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Ni-CeO₂/C Catalysts with Enhanced OSC for the WGS Reaction

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Abstract: In this work, the WGS performance of a conventional Ni/CeO₂ bulk catalyst is compared to that of a carbon-supported Ni-CeO₂ catalyst. The carbon-supported sample resulted to be much more active than the bulk one. The higher activity of the Ni-CeO₂/C catalyst is associated to its oxygen storage capacity, a parameter that strongly influences the WGS behavior. The stability of the carbon-supported catalyst under realistic operation conditions is also a subject of this paper. In summary, our study represents an approach towards a new generation of Ni-ceria based catalyst for the pure hydrogen production via WGS. The dispersion of ceria nanoparticles on an activated carbon support drives to improved catalytic skills with a considerable reduction of the amount of ceria in the catalyst formulation.

Keywords: WGS; cerium oxide; carbon support; OSC; Ni based catalysts

1. Introduction

Nowadays, synthesis gas (a mixture of hydrogen and carbon monoxide) is generally produced by steam reforming of hydrocarbons, especially if the principal objective is the generation of gas streams with high H₂/CO ratios. For clean energy production, pure hydrogen is required as a feed gas for electricity generation in low temperature fuel cells [1]. In this sense, some processes have been considered in order to minimize the reformat CO concentration for PEM fuel cell applications as for example water-gas shift (WGS). Conventionally, in an integrated fuel processor, the WGS reactor is the first clean-up unit, and it is the reaction that removes the most important amount of CO in the H₂ stream [2].

Due to its high oxygen storage capacity and reducibility (via the Ce⁴⁺ ↔ Ce³⁺ redox process), cerium oxide is widely used as catalyst support and promoter in the water-gas shift reaction [3]. The role of the ceria surface is determinant for this reaction, both in terms of reducibility but also in terms of extension (large exposed surface areas are needed). Furthermore ceria reducibility is favored by the presence of metals [4,5].

One of the key points that convert ceria in a highly suitable support for the shift reaction relies on its ability to provide oxygen to the process. Indeed the WGS is a redox reaction, thus the oxygen mobility of the catalyst is regarded as a main issue in the catalytic design [6]. The later makes obligatory an accurate study of the redox features exhibited by the WGS systems, namely, the oxygen storage complete capacity (OSCC) and oxygen storage capacity (OSC). Recently, a great increase in both the OSC and the OSCC has been proposed as one of the main reasons to explain the activity promotion when ceria is dispersed on a high surface alumina [7]. In this way, promoting redox properties of the catalysts, namely surface and bulk oxygen mobility should benefit the WGS performance. Therefore, oxygen supply from the support is a highly desired feature for an effective WGS catalyst. Dispersing ceria over a high surface support such as carbon provides higher surface/bulk ratios improving oxygen mobility. In addition, the limited supply and extensive applications of CeO₂ makes desirable to optimize its use [8].

On the other hand, ceria-supported noble metals are mostly used due to the high activity in the WGS reaction. However, their elevated prices motivate the search for cheaper and more abundant metals which can be useful in the shift reaction. Ni-based catalysts are widely employed in many industrial processes such as reforming of alcohols, hydrogenation reactions and hydrocracking or oxidation processes [9]. Previous studies have addressed the behavior of NiO/CeO₂ or Ni/CeO₂ systems as catalysts for the title reaction. Despite good activities were reported, Ni containing catalysts suffer for deactivation mainly due to the well-known metallic particles sintering process together with the accumulation of carbon deposits on the catalysts surface [10,11].

Another point to consider is the adaptation of the new catalysts formulation to the budding market demands. The emerging fuel cell technology for portable electronic devices is changing the requisites for the WGS catalysts. Apart from developing a solid with the properties mentioned above, an industrial catalyst for WGS reaction requires in addition high long term stability and good resistance toward start/stop situations [12].

