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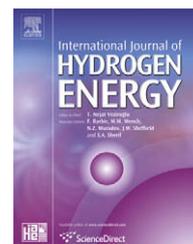
Stability improvements of Ni/α-Al₂O₃ catalysts to obtain hydrogen from methane reforming

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ARTICLE INFO

ABSTRACT

Ni catalysts supported on commercial α-Al₂O₃ modified by addition of CeO_2 and/or ZrO_2 were prepared in the present work. Since the principal objective was to evaluate the behavior of these systems and the support effect on the stability, methane reforming reactions were studied with steam, carbon dioxide, partial oxidation and mixed reforming. Results show that catalysts supported on Ce–Zr–α-Al₂O₃ composites present better reforming activity and stability noticeably higher than in the case of the reference support. With respect to composites, the presence of mixed oxides of $Ce_xZr_{1-x}O_2$ type facilitates the formation of active phases with higher interaction. This fact reduces the deactivation by sintering conferring to the system a higher contribution of adsorbed oxygen species, favoring the deposited carbon elimination. These improvements resulted in being dependent on the Ce:Zr ratio of the composite, thus obtaining more stable catalysts for Ce:Zr = 4:1 ratios.

1. Introduction

In the near future, we will find an important increase of hydrogen demand, which will be affected not only by applications in ammonium production, Fischer–Tropsch synthesis, processes in oil refineries and chemical industries, but also by the use of hydrogen in fuel cells [1–4]. Therefore, it is still interesting for R&D groups to continue with the study of processes for procurement of synthesis gas (CO and H₂) from natural gas using different reforming agents such as H₂O, O₂, CO₂, H₂O and O₂, and the development of catalysts that minimize the energetic requirement [5].

Supported Ni catalysts have resulted in being important due to comparative costs with precious metals, and to the excellent activity reported in reforming reactions. However, the particular problem is the strong deactivation by carbon deposition, which induces the search of modifications in the catalyst formulation and in selection of operative conditions to improve this aspect [6–8].

The support role on the stability of catalysts is well known. Although α-Al₂O₃ is an adequate support for reforming processes by its chemical and physical stability and mechanical strength, it presents the disadvantage that by its low reactivity it leads to a weak interaction metal-support with the active phase. In this sense, this research group has performed works oriented to modify the alumina by the addition of an aluminum oxide layer, facilitating a higher interaction with the metal and decreasing the sintering of the

active phase [9]. We have also used alkaline metals with marked Lewis basicity such as Li or K, which allowed a noticeable reduction in carbon deposition [10].

On the other hand, pure CeO_2, ZrO_2 and CeO_2–ZrO_2 supports were also used for favoring carbon gasification due to their oxygen storage capacity (OSC) [11,12]. The high cost of these supports makes them difficult to be applied in commercial formulations. For this reason, some proposals have been made including the addition of CeO_2 on γ-Al_2O_3 for dry reforming [13], Ce–ZrO_2 on θ-Al_2O_3 for steam and oxy-steam reforming [14,15], CeO_2–ZrO_2 on γ-Al_2O_3 for partial oxidation of methane [16,17], and CeO_2–ZrO_2 on SiO_2 for auto-thermal reforming [18]. In all these works, starting supports have surface area values higher than $160\,m^2\,g^{-1}$, and authors reported important improvements in the catalyst stability attributed to modification of supports.

In order to obtain an efficient Ni-containing catalyst supported on α-Al_2O_3 that has a surface area lower than $10\,m^2\,g^{-1}$, we have prepared and characterized Ce–Zr–α-Al_2O_3 composites. Our results demonstrate that the excellent refractory properties of α-Al_2O_3 are maintained and the presence of patches of mixed oxides of the type $Ce_{1-x}Zr_xO_2$ on the catalyst surface increases sites with strong basic nature [19].

The present work evaluates the fundamental catalytic properties of Ni systems supported on Ce–Zr–α-Al_2O_3 in different reforming reactions (partial oxidation (POM), steam reforming (SR), mixed reforming (MR) and dry reforming (DR)).

Special attention has been devoted to the study of the catalyst stability facing severe deactivation conditions to evaluate the support effect.

2. Experimental

Commercial α-Al_2O_3 Rhone Poulenc (Spheralite 512; surface area around $10\,m^2\,g^{-1}$) was used as base support. Modified supports were prepared by succesive impregnations of α-Al_2O_3 first with $ZrO(NO_3)_2$ xH_2O (Aldrich), and then with $Ce(NO_3)_3 \cdot 6H_2O$ (Alpha) aqueous solutions. They were dried at $120\,°C$ for 12 h and calcined in air for 4 h at $600\,°C$. The supports are designated as xCeyZrα, where x and y represent the % wt/wt of CeO_2 and ZrO_2 respectively and α the α-Al_2O_3 support. The Ni impregnation was carried out with an $Ni(NO_3)_3 \cdot 6H_2O$ (Aldrich) aqueous solution to reach a final

metallic content of 2 wt/wt%. After drying at $120\,°C$ for 12 h the samples were calcined in air flow at $750\,°C$ for 4 h.

