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Applied Catalysis A: General



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# Ni catalysts supported on modified ZnAl<sub>2</sub>O<sub>4</sub> for ethanol steam reforming

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# ARTICLE INFO

Article history: Received 5 January 2010 Received in revised form 8 March 2010 Accepted 10 March 2010 Available online 17 March 2010

Keywords: Ethanol steam reforming Hydrogen production Ni/ZnAl<sub>2</sub>O<sub>4</sub> catalysts

# ABSTRACT

Nickel catalysts supported over  $ZnAl_2O_4$  modified by Ce or/and Zr addition were studied in the steam reforming of ethanol under more severe reaction conditions such as a lower extent of feed dilution and lower space velocities. The catalysts were stable at 650 °C during 35 h in time on stream. The main reaction products were H<sub>2</sub>, CO<sub>2</sub>, CO, C<sub>2</sub>H<sub>4</sub>O and small amounts of CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>. The catalyst supported over CeO<sub>2</sub>–ZnAl<sub>2</sub>O<sub>4</sub> was the most active and showed the highest hydrogen selectivity. The addition of ZrO<sub>2</sub> decreased the activity and favored the CO production. The lowest degree of Ni<sup>2+</sup> reduction over Ni/ZAZr could explain the worst performance of this system. Otherwise, the highest Ni<sup>2+</sup> dispersion and the high oxygen mobility from ceria or from Ni–Ce boundary allowed a higher residual activity and an improved coking resistance.

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# 1. Introduction

The growing of the world population and the changes in the society behavior have produced a vertiginous increase in the energetic demand. The decrease in fossil resources, the lower profit in petroleum bore holes and the high price of petroleum barrel together with the increased necessity to protect the environment have led to the urgent search for energetic solutions.

The production of hydrogen from biomass is gaining increasing attention as a potential source of renewable energy. In this context, ethanol could be transformed in hydrogen by means:

 $C_2H_5OH\,+\,3H_2O\,\rightarrow\,2CO_2+6H_2$ 

As a consequence of the structure of ethanol molecule because of to the presence of a C–C bond and oxygen atom, this reaction presents significant differences to the steam reforming of methane (which is nowadays the most widespread and economic way of producing hydrogen). Then, the reaction mechanism is more complex and the number of potential by-products formed from ethanol is greater [1]. Ni catalysts have been used in a commercial scale in several reforming processes for more than 40 years [2]. Noble metals (Pd, Pt, Rh, Ru), nickel and cobalt catalysts have shown a very good performance in the ethanol steam reforming [3–9], although there is not a commercial catalyst yet. The main problem for most of these catalytic systems is the high deactivation rate related to the formation of carbonaceous deposits, in particular for inexpensive Ni catalysts. It is well known that carbon deposition is thermodynamically unfavorable at high temperatures and higher water/ethanol ratios. The deactivation could occur by covering the active phases due to encapsulating carbon and also by filamentous formation. The morphology and chemical properties of carbon deposits depend on catalysts, operation conditions and the carbon source employed [10]. The carbon amounts are not only a function of time on stream, they also depend on the deposition and removing rates. There are many studies about the carbon formation on Ni systems [3,4,6,11] and a lot of effort has been focused on developing new Ni stable catalysts with improved resistance to coke formation. In a previous work, the addition of Ce to NiZnAl unsupported catalysts was examined and an important decrease in carbon deposition was observed in ethanol steam reforming reaction [4]. These evidences were obtained from experiments carried out under a diluted feed (molar fraction of ethanol: 3%). However, the catalytic system was rapidly deactivated when it was submitted to more severe operation conditions. Ni catalysts supported ZnAl<sub>2</sub>O<sub>4</sub> modified by Ce and/or Zr were prepared in this work with the aim to improve the resistance to carbon deposition. Activity in the ethanol steam reforming reaction and deactivation studies together with characterization data from XRD, SEM-EDX, XPS, BET and TG are also presented.