In a previous work [13] Ni_xCeO₂/C catalysts with different CeO₂ contents ($x = 10, 20, 30, 40\%$ wt.) were tested in the WGS reaction. Detailed characterization was performed, deepening in both physical and chemical characteristics of these materials. The results showed that there was a clear effect of the ceria loading on the catalytic activity. It could be seen that the Ni-CeO₂-carbon system yielded catalysts which showed better performance than bulk Ni/CeO₂.

In this scenario, and taking into account our previous results [13] the objective of this work is to correlate the OSC of these catalysts with their high activity. A study of the enhancement of the oxygen storage capacity when ceria is dispersed on carbon is carried out. For this study, a sample with a 20 wt.% CeO₂ loading was chosen due to the interesting results obtained before. Additionally, and differently to our previous study, water-gas shift reactions employing more demanding WGS conditions were carried out. Further, stability tests and start/stop cycles were developed in order to evaluate the viability of this catalyst in real applications.

2. Results and Discussion

2.1. Catalysts Composition and Textural Properties

The chemical composition and the main textural properties of the prepared catalysts are presented in Table 1. The enhanced textural properties of the carbon materials are evidenced, all of them exhibiting larger surface area compared to the bulk solids. As previously reported, carbon is playing a role of textural promoter in these type of catalysts [13]. Data in Table 1 show a decrease of the BET surface area for ceria-carbon based samples, attributed to the blockage of porosity by ceria crystallites and/or an effect of mass increment and the much lower porosity of ceria as compared with carbon. The addition of nickel also produces a decrease in the BET surface area of the catalysts, which is also attributed to presence of high amounts of Ni (15 wt.%).

Regarding the elemental analysis, the actual Ni and CeO₂ content of the catalysts were determined by ICP (Inductively Coupled Plasma) measurements, and they are reported in Table 1. The obtained values are very close to the targeted ones, this validating the preparation method used.

Table 1. Catalysts composition and textural properties of the prepared samples.

Sample	S _{BET} (m ² /g)	V _{micro} (cm ³ /g)	V _{meso} (cm ³ /g)	Ni (wt.%) *	CeO ₂ (wt.%)*
C	1487	0.52	0.62	--	--
20CeO ₂ /C	1083	0.37	0.47	--	22.2
CeO ₂	101	0.04	0.07	--	--
Ni20CeO ₂ /C	807	0.28	0.34	12.7	21.6
Ni/CeO ₂	70	0.03	0.04	14.1	--

* Determined by ICP analysis.

2.2. OSCC and OSC

As mentioned above, redox properties constitute one of the main issues to be optimized for the successful design of an efficient WGS catalyst. An accurate understanding of such skills is obtained by the oxygen storage capacity measurements. In particular, OSCC measurements provide information

about the maximum reducibility of the samples, while OSC informs about the most reactive and most available oxygen atoms that are involved in the redox process [14]. This study was carried out at two different temperatures (150 °C and 250 °C) both of them low enough to avoid any possible carbon combustion due to the oxygen pulses. Actually our TGA data (not shown for sake of brevity) point that carbon combustion in our catalysts under air atmosphere starts at 320 °C. The selected temperatures are relevant points in the catalytic study. Therefore, the analysis of the redox behavior of both catalysts at these temperatures provides valuable information to understand their WGS performance. Figure 1 shows the OSCC results of the prepared solids. As expected, the OSCC increases with the temperature for both supports and catalysts, indicating higher degree of ceria reduction at 250 °C. In the case of the supports (Figure 1A) it must be underlined the superior OSCC exhibited for the CeO₂/C system at the studied temperatures. These data indicate that the dispersion of ceria nanoparticles on a high surface carrier as activated carbon results in a notorious improvement of its reducibility. In other words, enhanced redox properties are achieved for the CeO₂/C solid in comparison to the bulk CeO₂. Even though carbon is not playing a chemical role in the oxygen storage process, it acts as an ideal media to support ceria nanoparticles providing high surface area (as shown in Table 1). Similar results were obtained when CeO₂ is dispersed over gamma alumina [15]. In this sense, dispersing ceria over a high-surface carrier opens up the possibility of having higher surface/bulk ratios thus improving the oxygen mobility no matter the used support. However it is worth noting that our ceria/carbon based samples present higher OSCC values than those observed for ceria/alumina systems measured under the same conditions [15]. The latter indicates the suitability of carbon as a textural promoter allowing better dispersion of ceria nanoparticles.