In preliminary experiments it was determined that the intraphase transport of mass does not affect the reaction rate when the pellet size of the catalyst is between 0.495 and 0.104 mm. Similarly, the minimum feed flow rate (corresponding to GHSV: $3.1 \times 10^5\,cm^3\,g^{-1}\,h^{-1}$), above which interphase transport resistances were minimized, was also determined following standard procedures at $700\,°C$ [20].

Partial oxidation (POM), steam reforming (SR), mixed reforming (MR) and dry reforming (DR) reactions were studied in an experimental apparatus in continuous flow, at atmospheric pressure, in the temperature range 400–$700\,°C$ and GHSV $= 3 \times 10^5\,cm^3\,h^{-1}\,g^{-1}$. The composition of the feed mixtures was: POM, $N_2/CH_4/O_2 = 10/2/1$; SR $N_2/CH_4/H_2O = 10/2/2$; MR, $N_2/CH_4/H_2O/O_2 = 10/2/1/1$; DR, $N_2/CH_4/CO_2 = 6/1/1$; (partial pressure of CH_4 ∼0.15 bar and C/O ∼1).

The catalyst sample used was 0.025 g and the pellet size between 0.12 and 0.15 mm. The catalyst bed was diluted with 0.200 g of α-Al_2O_3 to avoid the development of hot points in particular for POM reaction. Samples were reduced at $700\,°C$ ($10\,°C\,min^{-1}$) for 1 h in pure H_2 flow ($30\,cm^3\,min^{-1}$) before catalytic runs. The analysis of reaction products was performed with a gas chromatograph Shimadzu GC-8A equipped with a column HayeSep D 100 and a detector of thermal conductivity.

Two tests were carried out to determine the catalyst stability under different reaction conditions. The sintering of the active phase and the carbon deposition were evaluated according to conditions of Tests (A) and (B) respectively. Test (A) consisted in the SR reaction at $700\,°C$. After 1 h reaction, the initial activity was determined. The sample was subsequently exposed to water steam and hydrogen flow at $800\,°C$ for 2 h and the activity was then measured under the SR condition at $700\,°C$. Test (B) consisted in the DR reaction at $700\,°C$ for about 72 h. The stability was evaluated in terms of the activity coefficient a_{CH4}, which represents the ratio between the CH_4 consumption rate at time t (hours) and the initial rate.

Mean particle size was determined by TEM and obtained in a TEM JEOL 100 C instrument. A graphite pattern was used for calibration. Histograms of particle size distribution arise from microphotographs using the technique of clear field image. The mean diameter of particles was obtained from the second distribution moment named diameter volume-area (d_{va}).

Table 1 – Particle diameter obtained by TEM, metallic dispersion determined by hydrogen chemisorption and from Brunelle equation [22] and hydrogen consumption from TPR analysis.

Catalyst	TEM		H₂ chemisorption		TPR	
	Average particle diameter (nm) d_{va}	Metal dispersion[a] (%)	Metal dispersion (%)	Metal surface area ($m^2\,g^{-1}$)	H₂ consumption (mmol $H_2\,g^{-1}$)	Reducibility (%)
Niα	18	4.7	2.3	0.32	0.27	80
Ni5Ceα	14	6.0	5.6	0.77	0.22	63
Ni4Ce1Zrα	12	7.0	7.0	0.95	0.25	74
Ni2.5Ce2.5Zrα	12	7.0	7.2	0.98	0.19	58
Ni1Ce4Zrα	14	6.0	5.7	0.78	0.24	69
Ni5Zrα	16	5.0	5.4	0.75	0.21	62

a From Brunelle equation [22].

Hydrogen chemisorption measurements were carried out in dynamic equipment with a TCD detector. Samples were reduced in H_2 at 700 °C for 1 h, cooled in hydrogen up to 400 °C, flushed with argon for 2 h at 400 °C and then cooled up to room temperature in argon flow. Hydrogen pulses were then injected up to saturation. Dispersions were estimated from the hydrogen amount consumed, assuming an adsorption stoichiometry H/Ni = 1.

Tests of temperature programmed reduction (TPR) were carried out in a dynamic conventional apparatus with a H_2/N_2 ratio in the feed of 1/9 and heating rate of 10 °C min^{-1} from room temperature up to 950 °C.

Carbon deposits were characterized by temperature programmed oxidation (TPO), measuring the weight variation as function of the temperature in a thermogravimetric instrument (Shimadzu TGA 50). Post reaction samples of 0.015 g were used with air flow of 10 cm^3 min^{-1} and heating of 10 °C min^{-1} from room temperature to 850 °C.

