Magnetic Properties of Efficient Catalysts Based on La-Doped Ceria-Supported Nickel Nanoparticles for rWGS Reaction. Influence of Ni Loading

Consuelo Alvarez-Galvan,* Jose Luis Martínez, Maricarmen Capel-Sanchez, Laura Pascual, and Jose Antonio Alonso*

The influence of Ni loading on Ce0.9La0.1O1.95-supported Ni catalysts for CO2 reduction with hydrogen (reverse water gas shift reaction) is studied. The samples are prepared by solution combustion synthesis (SCS), leading to materials with high thermal resistance, purity, and crystallinity, consisting of metallic nickel nanoparticles supported on La-doped ceria. The study of the ferromagnetic Curie temperature (\(T_C\)) and magnetization cycles suggest that the Ni nanoparticles are superparamagnetic, exhibiting magnetic order at room temperature, with \(T_C\) strongly dependent on the particle size; this spans from 1.9, up to 80 nm. The structural study from synchrotron X-ray diffraction data and Raman spectroscopy clearly show the presence of oxygen vacancies in the fluorite crystal structure of the Ce0.9La0.1O2−δ matrix, which increase in the spent catalysts by forming a greater proportion of Ce3+ compared with their fresh counterparts. This is confirmed from the Raman spectra, showing an increase in the relative intensity of the band placed between 520 and 610 cm⁻¹. All the catalysts show very high reaction rate per unit mass of catalyst; the CO2 conversion after 6 h for the catalyst with 10% Ni molar (Ni0.1/Ce0.9La0.1) is 57% (2.4 moles CO·h⁻¹·g catalyst⁻¹), very close to the thermodynamic equilibrium (59.3%).

1. Introduction

Carbon dioxide (CO2) is recognized as one of the main sources of the greenhouse effect. Nowadays, there are increasing attempts to consider it as a resource rather than a waste, since large amounts of low cost and relatively pure carbon dioxide will be soon available from current and planned plants for carbon sequestration and storage. The present use of CO2 is limited to a few processes: syntheses of urea, salicylic acid, and polycarbonates, but these only correspond to a few percentage of the potential CO2 suitable to be converted into chemicals and/or fuels.10

Conversion of CO2 into CO by catalytic hydrogenation has been recognized as one of the most promising processes for CO2 utilization. Synthesis gas (syngas) could then be used to produce hydrocarbons or oxygenated hydrocarbons via Fischer–Tropsch reaction, as well as for the synthesis of methanol. This is a basic chemical for the production of synthetic fuels and polymers, whose importance is increased by the progressing shift in resources used in the petrochemical industry from crude oil to natural gas. The syngas reaction is a process in two steps, in which the first and essential is the reduction of CO2 to CO with H2, or reverse water gas shift reaction (rWGS, CO2 + H2 ↔ CO + H2O), using renewable H2. This reaction is endothermic, being thermodynamically favored at high reaction temperatures and in excess of H2; therefore, the use of an active-selective-stable catalyst under these conditions is imperative.

Regarding the reaction mechanism, it has been widely reported that the reaction requires a bifunctional catalyst, consisting of a metal, which favors activation and dissociation of H2 and a reducible oxide, promoting CO2 adsorption and oxygen mobility in the lattice. The rate-determining step for the reaction depends on the catalyst composition and reaction conditions, being, at high temperature RWGS reaction: CO–O bond cleavage on Pt, Pd, and Cu, owing to the high barrier on the surfaces, while OH binding with H to form H2O is rate-determining on Co, Fe, Ru, Ni, and Rh.5–7 Copper-based catalysts, the most studied for WGS reaction, have been also applied to the rWGS reaction;8–10 however these systems are not suitable at high temperature because of their poor thermal stability.10 As alternative, ceria-supported nickel and noble-metals catalysts have shown excellent catalytic performance in terms of activity, selectivity, and stability for RWGS reaction.8–10