Nickel addition (Figure 1B) enhances the OSCC for both, bulk CeO₂ and CeO₂/C support. This result agrees with H₂-TPR data recently published for these solids evidencing a remarkable increase of the support reducibility due to the strong Ni-CeO₂ interaction [13]. Again, as observed for the bare supports, much higher OSCC values are obtained when ceria and nickel phases are dispersed on the activated carbon.

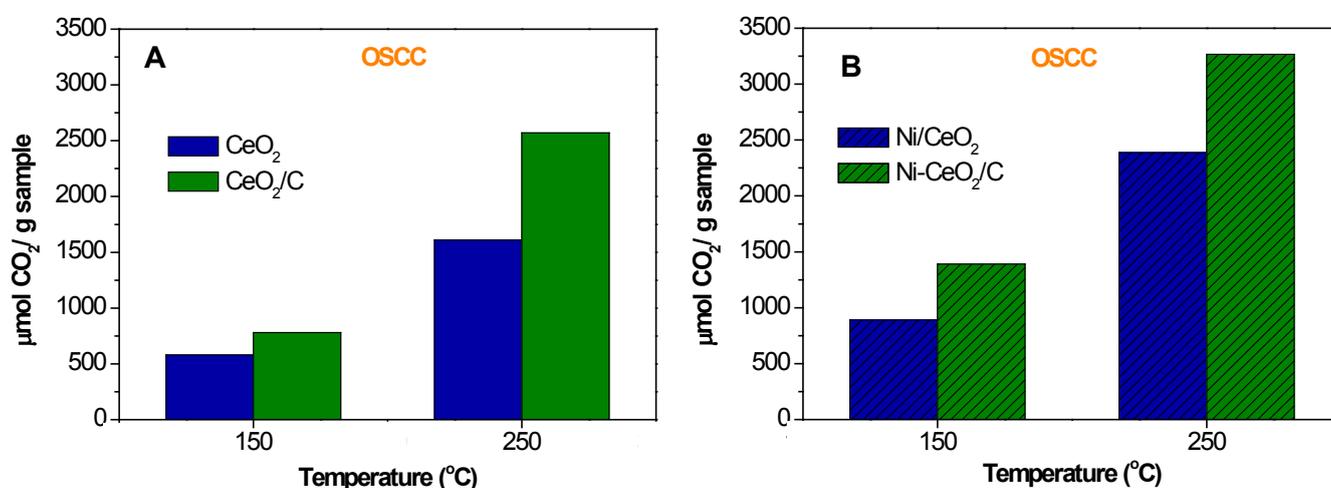


Figure 1. Oxygen storage complete capacity (OSCC) of the prepared solids. (A) supports (B) Ni based catalysts.

The OSC study is summarized in Table 2. At 150 °C the supports presented low oxygen mobility; however, the OSC improves when the temperature is raised. In a similar way to the OSCC, the OSC of the CeO₂/C sample is always higher than that of the bulk CeO₂ support. As stated above, Ni influences CeO₂ reducibility due to the intimate Ni-CeO₂ contact [16]. This effect is highlighted at low temperature (150 °C), where the metallic particles broadly boost the OSC of the parent supports. In any case, for all the studied temperatures, the Ni-CeO₂/C catalyst shows the best oxygen mobility. The promoted redox features of this catalyst are related with two inherent aspects of its composition: (i) the dispersion of ceria nanoparticles on the activated carbon, which increases the surface/bulk ratio, thus potentiating the oxygen mobility in the ceria lattice and, (ii) the facilitated CeO₂ reduction due to the presence of Ni, arising from a strong metal-support interaction.