XPS analysis was performed with a Leybold Heraeus LHS10 spectrometer operating in FAT mode (50 eV pass energy), with Al Kα (1486.6 eV) radiation. A computer sequentially acquired the following regions: Ce (3d), Ni (2p), O (1s), C (1s), Zr (3d), and Al (2p). Reduction treatments *in situ* in a flowing H_2/N_2 mixture (2 %vol) at 400 °C for 2 h were carried out on samples previously treated in H_2 at 700 °C for 1 h and exposed to air. Binding energy (BE) values, measured with an accuracy of ±0.2 eV, were referenced to C 1s at 285.0 eV, which always resulted in an Al (2p) peak at 74.5 eV (as for Al (2p) in Al_2O_3). Data analysis involved smoothing, X-ray satellite removal, non-linear Shirley-type background subtraction, curve fitting (mixed Gaussian–Lorentzian function by a least-square method) and peak area determination by integration of the appropriate signal after data analysis (Esca Tools 4.2 software, Surface Interface Inc., Mountain View, CA). Surface composition was determined by the peak area ratios using the empirically derived atomic sensitivity factors reported by Wagner [21].

Changes in the Ce 3d and Ni 2p signal shape on reduced samples were analyzed by a curve fitting procedure with Ce 3d

and Ni 2p doublets endowed with fixed spectroscopic parameters, but using variable position, full width at half maximum (FWHM) and intensities.

3. Results and discussion

The commercial α-Al_2O_3 used as base support presents a specific surface area around 10 m^2 g^{-1}. The supports obtained by the addition of Ce and/or Zr oxides (1% and 5%) showed a larger number of surface active sites at the expense of a slight decrease of α-Al_2O_3 surface area (7–8 m^2 g^{-1}). Since our results of characterization and catalytic activity are analogous for 1% and 5% of modifier oxides of the support, we only present results corresponding to 5% (Table 1).

In a previous work, we have demonstrated that the addition of Ce and Zr leads to α-Al_2O_3 supports with patches of

Fig. 1 – Particle size distribution determined by transmission electron microscopy (TEM).
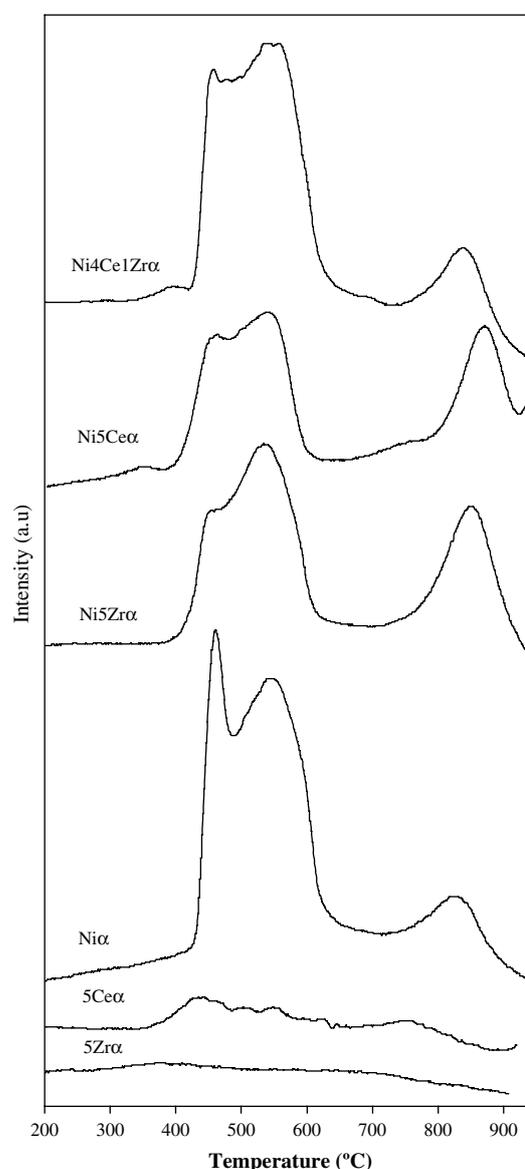
Fig. 2 – Temperature programmed reduction (TPR) profiles for Niα, Ni5Ceα, Ni4Ce1Zrα, Ni5Zrα catalysts and 5Ceα, 5Zrα supports.

CeO_2 and ZrO_2 respectively, while in CeZrα composites, patches of mixed oxides type $Ce_{1-x}Zr_xO_2$ are formed. Particularly, with Ce:Zr = 4 ratio, the presence of mixed oxide of $Ce_{0.8}Zr_{0.2}O_2$ stoichiometry was proved [19].

The average diameter of nickel particle obtained by TEM indicates a slight decrease for modified supports (Table 1). Histograms representing metallic particle sizes (Fig. 1) show a more homogeneous distribution for systems with modified supports. Although they are scarcely dispersed systems, property supports based on α-Al_2O_3, the presence of modifier oxide on the support improves the Ni dispersion. It is also possible to appreciate that values of metallic dispersion obtained from TEM measurements (Brunelle equation [22]) are similar to those obtained by the method of hydrogen dynamic chemisorption.

