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Abstract: The catalytic behavior of nanostructured catalysts based on nickel, cobalt and cerium oxide in ethanol steam reforming (ESR) was studied to investigate the effect of the nature of the metal, their combination and the method of preparation. Mono- and bimetallic catalysts with equal metal content (M:Ce = 4:6, M = Ni, Co, or Ni/Co=1) were prepared by two methods, impregnation and coprecipitation within reverse microemulsions, characterized by SBET, XRD, TPO and HRTEM, and tested for ESR at 500°C. The nickel catalyst prepared from microemulsions exhibited the best performance in terms of catalytic activity (close to 100% conversion), stability and hydrogen yield. Al the other catalysts deactivated at different paces due to formation of carbon deposits. The oxidative regeneration treatment of the deactivated catalysts recovered the initial activity of the impregnated catalysts but increased markedly those of catalysts from microemulsions. Thus, the catalytic behavior in ESR of the (Ni, Co)-Ce-O system depends on the preparation method, its composition and catalyst history.

Manuscript CATTOD-D-17-00073 Authors' replies to reviewers' comments:

Reviewer #1: In this work, authors tested the performance of nano-catalysts containing Ni, Co and Ce for ethanol steam reforming. This work is worthy of publication after revision as follows:

We thank the reviewer for his/her positive overall assessment

1) Please improve the usage of English.

Usage of English has been revised throughout

2) Introduction: Ethanol is a very good additive for liquid transportation fuel. Authors should explain the rationale for rather converting it to hydrogen.

The use of ethanol as fuel additive (in internal combustion engines) is out of the scope of this manuscript. Nevertheless we have included a sentence to address this matter in the introduction: Though it is a very good additive for liquid transportation fuel, the low energy efficiency of the internal combustion engines as compared to that fuel cells, makes preferable its transformation into hydrogen for its use in fuel cells."

The authors' review of the literature is incomplete. Many useful reviews on ethanol steam reforming and past works on Ni and Co catalysts are missing!

Our cited ref. [3] includes and discusses most of the reviews on ethanol steam reforming prior to 2012 (Benito et al, 2005; Haryanto et al, 2005; Vaidya et al, 2006; Ni et al, 2007; Subramani and Song, 2007; Bshish et al. 2011; Bin et al, 2012) that were not mentioned separately to avoid duplication, and more recent reviews were referred to in the discussion (refs. [20] and [21]). Nevertheless, following reviewer's comment we have added four additional recent reviews (now [10,11,14,15]) and moved the previous citations of reviews [20] and [21] to the initial set of references (now [12, 13]) for the convenience of the readers.

Eqs. 3 to 13 are well documented in literature. Unless authors link their results to these, any repetition is superfluous.

We agree with the referee but they are used for discussing the catalytic performances and their evolution in Section 3. Nevertheless, we have re-written and simplified the whole paragraph in order to show the reaction network involved and the positive or deleterious effect of each reaction on hydrogen yield.

3) Section 2.4 is titled oxidation! No accuracy in measuring temperature and flow is stated. What was system pressure? Did authors check for error in measurements and consistency of results? Section 2.4 title has been corrected. Accuracy of temperature or flow measurements is guaranteed by the automatized equipment Microactivity Reference we used, which usage among catalytic laboratories is widespread, so we did not mention it. Nevertheless, following reviewer's

comments we have extended the description of the tests indicating accuracy, reaction pressure, error and consistency of measurements in the Experimental section

4) Fig. 3: Any comparison with past works on ESR for impregnated Ni and Co catalysts?

The catalytic performances of Ni and Co catalysts for ESR are extremely dependent on reaction conditions such as temperature, residence time, feed composition and ethanol-to-steam ratio; this implies that, for having a meaningful comparison with other catalysts, their corresponding catalytic tests should be conducted at practically equal reaction conditions. The dispersion of the tested reaction conditions reported in literature did not allow us making useful comparisons.

5) Section 3.3 should include a comparison with the results shown in section 3.2.

Such a comparison of the results of both sections constitutes the content of the discussion in Section 3.5.

6) Conclusions: Please highlight the best conditions for producing hydrogen.

As the objective of the work was comparison of catalytic performances we used a single set of fixed reaction conditions (feed composition, W/F, reaction temperature and pressure). So, we cannot make any conclusion on the best conditions for producing hydrogen, but only on which is the best performing catalyst among those we have investigated.

Reviewer #2: The manuscript "Ethanol steam reforming on nanostructured catalysts of Ni, Co and CeO2: influence of synthesis method on activity, deactivation and regenerability" was reviewed and some issues must be addressed before it is suitable for publication in the journal.

Authors described the behavior of Ni, Co and Ni-Co catalysts before and after the ethanol steam reforming, based on different methods of preparation. They also evaluated the catalysts regeneration process. Catalysts were characterized by SBET, XRD, TPO and HRTEM. Although the authors have a reaction dataset for a good discussion, there is not a good dataset of catalysts characterization before the reaction. Then, this is not possible to understand the behavior of the some catalysts, which compromise the quality of this work.

Certainly, the characterization of the fresh catalysts could be more substantiated. It is however our main aim to get general characteristics of the systems which we get from the results reported in Table 1 and figures 1 and 2, which allowed us to describe most relevant structural features of the as-prepared catalysts (crystalline phases, base metal atoms insertion in ceria network, textural properties). The exploration of other important properties like the analysis of the metal dispersion was discarded because of the nature of the systems which imposes important difficulties for such analysis (chemisorption procedures are not of help due to difficulties to discard adsorption from the support itself; direct analysis by techniques like TEM is not able to characterize dispersed metals due to the absence of contrast between components). It must be taken into account that our main aim is to study the differences between nickel and cobalt (and/or

bimetallic nickel-cobalt) in terms of their most relevant ESR catalytic properties and how different catalyst configurations (as attained by changing the preparation method) could affect to such properties. In any case, it can be noted we have extended the characterization of used systems by including new analysis by EDX in order to substantiate the discussion about activity/deactivation characteristics of the catalysts.

Abstract: authors said that the effect of the history of catalysts was observed, however it was not evaluated in the manuscript.

The content of the manuscript describes how the catalytic performance of each catalyst composition varies depending on the pretreatment, time on stream in ESR, reactivation treatment and again on time on stream of the regenerated sample, i.e., on the history of the sample, and discusses all those effects. That is what we meant in the abstract.

Is it possible to change the references 23 and 24 for indexed manuscripts?

We are sorry that the content of these references, corresponding to oral communications to a national congress, have not been yet published in indexed journal. Nevertheless, a new sentence describing the main features of their content has been inserted in the last paragraph of the introduction for convenience of the readers.

Selectivity is commented in the results, but the equation of selectivity was not presented.

We thank the reviewer to point out this. Equations of selectivity for carbon containing products and for hydrogen have been included in Experimental.

How many times were the experimental reactions repeated? Are the Results obtained with Ni-Co-CeO2 (M) reproducible?

Catalytic tests were duplicated for all the impregnated catalysts, while those of catalysts prepared by microemulsion were repeated three times due to its unexpected behavior. Tests for each sample were reproducible within experimental error. A sentence stating this has been added to Experimental.

The effect of metal composition was not discussed.

We regret we may not understand this reviewer's comment as section 3.2 shows the effect of metal composition in impregnated catalysts and Section 3.3 the effect in impregnated catalysts, and the different effect of metal composition depending on the preparation method is discussed in Section 3.5.

The preparation of cerium oxide support by impregnation should be presented with more details. What were the quantities of compounds used ((NH4)2Ce(NO3)6 6H2O) and urea) and what about solutions concentration? Was calcination of cerium under oxidant atmosphere? What was the heating rate?

This ceria support was prepared by the method described by Kundakovic and Flytzani-Stephanopoulos [J. Catal.179 (1998) 203-221], which reference has been now added for providing all the relevant details.

The procedure of reverse microemulsion needs to be better explained. Two solutions were prepared: the first with organic/cosurfactant/surfactant/aqueous; the second had organic/cosurfactant/surfactant/base. Is that correct? What was the quantity of each solution used?

The procedure is detailed in the cited reference [29]. Both microemulsions are of the same characteristics in terms of proportion of components. The only change is the components of the aqueous solution in each case: a solution of the metal precursor salts in the first one and a solution of the TMAH base in the second. This has been extended in the corresponding section of Experimental in order to clear this point.

Catalysts were not well characterized before the reaction. Then, it is not possible to understand what are the structural and morphological differences between the active phases of the catalysts. It would be important to understand the behavior of the catalysts during the reaction.

Certainly most relevant characterization of this type of systems is the one which is made under reaction conditions. Furthermore, characterization should point to analyze details taking place at the interfaces between active metallic forms of nickel or cobalt and the ceria support in each case, which is in any case a very complicated task. We appreciate the comment by the reviewer but however consider that getting such details falls somewhat out of the scope of present manuscript while work is in progress to cover this issue and as it will be considered for a future contribution.

The authors evaluated the catalysts after the reaction in relation to deactivation and regeneration. It were observed some interesting and unexpected results. For example, the unexpected effect of regeneration for Ni-Co-Ce (M) catalyst needs to be better studied and explained. What induced this behavior? Could it be the preparation method? If yes, it is necessary to be clarified.

Our results show clearly that this effect depends on the preparation method, which determines the dispersion of the active metal and its interaction with the support (see reply to next comment). Microemulsion coprecipitation can lead to a higher insertion of the active metals in the network of the ceria support, as shown by the absence of segregated Ni- or Co-containing phases in the bimetallic system prepared by microemulsion, which means that, at variance of NiCo-I, there is probably a random surface distribution of both metal atoms. Further than such insertion of the metals in the fluorite ceria lattice, product distribution over the fresh NiCo-M sample points to a majority of Co atoms on its surface in relative terms while over the regenerated sample, product distribution is more similar to that of Ni-M, which points out to a majority of Ni atoms on the surface. Our hypothesis is that the effect of reaction followed by oxidative regeneration importantly affects the evolution of the metals in this system while the

effect of a localized heating at the surface leads finally to Ni atoms “emerged” from the network, thus changing the catalytic behavior. Additional sentences have been added to Discussion to better describe our hypothesis in this sense.