Table 2. OSC in $\mu\text{mol CO}_2/\text{g}$ sample for the studied samples at different temperatures.

Sample	OSC _{150 °C}	OSC _{250 °C}
CeO ₂	10	180
CeO ₂ /C	25	255
Ni/CeO ₂	410	726
Ni-CeO ₂ /C	620	850

2.3. WGS Behavior

The catalysts were evaluated under a surrogate post reforming stream (7 mol% CO, 30 mol% H₂O, 50 mol% H₂, and 9 mol% CO₂ balanced with He) with the aim to test their viability for a real application, for instance the use of a WGS reactor in an integrated fuel processor for pure hydrogen production. The catalytic activity of the prepared Ni-ceria based catalysts in the shift reaction is presented in Figure 2. It should be mentioned that the supports were also tested under the same conditions, showing an almost nil activity in the studied temperature range. This underlines the importance of the metallic phase to achieve good performance in the WGS when ceria-based solids are considered. As intended from the plot, the samples are not very effective in the low temperature range (<200 °C). At these conditions the solids present limited oxygen mobility (low OSC values) that may contribute to the observed low CO conversion. Nevertheless, the catalytic activity rapidly increases with the temperature. The Ni-CeO₂/C sample evidences superior WGS activity compared to the Ni/CeO₂ one in the whole temperature range. Taking into account that the amount of metallic phase (Ni) is comparable in both materials, as obtained by ICP, the higher activity in WGS correlates with the boosted OSC and OSCC demonstrated for this solid. In addition to the excellent redox skills, the Ni-Ce/C sample presents greater metallic dispersion and superior specific surface area contributing to activity enhancement. This catalyst quadruplicates the activity of the Ni/CeO₂ solid at 240 °C, and reaches equilibrium conversion at 260 °C. Compared to others Ni-ceria catalysts previously reported, our carbon-supported sample performs better even under harder WGS conditions [17,18]. This is a very promising result since this material seems to be as efficient as some well-known noble metal based catalysts for this reaction [19]. However, contrary to the noble metal based solids, Ni-ceria solids also catalyze the methanation reaction. As can be seen in Figure 2, both catalysts exceed the equilibrium conversion at high temperatures. The additional CO consumption is due to the

methanation process. The high concentrations of CO used in this stream favor the methanation reaction [20]. The good point is that the methanation reaction for both catalysts starts at temperatures higher than 260 °C and thus, this does not affect our WGS operating window.

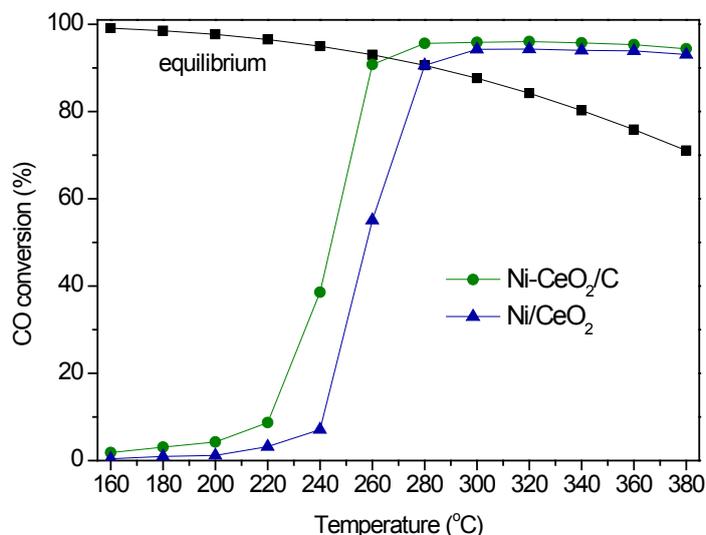


Figure 2. CO conversion vs. reaction temperature for catalysts reduced at 350 °C. Gas mixture: 7 mol% CO, 30 mol% H₂O, 50 mol% H₂, and 9 mol% CO₂ balanced in He.