Fig. 2 shows programmed temperature reduction profiles for catalysts under study. The H_2 consumption, Table 1, was calculated using CuO for calibration, and expressed as reduction degree estimation of samples, ''Reducibility (%)'': [(H_2 amount consumed by TPR)/(theoretical amount of H_2 consumption for total reduction)] × 100.

Three principal peaks of hydrogen consumption are observed in the Niα catalyst at 463, 555 and 835 °C, which would indicate the presence of three phases, (i) NiO bulk, ~30% of the total reduced Ni, very weakly interacting with the support, (ii) mixed nickel and aluminum oxides, as majority species ~60%, with quite a strong interaction with the support, and (iii) $NiAl_2O_4$ species, ~10% of the total reduced Ni, strongly interacting with the support.

In the systems with modified supports, both H_2 consumption profiles and reducibility differ from the system based on Niα; the differences are more evident in the distribution of peaks than in the shift of temperatures. The intensity decrease of the signal at low temperature (~450 °C), would indicate a decrease of the NiO bulk weakly interacting, whereas the increase of hydrogen consumption peaks at higher temperature could be related to NiO_x species strongly interacting with modifier oxides of the support (CeO_2, ZrO_2 and $Ce_xZr_{1-x}O_2$) [23].

Reduction of supported modifier oxides, 5Ceα and 5Zrα, show that the H_2 consumption is very low for 5Ceα and results negligible for 5Zrα; consequently, changes in reduction profiles cannot be attributed to the reduction of supports [24].

Up to this moment, it is apparent that the strong Ni-modified support interaction is evidenced not only by the higher Ni dispersion on the support surface but also by the presence of NiO_x (Ni^{2+}) species that are reduced at high temperatures and by the decrease of NiO bulk.

XPS analysis was used to determine the chemical composition of the catalyst surface and to better understand the nature of interactions between the dispersed Ni species and the supporting oxides. BE values for the different elements in the fresh samples (700 °C in air for 4 h) are consistent with the presence of Ni(II), Zr(IV) and Ce(IV). The O 1s peak is, in general, broad and complicated because of the non-equivalence of surface oxygen ions.

The occurrence of a strong interaction between ceria and zirconia in NiCeZrα specimen is evidenced by the decrease in the BE of Zr $3d_{5/2}$ (181.8 eV) with respect to the value for ZrO_2 (182.5 eV), as reported for ceria reach-side solid solution [25]. The relative dispersion of the various oxides on the alumina surface can be obtained from the atomic intensity ratios (Table 2). Comparing the bulk composition with the XPS derived surface composition, ceria–zirconia solid solution formation in NiCeZrα samples can be inferred from the agreement between bulk and surface nCe/nZr atomic ratios and from the increase of both nCe/nAl and nZr/nAl ratios. Niα and Ni5Zrα catalysts exhibit Ni surface enrichment, whereas Ni5Ceα and Ni4Ce1Zrα reveal a homogeneous Ni surface distribution.

Typical changes of the Ni 2p region for both Niα and Ni5Zrα catalysts after in-situ H_2 treatment are illustrated in Fig. 3 for Ni5Zrα, as an example. The Ni 2p spectra consisted of both Ni^{2+} and Ni^0, suggesting that the applied reduction procedure did not result in a complete reduction of the nickel. Curve fitting of the Ni 2p region allowed determination of the contribution of Ni^0 (853.2 ± 0.2 eV) and Ni^{2+} species (main peak and associated satellite separated by 6.1 eV) (856.7 ± 0.2 eV) as about 50% of the total intensity (Table 3). In

Table 2 – Bulk and surface atomic composition for catalysts after in situ treatment in flowing H_2/N_2 mixture.

Catalysts	nA/nB	(nNi/nCe)	(nNi/nZr)	(nNi/nAl)	(nCe/nZr)	(nCe/nAl)	(nZr/nAl)
Niα	Bulk	–	–	0.018	–	–	–
	Fresh[a]			0.110			
	H_2[a]	–	–	0.080	–	–	–
Ni5Zrα	Bulk	–	0.840	0.018	–	–	0.022
	Fresh[a]		1.650	0.103			0.065
	H_2[a]	–	1.210	0.075	–	–	0.060
Ni5Ceα	Bulk	1.17	–	0.018	–	0.015	–
	Fresh[a]	0.91		0.091		0.105	
	H_2[a]	0.80	–	0.090	–	0.110	–
Ni4Ce1Zrα	Bulk	1.46	4.20	0.018	2.86	0.012	0.004
	Fresh[a]	1.24	4.90	0.127	3.20	0.103	0.030
	H_2[a]	1.10	4.80	0.130	3.60	0.140	0.026

Surface atomic ratios were calculated according to the equation: $nA/nB = (I_A/S_A)/(I_B/S_B)$, were S_A and S_B refer to the empirically derived sensitivity factors [21].
a Flowing H_2/N_2 mixture.

Table 3 – XPS results from curve fitting of Ce 3d$_{5/2}$ and Ni 2p$_{3/2}$ regions after in situ H$_2$ reduction.

