Ni-supported catalysts for ethanol steam reforming: effect of the solvent and metallic precursor in catalyst preparation

Alejandra C. Villagrán Olivares1 · Manuel F. Gomez1 · Mariana N. Barroso1 · María C. Abello1

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Abstract
Ethanol steam reforming was studied over Ni/MgAl2O4–CeO2 catalysts. The catalysts were prepared using different impregnation media (ethanol or water) and Ni precursors (nitrate or acetate). The use of an alcoholic solution did not affect the specific surface area, but promoted the NiO formation reducible at lower temperature affecting the Ni-support interactions and the Ce3+/Ce4+ initial ratios. All catalysts were highly active in the reforming reaction of ethanol with a high initial conversion of ethanol under more severe conditions than those commonly used in literature. The best catalytic behavior was found over the catalyst prepared from an ethanolic solution of Ni(NO3)2. This sample showed a high Ce3+/Ce4+ ratio, an adequate interaction Ni-support and an average Ni diameter around 28 nm. This catalyst was stable under the reforming conditions used in this work: initial ethanol concentration: 9.4%, reaction temperature: 650 °C, W/F = 49 g min mol−1 C2H5OH and reaction time: 40 h. The ethanol conversion was almost complete with H2 selectivity around 78%.

Keywords Hydrogen · Ethanol reforming · Ni/MgAl2O4–CeO2 catalysts · Deactivation

Introduction

The climate change observed in the last few decades and its consequences have led the global society to minimize the emissions (mainly CO2) into the environment and to decrease the dependence on fossil fuels. The use of sustainable energy sources is imperative and it is widely accepted that a carbon-free society will not be possible without a hydrogen economy [1]. The hydrogen production from ethanol steam reforming is an interesting option, because ethanol has several advantages compared with other raw materials. The most important one is its renewable origin, because it can be obtained from biomass fermentation (e.g., sugar cane, corn, lignocelluloses, etc.) [2, 3]. The ethanol has relatively high hydrogen content and its reaction with water under steam reforming conditions is able to produce 6 mol of H2 per mole of reacted ethanol:

\[
\text{CH}_3\text{CH}_2\text{OH} + 3 \text{H}_2\text{O} \rightarrow 6 \text{H}_2 + 2 \text{CO}_2.
\]  

The other important advantage is that CO2 production slightly contributes to greenhouse effect since it is recycled through photosynthesis during the plant growth. The noble metals [4–7], nickel [8–13], cobalt [9, 14–21], etc., supported over several supports have been studied as catalysts for this reaction. Ni catalysts have been used in commercial scale in several reforming processes for more than 40 years [22], especially for its high activity to break C–C bond and its low cost compared to noble metals. The main disadvantage of Ni catalysts is related to deactivation by coke formation, sintering and inactive phase transformation. There are many studies about the carbon formation on Ni systems [13, 23–25] and a considerable effort has been focused on developing new Ni stable catalysts with an improved resistance to coke formation.

The type of metal present (base metal or noble metal) and the reaction conditions (initial ethanol concentration, water: ethanol molar ratio, temperature, etc.) affect the mechanism of carbon deposition [3]. The addition of alkaline metals, alkaline earth metals or rare earth metals has been frequently used on Ni catalysts to increase the carbon tolerance [23, 26, 27]. It has been reported that the addition of Na or K changes the surface acidity of catalyst and minimizes the ethylene formation known as coke precursor. The inhibition of carbon deposition has been also related to Ni particle sizes. Ni
particles lower than a critical size (around 10 nm [3]) and high dispersion levels could minimize the carbon deposition responsible for the irreversible deactivation or for the pressure increase in the catalytic bed [28]. Other important factor is the Ni-support interaction. Strong interactions of NiO with the support and/or Ni compound formation can hinder the formation of metallic Ni. The anchorage of Ni particles on the support could be also affected by the impregnation medium [29] and/or the Ni precursor nature [30].

The effect of the solvent used in the impregnation step has been investigated in Co-based catalysts. Song and Ozkan [29] have studied the influence of ethanol and water as impregnation media in Co/SiO₂ catalysts. The catalysts prepared in ethanol showed a significant improvement in the ethanol steam reforming reaction, ESR: higher H₂ yield, better stability and lower amount of by-products. The authors have assigned this positive effect to the presence of oxygen-ated carbon species which prevent sintering and exert a site blocking that suppresses the side reactions. Besides, they have suggested an “imprinting” effect that favors the surface acetate formation and provides an optimum surface geometry for the selective reactions. The impregnation with an ethanolic solution of cobalt nitrate instead of an aqueous one has also shown an improvement in the metallic dispersion in Fischer–Tropsch Co catalysts [31]. Ho and Su have reported that the presence of ethylene groups hinder the aggregation of Co₂O₃ during its formation from the thermal decomposition of cobalt nitrate [31]. The influence of other solvents in metallic dispersion has been also reported in literature [32, 33]. Lucredio et al. [32] have investigated the effect of methanol in the preparation of Co catalysts. They observed an improvement in the ESR when Co was supported on SiO₂. However, the performance of Co/Al₂O₃ resulted to be independent of the solvent used in preparation. The influence of methanol seems to depend on support nature.