This result is very interesting from the point of view of catalyst design since, according to our data, a much better catalytic activity is obtained when CeO₂ is dispersed on activated carbon. This approach permits to develop very active WGS catalysts reducing significantly the amount of ceria on the catalyst formulation. This outstanding behavior is linked to a strong enhancement of the redox properties when ceria nanoparticles are dispersed on a high surface carrier.

From the industrial perspective, the catalytic stability is as relevant as the activity. In this sense, a complete stability study of the selected sample was carried out. The stability test was developed at 250 °C, a reaction temperature at which the methanation reaction was not observed and good WGS activity was achieved. Figure 3 shows the long term stability test of the Ni-CeO₂/C catalyst. For the aim of comparison the same test was carried out with the Ni/CeO₂ solid; however, this catalyst exhibited fast deactivation and very poor CO conversion. Therefore it will not be longer considered. Regarding our Ni-CeO₂/C material, at the first stages of the reaction the system exhibits a good catalytic behavior. However, the CO conversion notably drops after 8 h of continuous reaction and remains stable after more than 120 h. Afterwards, several start/stop cycles were introduced simulating likely situations in real application. It was observed that the catalyst recovers the conversion after the start/stop operation. Apparently, once the initial deactivation occurs (at the early reaction stages) the start-up/shutdown actions do not influence the activity.

For a deeper understanding of this result, a second stability test was carried out. At this time, the catalyst was directly submitted to a series of start/stop cycles to check its actual tolerance under these conditions. Indeed, this type of stability experiment is considered as the most exigent test for a WGS catalyst, since during the stop stages the system is cooled down at room temperature with the reaction flow passing through the catalytic bed [21]. The later involves liquid water may condense on the pores of the catalyst damaging the system. Figure 4 reveals that the Ni-CeO₂/C catalyst withstands four

start/stop cycles within 6 h of reaction while preserving the initial activity. However, the activity drops after the fourth cycle, and it reaches practically the same value attributed to the steady state in the long term stability test. This result is very interesting from the catalyst deactivation point of view. Our data reveal that in a long term stability test high conversions are preserved during at least 10 h of reaction, but start-up/shutdowns cycles strongly affect the catalysts stability, in such a way that the activity drop takes place earlier (after 6 h of reaction).

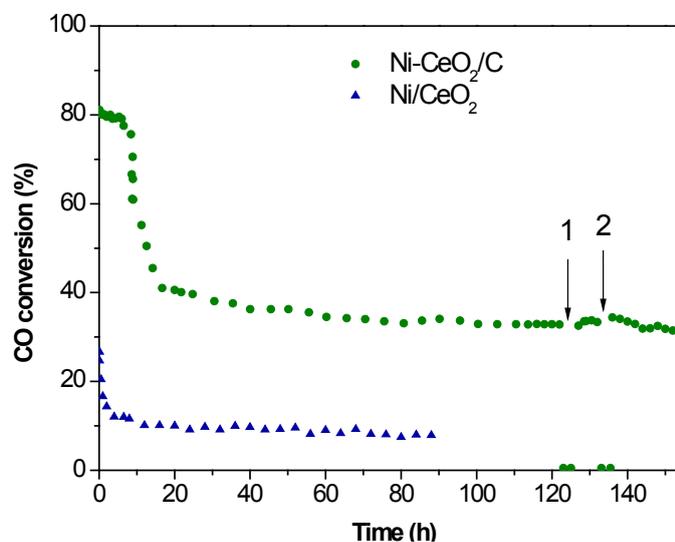


Figure 3. Long term stability test of the prepared catalysts at 250 °C. 1 and 2 start/stop cycles. Gas mixture: 7 mol% CO, 30 mol% H₂O, 50 mol% H₂, and 9 mol% CO₂ balanced in He.