What was the differences observed in the active phase obtained by the different preparation methods?

In principle, the active phase must be related in any case to the combination between metallic states of either nickel or cobalt and the underlying ceria support (more or less doped with nickel or cobalt heterocations), as also evidenced by XRD of the used samples. It is the physicochemical properties of such interfaces which must determine the ESR catalytic properties of the systems. The obtained results reveal in such sense that the generation of more intimate contacts between nickel and ceria in the system prepared by microemulsion can produce very active catalysts for the process. The presence of cobalt, further than showing some particular catalytic properties itself, generally affects such interaction in a detrimental way and the same apparently occurs when using impregnation as preparation method, most likely because of higher difficulties to establish most active interfacial configurations in such case.

Another question: it is important to observe that the hydrocarbons and alcohols steam reforming reactions occur on metallic catalysts and the active phase is the metal and not the metal oxide. Then, before the reactions, the catalysts are reduced to metallic phase, normally using hydrogen as reduction agent. In this work, the authors did not use this procedure and the catalysts were activated over an oxidant atmosphere. However, it is possible to the metal reduction to occur during the reaction, but it is important that the authors explain it clearly. Why did they decide to do it this way?

The pretreatment in pure hydrogen at high relatively high temperature may cause metal sintering, reducing metal dispersion. However a reduction by a softer reductant (as ethanol, for example, or, in fact the ESR reactant mixture) may allow keeping the initial cation dispersion in the oxidic precursor. As the activity of catalysts containing ceria is strongly dependent on the number of vacancies in its network, which in turn are dependent not only on the preparation method but also on its contact with environment and its storage. For these reasons we used oxidative activation to homogenize the initial oxidation state of ceria in the catalysts, and the reduction of the active metal component takes place by its interaction with the reaction medium. This has been observed in other metallic systems: Zeolite-supported nanosilver catalysts used for CO oxidation at low temperatures show much higher activity if they are pretreated consecutively first with oxygen and then with reduced with hydrogen than if they are just reduced in hydrogen [E. Kolobova et al., Fuel 188 (2017) 121-131]. A new paragraph and this reference has been added in Section 3.5.

It is weird that in the first few minutes of reaction the conversion has been 100% or near 100%. If this occur, the activation of catalysts with hydrogen is unnecessary, and this is an important result.

Regardless the catalyst activation procedure, total conversion could result from a variety of reaction conditions such as an excess of residence time for the reaction temperature used or a temperature too high for a given residence time. So, this result “per se” does not mean that activation with hydrogen is unnecessary.

Let us point out that our test conditions were selected to obtain an initial conversion as high as possible, but without reaching full conversion, in order to be able to observe big variations if they would occur.

Then, what is the active phase in the first minutes of reaction? Ni2+, Ni0, Co2+, Co0 ? and what is the mechanism of reaction?

Prior to reaction Ni and Co are in the 2+ state as shown by the fresh catalysts characterization, and the oxidation pretreatment excludes their reduction before contacting the reaction medium. As the active centers must basically correspond to the metallic state (as confirmed by used catalysts characterization), one may infer that both cations are reduced by the ethanol in the reactant mixture during the initial moments of their contact.

As our first product analysis is made after at least 15-30 minutes of the initial contact, the product distribution corresponds to catalytic ESR. This reasoning has been incorporated to discussion in Section 3.5.

Lines 207-211: This text is confuse, because when the catalyst contains only Ni or Co, the lattice parameter a of ceria increased, and it was due to reduced state of cerium in network. But, when the catalyst contains Ni and Co the lattice parameter a decreased and it was attributed to cerium oxidation.

The insertion of divalent cations in the network of ceria is typically proposed to occur through substitutional exchange with cerium cations. Such exchange requires the formation of oxygen vacancies for keeping charge neutrality in the lattice. On the whole, and despite the fact that oxygen vacancy formation can lead to a certain expansion of the lattice as a consequence of increased repulsion between cations, the lower ionic radius of the divalent (or trivalent) nickel or cobalt cations with respect to Ce4+ produces a lattice contraction upon mentioned substitutional incorporation. On the other hand, the reduction of Ce4+ to Ce3+ also has to be accompanied by oxygen vacancy formation while the ionic radius becomes increased and both effects lead to lattice expansion. Interpretation of the evolution of lattice parameters is made on these bases.

This broader description has been added to the corresponding paragraph in the text body

When the catalysts-I were regenerated, they showed a different trend in contrast with the fresh ones. This result needs to be more explored. What is happening?

The overall trend of deactivation for each sample was similar for the fresh and the regenerated state of each catalyst. Nevertheless, as mentioned above, we believe that main catalytic difference as a function of the preparation method is related to the fact that the microemulsion method may give rise to more intimate contact between nickel and the support. In addition to achieving most likely lower degree of metal dispersion through impregnation, the interfacial structure could also be different in each case. On the whole, all these aspects are believed to affect the differences observed

The catalyst Ni-Ce (M) was better than the other catalysts. Why did it happen? What was responsible for this behavior? Which was the difference observed in the active phase of this catalyst when compared with the others?

We believe that the interaction of components nickel and ceria becomes maximized in such case. First, the microemulsion preparation allows a more intimate contact between components. Second, the absence of cobalt allows maximizing mentioned interactions.

Acetaldehyde was not observed in the reaction with Ni-Ce (M) catalyst?

Formation of acetaldehyde was observed on each catalyst, but its yield on Ni-Ce (M) catalyst was so small it can be considered negligible. This implies that reforming of acetaldehyde on is catalysts is faster that its formation from ethanol.

Ni-Ce (M) catalyst not showed formation of acetone and ethylene.
Co-Ce (M) catalyst was the responsible by the formation of acetone and ethylene.
And, Ni-Co-Ce (M) showed higher formation of them.
Why? What is the explanation?

Nickel is much more active than cobalt to activate ethanol, which is the first step in the overall process. Thus, the higher formation of acetone and ethylene on the fresh NiCo-M catalysts compared to that of fresh Co-M could be due to the easier activation of ethanol on nickel while the product distribution is controlled by cobalt.

"Emergence" of the active metal atoms can be evaluated within situ techniques, as XAS, XPD, and it must be done before publishing this manuscript.

We appreciate the reviewer‘s suggestion but, as mentioned above, completing the work in the mentioned sense falls somewhat out of the scope of the present work and will in any case be object of another paper under preparation. Nevertheless, we have added EDX analysis of the regenerated NiCo-M sample after use in ESR that shows a surface enrichment in Ni, which is coherent with our hypothesis.

The explanation presented in lines 332-336 is only speculative.

We agree we do not have sufficient evidences for mentioned proposal but we are just posing such explanation as a possible hypothesis. The whole paragraph of explanation has been re-phrased to underline the hypothetical nature of our interpretation.

LIST OF THE MODIFICATIONS MADE

(all these changes are highlighted in red in the revised manuscript)

Usage of English has been revised throughout

Introduction:

New sentences considering the use of ethanol as fuel additive are included (l.54-56)

Paragraphs concerning the reaction network have been simplified, re-ordered and re-written (l. 62-83)

Four new references to ESR reviews have been added.

Description of preliminary results has been expanded (l.113-115)

Experimental:

A new reference and more details are included in catalyst preparation, and EDX details have been added.

Details of temperature and flow precision, reproducibility of results, carbon balance, and the formulae for selectivity of products have been added

Section 3.1

Discussion on interpretation of cell parameter changes has been expanded (l.218-224)

Section 3.4

Discussion of XRD results have been partially re-phrased to give additional details (l.268-278)

New data from EDX have been added in New Table 2, and a paragraph discussing them has been added (l.309-317)

Section 3.5

New paragraphs describing the choice of activation treatment (l.319-338) and on the effect of preparation method and metal composition (l.339-348) have been added.

Discussion on the effect of the reaction –regeneration cycle on NiCo-M catalyst have been re-written (l.377-391)

Conclusions

A new paragraph has been added (l.425-428)

Acknowledgement

A new line has been added

References

7 new references have been added and the numbering corrected accordingly.