Catalyst	Ni 2p$_{3/2}$ (eV)	Ce 3d$_{5/2}$ (eV)
Niα	853.3 (Ni^{2+}, 55%)	–
	856.9 (Ni^0, 45%)	
Ni5Zrα	853.2 (Ni^{2+}, 48%)	–
	856.6 (Ni^0, 52%)	
Ni5Ceα	853.2 (Ni^{2+}, 50%)	883.2 (v)
	856.7 (Ni^0, 50%)	885.9 (v′)
		916.8 (u‴, 9.5%)
Ni4Ce1Zrα	853.3 (Ni^{2+}, 75%)	883.0 (v)
	856.8 (Ni^0, 25%)	885.3 (v′)
		916.8 (u‴, 5.2%)

In parentheses: chemical state and corresponding reduction degree.
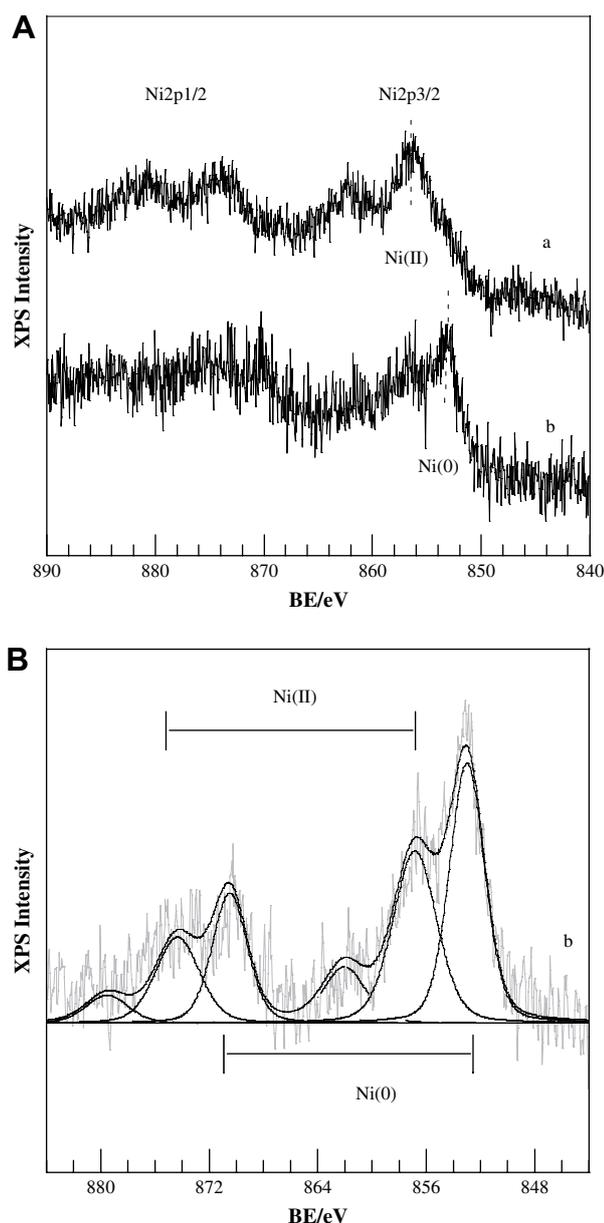
Fig. 3 – Ni 2p spectra of Ni5Zrα sample. (A) Curve a, fresh sample (700 °C in air for 4 h); curve b, reduced sample after in situ treatment in H$_2$. (B) Ni 2p$_{3/2}$ signal shape analysis of spectrum b.

addition the reduction treatment induced Ni species, clustering as indicated by the decrease of nNi/nAl and nNi/nZr ratios (Table 2). For Ni5Ceα and Ni4Ce1Zrα catalysts the complex Ce 3d and Ni 2p region (Figs. 4 and 5, respectively), collectively resolved by curve fitting, contained both Ni^0 (853.2 ± 0.2 eV) and Ni^{2+} species (856.7 ± 0.2 eV). The fraction of Ni^0 is higher in Ni4Ce1Zrα than in Ni5Ceα (Table 3), but no variation of Ni distribution on the surface is detected (Table 2).

The Ce 3d region shows complex but distinct features arising from final-state effects and from the presence of both Ce^{4+} and Ce^{3+} oxidation states.

For Ce^{4+} the Ce 3d$_{5/2}$ and Ce 3d$_{3/2}$ lines (separated by about 18.5 eV) are characterized by three contributions denoted as v, v″, v‴ and u, u″, u‴, respectively [26]. The presence of Ce^{3+} introduces in addition two contributions denoted as v$_0$, v′ and u$_0$, u′. Because the u‴ peak arises exclusively from Ce^{4+}, it can be used as quantitative measure of Ce^{4+} amount. The integrated area of the u‴ component with respect to the total Ce 3d area should constitute around 14% of total integral intensity [27]. Cerium is in reducible form in both Ni5Ceα and Ni4Ce1Zrα catalysts. Comparing the contribution of the u‴ component revealed in Ni5Ceα and Ni4Ce1Zrα samples (Table 3), it is apparent that the Ni4Ce1Zrα shows a higher reducibility than Ni5Ceα. In both samples, however, the surface compositions resemble that of bulk.