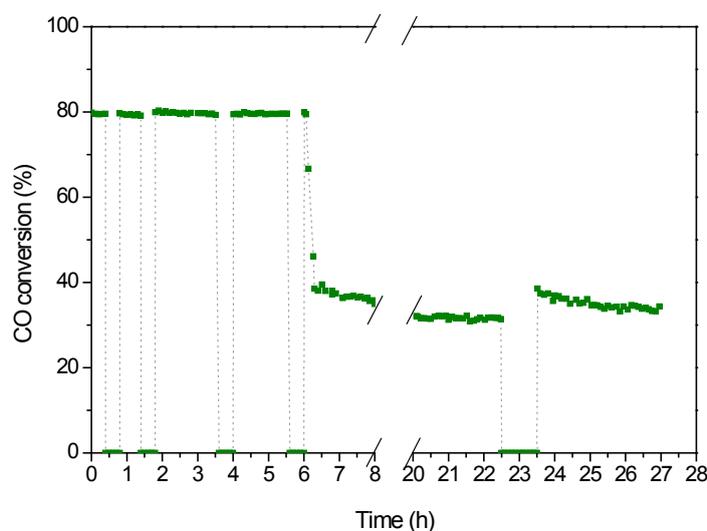


Figure 4. Stability test: start/stop cycles of the Ni-CeO₂/C catalyst at 250 °C. Gas mixture: 7 mol% CO, 30 mol% H₂O, 50 mol% H₂, and 9 mol% CO₂ balanced in He.

In both cases, long term and start-up/shut-down, the deactivation is related to the well-known phenomenon of Ni particles sintering. Actually, as previously proposed, the presence of water

potentiates Ni particles agglomeration especially at high temperatures [22,23]. TEM images presented in Figure 5, corresponding to the Ni-CeO₂/C catalyst, evidences the Ni sintering process.

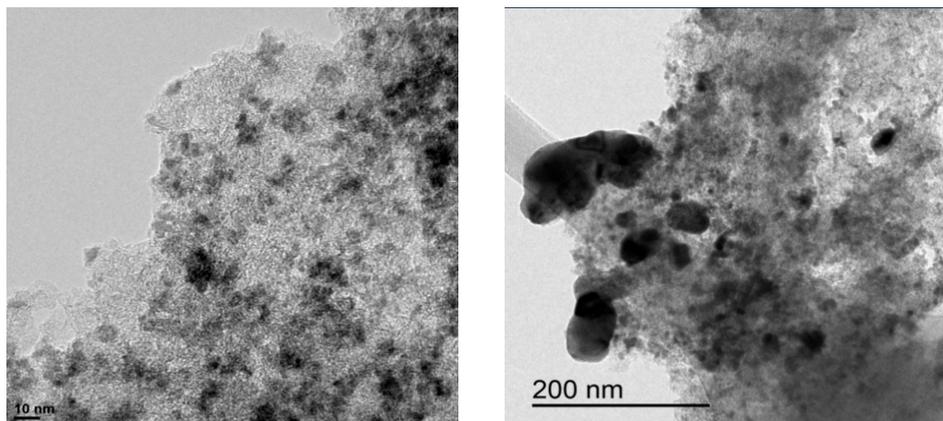


Figure 5. TEM micrographs of the Ni-CeO₂/C catalyst before (scale 10 nm) (a) and after (scale 200 nm) (b) the stability reaction test at 250 °C.

Our stability study indicates that water favors Ni agglomeration. This reduces the catalytic surface area and results in a decreased activity [24]. According to our data, the sintering process occurs earlier when liquid water (during the start/stop cycles) enters in contact with the catalyst.