In a previous work, Ni catalysts supported on MgAl₂O₄–CeO₂ showed a good performance in ESR, although they suffered deactivation mainly by carbonaceous species deposition [30]. As it was mentioned, high dispersion levels of Ni could depress coke formation. Then, it is interesting to examine the interaction of ethanol as impregnation medium in preparation of Ni/MgAl₂O₄–CeO₂ catalysts. In this work, the solids were synthesized by wet impregnation using ethanol with different Ni precursors: Ni(NO₃)₃ or Ni(CH₃COO)₂·4H₂O. The catalysts were characterized by different techniques and their catalytic results in ESR were compared with those obtained using catalysts prepared in an aqueous solution.

### Experimental

#### Catalyst preparation

MgAl₂O₄ support was prepared by the citrate method [26]. The sample was calcined in two steps: (1) under a N₂ flow (180 mL min⁻¹) from room temperature to 500 °C at 5° min⁻¹ and 2 h at 500 °C; cooling down in N₂ flow and then, (2) in static air from room temperature to 700 °C at 5° min⁻¹ and 1 h at 700 °C. The addition of Ce (5 wt%) on support was carried out by wet impregnation using an aqueous solution of Ce(CH₃COO)₃·xH₂O. The solvent was removed in a rotating evaporator at 75 °C under vacuum. The sample was dried in vacuum at 100 °C overnight. The modified support was used without calcination.

Four supported catalysts with a nominal loading of 8 wt% Ni were prepared by the wet impregnation technique using an aqueous solution (w) or an ethanolic solution (e) of Ni(NO₃)₂·6H₂O (n) or Ni(CH₃COO)₂·4H₂O (a). After impregnation, the solvent was evaporated in a rotavapor at 75 °C under vacuum and then, the samples were dried at 100 °C and calcined in air at 650 °C for 3 h. The catalysts are denoted as mentioned in Table 1. Hence, Ni(n–w) indicates a Ni catalyst prepared from an aqueous solution of nickel nitrate.

### Table 1 Characteristics of fresh Ni/MgAl₂O₄–CeO₂ catalysts

| Catalyst | Ni(n–w) | Ni(a–w) | Ni(n–e) | Ni(a–e) |
|----------|---------|---------|---------|---------|
| Ni, wt%   | 6.37    | 4.89    | 6.10    | 5.48    |
| Ce, wt%   | 4.23    | 3.36    | 4.30    | 3.93    |
| S_{BET}, m² g⁻¹ | 113     | 112     | 111     | 110     |
| H₂ consumption by TPR, μmol H₂ g⁻¹cat | 938     | 897     | 1167    | 1086    |
| mol H₂/mol Ni | 0.9     | 1.0     | 1.1     | 1.1     |
| % D      | 2.6     | 4.9     | 3.6     | 0.39    |
| Metallic surface area, m² g⁻¹cat | 1.10    | 1.62    | 1.45    | 0.14    |
| d_Ni, nm | 39      | 21      | 28      | 259     |

a wt% determined by ICP

b₅₀₈ (nm) = 101% D [32]. S_{BET} of unmodified support = 92 m²/g. S_{BET} of modified support without calcination = 161 m²/g.
Catalyst characterization

Chemical composition

Nickel and cerium contents were obtained with a sequential ICP spectrometer Baird ICP 2070 equipped with a monochromator [26].

BET surface area

Specific surface areas were determined by the BET method. They were measured using a Micromeritics Gemini V analyzer by adsorption of nitrogen at \(-196\text{ °C}\) on 100 mg of a sample previously degassed at \(300\text{ °C}\) for 16 h under flowing \(N_2\).

X-ray diffraction

XRD patterns were recorded with a RIGAKU diffractometer using CuK\(\alpha\) radiation (\(\lambda = 0.15418\text{ nm}\)) and a rate of 3° min\(^{-1}\) in the 2\(\theta\) range from 10° to 70° [26].

Infrared spectroscopy

IR spectra were recorded by a Nicolet Protegé 460 infrared spectrometer, in the region 4000–250 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\). Compressed KBr (spectroscopy quality) disks containing 1 wt% of catalyst were employed. The disks were prepared by applying a pressure of 200 kg m\(^{-2}\) for 5 min. Each spectrum was collected by co-adding of minimum 64 scans.

Temperature programmed reduction

The TPR profiles were recorded in a conventional TPR equipment [30]. Before the run, the sample was oxidized in a 50 mL min\(^{-1}\) flow of 20 vol% \(O_2\) in He at \(300\text{ °C}\) for 30 min. After that, helium was admitted to remove oxygen and finally, the system was cooled to 25 °C. The sample was subsequently contacted with a 50 mL min\(^{-1}\) flow of 5 vol% \(H_2\) in \(N_2\), heated at a rate of 10 °C min\(^{-1}\) from 25 °C to a final temperature of 700 °C and held at 700 °C for 2 h. The hydrogen consumption was determined by calibration with \(H_2\) (5 vol%)/\(N_2\) mixture injections.