The behavior of each catalyst, evaluated facing the different reforming reactions (see experimental section), indicates that the reactivity trend POM ≈ MR > DR ≈ SR does not change by support modifications (Fig. 6).

Similar reaction rates for SR and DR were found as already reported [28]. In MR reaction, the replacement of H$_2$O by O$_2$ in the reaction mixture (CH$_4$/O$_2$/H$_2$O = 2/1/1) provokes a marked increase in catalytic activity. This could be explained by the fast methane combustion with oxygen present in the feed, generating a temperature increase that produces the increase in the reforming rate [23,29–31].

The H$_2$/CO ratio in the synthesis gas results is higher than the stoichiometric value of each reaction: SR ∼3–3.5, POM ∼2–2.5, and MR ∼2–3, which suggests the important contribution of WGS reaction.

With respect to differences among catalysts, catalysts based on modified supports showed higher activity in all reactions, in agreement with the higher concentration of active sites on the surface (Fig. 6). In DR reaction, higher differences in activity are noticed by the support effect, in agreement with some authors who established the participation of Ce and Zr oxides in CO$_2$ chemisorption [32–34]. Among composites, the Ni4Ce1Zrα sample presented the highest activity, evidencing the importance of Ce$_{0,8}$Zr$_{0,2}$O$_2$ on the support surface in active phase generation.

We performed a deep analysis of catalyst stability against sintering and carbon deposition, which are critical properties of nickel catalysts. Sintering is a thermal degradation process difficult to prevent production of, generally, irreversible deactivation. Ferretti et al. demonstrated that the water steam in the feed produces a marked metallic area decrease in
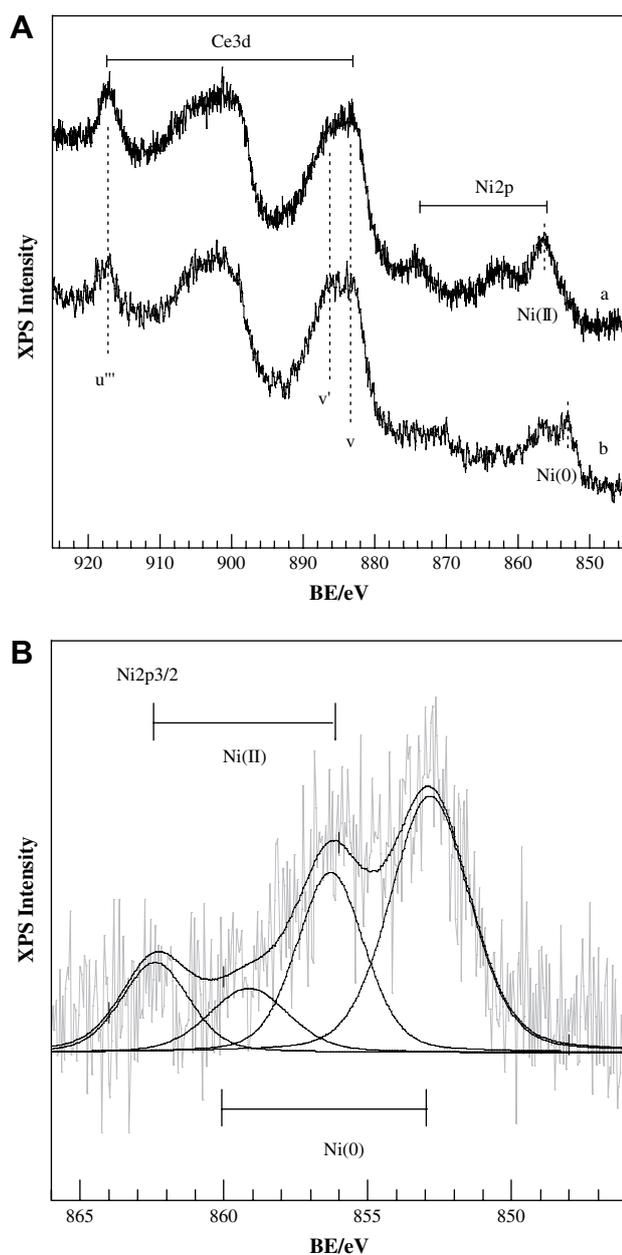
Fig. 4 – Ce 3d and Ni 2p spectra of Ni5Ceα catalyst. (A) Curve a, fresh sample (700 °C in air for 4 h); curve b, reduced sample after in situ treatment in H_2. (B) Ni $2p_{3/2}$ signal shape analysis of spectrum b.

Fig. 5 – Ce 3d and Ni 2p spectra of Ni4Ce1Zrα catalyst. (A) Curve a, fresh sample (700 °C in air for 4 h); curve b, reduced sample after in situ treatment in H_2. (B) Ni $2p_{3/2}$ signal shape analysis of spectrum b.

supported nickel catalysts [35]. Among all reforming processes investigated in this work, the SR reaction allows the most favorable conditions for sintering.