# 2. Experimental

# 2.1. Catalyst preparation

 $ZnAl_2O_4$  modified by the addition of Ce and/or Zr were used as supports. They were prepared by a sol-gel method using aluminium isopropoxide (AIP) as a source of Al. The procedure was similar to that reported in the literature [12]. The hydrolysis of AIP

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was carried out at 95 °C in a batch reactor. A bohemite stable sol was obtained by using a molar ratio of 200 mol H<sub>2</sub>O/mol AIP. A solution of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in isopropyl alcohol was added dropwise to the sol and then a  $Ce(NO_3)_3 \cdot 6H_2O$  and/or  $ZrO(NO_3)_2$  aqueous solutions, in the necessary amounts to obtain a final loading of 5 and 10 wt.% in Ce and/or Zr. After the addition of 0.7 mol H<sup>+</sup>/mol AIP transparent gels with low viscosity were obtained and they were submitted to evaporation until the volume was reduced in 1/3. The aging was carried out in a thermostatic bath at 65 °C overnight. The solids were dried at 110 °C for 10 h and finally, they were decomposed in N<sub>2</sub> flow (100 mL min<sup>-1</sup>) under the following temperature program: from room temperature to 150°C; at 150°C for 2h to eliminate the remained water; from 150 to 350 °C at a heating rate,  $\beta$ , of 5 °C min<sup>-1</sup>; at 350 °C for 2 h; from 350 to 500 °C at the same  $\beta$ ; at 500 °C for 5 h and then cooling to room temperature. Then, the solids were calcined at 700 °C under static air for 2 h to eliminate any carbonaceous residues and stabilize the support structure. The samples were denoted as ZACe (10 wt.% Ce), ZAZr (10 wt.% Zr) and ZACeZr (5 wt. %Ce + 5 wt.%Zr).

Nickel was impregnated over the supports by the incipient wetness impregnation technique using an aqueous solution of  $Ni(NO_3)_2 \cdot 6H_2O$ . After impregnation of 7 wt.% of Ni, the samples were dried at 110 °C overnight and calcined in air at 700 °C for 2 h. The catalysts were labeled as Ni/ZACe, Ni/ZAZr and Ni/ZACeZr, respectively.

# 2.2. Catalyst characterization

All samples were characterized using different physical-chemical methods.

## 2.2.1. BET surface area

BET surface areas were measured using a Micromeritics Gemini V instrument by adsorption of nitrogen at -196 °C on 200 mg of sample previously degassed at 250 °C for 3 h.

#### 2.2.2. X-ray diffraction (XRD)

XR diffraction patterns were obtained with a RIGAKU diffractometer operated at 30 kV and 20 mA by using Ni-filtered CuK $\alpha$  radiation ( $\lambda = 0.15418$  nm) at a rate of 3° min<sup>-1</sup> from  $2\theta = 20^{\circ}$  to 80° for fresh samples and in the step mode ( $0.05^{\circ}$ , 5 s) for the used samples. The powdered samples were analyzed without previous treatment after deposition on a glass sample holder. The identification of crystalline phases was made by matching with the JCPDS files.

#### 2.2.3. Thermal gravimetry (TG)

The analyses were recorded using TGA 51 Shimadzu equipment. The samples, ca. 15 mg, were placed in a Pt cell and heated from room temperature to  $800^{\circ}$ C at a heating rate of  $10^{\circ}$ C min<sup>-1</sup> with an air flow of 50 mL min<sup>-1</sup>.

#### 2.2.4. Temperature programmed reduction (TPR)

Studies were performed in a conventional TPR equipment. This apparatus consists of a gas handling system with mass flow controllers (Matheson), a tubular reactor, a linear temperature programmer (Omega, model CN 2010), a PC for data acquisition, a furnace and various cold traps. Before each run, the samples were treated in He at 300 °C for 30 min. After that, the system was cooled down to 25 °C. The samples were subsequently contacted with a  $30 \text{ mLmin}^{-1}$  flow of 5 vol.% H<sub>2</sub> in N<sub>2</sub>, heated at a rate of 5 °C min<sup>-1</sup> from 25 °C to a final temperature of 700 °C and held at 700 °C for 1 h. Hydrogen consumption was monitored by a thermal conductivity detector after removing the water formed. Some TPR experiments were carried out from 25 to 1000 °C under the same conditions.

#### 2.2.5. SEM-EDX

Scanning electron micrographs were obtained in a LEO 1450 VP. This instrument is equipped with an energy dispersive X-ray microanalyzer, EDAX Genesis 2000 with Si(Li) detector which permitted analytical electron microscopy measurements. The samples were sputter coated with gold.

# 2.2.6. Hydrogen chemisorption

Nickel metal dispersion was determined by dual isotherm method. The samples were reduced *in situ* at 500 °C for 90 min and the uptakes of strongly chemisorbed  $H_2$  at 25 °C were measured between 5 and 100 Torr. A back sorption isotherm was measured by repeating this procedure after evacuation at 25 °C for 30 min. The difference between chemisorption and backsorption isotherms was used to estimate strongly chemisorbed hydrogen uptakes. A H/Ni titration stoichiometry equal 1 was considered [13]. The reduced nickel surface area was estimated assuming a cross-sectional area of 0.065 nm<sup>2</sup> for a Ni atom and the average crystallite diameter was calculated for spherical particles [14].