Chemisorption of hydrogen

\(H_2\) pulse chemisorption was carried out in a Micromeritics Autochem II 2920 instrument. The samples were reduced at 650 °C for 45 min under a \(H_2\) (10%)/Ar (100 mL min\(^{-1}\), 20 °C min\(^{-1}\)). Then, they were cooled down in Ar flow (100 mL min\(^{-1}\)) until 50 °C. The chemisorption was carried out by pulses of a \(H_2\) (10%)/Ar mixture (50 mL min\(^{-1}\)) until the peak areas remained constant. The nickel dispersion, \(\%D\), was calculated from the \(H_2\) adsorbed volume assuming the stoichiometric ratio \(H_{\text{adsorbed}}:\text{Ni}_{\text{surface}} = 1\) and the cross-sectional area of the nickel atom = 0.0649 nm\(^2\) atom\(^{-1}\). Spherical particles were assumed to calculate average nickel particle sizes and \(d_{\text{Ni}}\) represents the surface-weighted average crystallite diameter in nm [34].

X-ray photoelectron spectroscopy

The XPS spectra were collected with a multitechnique system (SPECS). The conditions were similar to those used in Ref. [35]. The residual pressure inside the analysis chamber was kept at values below \(2 \times 10^{-8}\) mbar. \(\text{Ni}\) 2p, \(\text{Al}\) 2p and \(\text{Ce}\) 3d spectra were recorded for each fresh sample. All binding energies (BE) were referred to the C 1 s peak at 284.6 eV as a consequence the BE for the \(\text{Al}\) 2p was about 74.1 eV. The samples were ex situ reduced to 650 °C in a \(H_2\) (5%)/\(N_2\) flow for 45 min. In addition, they were treated inside the pre-chamber in a reductive flow \(H_2\) (5%)/Ar at 400 °C for 10 min and atmospheric pressure before the XPS measurements. The procedure for data treatment was the same as described in [35].

Thermal gravimetry

The TG-TPO analyses were carried out in a DTG-60 Shimadzu instrument. The samples were heated from room temperature to 1000 °C at 10 °C min\(^{-1}\) under an air flow (50 mL min\(^{-1}\)). The carbon amount was expressed as %C, [30].

Scanning electron microscopy and energy dispersive X-ray spectroscopy

SEM micrographs of samples after being used in reaction were obtained in a LEO 1450 VP equipped with an energy dispersive X-ray microanalyzer (EDAX Genesis 2000) [26].

Catalytic test

The ethanol steam reforming reaction was carried out in the experimental set-up described elsewhere [26]. The reactor was operated at 650 °C and atmospheric pressure. The feed to the reactor was a gas mixture of ethanol, water and inert. The molar ratio in the feed was \(H_2O: C_2H_5OH: \text{inert} \approx 5:1:5\) being the initial ethanol concentration around 9.4%. In all experiments, the \(W/F^{C_2H_5OH}_{C_2H_5OH}\) was 49 g min mol\(^{-1}\). To observe the catalyst deactivation within a short operation time (6 h on stream), a small amount of catalyst (50 mg) without dilution in an inert material was used. For the stability test, the catalyst was diluted with SiC in a weight ratio.
1:1. Before reforming experiments, the catalyst was in situ reduced in H₂ (5%)/N₂ flow at 650 °C for 45 min. The reactants and reaction products were analyzed online by gas chromatography. Ethanol conversion (X_{C₂H₅OH}), selectivity to carbon products (S_i) and the hydrogen yield (Y_H₂) were estimated as described elsewhere [26]. The selectivity to H₂ was calculated taking into account that 6 mol of H₂ represents 100% of selectivity (Eq. 1).

**Results and discussion**

**Characterization of fresh catalyst**

The chemical composition determined by ICP spectroscopy and the specific surface areas for calcined catalysts are shown in Table 1. The average Ni and Ce compositions are 6 and 4 wt%, respectively. The use of hydrated reactives in the preparation could explain that Ni and Ce compositions are lower than the nominal ones. The BET values are similar (110–113 m²g⁻¹) and quite high after the thermal treatment (650 °C for 3 h), regardless of the solvent or the precursor used for Ni impregnation.

The diffraction patterns of fresh samples shown in Fig. 1 reveal the presence of MgAl₂O₄ (2θ = 19.03°, 31.3°, 36.8°, 44.8°, 55.6°, 59.4°, 65.2°, JCPDS-21-1152), CeO₂ (2θ = 28.5°, 47.5°, 56.3°, JCPDS 30-0394) and NiO (2θ = 43.3°, 37.3°, 62.9°, JCPDS-4-835). The particle sizes of NiO could be inferred from XRD. From the broadening of peaks and the Scherrer equation (2θ = 43.3°), the NiO particle size follows the order of Ni(a–e) (d_{NiO} = 17 nm) > Ni(n–e) (d_{NiO} = 11 nm) > Ni(n–w) (d_{NiO} = 9 nm) > Ni(a–w) (d_{NiO} = 7 nm). They are more affected by the impregnation medium than by precursor salt. These differences could affect the catalytic activity in ESR and the carbon accumulation rate [36, 37].