These supported metals present high ability for activation and dissociation of H2 molecules,7 being Ni preferred due to its lower prices compared to expensive noble metals.14 Ceria is a suitable support due to their basic properties.14 Moreover, the...
existence of oxygen vacancies in ceria promotes CO₂ adsorption and favors oxygen mobility, readily available to form water. When CeO₂ is doped with a certain proportion of La³⁺, these ions occupy Ce⁴⁺ positions increasing oxygen vacancies. Several studies suggest that the active site of the rWGS reaction is related to the interface between metallic particles of transition metals and a reducible oxide support, in order to promote de adsorption of CO₂. As reported in literature, the preparation method that achieves a higher interface between the metallic particles and the support is coprecipitation; however the catalysts prepared by this method are bulk materials, without internal porosity, being the dispersion of the active phases quite low.

Considering the very high efficiencies of certain supported catalysts based on Ni nanoparticles supported on lanthanide-doped ceria prepared by solution combustion synthesis (SCS) applied to the rWGS reaction, once optimized the proportion of lanthanide proportion, we focus on the effect of Ni amount establishing activity-structure correlations.

In order to get knowledge over the influence of Ni loading on the catalytic properties, trying to elucidate the structure-activity dependence, different physicochemical characterization techniques have been used: Synchrotron X-ray diffraction (SXRD), transmission electron microscopy (TEM), temperature programed reduction, Raman spectroscopy, and N₂ adsorption-desorption and magnetic properties arising from Ni nanoparticles.

2. Results and Discussion

2.1. Crystalline Phases by X-Ray Diffraction Analyses

Figure 1a shows the SXRD patterns collected at RT; they correspond entirely to the ceria-based matrix, consisting of Ce₀.9La₀.1O₂₋δ oxide with fluorite crystal structure, since the Ni nanoparticles are not visible to X-ray diffraction (XRD), by the small crystallite (or crystalline domain) size with insufficient large diffraction domains to be detected by this technique (below ≈2 nm). However, certain synthesis conditions promote the reduction of nickel oxide to metallic nickel, which is revealed by the characteristic grey color of the samples and the magnetic properties of the obtained materials. A SXRD study for a representative Ce₀.9La₀.1O₂₋δ:7%Ni sample was essential to unveil some structural features that could not be determined from laboratory XRD, in particular to envision the oxygen vacancies associated with the partial replacement of tetravalent Ce by La³⁺ ions. Although oxygen atoms are weak scatterers to X-ray radiation, the short wavelength of SXRD allows accessing to a wide region of the reciprocal

![Figure 1. a) X-ray diffraction profiles of support and catalysts. b) Rietveld plots from SXRD data for Ni₀.07/Ce₀.9La₀.1O₂₋δ at RT and 800 °C, corresponding to structural refinements in the cubic Fm-3m space group. The insets show a close up of the high-angle region, highlighting the quality of the fit. The presence of metal Ni is not detected in the SXRD patterns.](image)
space, thus allowing the simultaneous refinement of the oxygen thermal factors and occupancies at the anionic sites of the fluorite structure. In the cubic Fm-3m (#225) space group, \( Z = 4 \), Ce and La are placed at random at the 4a (0,0,0) sites, and oxygen atoms O at 8c (1/4,1/4,1/4) positions. The quality of the Rietveld fit is illustrated in Figure 1b for the patterns at RT and 800 °C. The occupancy factors of oxygen atoms were refined in the final run. At RT (28 °C) the unit-cell parameter of the fluorite is 5.44435(7) Å, which increases to 5.49015(9) Å at 800 °C by the thermal expansion. Regarding the occupancy factor for oxygen positions, a value of 1.86(2) oxygen atoms per formula unit is obtained at RT, which decreases to 1.83(3) per f.u. at 800 °C, as the ceria matrix releases additional oxygen at elevated temperature by partial reduction of Ce\(^{4+}\) to Ce\(^{3+}\).