## 2.2.7. X-ray photoelectron spectroscopy (XPS)

The XP spectra were recorded with a multitechnique equipment (SPECS) with a hemispherical electron analyzer PHOIBOS 150 and a dual Mg/Al X-ray excitation source. The spectra were obtained by using an Al anode with 30 eV of energy step operated at 100 W and 10 kV. Each spectral region was obtained scanning a number of times in order to get good signal-to-noise ratios. The residual pressure inside the analyses chamber was kept at values below  $5 \times 10^{-9}$  mbar. All binding energies (BE) were referred to Al2p line at 74.5 eV. Al2p, Ni2p, Zn2p, O1s, Ce3d, Zr3d and C1s spectra were recorded for each catalyst. The surface atomic ratio was estimated by area integration after the correction with the corresponding sensitivity factor.

# 2.3. Catalytic test

The ethanol steam reforming reaction was carried out in a stainless steel tube with an internal diameter of 4 mm operated at atmospheric pressure. The reactor was placed in a vertical furnace, which was controlled by a programmable temperature controller. The reaction temperature was measured with a coaxial K thermocouple. The feed to the reactor was a gas mixture of ethanol, water and helium (free of oxygen). Ethanol-water was fed to an evaporator (operated at 130°C) through an isocratic pump operated at 0.15 mLmin<sup>-1</sup>. The flow rates of gas stream were controlled by mass flowmeters. The molar ratio in the feed was  $C_2H_5OH:H_2O:N_2:He = 1:4.9:0.9:6$  being the ethanol flow  $1.02 \times 10^{-3}$  mol min<sup>-1</sup>. The catalyst weight was pure 50 mg (0.3-0.4 mm particle size range) in the stability tests and it was changed (25, 50 and 100 mg diluted in quartz) in those experimental tests to reach different conversion levels. The catalyst was heated to reaction temperature under He flow, then the mixture with C<sub>2</sub>H<sub>5</sub>OH+H<sub>2</sub>O was allowed to enter into the reactor to carry out the catalytic test. In all the cases fresh samples were used. The reactants and reaction products were analyzed on-line by gas chromatography.  $H_2$ ,  $CH_4$ ,  $CO_2$  and  $H_2O$  were separated by a 1.8 m carbosphere (80–100 mesh) column and analyzed by TC detector. Nitrogen was used as an internal standard. Besides, CO was analyzed by a flame ionization detector after passing through a methanizer. Higher hydrocarbons and oxygenated products (C<sub>2</sub>H<sub>4</sub>O, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>O, C<sub>2</sub>H<sub>5</sub>OH, etc.) were separated in Rt-U PLOT capillary column and analyzed with FID using N<sub>2</sub> as carrier gas. The homogeneous contribution was tested with the empty reactor. These runs showed no activity at 500 °C whereas the ethanol conversion was 3% at 600 °C being acetaldehyde the only product.



**Fig. 1.** Catalytic activity and stability in ethanol steam reforming. (a) Ethanol conversion:  $\triangle$ : Ni/ZACe;  $\bigcirc$ : Ni/ZACeZr;  $\square$ : Ni/ZAZr. Product selectivity for: (b) Ni/ZAZr, (c) Ni/ZACeZr and (d) Ni/ZACe.  $\blacksquare$ : H<sub>2</sub>;  $\bigoplus$ : CO;  $\blacktriangle$ : CH<sub>4</sub>;  $\forall$ : CO<sub>2</sub>;  $\blacklozenge$ : C2;  $\blacktriangleleft$ : C<sub>2</sub>H<sub>4</sub>O. Reaction temperature: 650 °C,  $W/F_{C_2H_5OH} = 49$  g min mol<sup>-1</sup>, molar ratio H<sub>2</sub>O:C<sub>2</sub>H<sub>5</sub>OH = 4.9.

