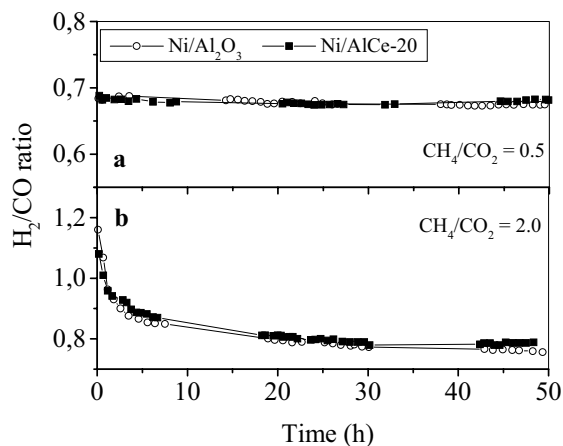

Fig. 9- Profiles of H_2/CO performance for the catalysts on CH_4 conversion with time-on-stream at different CH_4/CO_2 ratios

In a simple form, CO_2 plays an important role in the coke elimination by reacting with the carbon (Eq. 5) deposited by CH_4 decomposition (Eq. 2). If the equilibrium reaction presented in Eq. 5 is not fast enough to simultaneously eliminate the carbon generated by the CH_4 decomposition reaction, as it is deposited, the coke is accumulated.

$$CO_2 + C \longleftrightarrow 2CO \qquad (5)$$
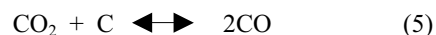
The reactions of Eq. 2 and Eq. 5 are endothermic and the equilibrium constants increase with the increase of the temperature, promoting the CH_4 decomposition and the CO_2 reaction with the deposited carbon (Eq. 5). This is in agreement with thermodynamic calculations (Reitmeier *et al.*, 1948; Gadalla and Bower, 1988) that point to a lower carbon deposition with high reaction temperature and high CO_2/CH_4 ratio.

In addition, the CH_4 decomposition reaction (without CO_2) carried out for the Ni/Al_2O_3 and Ni/AlCe-20 samples, presented a CH_4 conversion of 25 and 16% at 2min of reaction time, respectively, and at 7min the CH_4 conversion was near 1%.

IV. CONCLUSIONS

The activity and stability of Ni/Al_2O_3 catalysts are improved by CeO_2 addition. The catalyst deactivation is promoted by carbon deposition, which is mainly due to the CH_4 decomposition reaction.

The main CeO_2 contribution is on the CO_2 adsorption increase, which plays an important role on the coke elimination.

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