2.2. Magnetic Properties Determination

The La\(_{0.9}\)Ce\(_{0.1}\)O\(_2\) matrix, from the magnetic point of view, is mostly a diamagnetic system. The presence of small amounts of nickel particles gives rise to a very clear and strong paramagnetic/ferromagnetic signal, which is easy to measure and to study from the field and temperature dependence. In Figure 2a we present the magnetic susceptibility data in the low temperature range (below 130 °C) for the samples with Ni content between 1 and 10% Ni. Assuming that the pure bulk nickel Curie temperature (\( T_C \)) = 358 °C,[15] the first important observation is the very strong reduction in the \( T_C \) for the 1% Ni doped sample, down to \( \approx \)100 °C. For the different Ni contents from 4 to 10% Ni, the \( T_C \)s are well above 130 °C, as corresponds to the \( T_C \) value of bulk Ni.

In order to determine the \( T_C \) for higher doping levels, we measured the magnetic susceptibility in the temperature range from 130 up to 530 °C, and the data are presented in Figure 2b. On the other hand, the different amount of nickel particles strongly affects the saturated magnetization at low temperature in the ferromagnetic state. The hysteresis loops (field dependence of the magnetization) was measured for the different samples at very low temperature (5 K = -268 °C), and the results are presented in Figure 2c.

The low-temperature saturation magnetization is correlated to the amount of nickel contents from 1% up to 10% molar. The magnetic signal for the sample with only 1% Ni is mostly dominated by the Ce\(_{0.9}\)La\(_{0.1}\)O\(_2\) matrix, which is diamagnetic. The main reduction of \( T_C \) in nickel nanoparticles is coming from the particle size, as discussed in literature.[16] In this paper, different nickel nanoparticles were prepared with a different particle size and the magnetic characterization yields very different \( T_C \)s, with a clear dependence on the particle size. From these results, these authors are able to propose a simple formula for the size dependence of \( T_C \) for Nickel nanoparticles (Equation (4) in the above mentioned paper), that is, \( T_C \) (°C) = 358 – 482.38/D (nm).

From our data, we are able to determine the approximate value of \( T_C \) of the different samples, and then to estimate the particle size for the different Ni contents, by comparison with the data of Ref. [16]. Our data together with those given in Ref. [16] are presented in Figure 3. This figure shows that the average particle size for the lowest \( T_C \) (1% Ni) is rather small, that is, 1.9 nm, increasing for the 4% Ni to 15.6 nm, for 7% Ni to 32 nm, and finally for 10% Ni at least to 80 nm. The \( T_C \)s obtained for the four samples perfectly fit with the previous data.[16] In conclusion, this simple method of sample

---

**Figure 2.** a) Temperature dependence of the magnetic susceptibility for different doped samples of Ce\(_{0.9}\)La\(_{0.1}\)O\(_2\)\(_{\delta}\) in the range from 1 up to 10% Ni. b) Temperature dependence of the magnetic susceptibility for Ni contents of 4%, 7%, and 10%, in the high temperature part (up to 800 K). c) Hysteresis loops for the different samples Ni\(_x\)/La\(_{0.9}\)Ce\(_{0.1}\)O\(_2\) at \( T = 5 \) K.

**Figure 3.** Size dependence of the Curie Temperature (\( T_C \)) for the different nanoparticles of this work (Triangles) and Ref. [16] (Circles).
preparation by SCS is able to produce nanoparticles of nickel with a precise particle size, depending on the Ni amount introduced in the preparation, which present the characteristics of the bulk nickel in the nanometric size.

2.3. Redox Properties

H₂ reduction profiles during temperature-programmed reduction (TPR) experiments of the support (Ce₀.₉La₀.₁O₂-δ) and the samples with 1%, 7%, and 10% of Ni supported on Ce₀.₉La₀.₁O₂-δ are depicted in Figure S4, Supporting Information. Although Ni particle core is metallic, there exists an external layer consisting of NiO, formed by the contact of metallic nickel with atmospheric air that is reduced during the TPR analyses. Taking into account the previous quantification of H₂ consumption using high-purity CuO as a calibration standard, the proportion of nickel oxide in nickel particles is between 1% and 5%.