Ethanol conversion and selectivity to products were defined as follows:

$$X_{C_{2}H_{5}OH} = \frac{F_{C_{2}H_{5}OH}^{III} - F_{C_{2}H_{5}OH}^{out}}{F_{C_{2}H_{5}OH}^{in}} \times 100$$
$$S_{i} = \frac{\nu_{i}F_{i}^{out}}{2(F_{C_{2}H_{5}OH}^{in} - F_{C_{2}H_{5}OH}^{out})} \times 100$$

$$S_{\rm H_2} = \frac{F_{\rm H_2}^{\rm out}}{3(F_{\rm C_2H_5OH}^{\rm in} - F_{\rm C_2H_5OH}^{\rm out}) + (F_{\rm H_2O}^{\rm in} - F_{\rm H_2O}^{\rm out})} \times 100$$

Being  $F_i^{\text{in}}$  and  $F_i^{\text{out}}$  the molar flow rates of product "i" at the inlet and outlet of the reactor, respectively and  $v_i$  the number of carbon atoms in "i".

# 3. Results and discussion

The activity and stability of catalysts are tested in steam reforming of ethanol on pure catalysts at 650 °C for 35 h. As shown in Fig. 1, all fresh catalysts (used in reaction without pre-reduction) exhibit an immediate high activity that then markedly decreases until almost 200 min. After this long induction period a pseudosteady state regimen is reached where an oscillatory behavior in the reaction temperature is observed. The temperature changes  $\pm 4$  °C respect to the reference temperature (650 °C). Although the oscillation period cannot be accurately determined, it is nearly 30 s with asymmetric amplitudes. It is the first time that this behavior is reported in reforming reaction, although a similar effect has been observed for several authors in the partial oxidation of methane Table 1

Catalytic results in stability tests.				
	Ni/ZACe	Ni/ZACeZr	Ni/ZAZr	
S <sub>H2</sub>	34.3	18.5	9.6	
S <sub>CO</sub>	26.0	22.1	23.5	
S <sub>CH4</sub>	5.4	4.1	5.1	
S <sub>CO<sub>2</sub></sub>	40.3	31.2	18.5	
S <sub>C2H4</sub>	2.2	2.6	2.7	
S <sub>C2H40</sub>	24.0	33.0	45.7	
X <sub>SS</sub>	48.2	30.6	24.2	
$R_{\rm CO/CO_2}(*)$	0.64	0.7	1.27	

S<sub>i</sub>: % selectivity; X<sub>SS</sub>: % ethanol conversion (averaged values in steady state period); (\*) molar ratio.

Reaction temperature =  $650 \degree C$ ,  $W/F_{C_2H_5OH} = 49 \text{ g min}^{-1} \text{ mol}$ , and molar ratio  $H_2O:C_2H_5OH = 4.9$ , TOS: 35 h.

[15,16]. This behavior could be related to the simultaneous occurrence of carbon removal-deposition reactions and main reaction and needs further studies.

In Table 1, the average values corresponding to the steady state are shown. Ni/ZACe shows the highest ethanol conversion ( $X_{ss}$  = 48.2%), the highest hydrogen selectivity ( $S_{H_2}$  = 34.3%) and the lowest CO/CO<sub>2</sub> molar ratio (0.64), whereas Ni/ZAZr is less active ( $X_{ss}$  = 24.2%) with high CO/CO<sub>2</sub> ratio (1.27) and the lowest hydrogen selectivity ( $S_{H_2}$  = 9.6%). The Zr addition favors the acetaldehyde formation or inhibits its reforming. The Ni/ZACeZr catalyst shows an intermediate behavior.

The characterization of fresh samples and those after being used during 4 h in time on stream (once the induction period has finished) can explain the residual activity and the best catalytic performance of Ni/ZACe.