Table 2 has been added

HIGHLIGHTS

Synthesis by reverse microemulsions makes more efficient catalysts than impregnation

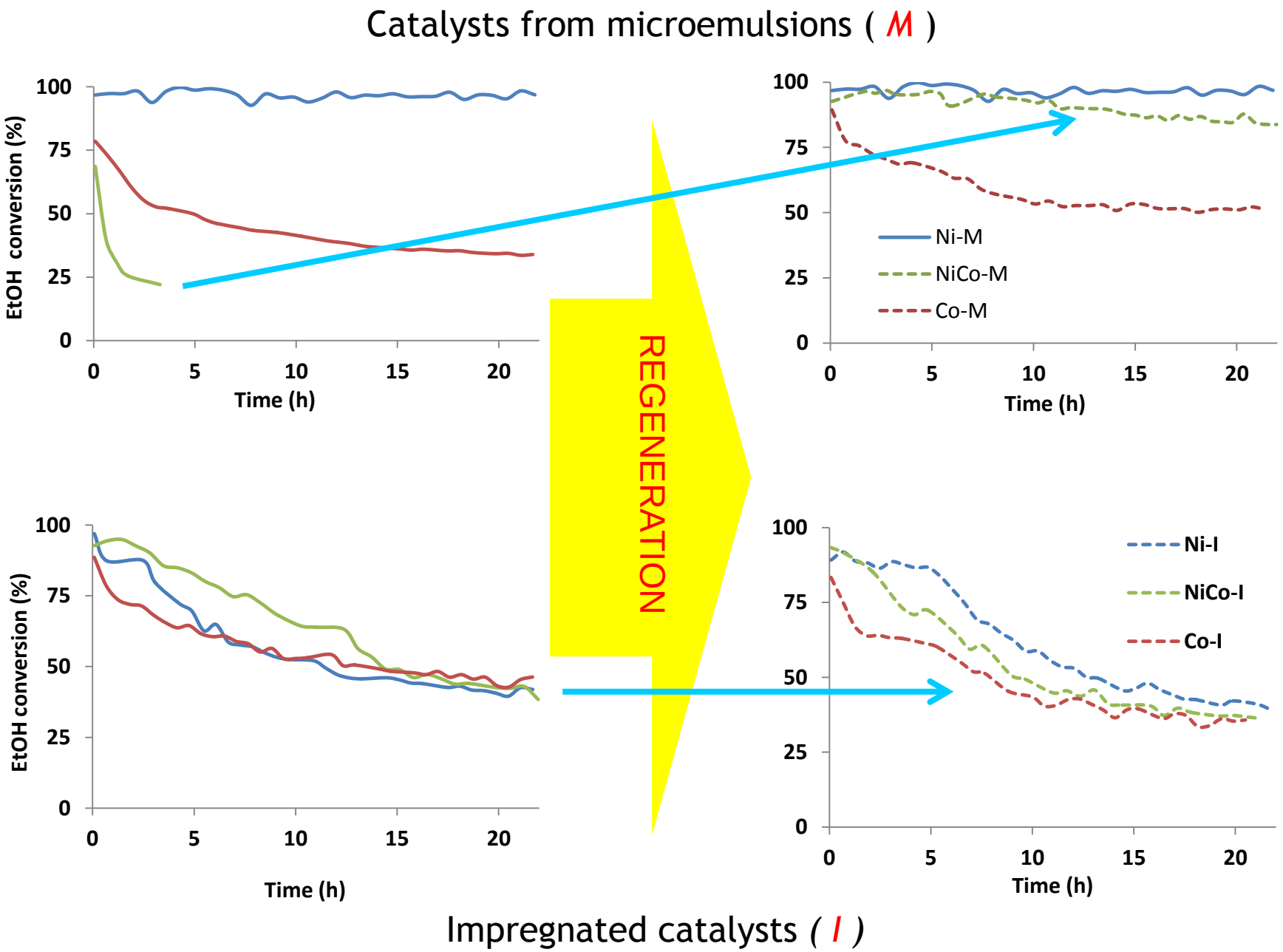
Catalytic activity and stability depend on the metal and the synthesis method

Deactivated catalysts activity can regenerated by oxidative treatment

Synthesis method influences nature of deposited carbon and catalyst regenerability

Unexpected effect of regeneration found for bimetallic NiCo-CeO_2 catalyst

*Graphical Abstract (for review)



Ethanol steam reforming on nanostructured catalysts of Ni, Co and CeO_2: Influence of synthesis method on activity, deactivation and regenerability

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Abstracts

The catalytic behavior of nanostructured catalysts based on nickel, cobalt and cerium oxide in ethanol steam reforming (ESR) was studied to investigate the effect of the nature of the metal, their combination and the method of preparation. Mono- and bimetallic catalysts with equal metal content (M:Ce = 4:6, M = Ni, Co, or Ni/Co=1) were prepared by two methods, impregnation and coprecipitation within reverse microemulsions, characterized by S_{BET}, XRD, TPO and HRTEM, and tested for ESR at 500°C. The nickel catalyst prepared from microemulsions exhibited the best performance in terms of catalytic activity (close to 100% conversion), stability and hydrogen yield. Al the other catalysts deactivated at different paces due to formation of carbon deposits. The oxidative regeneration treatment of the deactivated catalysts recovered the initial activity of the impregnated catalysts but increased markedly those of catalysts from microemulsions. Thus, the catalytic behavior in ESR of the (Ni, Co)-Ce-O system depends on the preparation method, its composition and the catalyst history.

Keywords: Ethanol steam reforming, hydrogen production, nickel, cobalt, bimetallic catalysts, reverse microemulsions, catalyst deactivation, catalyst regeneration

1. Introduction

The environmental impact of the massive use of fossil fuels on the emission of greenhouse gases requires the restructuring of existing energy systems, a major technological development of new alternatives and the use of new, cleaner energy carriers. In this framework, hydrogen can play a crucial role as a clean fuel (in combustion engines and fuel cells) in addition to its use as raw material in the Chemical Industry [1]. Hydrogen is mainly consumed in oil refining processes,

ammonia and methanol synthesis and employed as fuel only in spaceships and in some vehicle prototypes. Promising technologies like fuel cells allow converting the chemical energy contained in the H-H bond in electric energy through the clean combustion of H_2 in presence of an oxidant. However, to extend these promising and clean technologies to a large scale, some issues linked with hydrogen physical and chemical properties must be considered. Hydrogen is a very light gas, non toxic, colourless, but easily flammable in air in the range of concentrations 4-75% by volume. It has a low energy density on a volume basis (gasoline density is 0.7 kg/L whilst H_2 density is 0.03, 0.06 and 0.07 kg/L at 350 atm, 700 atm and liquefied (20 K), respectively). So, it is clear that hydrogen economy needs safe and cheap storage systems or, alternatively, technologies to produce it *in situ* (or on board for mobile uses) from easily transportable liquids. On the other hand, currently hydrogen is mostly produced from fossil fuels in processes like methane steam reforming or coal gasification; this means that, though hydrogen combustion is clean, the overall cycle (hydrogen production - hydrogen combustion) involves no reduction of CO_2 emissions. Thus, the reduction of the environmental impact thanks to its use as energy vector requires hydrogen to be produced from renewable resources. This makes biomass a promising resource for generating hydrogen through an easily scalable production process, because it is renewable and continuously available [2]. In this frame, ethanol can play an important role [3]. Ethanol, when obtained by biomass fermentation, is a renewable resource and about 95% of ethanol produced in the world comes from agricultural products, mainly from edible plants like sugarcane, sugar beet and corn [4, 5]. It has a high hydrogen-to-carbon ratio (H/C = 3) and high hydrogen content per unit of volume in the liquid state. Ethanol is a very good additive for liquid transportation fuel, the lower energy efficiency of the internal combustion engines as compared to that of fuel cells, makes preferable its transformation into hydrogen for its use in fuel cells.

Among the various catalytic pathways that can be used to produce hydrogen from ethanol, ethanol steam reforming (ESR) is an efficient and cost-effective technology [6] that gives the highest hydrogen production per ethanol molecule, as it extracts hydrogen not only from ethanol but also from water:

$$CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \qquad \Delta H^\circ_{298} = 173.4 \text{ kJ/mol} \qquad (1)$$

However, in spite of the apparent simplicity of its stoichiometry, ethanol reforming follows a complex reactive scheme which, in addition to H_2 and CO_2, can give rise to a large number of by-products such as CO, ethylene, acetaldehyde and CH_4 among others, due to other simultaneous reactions which negatively affect the selectivity to hydrogen [3, 7]. Thus, ethanol, as an alcohol, can go through the dehydrogenation to acetaldehyde (2) and dehydration to ethylene (3) even at low temperatures:

$C_2H_5OH \rightarrow CH_3CHO + H_2$ $\Delta H°_{298} = 68$ kJ/mol (2)

$C_2H_5OH \rightarrow C_2H_4 + H_2O$ $\Delta H°_{298} = 45$ kJ/mol (3)

While ethylene represents the main precursor of coke, acetaldehyde plays an important role in the pathways leading to hydrogen formation through reforming:

$CH_3CHO + 3H_2O \rightarrow 2CO_2 + 5H_2$ $\Delta H°_{298} = 105$ kJ/mol (4)

$CH_3CHO + H_2O \rightarrow 2CO + 3H_2$ $\Delta H°_{298} = 187$ kJ/mol (5)

CO formation by this latter reaction leads to lower hydrogen production from ethanol:

$C_2H_5OH + H_2O \rightarrow 2CO + 4H_2$ $\Delta H°_{298} = 256$ kJ/mol (6)

though additional hydrogen can be recovered via water gas shift (WGS):

$CO + H_2O \rightarrow CO_2 + H_2$ $\Delta H°_{298} = -41$ kJ/mol (7)

In addition, acetaldehyde decomposition to methane (7) or condensation to acetone (8), and methanation (9):

$CH_3CHO \rightarrow CO + CH_4$ $\Delta H°_{298} = -19$ kJ/mol (7)

$2CH_3CHO \rightarrow CH_3COCH_3 + CO + H_2$ $\Delta H°_{298} = 5$ kJ/mol (8)

$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ $\Delta H°_{298} = -165$ kJ/mol (9)

decrease the hydrogen yield, what must be avoided by the catalysts. Furthermore, polymerization of ethylene and polycondensation of acetone can lead to coke formation, causing catalyst deactivation. This complexity requires the catalysts to be polyfunctional to direct the process to a maximum hydrogen yield and selectivity, as they have to break the C-C bond at relatively low temperatures, to keep low the production of CO, to resist the deactivation caused by coke deposition, to be stable in operative conditions and to limit the hydrogenation of the products. In addition, their practical application requires that catalysts may be regenerated after the almost unavoidable catalyst deactivation.