The Ce₀.₉La₀.₁O₂-δ-Ni samples show a reduction profile with another peak located between 240 and 300 °C due to the reduction of NiO₅ particles with different degree of interaction with the support. The higher reduction temperature of NiO phase in nickel particles existing in the sample with 1% Ni, is due to the higher interaction of the very small nickel particles present in this sample. Typically, the peak assigned for free NiO species has a maximum at around 400 °C,[28] so the shift to lower reduction temperature is ascribed to the surface oxygen vacancies on the support that might promote nickel oxide reduction.[19] In the case of NiOₓ/CeO₂ samples, another wide and low intense reduction contribution was observed at 500–600 °C, attributed to the simultaneous reduction of NiOₓ and surface CeO₂, being the reducibility of the CeO₂ surface improved by the interaction with nickel species. Therefore, it means that both phases interact, favoring one to each other to be reduced at lower temperatures.[20] A shift of the reduction of this last contribution, related to surface ceria reduction, is observed toward lower temperatures as Ni loading increases. Bulk reduction of ceria is produced over 800 °C, being not registered in these analysis.[21,22]

2.4. Textural Properties

The BET surface areas of the catalysts have been determined by N₂ adsorption-desorption at −196 °C and the values, which are reported in Table S1, Supporting Information, are between 15 and 20 m²·g⁻¹. The relative low surface areas are derived from the essentially macroporous nature of the samples, having porosity values of around 90%.[23] This fact is supported by TEM micrographs, which will be commented in Section 2.5. As an example, pore size distribution for the sample with 1% Ni is depicted in Figure S1, Supporting Information. Some mesoporosity is observed, finding a relative maximum that corresponds to a pore size around 44 nm. However, the average pore size is larger, being in the macroporous range. The Ni particle size is below the average pore size of this spongy structure, and therefore, an increase in the Ni loading does not decrease progressively the surface area of the material. An increase of this value is found for the samples with 7% Ni in relation to the counterpart with 4%, which could be influenced by the contribution of Ni particles to the surface area. For the sample with higher Ni loading (10% molar, Ni₀.₁/Ce₀.₉La₀.₁) a slight decrease in the surface area is observed in relation to the sample with 7% Ni, since the Ni particle size is close to the average pore size of the matrix, plugging part of the porous structure of the support, as derived from magnetic measurements (see Figure 3).

2.5. Morphological Properties

Ni₀.₀₁/Ce₀.₉La₀.₁, Ni₀.₀₇/Ce₀.₉La₀.₁, and Ni₀.₁/Ce₀.₉La₀.₁ samples have been studied by TEM and related techniques; electron diffraction, high-resolution TEM (HRTEM), and X ray energy dispersive spectroscopy (XEDS). Figure 4a,d shows low-magnification micrographs of the Ni₀.₀₁/Ce₀.₉La₀.₁ and Ni₀.₀₇/Ce₀.₉La₀.₁ samples, respectively. Here, the morphology of the Ce₀.₉La₀.₁O₂-δ support phase it was difficult to isolate and characterize the Ni phase properly, being thus unable to perform a particle size distribution of the Ni particles in both samples. In the case of 7% Ni sample (Figure 4e) at medium magnifications, the presence of Ni agglomerates on the surface of the support (marked with arrows) can be appreciated. However, the HRTEM image of Figure 4f indicates the presence of one agglomerate of ~20 nm composed of very small Ni nanoparticles in which neither the shape nor the size can be distinguished. The EDX spectrum shows that indeed the agglomerate is composed of Ni. Even though XEDS analysis in several areas detects a proportion of Ni close to the nominal loading.

With these results in mind, we have made a spatial distribution of the elements using EDX analysis in STEM mode. The results are shown in Figure 4g, where the distribution maps of Ce, La, O, and Ni indicate that, in both cases, Ni is homogeneously distributed over the surface of the support.