The X-ray patterns of fresh, reduced and used samples are shown in Fig. 2. In all the cases the  $ZnAl_2O_4$  spinel phase ( $2\theta = 31.3^\circ$ , 36.8°, 44.8°, 55.6°, 59.4° and 65.3°, JCPDS-5-669) is observed. The four strongest peaks of fluorite structured CeO<sub>2</sub> at 28.5°, 33.3°, 47.5° and 56.3° (JCPDS-34-394) are also observed in the Ni/ZACe sample. In the Ni/ZAZr sample, ZrO<sub>2</sub> is mainly in a tetragonal structure, although it cannot be ruled out the presence of ZrO<sub>2</sub> in monoclinic phase. For the sample prepared from the mixed support ZACeZr the formation of solid solutions as  $Zr_xCe_{1-x}O_2$  are not clearly observed by XRD. The broadening of the peaks makes difficult to establish whether the Zr, Ce and O atoms are arranged in a single mixed phase or in separated phases. However, the slight shift of  $2\theta$  around  $0.15^{\circ}$ to a higher angle observed for the high intensity peak of CeO<sub>2</sub> could be an indication that a solid solution is also formed. Similar shifts have been reported in the literature and they were assigned to the solid solution formation [17]. In all the fresh catalysts, peaks of NiO  $(2\theta = 43.3^{\circ}, 37.3^{\circ}, 62.9^{\circ}, \text{JCPDS-4-835})$  are detected. Since reflections of NiAl<sub>2</sub>O<sub>4</sub> are coincident to ZnAl<sub>2</sub>O<sub>4</sub> its presence cannot ruled out. The ZnAl<sub>2</sub>O<sub>4</sub> used as support is a highly stabilized spinel and the Ni impregnation was carried out in one step by dry impregnation method, consequently the stoichiometric NiAl<sub>2</sub>O<sub>4</sub> formation should be very low. However, nickel could be incorporated into the subsurface of the zinc spinel and a surface Ni compound related to Ni strongly interacting with spinel matrix could be formed. Jongsomjit et al. have found similar results on alumina-supported cobalt catalysts prepared by impregnation method. These authors have reported the formation of a surface Co aluminate which it is not identical to CoAl<sub>2</sub>O<sub>4</sub> (spinel) but probably a surface compound deficient in Co [18]. The peaks corresponding to Ni<sup>0</sup> ( $2\theta = 44.5^{\circ}$ , 51.8°, 76.4°, JCPDS 4-0850) are clearly observed in used samples indicating that the catalyst undergoes a reduction under reforming conditions. The XRD patterns of used samples are similar to those of reduced samples except for the weak broad diffraction peak around  $2\theta = 26^{\circ}$  which is assigned to the formation of carbon. Carbon is readily deposited under the reaction conditions as it is shown in the TPO-TG experiments.



**Fig. 2.** Diffraction patterns of catalysts at 650 °C for 4 h TOS. (A) Ni/ZACe, (B) Ni/ZACeZr, (C) Ni/ZAZr.  $\times$ :  $ZrAl_2O_4$ ,  $\Leftrightarrow$ :  $CeO_2$ ,  $\bigcirc$ : NiO,  $\Leftrightarrow$ :  $Ni^0$ ,  $\blacksquare$ :  $ZrO_2$  (monoclinic), and  $\Box$ :  $ZrO_2$  (tetragonal); (F) fresh, (U) used in reaction, and (R) after TPR.

The reducibility of Ni<sup>2+</sup> is a very important issue in connection with the ability to self-active in reaction conditions, particularly taking into account that Ni<sup>0</sup> represents the active center for reforming reaction. In Fig. 3 the TPR profiles are shown. The catalysts with CeO<sub>2</sub> (Ni/ZACe and Ni/ZACeZr) exhibit a low intensity peak around 260–280 °C. This hydrogen consumption could be assigned to the reduction of weakly interacted NiO with the spinel support and also to a partial reduction of CeO<sub>2</sub> surface oxygen. This peak is not observed on Ni/ZAZr. CeO<sub>2</sub> reduction has been thoroughly investigated and most of the previous investigations agree on ascribing a peak at low temperature to surface reduction. The redox behavior of CeO<sub>2</sub> strongly depends on textural properties because a decrease of surface area depresses all the surface related redox processes [19,20]. The Ce signal in oxidized samples given by XPS is very weak then the surface reduction of ceria should be low. However, once NiO weakly interacting with the support



Fig. 3. TPR profiles of (a) Ni/ZACe, (b) Ni/ZACeZr, and (c) Ni/ZAZr. Insert presents TPR profiles up to 1000 °C of (a') Ni/ZACe and (c') Ni/ZAZr and ZACe.

Table 2
Characteristics of Ni supported catalysts

Specific surface areas BET $(m^2 g^{-1})$			C (wt.%)
Bare support	Fresh	Used <sup>a</sup>	
42.4	35.4	94.4	42.5 (60.1)
56.6 60.4	46.2 48 5	58.8 79 7	11.2 (32.7) 20 9 (32.4)
	Specific surface a Bare support 42.4 56.6 60.4	Specific surface areas BET (m²Bare supportFresh42.435.456.646.260.448.5	Specific surface areas BET $(m^2 g^{-1})$ Bare support      Fresh      Used <sup>a</sup> 42.4      35.4      94.4        56.6      46.2      58.8        60.4      48.5      79.7

<sup>a</sup> After being used at  $650\,^{\circ}$ C for 4 h over undiluted catalyst. Parenthesis values correspond to medium ethanol conversion during 4 h.