3. Experimental Section

3.1 Catalysts Preparation

The procedure used for the catalyst synthesis was the same than in our previous work [13]. The support was an industrial activated carbon (RGC30, from Westvaco, New York, NY, USA). This carbon was grinded and meshed (300–500 μm). The corresponding amount of Ce(NO₃)₃·6H₂O (99.99%, Sigma–Aldrich, St. Louis, MO, USA) to obtain 20 wt.% of CeO₂ was dissolved in acetone. Dried carbon was added to the solution, in a proportion of 10 mL/g of support, with stirring. After 12 h, the excess of solvent was slowly removed under vacuum at 40 °C and the solid was then dried in the oven overnight. Finally, the dried solid was heat treated during 4 h at 350 °C under flowing He (50 mL/min), with a heating rate of 1 °C/min, in order to slowly decompose the cerium nitrate to form CeO₂, trying to avoid the modification of the carbon surface by the evolved nitrogen oxides [25].

Nickel addition to the CeO₂/C solid was carried out using the proper amount of Ni(NO₃)₂·6H₂O (99.9%, Sigma-Aldrich, St. Louis, MO, USA) in acetone to obtain 15 wt.% Ni, using 10 mL of solution per gram of solid. After stirring for 12 h, the solvent was removed under vacuum at 40 °C. Finally, the solid was treated at 350 °C for 4 h under flowing He (50 mL/min). The catalyst prepared was labeled Ni-CeO₂/C. For the sake of comparison, a Ni/CeO₂ catalyst was also synthesized. The ceria support was prepared by homogeneous precipitation from an aqueous solution of Ce(NO₃)₃·6H₂O (99.99%, Sigma-Aldrich, St. Louis, MO, USA) containing an excess of urea. The solution was heated at 80 °C and kept at this temperature, with slow stirring, during 12 h. The solid formed was filtered and calcined at 350 °C for 4 h. The CeO₂ support prepared in this way was impregnated with the Ni precursor as described for the carbon supported catalysts.

3.2 Textural Properties

The textural properties of the supports were characterized by nitrogen adsorption measurements at $-196\text{ }^{\circ}\text{C}$. Gas adsorption experiments were performed in home-made fully automated manometric equipment. Prior to the adsorption experiments, samples were out-gassed under vacuum (10^{-4} Pa) at $250\text{ }^{\circ}\text{C}$ for 4 h. The specific surface area was estimated after application of the BET equation.

3.3 Elemental Analysis

The actual metal loading of the different catalysts was determined by ICP-OES in a Perkin Elmer device (Optimal 3000). To this end, the metal was extracted from the catalysts by digestion in $\text{HNO}_3/\text{H}_2\text{O}_2$ (4:1) for 30 min, in a microwave oven at $200\text{ }^{\circ}\text{C}$.

3.4 OSCC and OSC Experiments

For the Oxygen Storage Complete Capacity (OSCC) 100 mg of catalyst was loaded into a U-shaped quartz reactor and the temperature was raised in a He flow (50 mL/min) until $350\text{ }^{\circ}\text{C}$. Then, the system was cooled and set to the desired temperature (150 , 250 and $350\text{ }^{\circ}\text{C}$). For each temperature 10 O_2 pulses of 1 mL were injected every 2 min. After that, the sample was submitted to 10 CO pulses of 1 mL each (every 2 min). The OSCC was calculated from the sum of the CO_2 formed after each CO pulse. The sample was then degassed during 10 min in a He flow to perform the OSC measurements. Four alternating series of pulses ($\text{CO-O}_2\text{-CO-O}_2\text{-CO-O}_2\text{-CO-O}_2$) were applied for each temperature. The OSC was determined by the average amount of CO_2 per pulse formed after the first CO pulse of the alternated ones. This method is based on the one proposed by Duprez *et al.* [26]. The gas composition at the exit of the reactor was analyzed by a mass spectrometer PFEIFFER Vacuum PrismaPlus controlled by Quadera[®] software (version 4.0, INFICON, LI-9496 Balzers, Furstentum Liechtenstein).