The reduction profiles are presented in Fig. 2. With the exception of Ni(n–e), the TPR profiles show two well-defined reduction peaks. The small peak (α peak) at low temperature could be assigned to Ni²⁺ species weakly interacted with the MgAl₂O₄, to Ni²⁺ interacted with CeO₂ particles and to the surface reduction of Ce⁴⁺ [38–40]. From thermodynamics bulk CeO₂ is reduced to Ce₂O₃ at high temperature (1300 °C, [41]). However, the reduction behavior of ceria has been reported to dramatically change in the presence of a metal. Recently, Lörberg et al. have reported TPR results on Ni/CeO₂ catalysts and these authors have also attributed the reduction peak around 270 °C to the presence of Ni species in very small NiO crystallites, Ni species in strong interaction with Ce species at the NiO–CeO₂ interface and/or in a Ce–Ni–O solid solution [40]. In our case, there is no evidence of solid solution formation, the presence of a strong interaction between NiO and CeO₂ cannot be ruled out. The β peak at high temperature that was attributed to the reduction of Ni²⁺ species strongly interacted with MgAl₂O₄ and surface Ni spinel-like species. A surface Ni compound species related to Ni strongly interacting with the Mg spinel as a “Ni aluminate” could be formed. This “Ni aluminate” is suggested to be different from pure NiAl₂O₄ [42]. In fact, a XPS signal of Ni²⁺ near to that attributed to pure Ni spinel was clearly observed indicating this interaction (see further). The TPR profiles for Ni(n–w) and Ni(a–w) do not show significant differences neither in the maximum temperature nor in H₂ consumption, Table 1. These results suggest that similar species were formed on the surface when the impregnation medium is water regardless of the Ni precursor. On the contrary, those prepared with an ethanol solution showed
a marked improvement in reducibility without significant changes in the extent of reduction. An improvement in reducibility was also reported for Co/CeO$_2$ catalysts synthesized using ethanol as an impregnation solvent [29]. For Ni(a–e) sample, the α peak decreases its intensity without changes in the maximum temperature. This could indicate an inhibition in the surface reduction of ceria. This inhibition could be associated with the blocking of reduction sites arising to ethoxy groups of solvent and/or to acetate groups of Ni precursor. The β peak (at 450 °C) is shifted in 200 °C at lower temperatures and could be assigned to the reduction of large NiO particles observed by XRD. The profile for Ni(n–e) is more complex. The peak at a high temperature for Ni(n–e) is clearly split, β’ (520 °C) and β” (665 °C), suggesting that Ni species (NiO and surface Ni spinel) have different interaction extent with support.

Carbon contamination in fresh catalysts was confirmed by IR spectroscopy, Fig. 3. Bands between 1600 and 1400 cm$^{-1}$ clearly reveals the presence of organic remains. Organic species remains on MgAl$_2$O$_4$ after calcination at 700 °C (curve e). The intense bands at 1573, 1435 and 1344 cm$^{-1}$ for MgAl$_2$O$_4$–CeO$_2$ (curve f) without calcination correspond to $\nu_{as}$(COO), $\nu_{s}$(COO) and CH$_3$ bending of acetate groups (the support was modified by using Ce(CH$_3$COO)$_3$) [43]. In all samples, multiples bands in the COO band region are observed (1640, 1512, 1400 and 1260 cm$^{-1}$) and they are more intense for samples prepared from Ni(CH$_3$COO)$_2$. The organic remains left on the Ni(a–w) and Ni(a–e) catalyst surface are similar and stable enough to withstand calcination at 650 °C for 3 h and they could certainly contribute to the early deactivation observed in ESR reforming on these catalysts.

The XRD patterns of reduced samples after TPR reveal the presence of MgAl$_2$O$_4$ and CeO$_2$ without significant changes, Fig. 4. The NiO peaks are not detected whereas that corresponding to Ni$^0$ at $2\theta = 51.8^\circ$ (JCPDS-04-0850) is clearly observed. The peak at 44.4$^\circ$ would be overlapped with that of MgAl$_2$O$_4$. From the broadening peak at $2\theta = 51.8^\circ$, the particle metallic size are lower for Ni(n–w), Ni(a–w) and Ni(n–e) samples.