Deactivation by carbon deposition is also critical. The formation of a carbon film covering the active site as well as the formation of carbon filaments or whiskers represents serious operational problems. Among all reactions studied, reforming with CO_2 (DR) is the one that mostly favors the deactivation by carbon deposition, because of the high carbon contribution in the feed and the high temperature required. Besides, the thermodynamic analysis indicates that for reaction temperatures in the range 550 and 700 °C, the carbon

deposition could come from methane cracking reaction as well as from "Boudouard" reaction [36].

In order to evaluate the resistance to the two principal deactivation sources, sintering and carbon deposition, stability tests were applied in two different deactivating conditions. In the first test, Test (A), SR reaction is performed with intervals of steam flow at 800 °C (for more details see Section 2). The results (Table 4) indicate the high deactivation degree for Niα and Ni5Zrα, with a_{CH4} equal to 0.35 and 0.15, respectively.

Sintering resulted the prevailing source in the deactivation, as evidenced by the mean post-reaction particle diameter (d_{va}) and carbon deposited (%wt/wt C) (Table 4): carbon content
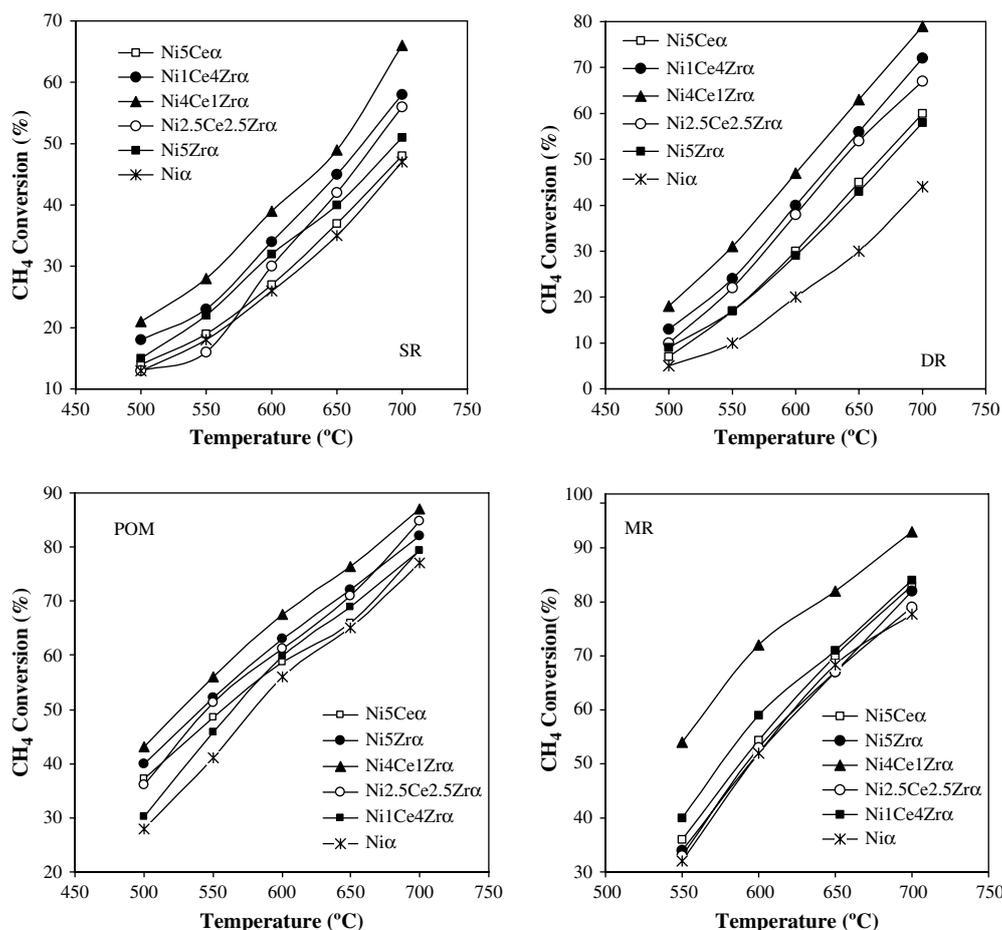
Fig. 6 – Methane conversions as function of the temperature in reforming reactions: steam reforming (SR), partial oxidation (POM), dry reforming (DR) and mixed reforming (MR). GHSV = 3×10^5 cm^3 h^{-1} g^{-1}.

was very low (less than 0.35% wt/wt), whereas the increase of metallic particle size was significant in catalysts with the higher deactivation (60% and 47%). In this way, Niα and Ni5Zrα systems resulted in less resistance to sintering. In Ni5Zrα,

Table 4 – Results obtained after sintering process.