Several assumptions were contemplated for the OSC calculations. Concretely, it was considered that (i) only oxygen atoms bonded to the cerium participate in the oxygen storage process; (ii) the surface is assumed homogeneous and (iii) only one of the four oxygen atoms is involved in the storage ($2\text{CeO}_2 \rightarrow \text{Ce}_2\text{O}_3 + \text{“O”}$)

3.5 TEM

TEM images were taken with a JEOL electron microscope (model JEM-2010) working at 200 kV. It was equipped with an INCA Energy TEM 100 analytical system and a SIS MegaView II camera. Copper grids with a holey-carbon film support were used for the microscopy measurements. The samples were suspended in ethanol and placed on the grids for the analysis.

3.6 WGS Catalytic Tests

The catalytic behavior of the prepared samples in the low temperature water-gas shift reaction was evaluated in a fixed bed flow reactor under atmospheric pressure in the range of temperatures from $160\text{ }^{\circ}\text{C}$ to $380\text{ }^{\circ}\text{C}$. For the stability tests the temperature employed was $250\text{ }^{\circ}\text{C}$. Trying to simulate a more

close to real outgas mixture from a reformer, experiments with a feed gas composition of 7 mol% CO, 30 mol% H₂O, 50 mol% H₂, and 9 mol% CO₂ balanced to 100 mL/min with helium was tested. Activity tests were performed using 0.150 g of catalyst diluted with SiC, to avoid thermal effects. The corresponding contact time was 0.09 g·s/mL. Prior to reaction, the catalysts were reduced under flowing H₂ (50 mL/min) during 2 h at 350 °C. The composition of the gas stream exiting the reactor was determined by mass spectrometry (Pfeiffer, OmniStar GSD 301). The stabilization time for each temperature was 1 h and the CO conversion percentage was calculated by this equation:

$$\text{CO conversion (\%)} = 100 - (x_{\text{CO}}/x_{\text{COinitial}}) \cdot 100 \quad (1)$$

where x_{CO} is the molar concentration of CO in the outlet of the reactor and $x_{\text{COinitial}}$ is the CO concentration in the initial gas mixture. The carbon balance was checked taking into account all the carbon containing products.

4. Conclusions

The impact of the oxygen storage capacity on the WGS behaviour of a Ni/CeO₂ based catalysts is underlined in this paper. The dispersion of ceria nanoparticles on a high surface activated carbon drives to a strong enhancement of the catalyst's oxygen mobility. The excellent redox skills together with the better metallic dispersion of the Ni-CeO₂/C catalyst due to the carbon textural promotion, result in a remarkable improvement of the WGS activity.

The stability of the Ni-CeO₂/C catalysts under continuous operation, as well as interrupting cycles, was tested. Although high activity was found under these conditions at early stages of the reaction, a notable activity loss was observed and attributed to the sintering of Ni particles. Despite the issue of the stability should be improved, the Ni-CeO₂/C catalyst could be considered as an interesting alternative for the low temperature WGS reaction and merits further investigations.

As final remark, it should not be disregarded that the high WGS activity observed for the developed sample was achieved with a relatively low amount of cerium oxide on its composition. This fact indicates that our preparation procedure could constitute an alternative approach towards a new generation of Ni/CeO₂ based catalysts.

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Author Contributions

Laura Pastor Pérez was the main author of this paper. Tomás Ramírez Reina carried out the OSC experiments and he provided assistance in the manuscript writing. Svetlana Ivanova, Miguel Ángel Centeno, José Antonio Odriozola and Antonio Sepúlveda Escribano took part in the article revision and they contributed in the response to reviewers' comments

Conflicts of Interest

The authors declare no conflict of interest.

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