The dispersion values, $D$, estimated by chemisorption of H$_2$ are presented in Table 1. This technique is not completely adequate for Ni dispersion determination due to the presence of ceria which is also reduced in the first steps of the procedure. Taking into account that the ceria reduction occurs almost in the same extent (see TPR, Fig. 2), the dispersion values could be compared. The $D$ values for the samples except to Ni(a–e) are between 2.6 and 4.9%, leading to average $d_{Ni}$ of 39–21 nm. These values follow the same trend of those obtained by XRD. However, Ni particle sizes predicted by H$_2$ chemisorption are around twice those from XRD. In fresh samples, several Ni$^{2+}$ species are present on the support: dispersed Ni$^{2+}$ species, NiO particles and surface spinel-like species (different to NiAl$_2$O$_4$). The particle size of Ni estimated by Scherrer only corresponds to Ni detected by XRD. Ni$^0$ becoming from the surface spinel-like species observed by XPS (see

![Image of IR spectra](Fig. 3)  ![Image of XRD patterns](Fig. 4)
further) and/or from amorphous NiO would be undetectable by XRD. The dispersion for Ni(a–e), 0.39%, was markedly lower, probably related to its reduction behavior. The TPR profile of this sample presented a maximum at 450, 200 °C below the others, Fig. 2. In the chemisorption experiments, the samples were in situ reduced at 650 °C (it is the temperature at which the major fraction of Ni2+ of the other samples was reduced). Therefore, the metallic particles generated at 450 °C have different ages than those generated at 650 °C and have a higher possibility to be sintered. This could explain the differences in dispersion and in the behavior against carbon deposition. The catalyst is reduced in H2(5%)/N2 flow at 650 °C for 45 min before carrying out the ESR catalytic experiments. As a consequence, the particle size of metallic nickel over Ni(a–e) would be seven to twelve times as large as the other catalytic systems.

The redox properties of catalysts were analyzed by XPS. As it was mentioned, first the samples were ex situ reduced at 650° during 45 min (to simulate its surface state at the beginning of reaction) and then, in the XPS pre-chamber at 400 °C for 10 min (to reduce NiOx species formed during air exposure of the sample). The XP spectrum of Ni 2p presented peaks at binding energies corresponding to Ni0 and Ni2+, Fig. 5-I and Table 2. The presence of Ni2+ could be indicating that the additional in situ reduction at 400 °C for 10 min in the pre-chamber was insufficient to clean the surface oxidation due to the handling of samples or the reduction treatment was incomplete. The in situ reduction at 650 °C cannot be made in the XPS equipment used in this work. The XP spectrum for Ce 3d, Fig. 5-II, exhibited peaks at 879.8–880.1, 882.2–882.3, 885.2–885.3, 887.7–887.9, 897.5–898.0 eV corresponding to Ce3+ and Ce4+ [35].

![X-ray photoelectron spectra](image)

**Fig. 5** X-ray photoelectron spectra of (a) Ni(n–w), (b) Ni(a–w), (c) Ni(n–e) and (d) Ni(a–e) in: I the Ni 2p region and (II) the Ce 3d region, peak assignments for Ce3+, Ce4+ and Ni 2p1/2

**Table 2 XPS results for reduced catalysts**

| Catalyst | Ni 2p3/2 | Ce 3d5/2 | Surface ratio |
|----------|---------|---------|---------------|
|          | Ni0     | NiO     | NiAl2O4 Sat.NiO | Ni/Ce + Ni |
| Ni(n–w)  | 852.2   | 855.4   | 858.0          | 861.4      | 879.8  | 882.2  | 885.2  | 887.7  | 898.0  | 0.25   | 0.53   | 0.68   |
| Ni(a–w)  | 852.1   | 855.3   | 857.7          | 861.1      | 880.1  | 882.3  | 885.3  | 887.9  | 897.6  | 0.30   | 0.74   | 0.64   |
| Ni(n–e)  | 852.1   | 855.1   | 857.7          | 860.8      | 880.1  | 882.3  | 885.3  | 887.9  | 897.6  | 0.38   | 0.70   | 0.69   |
| Ni(a–e)  | 851.9   | 854.4   | 857.2          | 860.2      | 879.9  | 882.2  | 885.2  | 887.8  | 897.5  | 0.37   | 0.54   | 0.67   |
The Ni/(Ce + Ni) surface ratios show non-significant changes, between 0.64 and 0.69, Table 2. The Ce$^{3+}$/Ce$^{4+}$ ratio was determined from curve fitting and integration of the Ce 3d region. There is not a clear dependence with the precursor nature or the impregnation medium. The Ce$^{3+}$/Ce$^{4+}$ ratio for Ni(a–e) was lower than the value for Ni(n–e), 0.54 against 0.7; whereas the Ce$^{3+}$/Ce$^{4+}$ ratio for Ni(a–w) was higher than the one corresponding to Ni(n–w), 0.74 against 0.53. The presence of the redox couple Ce$^{3+}$/Ce$^{4+}$ is crucial to increase the carbon tolerance [35]. The Ni$^0$/Ni ratios were higher for the samples prepared in presence of ethanol.

**Catalytic results in ethanol steam reforming**

Catalytic results are shown in Fig. 6. High ethanol conversions were reached from the beginning of the reaction. The samples prepared from acetate precursor showed a faster deactivation, in agreement with previous results [44, 45]. The Ni(a–e) catalyst exhibited a marked loss of conversion from 100 to 72% after 350 min in time on stream. The loss of conversion was lower for catalysts prepared from Ni(NO$_3$)$_2$ regardless of impregnation solvent.