or interacting with ceria begins to be reduced, the presence of reduced Ni species should facilitate the reduction of surface ceria. In all the cases a high temperature H<sub>2</sub> uptake peak is observed up to 400 °C centered at 586 °C for Ni/ZACe, 597 °C for Ni/ZAZr and 652 °C for Ni/ZACeZr. The peak observed at high temperature is attributed to the Ni<sup>2+</sup> reduction with a high degree of interaction with the modified support. The extent of Ni<sup>2+</sup> reduction is lower than 100% in Ni/ZAZr (H<sub>2</sub>/Ni=0.65 mol H<sub>2</sub>/mol Ni). XRD of reduced sample reveals NiO remains, Fig. 2. The H<sub>2</sub> consumption is higher in Ni/ZACe  $(H_2/Ni = 1.01)$  and Ni/ZACeZr  $(H_2/Ni = 0.92)$ , suggesting an improved reducibility by the Ce addition or a contribution of ceria reduction. The low degree of Ni<sup>2+</sup> reduction over Ni/ZAZr could explain the lowest residual activity of this catalyst. TPR experiments of Ni/ZACe and Ni/ZAZr carried out from 25 to 1000 °C are also shown in Fig. 3. Non-significant differences are revealed for Ni/ZAZr sample whereas a new highest temperature peak is observed in Ni/ZACe profile. This peak could be attributed to Ni<sup>2+</sup> species reduction in a spinel structure. TPR of ZACe support also shown is almost flat up to 700 °C.

In Table 2 some properties of supports and catalysts are shown. For fresh samples an increase in the specific surface areas is observed with Zr content increasing. This increase could be an intrinsic result of the acid-catalyzed sol–gel preparation. Zr is able to hydrolyze, condense and become gel forming structures with a higher ramification degree more than Ce. After the induction period an important increase in specific surface areas is observed what is related to carbon deposition. The higher value corresponds to the sample exposed at high conversion levels.

In Fig. 4 the results of temperature programmed oxidation carried out by thermogravimetric analysis are shown. Two peaks are clearly observed on Ni/ZAZr and Ni/ZACeZr. The peak at low



**Fig. 4.** TPO–DTG of catalysts used under reforming conditions. (a) Ni/ZACe, (b) Ni/ZAZr, and (c) Ni/ZACeZr. Reaction temperature:  $650 \degree$ C, TOS: 4 h and Molar ratio H<sub>2</sub>O:C<sub>2</sub>H<sub>5</sub>OH=4.9.



Fig. 5. SEM micrographs of Ni/ZACe (top) fresh and (bottom) after being used in reaction.

temperature (around 470 °C) is assigned to a reactive carbon associated to metallic particles. This carbon deposit could be partially removed on Ni/ZACe under reaction conditions and the peak is not clearly observed in TPO-TG. ZnAl<sub>2</sub>O<sub>4</sub> is an irreducible support [5]. However, CeO<sub>2</sub> is a reducible oxide which could provide oxygen under reforming conditions and contribute to eliminate the surface carbon on Ni<sup>0</sup>. The intensity of combustion peak at high temperature follows the order Ni/ZACe > Ni/ZAZr > Ni/ZACeZr and could be attributed to carbon associated to other fraction of metallic particles and also to carbon deposited over the support surface. The weight losses determined as regards free carbon mass (Table 2) are 42.5, 20.9 and 11.2 wt.% for Ni/ZACe, Ni/ZAZr and Ni/ZACeZr, respectively, which represent 8.8, 4.5 and 2.3 mmol C g<sup>-1</sup> h<sup>-1</sup>. From these results the carbon resistance seems to be higher for Ni/ZACeZr but the best performance in reforming reaction is over Ni/ZACe. The discrepancy could be attributed not only to the differences in ethanol conversion but also to the differences in surface properties.

The presence of carbon deposits over the catalysts used in reaction is also examined by SEM. Within the detection limit of the technique, carbon filaments are not observed but a high intensity peak of carbon could be detected by EDX. In Fig. 5, the SEM micrographs of Ni/ZACe are shown as example. Similar results were observed on a previous report over unsupported NiZnAl catalysts with Ce addition [4]. Sanchez-Sanchez et al. [21] also found that Ce and La additives prevent the formation of carbon filaments on nickel surfaces. However, these authors have considered significant



Fig. 6. XP spectra in Ni2p region of catalysts: (a) fresh and (a') used Ni/ZACe; (b) fresh and (b') used Ni/ZACeZr. Insert: XP spectra in C1s region of used samples: (c) Ni/ZACe and (d) Ni/ZACeZr.