Catalyst	Test A (sintering)			Test B (carbon deposition)		
	a_{CH4} (24 h)	C (%wt/wt) (TPO/TGA)	Particle size increase (%) (TEM)	a_{CH4} (70 h)	C (%wt/wt) (TPO/TGA)	Particle size increase (%) (TEM)
Niα	0.35	0.33	60	0.24	6.9	40
Ni5Zrα	0.15	0.25	47	0.44	1.8	32
Ni4Ce1Zrα	0.84	0.10	25	0.86	0.3	24
Ni2.5Ce2.5Zrα	0.80	0.15	28	0.78	0.6	27
Ni1Ce4Zrα	0.74	0.12	30	0.70	0.4	27
Ni5Ceα	0.65	0.22	37	0.58	2.1	29

Particle size increase %: [(dTEM post-reaction – dTEM fresh/dTEM fresh × 100].

besides the increase of metal particle size, the zirconia migration on metallic particles covering the active sites was determined by XPS, in agreement with previous findings [37].

The composite systems show the lowest deactivation degree (a_{CH4}: 0.74–0.84). The presence of mixed oxides of the type Ce$_x$Zr$_{1-x}$O$_2$ improves noticeably the thermal stability of the catalyst, as indicated by other authors [23].

The second stability test, Test (B), carried out under conditions favoring carbon deposition (Fig. 7), indicates that all the catalysts based on modified alumina are more stable than the Niα catalysts. Catalysts modified with Ce and those containing composites show the best improvements. The carbon content on Ni4Ce1Zrα, Ni2.5Ce2.5Zrα and Ni1Ce4Zrα samples (<0.6% wt/wt C) was an order of magnitude lower than Niα catalysts (6.9% wt/wt C). TEM micrographs show "whiskers" type carbon filaments and an increase of particle size in post-reaction samples of about 24–27% (Fig. 8). These results allow one to conclude that improvements in stability are produced by the low carbon deposition.

Our results can be analyzed according to the reaction mechanisms proposed by Qin et al. [38] and Rostrup-Nielsen [39] that allow an explanation of the significant differences in activity and stability depending on the support type. Scheme 1 shows the steps corresponding to methane activation (from 1 to 2),

Fig. 7 – Deactivation tests of the studied catalysts. Reaction: dry reforming. Feed flow rate 130 cm^3 min^{-1} (N$_2$/CH$_4$/ CO$_2$ = 14/2/2), T = 700 °C, a_{CH4} = XCH$_4$(t)/XCH$_4$(i).

1. $CH_x + 2S \rightarrow CH_{x-1} - S + H - S \quad (2 < x < 4)$

2. $CH - S + S \rightarrow C - S + H - S$

3. $CO_2 + 2S \rightarrow CO - S + O - S$

4. $O_2 + 2S \rightarrow 2O - S$

5. $H_2O + 3S \rightarrow O - S + 2H - S$

6. $CH_x - S + O - S + (x-1)S \rightarrow CO - S + xH - S$

7. $CO - S \rightarrow CO + S$

8. $2H - S \rightarrow H_2 + 2S$

Scheme 1 – Reaction scheme to obtain synthesis gas [38].

generation of adsorbed oxygen on surface sites, O-S (from 3 to 5), and formation of CO and H$_2$ (from 6 to 8). By assuming that the global activity results by the activation rate of CH$_4$ and by the reaction between species CH$_x$-S and O-S (stage (6)), the difference in the rates between reactions POM, MR and DR would be produced by the higher amount of sites O-S in the POM and MR (stage (4) versus stage (3)) than in DR.

The small contribution of O-S in DR could be responsible for the lower reaction rate, allowing the development of intermediate species that lead to higher carbon formation. In addition, the activity improvement in DR measured on composites could be due to the role played by the support in step dealing with O-S formation.

With respect to stability, the higher availability of adsorbed O-S species allows the CO production with lower carbon formation. Our results indicate that the provision of these O-S sites by the support property follows the order: Ni4Ce1Zrα > Ni1Ce4Zrα, Ni2.5Ce2.5Zrα > Ni5Ceα > Ni5Zrα > Niα. The same stability order is established for catalysts with 1% wt/wt of modifier oxides.

4. Conclusions

The present study indicates that the addition of small amounts of CeO$_2$ and ZrO$_2$ to α-Al$_2$O$_3$ allows procurement of a support with patches of Ce$_x$Zr$_{1-x}$O$_2$ mixed oxide on the surface. This support, improving the Ni dispersion and the metal particle reducibility, leads to catalysts with a high activity for all methane reforming reactions in the temperature range investigated (450–700 °C). The improvement is more marked for reactions involving CO$_2$ and O$_2$ as reagent (DR and POM) due to the contribution of the support in generating reaction steps with surface adsorbed oxygen species. As for stability, the Ce$_{0.8}$Zr$_{1-x}$O$_2$ patches provide the highest benefits not only by the high oxygen storage capacity (OSC) which prevents the carbon deposition but also by the metal–support interaction that prevents deactivation by sintering.

Fig. 8 – TEM micrographs of Ni4Ce1Zrα catalyst, after DR deactivation test at 700 °C.

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