As regards to performance to H$_2$, the catalysts prepared in aqueous medium presented higher values than those prepared in an ethanolic medium. The Ni(n–w) catalyst showed an initial yield close to 5.2 mol H$_2$/mol C$_2$H$_5$OH decreasing to 4.5. Furthermore, this catalyst showed the highest selectivity (an average of 80% value). For the system Ni(a–w), H$_2$ yield also decreased from 4.5 to 4 mol H$_2$/mol C$_2$H$_5$OH. However, for Ni(n–e), the H$_2$ yield was kept constant near to 4.2 mol H$_2$/mol C$_2$H$_5$OH. The lowest value of H$_2$ yield was 3 mol H$_2$/mol C$_2$H$_5$OH for Ni(a–e) catalyst due to the formation of C$_2$H$_4$O ($\delta$C$_{C,H,O}$ ~ 14%), CH$_3$COCH$_3$ ($\delta$CH$_{CH,COCH}$ ~ 9%) and C$_2$H$_4$ ($\delta$C$_{CH,H}$ = 3.6%, known as coke precursor). The CH$_4$ selectivity for all catalysts was near to 3%. The carbon balances were relatively low indicating a continuous carbon deposition on the catalysts.

The Ni particles size is substantially higher on Ni(a–e) which could explain the different catalytic behaviors. The

![Fig. 6](image-url) Ethanol conversion and products distribution over a Ni(n–w), b Ni(a–w), c Ni(n–e) and d Ni(a–e) as a function of time on stream brown filled downward triangle: ethanol conversion; o: mol H$_2$/mol C$_2$H$_5$OH; selectivity to blue filled upward triangle CO$_2$, red filled square CO, light green filled circle CH$_4$ and aqua blue filled diamond C$_2$H$_4$O. Initial ethanol concentration: 9.4%, reaction temperature: 650 °C, W/F = 49 g min/mol$_{C_2H_5OH}$
simultaneous presence of ethoxy groups in the solvent and acetate groups from Ni precursor during the thermal decomposition could also affect the morphology of Ni particles and change the Ni–CeO₂ interactions. The difference in size and shape of Ni particles with the different types of lattice planes exposed has been reported to have a significant effect on the ESR reaction rate and carbon deposition [46, 47]. Besides, it cannot be ruled out that the organic remains could be blocking the active sites for selective reactions. This hypothesis cannot be conclusively confirmed based on the available characterization data.

All catalysts were active in the reforming reaction of ethanol with a high initial conversion of ethanol under more severe conditions than those commonly used in literature (inlet ethanol concentration around 10% and 50 mg of catalyst without dilution to observe the catalyst deactivation within a short operation time). As it is known that the activity, selectivity and stability are strongly affected by the reaction conditions (temperature, feed composition, residence time, etc.) and the nature of catalyst. Recent catalytic results in this reaction over similar Ni catalysts are reported in Table 3. The differences observed with the present results could be explained from the different operating conditions and also the nature of catalyst. The carbon deposition rate could be an indicator of performance in similar operation conditions (see further).

### Table 3: Catalytic results in ESR over Ni-based catalysts

| Catalytic system | Operating conditions in ESR | X₃C₂H₅OH | Main products | Carbon deposition | References |
|------------------|-----------------------------|----------|--------------|------------------|------------|
| NiMAl (M: Mg, Ca, Zn) and NiMgN (N: La, Ce) With Ni loadings around 7 wt% (A) NiMgAl, (B) NiMgCe | Catalyst weight = 315 mg Reaction temperature = 600 °C Atmospheric pressure Nitrogen flow = 30 N mL/min H₂O:C₂H₅OH molar ratio = 3, 7 Flow rate = 0.075 mL/min W/F = 12.7 h⁻¹ | (A) 100% TOS: 8 h (B) From 100 to 60% TOS: 8 h | Selectivity (A) H₂: 78%, CO₂: 46%, CO: 27%, CH₄: 26%, CH₃CHO: 2% (B) H₂: 82%, CO₂: 58%, CO: 14%; CH₂: 13%, CH₃CHO: 15% | (A) 1583 mg C/gcat h (B) 41 mg C/gcat h Coke amount: NiMgAl ≫ NiZnAl > NiCaAl > NiMgLa > NiMgCe | [48] |
| Ni₁₀%MgO–CeO₂ Mg molar fraction in the support 10 mol % | Catalyst weight: 200 mg mixed with 1 mL quartz particles Reaction temperature = 400 °C H₂O:C₂H₅OH molar ratio = 8 W/F C₂H₅OH = 33 g h/mol | 100% TOS: 10 h | Selectivity H₂: 65% CO: 2% CO₂: 60% CH₄: 40% C₂H₆ + C₂H₅OH + CH₃CHO + CH₃C-OCH₃: 0.25% | 15 mg C/gcat h | [49] |
| Ni(8.2%)/MgAl₂O₄ | Catalyst weight = 500 mg Reaction temperature = 590 °C H₂O:C₂H₅OH molar ratio = 6 Inlet ethanol concentration = 3, 3.3% Flow rate = 1600 N mL/min | From 83 to 75% TOS = 4 h | Selectivity H₂: 69% CO₂/CO molar ratio = 3.7 | 28 mg C/gcat h | [50] |
| Ni–Ce–Mg–Al Ni(5.5%), Ce(10.5%) | Catalyst weight = 3 Reaction temperature = 540 °C H₂O:C₂H₅OH molar ratio = 6 Flow rate = 0.02 mL/min Special time = 22.04 kgcat h/kmol feed ethanol | ≈ 96% TOS: 10 h | Yield in mol/mol C₂H₅OH H₂: ~ 2.5 CO₂: ~ 0.5 CO: ~ 1 CH₂: < 0.3 | 16.5 mg C/gcat h | [51] |
| Ni (7%)/MgO–CeO₂ | Catalyst weight = 30 mg Reaction temperature = 600 °C H₂O:C₂H₅OH molar ratio = 6 (54 and 9% of water and ethanol in the inlet feed, respectively) Liquid feed flow = 1 mL/h to 15 mL/h GHSV = 4895 mL/gcat/h W/F = 0.735 g s/mL | ≈100% TOS = 18 h | Selectivity H₂: ~ 70% CO₂: ~ 20% CO: ~ 10% CH₂: < 5% | 13.9 mg C/gcat h | [52] |
Characterization of used catalysts in ethanol steam reforming