amounts of filaments covering the Ni particles on Ni/Al<sub>2</sub>O<sub>3</sub>–Zr. As the nickel lattice could be changed by the inclusion of Ce (Zr) atoms, it is possible to avoid or limit the dissolution of C in the same lattice which is a crucial step in filament formation. In Fig. 2, the XRD of catalysts used at 650 °C for 4 h show a broad incipient peak at  $2\theta = 26.4^{\circ}$  (JCPDS: 41-1487) of graphitic carbon. The presence of Ce and Zr could promote the formation of amorphous carbon which is thermodynamically feasible to be partially removed at the reaction temperature used in this work [4].

XPS measurements are carried out for Ni/ZACe and Ni/ZACeZr. The Ni2p spectra of fresh samples, shown in Fig. 6, exhibit peaks assigned to  $Ni^{2+}$  with  $Ni2p_{3/2}$  and  $Ni2p_{1/2}$  binding energies at 855.1 and 872.6 eV, respectively. The signal of  $Ni^{2+}$  species could be assigned to NiO according to XRD patterns, although the pos-

sibility of NiAl<sub>2</sub>O<sub>4</sub> cannot be excluded. For the used catalysts the Ni2p signal is low as a consequence of the coke deposition and the valence state of nickel is unclear. However, the nickel signal does not disappear indicating that some nickel remains exposed to the reactants. The XP spectra of Ce3d show a very low signal in fresh and used samples suggesting a covering of Ce by Ni during impregnation. On the other hand, the XP spectrum of Zr3d for Ni/ZACeZr sample clearly shows peaks at 181.7 eV (Zr3d<sub>5/2</sub>) and 183.8 eV (Zr3d<sub>3/2</sub>) assigned to Zr<sup>4+</sup> in ZrO<sub>2</sub> [21–23]. The presence of solid solution cannot be unequivocally confirmed by XPS. The high surface ratio Zr/(Zn + Al) on fresh sample (0.048) near the nominal one (0.037) indicates that ZrO<sub>2</sub> is in a high dispersion on the support and it is not covered by Ni during impregnation.

# Table 3

XPS atomic ratio of the catalysts before and after 4h in ethanol steam reforming.

Surface atomic ratio	Ni/ZACe		Ni/ZACeZr	
	Fresh	Used	Fresh	Used
Ni/(Zn + Al)	0.083 (0.087)	0.078	0.107	0.045
Ni/Zr	-	_	2.215 (2.340)	1.003
C/Ni	4.136	58.82	2.331	100
C/(Zn + Al)	0.405	4.466	0.250	4.283
Zr/(Zn + Al)	-	-	0.048 (0.037)	0.044

Parenthesis values correspond to nominal ones.



**Fig. 7.** Product distribution as a function of ethanol conversion for (a) Ni/ZACe and (b) Ni/ZACeZr. ■: H<sub>2</sub>, •: CO, ▲: CH<sub>4</sub>, ▼: CO<sub>2</sub>, ♦: C2, and ≺: C<sub>2</sub>H<sub>4</sub>O. Reaction temperature = 650 °C, TOS: 13 h, molar ratio H<sub>2</sub>O:C<sub>2</sub>H<sub>5</sub>OH = 4.9.

The surface atomic ratios given by XPS are collected in Table 3 and compared with the nominal ones. An idea of Ni dispersion degree could be obtained from the surface Ni/(Zn+Al) atomic ratio. This ratio on oxidized samples is near the nominal value and indicates a high amount of oxidized Ni exposed across the support surface. Before reaction the Ni/(Al+Zn) atomic ratio is higher on Ni/ZACeZr sample. However, after reaction the decrease in Ni/(Zn + Al) ratio for Ni/ZACe (6%) is significantly lower than that for Ni/ZACeZr catalyst (58%). This could indicate that carbon is covering metallic particles and support as well. The C/Ni values also suggest that the amount of carbon on metallic particles is substantially lower over Ni/ZACe. However, the intensity of combustion peak at high temperature in TPO-TG curves is higher over Ni/ZACe. These results lead to infer that an important fraction of this carbon is deposited in multilayers with loose structure over support surface and does not hamper the reactant gases diffusion to the catalyst. This idea is supported by the important increase in specific surface area, Table 2. Besides, it can be suggested that a major fraction of Ni over Ni/ZACe is accessible to the reactant gases during reaction in spite of the formation of large amounts of carbon. The XP spectra of C1s for used samples, insert in Fig. 6, show one strong peak with similar intensity at 284.5 eV corresponding to carbon atoms in a state close to graphitic sp<sup>2</sup> configuration. This result indicates that the surface of both catalysts is covered by the same type of carbon.