Many catalytic systems are active for ESR [3, 8-15], based on both noble metals (Rh, Pt and Pd) [8, 9] and on transition metals (Ni, Co, Cu-Ni) [14,15]. The lower cost of the latter makes them an attractive alternative as Ni and Co show catalytic performance and stability comparable with those of the best noble metal systems. [16]. Bimetallic catalysts have the main goal to create a synergy of positive effects of two non-noble metals. Many combinations can be found in literature, like Fe-Co [17], Co-Cu [18] or Ni-Cu [19], supported on a variety of supports.

The role of the support is fundamental. Acid solids like Al_2O_3 promote the dehydration of ethanol to ethylene, the most common coke precursor [20, 21], while basic supports like MgO are way more resistant to coke deposition, but generate more oxygenate products [22]. Redox supports like ZrO_2 and CeO_2 have a high oxygen storage capability, high oxygen mobility and are active in the WGS reaction [23-25]. On the other hand, sintering of metal nanoparticles also causes irreversible catalyst

deactivation. This phenomenon is due mainly to a local and rapid temperature increase and in this process the role of the support is also significant. Acid supports have been reported to promote in particular Ni sintering, while redox supports, and in particular CeO_2, give an increased thermal stability to the metallic phase [12].

The preparation method influences the textural properties, such as specific area, structural features like crystalline phases, and also activity, stability and life of the catalysts. Previous studies of copper-ceria catalysts for preferential CO oxidation (PROX) have found that support surfaces with different nature and interaction with the active phase can be produced by impregnation of ceria and by coprecipitation of the two components within reverse microemulsions, method that allows obtaining nanostructured systems with high structural, morphological and chemical homogeneity [26].

The preliminary results obtained for ESR with Ni-Ce-O and Co-Ce-O catalysts prepared in reverse microemulsions were promising [27, 28], showing that both systems were active with maximum activity for atomic ratio Ce/M = 6/4 for both systems (M = Ni, Co), and while Ni-Ce-O catalysts were more active, Co-Ce-O catalysts showed a very low formation of CO. This motivated the present study on the combination of both active metals (Ni and Co) with cerium oxide, as bimetallic Ni-Co may combine the ability of nickel to break C-C bond with the cobalt resistance to coke deposits [17-19]. We have investigated the influence of the preparation method on the activity, hydrogen yield, catalyst deactivation and regeneration of the bimetallic catalysts Ni-Co on ceria and compared them with their monometallic counterparts, and with their homologues prepared by wet impregnation. It has been found that the effect of both metals is not additive, and that the catalytic behavior strongly depends on the metal composition, the method of preparation and the history of the catalyst.

2. Experimental

2.1 Catalysts preparation

Two series of catalysts with equal chemical compositions (atomic ratio Ce/M = 6/4; M = Ni, Co or Ni-Co in a ratio Ni/Co = 1) were prepared using two different methods: wet impregnation *(I)* and coprecipitation in reverse microemulsions *(M)* [29]. In the first case, cerium oxide was chosen as a support for the active phase of nickel oxide and cobalt oxide. In the second, cerium is present in the structure of the mixed oxide system with the two non-noble metals.

A) *Impregnation (I)*

$Ni(NO_3)_2{\cdot}6H_2O$ 99% and $Co(NO_3)_2{\cdot}6\ H_2O$ 99% (Sigma-Aldrich) were used as metal precursors. Cerium oxide support was prepared mixing aqueous solutions of $(NH_4)_2Ce(NO_3)_6{\cdot}6H_2O$ and urea at 100°C following the method described by Kundakovic and M. Flytzani-Stephanopoulos [30]. The precipitate was then filtered, washed with deionized water and dried overnight at 110 °C. The solid

136 was then ground and calcined in a tubular oven at 500 °C. Metals were incorporated by wet
137 impregnation of calcined CeO_2 with an aqueous solution of the metallic precursor in the proper
138 concentration in order to obtain the desired loading in a flask under inert atmosphere of nitrogen, to
139 avoid CeO_2 carbonation. The suspension was kept gently stirring overnight. The exceeding water
140 was removed and ultimately the samples were calcined at 500 °C for 4 h.
141 B) *Reverse microemulsion (M)*
142 The reverse microemulsion was prepared with n-heptane 99% as the organic phase, 1-hexanol 98%
143 as cosurfactant, and Triton X-100 Sigma Pro as non-ionic surface surfactant (all from Sigma-
144 Aldrich). $Ce(NO_3)_3{\cdot}6H_2O$ 99% (Adrich Chemistry), $Ni(NO_3)_2{\cdot}6H_2O$ 99% (Sigma Aldrich) and
145 $Co(NO_3)_2{\cdot}6\ H_2O$ 99% (Assay) were used as metal precursors and $(CH_3)_4N(OH)$ (TMHA) 25% w/w
146 (Alfa Aesar) as base. The volume ratio organic/cosurfactant/surfactant/aqueous was 66/14/13/7 in all
147 the preparations.
148 Organic phase, cosurfactant and surfactant were mixed with the aqueous solutions of the metals salts
149 to produce the saline microemulsion. Similarly, basic microemulsion with the same proportion of
150 components was prepared by replacing the aqueous solution of the metal salts with the TMAH one.
151 Both microemulsions were stirred at 100 rpm for 1 h. Then, basic microemulsion was added slowly
152 to the saline microemulsion to avoid abrupt changes in the pH. The resulting mixture was stirred at
153 100 rpm for 24 h (oxides precipitation occurred in this time). After centrifugation and washing with
154 methanol, the precipitate was dried overnight at 120ºC and calcined in air at 500°C for 2 h.
155 Hereinafter catalysts are denoted with the component metal elements, followed by an *"I"* (if they
156 were prepared by impregnation) or an *"M"* (if prepared by microemulsion).
157 2.3 Catalyst characterization
158 The specific surface area (S_{BET}) and pore volume were measured by the analysis of N_2 adsorption
159 isotherms at -196 ºC by a Micromeritrics ASAP 2010 equipment. X-ray diffractograms were
160 obtained on a Seifert XRD 3000P diffractometer using nickel-filtered Cu Kα radiation operating at
161 40 kV and 40 mA, using a 0.02^o step size and 2 s counting time per point. Analysis of the diffraction
162 peaks was done with the software ANALYZE Rayflex Version 2.293. Temperature programmed
163 oxidation (TPO) experiments were conducted in a quartz reactor, using a flow of 5% O_2 in He and a
164 heating rate of 10 ºC/min, and analyzing the effluent gases by means of a quadrupole mass
165 spectrometer Pfeiffer Vacuum OmniStar™. High resolution transmission electron microscopy
166 (HRTEM) tests were made at a TEM/STEM instrument JEOL 2100F operating at 200 kV with a
167 Field Emission Gun (point resolution: 0.19 nm), which has an attached energy-dispersive X-ray

spectroscopy (EDX) detector INCA x-sight (Oxford Instruments) for semiquantitative chemical analysis.

2.4 Catalytic tests

Catalysts were tested for ESR at 500 ºC and near atmospheric pressure, with a feed of molar composition water:ethanol:He = 18.4:3.1:78.5 and W/F = 0.12 g_{cat}.h/mol ethanol, in a stainless steel, fixed bed tubular reactor placed in an equipment Microactivity Reference model MAXXXM3 (PID Eng & Tech) which allows controlling the reaction temperature within ± 1ºC thanks to a coaxial thermocouple placed in the center of the catalytic bed. Reactants flows were controlled by mass flow controller with a precision of ± 1% of full scale. Prior to the reaction, fresh (unused) catalyst samples were activated under flow of 10% O_2 diluted in He, at 650 °C for 1 h. Catalytic stability tests were conducted at 500°C for 22 hours. After the first run, if the catalyst suffered a deactivation, it was cooled down and flushed under inert flow, and then reactivated using the same procedure of the initial activation, i.e., heating up to 650 ºC at 10 ºC/min and keeping this temperature for 1 h, under a flow of 10% O_2 in He. Then, after cooling down to 500 ºC in inert flow, a second run was conducted with the regenerated samples under the same conditions of the first run. Catalytic tests were duplicated for all the impregnated catalysts, while those of catalysts prepared by microemulsion samples were repeated three times due to its unexpected behavior. Tests for each sample were reproducible within experimental error. Carbon balance in the reported data were within 100 ± 5%

Reactants and products were analyzed on line by GC on a Varian Star 3400 CX instrument equipped with two columns, one filled with molecular sieve (for H_2, CO and CH_4) and other with Porapak Q (for the rest of compounds), and a thermal conductivity detector.

Yield (Y_i) and selectivity (S_i) of carbon-containing products and ethanol conversion (X_{EtOH}) were calculated on a C atom basis and expressed as mol%:

$$Yi = \frac{f_i \cdot nC_i}{2f_{EtOH\ in}} \cdot 100 \qquad X_{EtOH} = \sum Yi \qquad S_i = Y_i / X_{EtOH}$$

where nC_i is the number of C atoms contained in the product *i* and f_i is its molar flow (mol/h).

According to the stoichiometry of the reforming reaction (1), the maximum possible yield of hydrogen is 6 mol H_2/mol ethanol; therefore hydrogen yield (Y_{H2}) and selectivity (S_{H2}) were calculated (in mol%) as:

$$Y_{H2} = \frac{f_{H_2 out}}{6 \cdot f_{EtOH\ in}} \cdot 100 \qquad S_{H2} = \frac{f_{H_2 out}}{6 \cdot (f_{EtOH\ in} - f_{EtOH\ out})} \cdot 100$$

3. Results and discussion

3.1 Catalyst characterization

Table 1 summarizes the results of S_{BET} and average pore diameter. All catalysts could be classified as mesoporous materials, as they all show a type IV isotherm with H2 hysteresis (not shown), but impregnated catalysts (I) presented a multimodal pore size distribution in contrast with the unimodal distribution of the (M) samples from microemulsions.