The presence of carbon deposits was detected in all the used catalysts. Characterizations of used catalysts were carried out with the aim to determine types and amounts of deposited carbon.

The diffraction patterns of used catalysts are shown in Fig. 7. Non-significant changes are observed in MgAl₂O₄ and CeO₂. The presence of Ni⁰ is clearly detected by the characteristic peak at 2θ = 51.8° indicating that the catalyst is kept activated under the reaction conditions. The patterns also reveal a peak at 2θ ≈ 43° which could be assigned to NiO which appears very evident in the pattern of Ni(a–e). This peak could be also assigned to MgO, due to the high similarity with the NiO XRD pattern. Since this peak does not appear in the XRD of reduced samples, Fig. 4, it could be inferred that it mainly corresponds to NiO. The presence of NiO can be explained if a fraction of metallic nickel is reoxidized under reforming conditions induced by the organic remains from preparation. The oxidation by H₂O cannot be discarded. The peak of NiO is weak in the case of Ni(n–e). The intense peak in Ni(a–e) catalyst suggests a higher amount of this phase and its presence contributes to a major deactivation. Hou et al. [53] have reported similar results in the methane autothermal reforming.

For all the used catalysts, a peak corresponding to graphitic carbon at 2θ = 26.4° is also observed. The intensity of this peak follows the order of Ni(a–e) > Ni(a–w) > Ni(n–w) ≈ Ni(n–e) in a reasonable agreement with TPO-TG results (see forward). This type of carbon has been reported on Ni catalysts supported on MgAl₂O₄ modified by CeO₂ or ZrO₂ [30, 54].

The carbon deposition on the used samples was also studied by TG-TPO analysis in air, Fig. 8. In all the cases, a mass loss was observed between 520 and 700 °C and it was attributed to the carbon combustion [55, 56]. The TPO profiles displayed one peak at a high burning temperature (between 613° and 645 °C, Table 4) suggesting a high extent of carbon deposit graphitization [57, 58] mainly filaments or carbon nanotubes. The carbon amounts are shown in Table 4. A great amount of carbon (105%) was determined on Ni(a–e) catalyst in agreement with its high particle size (XRD and H₂ chemisorption), its minor Ni-support interaction (TPR) and the low Ce³⁺/Ce⁴⁺ ratio (XPS). Comparing the carbon deposition rates expressed as mg C g⁻¹ cat h⁻¹ (Tables 3, 4), the observed rate over Ni(n–e) is markedly lower. This catalyst seems to be a promising system for ESR.

Taking into account the %C and Ni diameter, it is clear the importance of controlling the ensemble size to minimize carbon formation. The carbon amounts for Ni(a–w)

| Sample  | TPO-TG | C rate | EDX result |
|---------|--------|--------|------------|
|         | %C    | T_burning (°C) | (mg C g⁻¹ cat h⁻¹) | %C Zone A | %C Zone B |
| Ni(n–w) | 14    | 623    | 23         | 45       | n.d       |
| Ni(a–w) | 27    | 613    | 45         | 65       | 3.5       |
| Ni(n–e) | 3     | 645    | 5          | 57       | 5.3       |
| Ni(a–e) | 105   | 640    | 175        | 81       | 11.2      |

n.d not determined

Fig. 7 Diffraction patterns of catalysts after being used in ESR. (a) Ni(n–w); (b) Ni(a–w); (c) Ni(n–e) and (d) Ni(a–e), dark green open square: MgAl₂O₄, purple filled diamond: CeO₂, navy blue filled circle: NiO, *: Ni⁰ and black filled downward triangle: C

Fig. 8 Weight loss (inserted) and its TGA derivative for used catalysts in ethanol steam reforming. (a) Ni(n–w); (b) Ni(a–w); (c) Ni(n–e) and (d) Ni(a–e)

Table 4 Carbon amounts on used Ni/MgAl₂O₄-CeO₂ catalysts in ESR after 6 h run
and Ni(n–w) were 27 and 14%, respectively. The lowest carbon amount (3%) corresponded to Ni(n–e), although the Ni particle size was higher (28 nm) than the critical size (10 nm, [3]) and related probably to its reduction behavior and to the high Ce³⁺/Ce⁴⁺ value. Besides, this catalyst showed a very weak XRD peak at \(2\theta = 43^\circ\). These evidences could explain the major tolerance to carbon deposition.