The Ni dispersion on reduced samples shown in Table 4 and determined by  $H_2$  chemisorption follows the order: Ni/ZACe > Ni/ZACeZr > Ni/ZAZr in agreement with the ethanol conversion. In comparison with XPS results where the Ni/(Zn+AI) ratio is near the nominal value in fresh oxidized catalysts, the amount of exposed nickel atoms in reduced samples is low. The reduction at 500 °C for 90 min leads to a low Ni<sup>0</sup> amount exposed over the surface probably due to an incomplete reduction under these conditions and/or a sintering of nickel particles. Experimental limitations in H<sub>2</sub> chemisorption equipment do not allow sample reduction at the reaction temperature. Considering that

Table 4				
Hydrogen	chemisorption	results of	reduced	samples.

Sample	Dispersion %	d <sub>Ni</sub> (nm)	Metal surface area (m <sup>2</sup> g <sup>-1</sup> )
Ni/ZACe	2.4	42	1.1
Ni/ZACeZr	1.3	78	0.61
Ni/ZAZr	0.8	126	0.36

the TPR indicated the reduction around 600  $^\circ\text{C}$ , dispersion could be higher under reforming conditions.

With the aim to elucidate which catalytic system is the most carbon resistant, the samples were tested at 650 °C for 13 h under different space velocities. In these experiments diluted catalysts are used. The dilution is variable to provide the same height of bed length. The Ni/ZAZr system is excluded from this study due to the high CO/CO<sub>2</sub> molar ratio and low H<sub>2</sub> selectivity, Table 1. In Fig. 7, the product distribution for Ni/ZACe and Ni/ZACeZr is shown as the function of conversion. An analysis of product distribution suggests that the reaction starts with a very high dehydrogenating activity. The acetaldehyde selectivity decreases with ethanol conversion while the selectivity to CO and H<sub>2</sub> increase. Comparing the catalytic behavior of both samples, the main difference is in the  $CO/CO_2$  molar ratio. In Fig. 8, the corresponding weight losses as a function of conversion in the steady state regime are shown. The carbon deposition is almost the same at low conversion level  $(X_{SS} < 30\%)$  but it is clearly higher on Ni/ZACeZr at increasing conversion. For Ni/ZACe, the ethanol conversion on pure catalyst is higher than that on diluted catalyst (48.2% and 29.9%, respectively,



**Fig. 8.** Carbon amount as a function of ethanol conversion over ( $\blacksquare$ ) Ni/ZACe and ( $\bullet$ ) Ni/ZACeZr. Reaction temperature: 650 °C, TOS: 13 h and molar ratio H<sub>2</sub>O:C<sub>2</sub>H<sub>5</sub>OH=4.9.

at the same experimental conditions). The selectivity to acetaldehyde decreases from 31.8% with dilution to 24% without dilution while the selectivities to CO and to  $H_2$  increase from 20.5% and 22.7% to 26% and 34%, respectively. No noticeable changes are observed in the other reaction products. On Ni/ZACeZr this effect is not so significant in ethanol conversion or in the product distribution. Further studies on this subject are necessary to obtain more quantitative information but it could be related to catalyst and inert particles distribution.

# 4. Conclusions

Catalytic experiments in ethanol steam reforming over Ni supported on modified  $ZnAl_2O_4$  (CeO<sub>2</sub> and/or ZrO<sub>2</sub>) combined with post-reaction characterization showed a significant deactivation during a long induction period (around 200 min). The catalytic results with no pre-reduction step and more severe operation conditions clearly showed that the introduction of Ce in sol-gel ZnAl<sub>2</sub>O<sub>4</sub> support significantly enhances the activity of Ni catalyst in the steam reforming of ethanol. The total or partial replacement of Ce by Zr decreased the activity and hydrogen selectivity. The lowest degree of Ni<sup>2+</sup> reduction over Ni/ZAZr could explain the worst performance of this system. Otherwise, the higher Ni<sup>2+</sup> dispersion and high oxygen mobility from ceria or from Ni–Ce boundary allowed a higher residual activity and an improved coking resistance.

## Acknowledgments

Financial supports are acknowledged to CONICET, ANPCyT and Universidad Nacional de San Luis.

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