X-ray diffraction patterns of all fresh samples (Fig 1 y 2) showed the characteristic reflections of the fluorite-like cubic phase of CeO_2, with similar intensity and width within each series. Table 1 also shows the lattice constant and size of the crystals calculated from the analysis of the most intense diffraction, corresponding to the (111) plane of this CeO_2 cubic phase. The patterns of the impregnated catalysts (Fig. 1) show sharper and more intense peaks, meaning that the particles of the support are bigger and more crystalline, while the preparation via microemulsions leads to more amorphous materials (Fig. 2); nevertheless, within each series there were no meaningful differences in crystal sizes. The diffractograms of monometallic catalysts Ni-I and Co-I evidenced also the presence of the cubic phases NiO and Co_3O_4, respectively, while bimetallic NiCo-I contained $NiCo_2O_4$ and NiO phases. Ceria crystalline particles were smaller and less crystalline in the (M) samples but the phase composition of the homologous catalysts was similar in both series, excepting sample NiCo-M which pattern did not present any diffraction lines that could be assigned to nickel or cobalt containing compounds. The lattice parameter *a* of ceria increased in all the monometallic catalysts in relation to that of the pure ceria phase (0.541 nm), which suggests that cerium is in a partially reduced state in the network: the reduction of Ce^{4+} to Ce^{3+} leads to lattice expansion because of the increase in the ionic radius as well as the fact that it has to be accompanied by oxygen vacancy formation. Catalysts NiCo-M and NiCo-I showed slightly lower lattice parameter values, probably due to the insertion of heterocations, either of Ni or Co, into the ceria network probably through substitutional exchange with cerium cations; the lower ionic radius of the divalent (or trivalent) nickel or cobalt cations with respect to Ce^{4+} produces a lattice contraction that may compensate the network expansion expected upon associated formation of oxygen vacancies.

3.2. Catalytic performance of impregnated catalysts

Preliminary tests, conducted in the range 400-650 ºC, showed all catalysts deactivated but each one with a different pace. Thus, we selected the temperature of 500 ºC to study and compare the catalytic performance and stability in isothermal experiments for 22 h. Under the tested conditions, reaction in the absence of catalysts reached an ethanol conversion < 6% with Y_{H2} < 1%.

Figure 3 shows the effect of run time on ethanol conversion and hydrogen yield of ESR on the impregnated catalysts (I). The three showed a high initial activity (near total conversion) but suffered a gradual deactivation for the first 15 hours, and later the values of conversion remained similar for

the three catalysts (45-50%) and deactivation was slower. Evolution of the hydrogen yield was parallel to that of conversion (fig. 3), indicating that deactivation was not affecting the hydrogen selectivity (around 60%). The bimetallic NiCo-I was the most active, selective and stable catalyst, with 95% ethanol conversion and Y_{H2} = 59% after 1.5 h, and keeping values above 63% conversion and 37% hydrogen yield for about 12 h.

TPO tests of the used samples (Section 3.4) evidenced the presence of carbon deposits on them. As this coke deposition was considered the most probable cause of the activity loss, to regenerate their catalytic activity, the used samples were submitted to oxidative reactivation in order to clean the surface by burning the deposited carbon that covered pores and active phases. After this treatment, initial conversion values were similar to those of the fresh samples, but the reactivated samples showed a different order of activity than the fresh ones (Fig. 4): the Ni-I was the most active, selective and stable, keeping the order along the run time: Ni-I > NiCo-I > Co-I. Anyway, reactivated samples also suffered deactivation and the overall deactivation trend shown was parallel to that of their fresh samples, so further characterizations were conducted on these used catalysts.

3.3. Catalytic performance of catalysts from microemulsions

Coprecipitated catalysts prepared via microemulsions displayed a quite different behavior and evolution under the same operative conditions (Fig. 5). Ni-M was the most active and stable catalyst, as it kept conversion above 95% and near constant hydrogen yield around 57% (equivalent to 3.4 mol H_2/mol ethanol) during the 22 h of our test. Fresh Co-M showed a lower initial conversion, and deactivated following the same evolution than its impregnated equivalent Co-I, but with lower performance: some 15-20 percentage points of conversion less at equal run times. After regeneration treatment, the reactivated Co-M sample showed similar initial activity than the fresh one, but it became more stable, losing only 10% of its activity (vs. a 40% loss for the fresh sample) after 7 h and remaining practically stable thereafter.

The catalytic behaviour of NiCo-M was unique: the fresh sample showed the lowest initial activity and quickly deactivated in 3 hours. This lowest initial activity could be related to a limited accessibility to Ni and/or Co atoms, as XRD showed this was the only catalyst for which no segregated oxide phases of Ni or Co were detected (Fig. 2) while showing the lowest lattice parameter in its ceria fluorite phase (Table 1). But, surprisingly, after the reactivation treatment it became almost as active as the most active one, Ni-M, as its ethanol conversion was very high, above 85%, and remained stable for 22 hours. Hydrogen yields trends were parallel to that of the ethanol conversion: reactivated NiCo-M and Ni-M were also the most selective catalysts with Y_{H2}>56% for

22 h of reaction (Fig. 5). These results point to a restructuration of its surface and/or active centers caused by the regeneration process.

3.4. Characterization of the used catalysts

XRD patterns of all the used catalysts, independently from the preparation method, presented reflections attributable to carbon species, probably with a graphite-like structure (Fig. 6). In all cases, after the activation and use in the ESR test the crystal particle size of the CeO_2 phase increased and the oxidic phases of the active metals were reduced to the respective zero state metals. In the impregnated bimetallic sample NiCo-I only the diffraction lines of Ni° can be identified, while no evidence of crystalline cobalt can be found. Used Ni-M sample was fully active after 22 hours, when the test was stopped; so, considering its XRD pattern, it can be concluded that Ni° particles may be the real active phase, responsible of the catalytic performance of this catalyst. It can be reasonable to think that the nickel reduction occurred at the beginning of the ESR test and may be caused by the reduction of the precursor oxide with ethanol in the reactant mixture while the presence of hydrogen produced by ESR can also help to maintain the reduced state of nickel.

The evolution of CO_2 during the TPO (5% O_2/He) of the used catalyst samples was monitored, and the resulting CO_2 profiles evidenced different types of carbonaceous species with different thermal stabilities (Fig. 7). Both Co-containing impregnated catalysts profiles show a very broad and intense peak in the range 525-700 ºC, with maxima at 625 and 700 ºC for NiCo-I, along with minor peak at lower temperature (500 °C), while the Ni-I profile showed only the broad peak at 700 ºC. This peak, present in the three profiles, indicates that the same type of carbonaceous compounds, with relatively strong thermal stability, was deposited on the surface of the samples during ESR. For NiCo-I the predominant contribution is the peak at 620 ºC, probably corresponding to polymeric non-structured coke species, with a weaker interaction with the catalytic surface. The minor peaks around 500 ºC can correspond to the decomposition of carbonates stabilized during ESR reaction.

TPO profiles of the used catalysts from microemulsion are quite different and show basically two peaks at 550°C and 630°C. The first peak is predominant, so this corresponds to the main carbonaceous compounds formed on the catalysts during the reforming reactions, which could correspond to carbon filaments, as confirmed by further TEM analysis. Figure 8**¡Error! No se encuentra el origen de la referencia.** shows two TEM images obtained for the used Ni-I sample. The nickel particles can be discriminated due to their stronger contrast. The light grey structures have been attributed to the carbonaceous species. A large presence of amorphous carbon can be identified along with a small portion of carbon nanotubes. The TPO peak at higher temperatures, corresponding to the type of carbon deposit with the strongest interaction with the catalyst, may be attributed to this

298 amorphous polymeric carbon compound that seems to block the metal particles, limiting the access
299 to the active sites with a consequent loss of activity. Another relevant contribution to the catalyst
300 deactivation can be assigned to the sintering of nickel particles which appear bigger in the used
301 sample than in the fresh one.
302 On the contrary, in the used Ni-M catalyst prepared from microemulsions the nickel particles
303 remained well dispersed and with an average dimension of 10 nm (Fig. 9). These morphological
304 properties may be linked to the high stability, activity and selectivity of these samples in the reaction
305 as it must be remembered that Ni-M did not experience any deactivation after 22 hours. This sample
306 exhibits a lower amount of carbon which appears mainly as nanotube structures along with a small
307 amount of amorphous coke. However, these carbonaceous deposits did not affect the catalytic
308 performance of this sample probably because carbon nanotubes do not block the access to the active
309 phase as non-structured coke do in the Ni-I sample (Fig. 9).
310 Table 2 summarizes atomic ratios estimated from the EDX spectra of catalyst Ni-M and the
311 regenerated sample of catalyst NiCo-M after their use in ESR test for 22h (and exposure to
312 atmospheric air at room temperature). As shown, a huge amount of carbon is observed in both cases
313 in agreement with TPO analysis, though a more moderate amount is detected in the case of Ni-M
314 which agrees with the fact that this sample appears the most stable one among those examined in this
315 work. This means that this type of carbon deposits does not impede catalytic activity, which is
316 coherent with the nature of the carbon deposits observed by TEM. Interestingly, the surface atomic
317 ratio of the used regenerated NiCo-M sample, Ni:Co = 3:2 suggests a surface enrichment in Ni, as
318 compared with that of the fresh sample, Ni:Co=1.