The SEM micrographs and EDX results of the used catalysts are shown in Fig. 9 and Table 4, respectively. The results shown in Fig. 9 reveal that carbon deposition is clearly not homogeneous. Two different regions A and B are observed. In the A zone, an abundant filament formation was observed.

![Fig. 9 SEM micrographs of used catalysts in ESR. (a) Ni(n–w); (b) Ni(a–w); (c) Ni(n–e) and (d) Ni(a–e)](image)
detected in all the samples and Ni and Ce signals were also observed by EDX. It could be inferred that the metallic Ni is exposed at the tip of fibers and that the Ce could be interacting with a fraction of Ni particles more than with MgAl2O4. The amount of carbonaceous deposits is markedly lower in the B zone and a fraction of the support is coke free. The %C values, except for Ni(n–e), satisfactorily agree with the trend observed by TG-TPO and XRD, Table 4. The high %C value estimated for Ni(n–e) is due to the EDX analysis that was carried out on the A zone where the amount of filaments was abundant and it does not represent the whole carbon deposit.

Stability test

From a catalytic result analysis, Ni(n–e) and Ni(n–w) samples showed good catalytic performances in ESR. However, in spite of the good hydrogen selectivity, the system Ni(n–w) showed a high formation to CO, a moderate amount of carbon after 6 h in reaction, a low surface Ce3+/Ce4+ ratio (0.53), a lower reducibility and a high Ni particle size (39 nm). Although Ni(a–w) sample also showed good surface properties (Ce3+/Ce4+= 0.74 and dNi = 21 nm) similar to those of Ni(n–e), the extent of reduction was the lowest one (Table 1) and a loss of conversion was observed to 250 min of time on stream. The formation of different graphitic structures could also be affected by the presence of organic remains. This behavior is not clear enough at this moment. Wang and Lu have determined that carbon deposits on catalysts prepared from nitrate precursor were predominately formed by −C−C− graphitic structures, but inactive −CO−C− species were formed on catalysts prepared from organic precursor which leading to more severe deactivation [45]. Similar results were found over Ni/ZnAl2O4–CeO2 catalysts [44].

The Ni(n–e) catalyst was chosen to study the stability. This long-time run was carried out in the same reforming conditions indicated in the experimental part with an intermediate overnight stay at room temperature in He flow. An increase of temperature due to the endothermic effect of reaction (ΔHºfC2H4O = 206.4 kJ mol⁻¹, calculated using HSC Chemistry for Windows [41]) was observed when the feed was stopped. Then, the catalyst (50 mg) was diluted with SiC in a weight ratio of 1:1. Thus, the strong variation of temperature when the feed was stopped was avoided and the thermally induced changes in catalytic surface were minimized. Ni(n–e) catalyst operated without problems during 40 h. In Fig. 10, the ethanol conversion and products distribution are shown. The catalytic results reveal a very good behavior in ESR with an increase in the H2 selectivity (78%) at the expense of decreasing the selectivity of C2H4O and the CO/CO2 molar ratio. The dilution improved the isothermal reactor condition and it could be affecting the reforming/decomposition of acetaldehyde and water gas shift reactions, known contributions during the whole process. No sign of deactivation was observed, but carbon was determined by TPO-TG. The maximum combustion temperature was 690 °C and the accumulation rate of C was 17.7 mg C g⁻¹cat h⁻¹. The coke formation is still important and may lead to a considerable deactivation in higher long-term operation. Regeneration strategies should be studied and optimized taking into account whether the reforming reactor will be used for mobile or stationary applications.

Conclusions

Ni catalysts supported over MgAl2O4–CeO2 were prepared using different impregnation media (ethanol or water) and Ni precursors (nitrate or acetate). The use of an alcoholic solution did not affect the specific surface area, but promoted the NiO formation reducible at lower temperature affecting the Ni-support interactions and the Ce3+/Ce4+ initial ratios. All the catalysts were highly active in the reforming reaction of ethanol with a high initial conversion of ethanol under more severe conditions than those commonly used in literature. The catalysts obtained from Ni acetate suffered deactivation from the beginning of reaction regardless of the solvent used in the impregnation step. The Ni(n–w) system showed high selectivity to H2, the highest CO formation and an amount of deposited carbon of 14% after 6 h in reaction. However, the system Ni(n–e) was better in terms of resistance to carbon deposition with a similar selectivity to H2. This behavior was associated with the high Ce3+/Ce4+ initial ratio and an adequate Ni-support interaction. These
properties of Ni(n−e) increased the tolerance to carbon despite the Ni particles being relatively large.

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