319 3.5. General discussion

320 The most usual way to activate supported metal catalysts for steam reforming of alcohols is to reduce
321 them in hydrogen to obtain the active metallic phase. However, pretreatment in pure hydrogen at
322 relatively high temperature may cause metal sintering, decreasing the metal dispersion. The
323 reduction by a softer reductant (as ethanol, for example; furthermore when combined with water in
324 the ESR reactant mixture) may allow keeping metal dispersion closer to the initial one in the oxidic
325 precursor. On the other hand, the activity of catalysts containing ceria is strongly dependent on the
326 number of vacancies in its network, which in turn are dependent not only on the preparation method
327 but also on its contact with the environment and its storage. For these reasons we used oxidative
328 activation to homogenize the initial oxidation state of ceria in the catalysts, and let the reduction of
329 the active metal component to take place by its interaction with the reaction medium. The positive
330 effect of consecutive oxidation and reduction pretreatments has been reported in other supported

metallic systems: zeolite-supported nanosilver catalysts used for CO oxidation at low temperatures show much higher activity if they are pretreated consecutively first with oxygen and then reduced with hydrogen than if they are just only reduced in hydrogen at the same conditions [31]. XRD patterns evidenced that the base metal oxides phases present in the fresh samples are converted into metallic phases in all the used catalysts. Therefore, one may infer that both cations (Ni^{2+} and Co^{2+}) are reduced by the ethanol in the reactant mixture during the initial moments of their contact and then the ESR proceeds on the metallic centers generated. As our first product analysis is made after at least 15 minutes of the initial contact, the product distribution already corresponded to catalytic ESR and not to the initial stoichiometric redox reaction between the cations and ethanol.

The main effect of the preparation method was observed on the deactivation and the regenerability of the catalysts. Oxidative regenerations of the three impregnated catalysts recovered initial conversion values but the overall trend of catalyst deactivation, compared to that observed with the fresh samples, did not change, despite the initial different order of activity for the regenerated samples. The situation was quite different among the catalysts prepared by microemulsions. Monometallic Co-M showed deactivation trends similar to that of its impregnated homologous, Co-I, but its activity increased slightly after regeneration.

On the contrary, the catalytic performances, deactivation trends and effect of oxidative regeneration of the Ni-containing catalyst prepared by microemulsions (Ni-M, NiCo-M) was quite exceptional and totally different to their impregnated counterparts (Ni-I, NiCo-I).

Analysis of the distribution of the carbon-containing products and its evolution provides a key to understand the different behavior of the three catalysts prepared by microemulsions and the drastic change with the bimetallic catalyst. Besides H_2, the only products on the stable and most active catalyst, monometallic Ni-M, were CO_2, CO and CH_4, whose selectivity (55, 25 and 15%, respectively) did not vary along the run time, and traces of acetaldehyde. This suggests that the nickel active sites were very active in ethanol dehydrogenation to acetaldehyde (2), whose very little yield indicates it is rapidly transformed by steam reforming (4-5).

On the contrary, the main products on the fresh bimetallic NiCo-M were acetone and ethylene, which summed up 50 % of the carbon containing products. These two intermediates are known precursors of coke, which may have caused the quick deactivation; their absence among the products of Ni-M might explain its outstanding stability.

Acetone and ethylene were also formed in the initial test stages on fresh Co-M catalyst, but in lower proportion (the maximum joint yield was 32 %), and decreasing very fast until almost disappearing at 4 h on stream, a time after which the pace of deactivation slowed down. This similarity of their

product distribution seems to indicate that activity of the fresh NiCo-M catalysts is mostly determined by the Co atoms on its surface.

At a variance of the impregnated catalysts, the regeneration treatment of the two deactivated catalysts (both containing Co) improved their initial catalytic activity and their stability (Fig. 5, hollow symbols), overcoming their impregnated counterparts. The product distribution on reactivated Co-M catalyst was similar to the observed for the fresh sample, but formation of acetone and ethylene was much lower (combined selectivity 13 %), which may explain its smaller deactivation.

The most radical change caused by regeneration was observed with catalyst NiCo-M, which started to work almost like the most active Ni-M catalyst. Contrary to the first run of this sample, no formation of acetone and ethylene was observed on this regenerated sample; this fact (and the higher initial activity) would indicate a change in the chemical nature of its active sites, and an increase of their number, due to reactivation, thus resulting in a higher efficiency. The similarity of their product distribution to that of Ni-M catalyst seems to indicate that activity of the regenerated NiCo-M catalysts is mostly determined by the Ni atoms on its surface.

While in the impregnation the metal precursors are deposited onto the support surface, the reverse microemulsions method forms a precipitate in which the metal precursors can be mostly distributed in the bulk of the nanoparticles formed. The observed change in the NiCo-M behavior and the ESR product distribution after regeneration points to a change in its surface metal composition caused by the regeneration process. One may hypothesize that this could be due to an "emergence" of the active metal atoms from the bulk to the ceria nanoparticles surface. This can most likely be produced during the reduction of the system under the ESR mixture. Note a similar mechanism of metal surface segregation upon reduction of cations inserted in the ceria fluorite lattice was observed to occur in copper-doped ceria systems subjected to redox treatments [32]; as a difference with such case in which the bulk-surface migration of copper appeared basically reversible upon redox cycling [32], in our case the reoxidation during catalyst regeneration could apparently keep the metals at the sample surface with consequent increase in the activity. Indeed, the catalytic performance of this regenerated system is similar to that of Ni-M one. This is coherent with an emergence of Ni atoms in the regenerated NiCo-M, and the EDX analysis of this sample in fact suggests a surface enrichment of Ni, consistent with this hypothesis. Even so, the two samples have product distributions that suggest a difference in the nature of the active sites, as on the bimetallic NiCo-M acetaldehyde, the primary product in the reaction network, was never fully converted while on the catalyst Ni-M it is absent among the products, indicating its total transformation. This indicates that the active metal surface composition is not exactly the same, which is coherent with the slightly lower stability of regenerated NiCo-M.

Another point that may affect the evolution of the metals during reaction/regeneration is the presence of a big amount of coke present on the used sample after the ESR test. TPO profile shows that practically all the carbonaceous deposits on this sample are burned out below 650 ºC. Even considering that the regeneration is made with a slow heating rate of 10 ºC/min and with diluted oxygen, one may assume that such combustion can create very localized hot spots (or hot narrow regions) in the catalyst surface, where the much higher local temperature could alter the mobility of the atoms in the vicinity of the surface.

4. Conclusions

The catalytic behavior in ESR of the (Ni, Co)-Ce-O system depends on the preparation method, the composition and its history. Freshly prepared catalysts are basically constituted by combinations of the cubic phases CeO_2, NiO and Co_3O_4, but the latter are reduced to metallic Ni and Co during ESR reaction. All catalysts show high initial conversion but also deactivation, albeit at different rates, caused by carbonaceous deposits most likely formed from acetone and ethylene, which can be reversed by oxidation treatment with dilute O_2.

The preparation methods investigated cause differences in the textural properties and crystallinity of the phases of the catalysts of the same composition, which influences their activity, stability, the type of the carbonaceous deposits formed during ESR and, therefore, their oxidative regenerability after their catalytic use. All this causes that the effect of the combination of Ni and Co in the bimetallic catalysts depends very much on its route of synthesis, producing a slight improvement, with respect to the monometallic Ni catalyst, only in the impregnated ones.

The reverse microemulsions method generates larger surface areas and a better dispersion of nickel, more homogeneous, which improves its activity and stability, as well as the yield and selectivity to H_2. This made the Ni-CeO_2 (Ni:Ce = 4:6) catalyst prepared by this method (Ni-M) to be the most active one among those examined in this study. A significant improvement in performance and a change in the product distribution during the initial reaction stages is observed with the Co-containing catalysts prepared by microemulsion after oxidative regeneration, especially for the bimetallic NiCo-M catalyst, which points to a restructuring of the active centers during the reaction-regeneration cycle. We hypothesize that this could be due to the emergence of Ni atoms from the bulk to the ceria surface during reduction of the catalyst under ESR conditions and which can be affected by local overheating as a consequence of the burning of the carbon deposits during the oxidative regeneration treatment. Further characterization studies are in any case under way to verify this hypothesis.

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Table 1: Textural and phase characterization of as-prepared catalysts

Catalyst	**BET**		**XRD**	
	Surface area (m^2/g)	Average pore diameter (nm)	Lattice parameter *a* (nm)	Crystal size (nm)
Ni-*I*	76	4.0	0.5411	8.0
NiCo-*I*	72	5.7	0.5389	7.5
Co-*I*	70	4.2	0.5411	7.8
Ni-*M*	136	4.0	0.5454	3.7
NiCo-*M*	132	4.2	0.5330	3.9
Co-*M*	125	5.2	0.5482	4.2

Table 2: EDX analysis of Ni-M and regenerated NiCo-M catalysts after their use in ESR

Catalyst	EDX atomic composition (at. %)				
	C	O	Ni	Co	Ce
Ni-M	93.34	3.68	0.84	-	1.11
NiCo-M	99.51	1.36	0.29	0.19	0.02

Legend of the figures

Fig. 1. XRD patterns of the CeO_2 support (orange) and the impregnated catalysts: Ni-I (blue), NiCo-I (green), Co-I (red)

Fig. 2: XRD patterns of the catalysts prepared by reverse microemulsions method: Ni-M (blue), NiCo-M (green), Co-M (red).

Fig. 3. Ethanol steam reforming on fresh impregnated catalysts at 500°C: ethanol conversion (left) and hydrogen yield (right) as function of reaction time.

Fig. 4. Ethanol steam reforming on used impregnated catalysts *(I)* after reactivation: ethanol conversion as function of reaction time. Reaction conditions in text.

Fig. 5. Ethanol steam reforming on fresh (solid symbols) and reactivated (hollow symbols) catalysts prepared by reverse microemulsions (M): ethanol conversion (left) and hydrogen yield (right) as function of reaction time. Reaction conditions in text.

Fig. 6. XRD patterns of the used samples of catalysts of Ni (blue) NiCo (green) and Co (red) prepared by impregnation (I, top) and reverse microemulsions method (M, bottom). Sharp peaks at $2\theta = 35^{o}$ correspond to sample contamination with SiC, used as catalytic bed diluent during the tests.

Fig. 7. CO_2 formation profiles during TPO of the used samples of catalysts of Ni (blue) NiCo (green) and Co (red) prepared by impregnation (I, top) and reverse microemulsions method (M, bottom).

Fig 8. TEM images of fresh (left) and used (right) samples of impregnated Ni-I catalyst.

Fig 8. TEM images of the used sample of impregnated Ni-M catalyst.

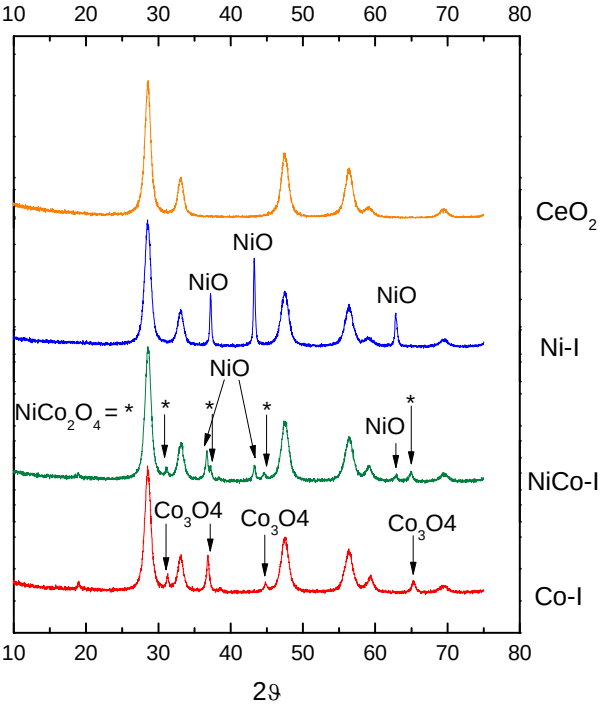


Fig. 1: XRD patterns of the CeO_2 support (orange) and the impregnated catalysts: Ni-I (blue), NiCo-I (green), Co-I (red)

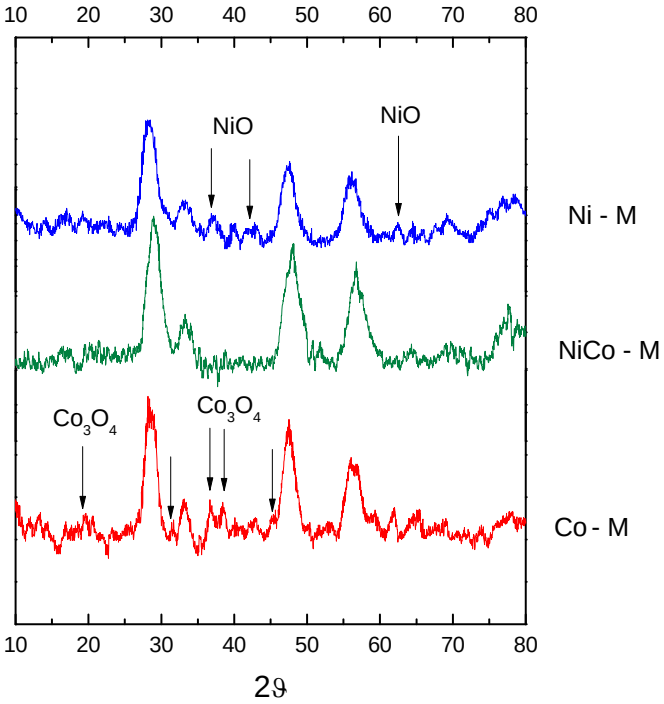


Fig. 2: XRD patterns of the catalysts prepared by reverse microemulsions method: Ni-M (blue), NiCo-M (green), Co-M (red).

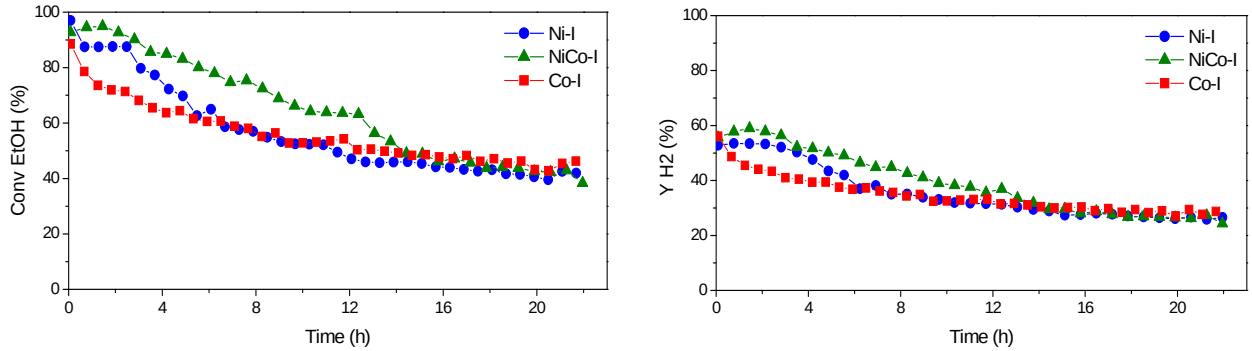


Fig 3: Ethanol steam reforming on fresh impregnated catalysts *(I)*: ethanol conversion (left) and hydrogen yield (right) as function of reaction time. Reaction conditions in text.

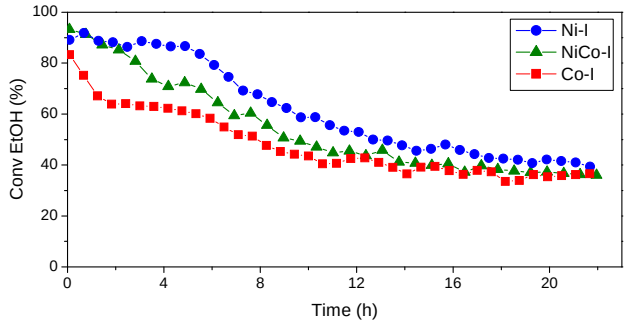


Fig 4: Ethanol steam reforming on used impregnated catalysts *(I)* after reactivation: ethanol conversion as function of reaction time. Reaction conditions in text.

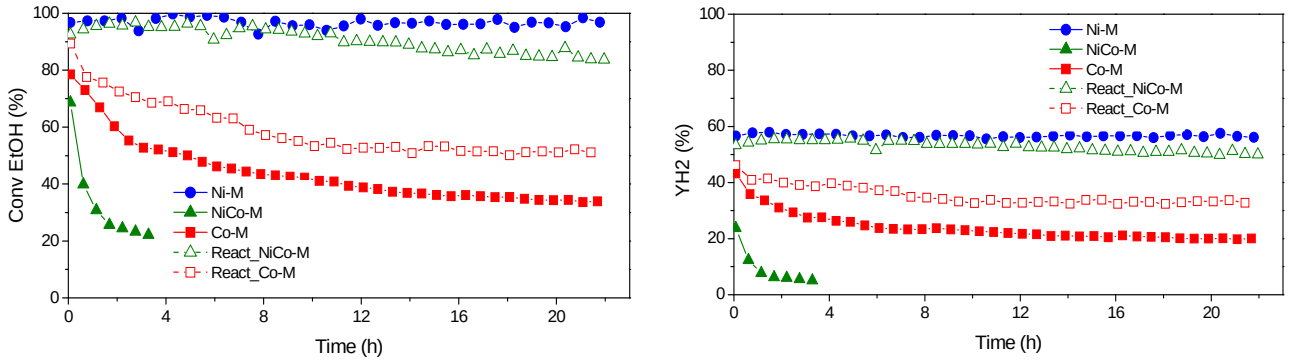


Fig 5: Ethanol steam reforming on fresh (solid symbols) and reactivated (hollow symbols) catalysts prepared by reverse microemulsions *(M)*: ethanol conversion (left) and hydrogen yield (right) as function of reaction time. Reaction conditions in text.

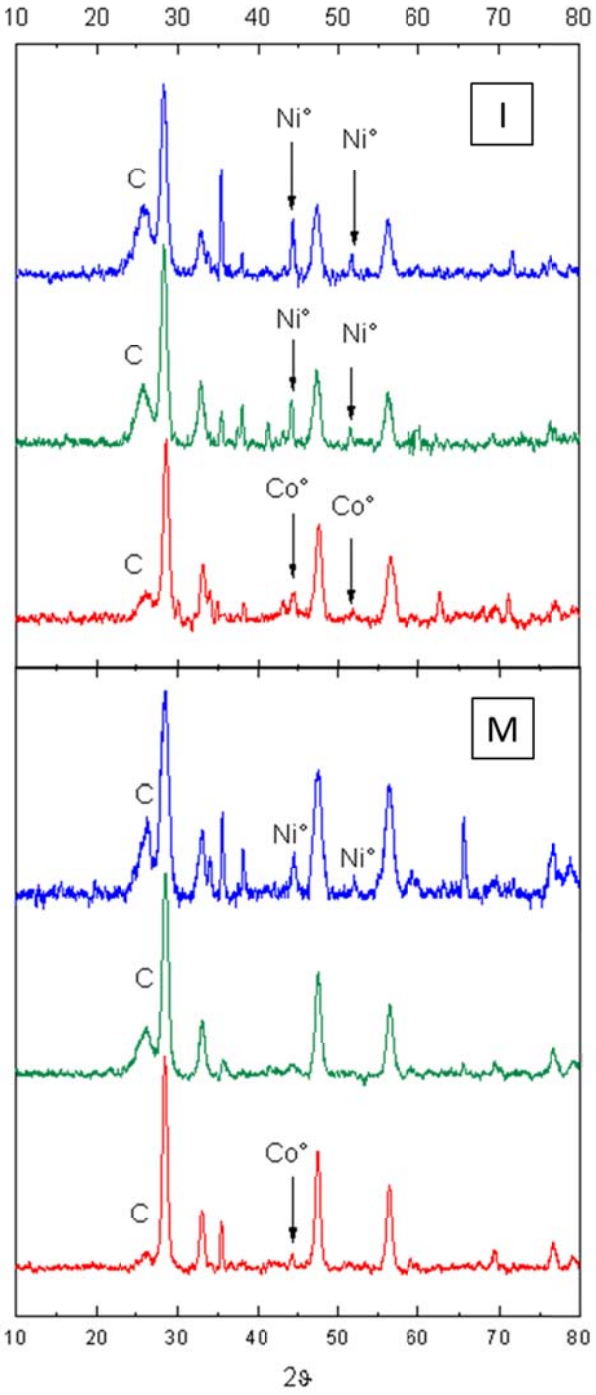
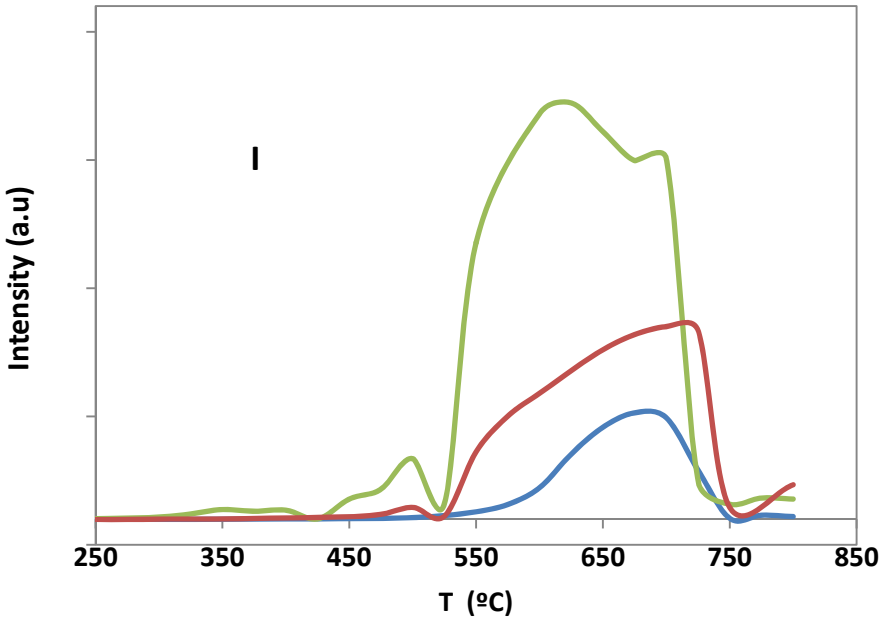


Fig. 6: XRD patterns of the used samples of catalysts of Ni (blue) NiCo (green) and Co (red) prepared by impregnation (I, top) and reverse microemulsions method (M, bottom). Sharp peaks at $2\theta = 35^{o}$ correspond to sample contamination with SiC, used as catalytic bed diluent during the tests.



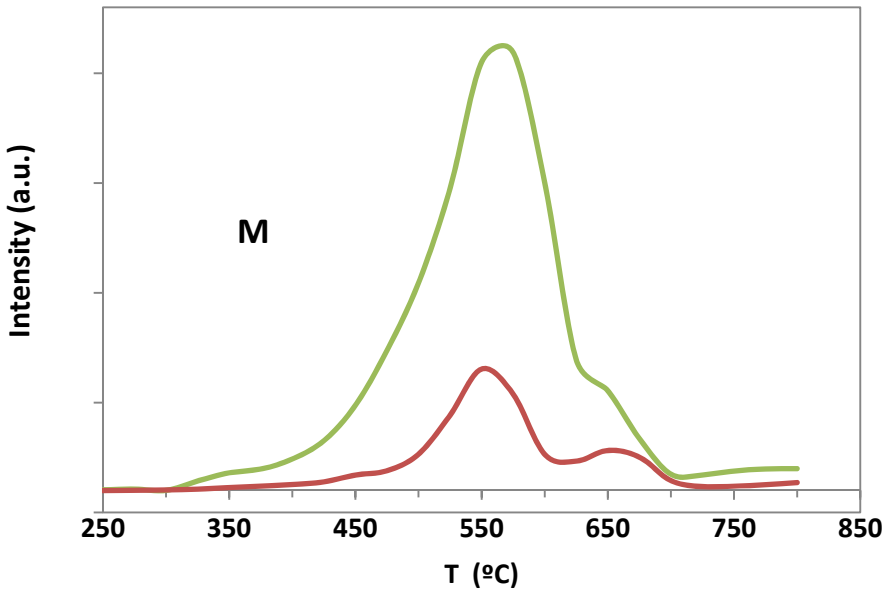


Fig. 7. CO_2 formation profiles during TPO of the used samples of catalysts of Ni (blue) NiCo (green) and Co (red) prepared by impregnation (I, top) and reverse microemulsions method (M, bottom).

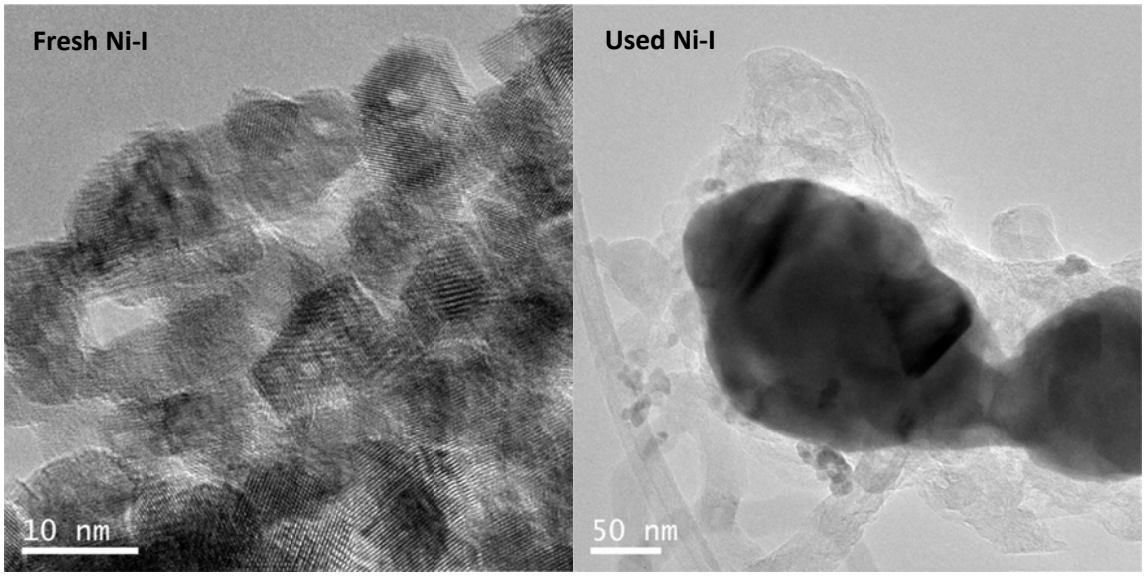


Fig 8. TEM images of fresh (left) and used (right) samples of impregnated Ni-I catalyst.

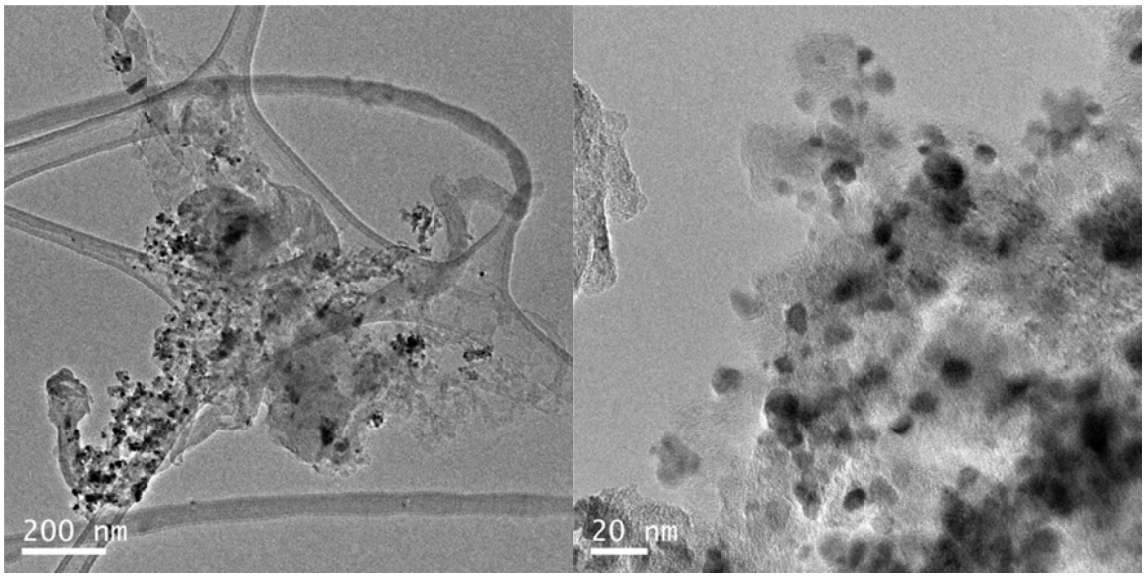


Fig 8. TEM images of the used sample of Ni-M catalyst from microemulsions