Other remarkable aspect is the presence of holes. Figure S5, Supporting Information shows a HRTEM image of the Ni₀.₀₁/Ce₀.₉La₀.₁ sample, in which the presence of holes of a few nanometers and with a well-defined hexagonal shape is observed. These holes are also present in the Ni₀.₀₇/Ce₀.₉La₀.₁ sample (Figure S5, Supporting Information), however holes here are bigger and with a rhombohedral shape. These holes are associated with former Ni existing particles, with hexagonal and cubic structures, respectively, which could melt or volatilize during the high temperature reached in the ignition produced during their synthesis by SCS method.[24] This structure transition with Ni particle size has been reported to occur around 6 nm.[25]
Finally, the spent sample of 7% Ni has also been characterized by TEM (Figure 5). The morphology and structure of the support seems to be maintained after the reaction, as indicated by its SAED (b) of a representative area. The most remarkable aspect in this case is the presence of a disordered surface (marked in the image (c,d)), due to traces of carbon after the
reaction. The elemental map of C obtained by EDX shows, in fact, the presence of carbon scattered over the support (Figure 5e).

2.6. Catalytic Performance

To explore the effect of Ni loading on the reaction performance of Ce0.9La0.1O2−δ-supported Ni catalysts, Ni0.01/Ce0.9La0.1, Ni0.04/Ce0.9La0.1, Ni0.07/Ce0.9La0.1, and Ni0.1/Ce0.9La0.1 have been evaluated for CO2 reduction with H2. Figure 6 plots CO2 conversion (Figure 6a), CO selectivity (Figure 6b), and CO yield (Figure 6c) versus reaction time. Different behaviors for the catalysts have been observed depending on Ni proportion. For the catalysts with 7% and 10% molar of Ni, after the first hour and half of reaction, which is how long it lasts the induction period observed for the sample with higher Ni loading (Ni0.1/Ce0.9La0.1), the conversions and yields are very similar for the whole reaction period. In case of the catalyst with 4% Ni, a slight trend of deactivation is observed. This induction period is explained by the greater time needed to completely reduce the nickel oxide layer that covers Ni metallic particles. The CO2 conversion after 6 h for the catalyst with 10% Ni molar (Ni0.1/Ce0.9La0.1) is 57% (2.4 moles CO·h−1·g catalyst−1), and very close to the thermodynamic equilibrium (59.3%). Considering the very high space velocity used in the activity tests, it is remarkable the excellent performance of these catalysts for the rWGS reaction, showing a very high reactivity per catalyst weight. This fact is directly influenced by the foamy morphology with large macroporosity of the catalyst derived

![Figure 5. TEM micrographs for Ni0.07/Ce0.9La0.1 spent catalyst. a) Low magnification image b) selected area electron diffraction c,d) TEM images e) distribution maps.](image-url)
H2O together with CO by the RWGS reaction, is being limited, function provided by metal sites, supplying H atoms to form proportionation reaction). Thus, when the Ni content is too small, the carbon formation by the Boudouard reaction (or CO disproportionation). The band between 520 and 610 cm\(^{-1}\) is related to intrinsic oxygen vacancies of the studied catalysts. The main peak of pure ceria is present at 466 cm\(^{-1}\) in F2g vibrational mode. In this mode, only oxygen atoms can turn around the cerium ions Ce\(^{4+}\); this mode corresponds to the symmetrical stretching mode (vs (Ce–O)) of the CeO\(_x\) vibrational unit, in the cubic fluorite lattice of ceria, being very sensitive to any disturbance in the symmetry of the oxygen sublattice, including changes in the oxygen stoichiometry of cerium dioxide.[27]

Figure 7 shows Raman spectra of fresh and after reaction catalysts. The main band is assigned to the F2g Raman-active mode at 465 cm\(^{-1}\) in CeO\(_2\), as well as additional peaks at around 560 and 610 cm\(^{-1}\), which are indicative of the creation of oxygen vacancies and/or structural defects in CeO\(_2\).[28] due to La doping and to oxygen vacancies originated from reducing Ce\(^{4+}\) to Ce\(^{3+}\), which both can promote the catalytic activity of ceria for RWGS reaction.[29] The band at \(\approx 520\) cm\(^{-1}\) is known as to be formed by extrinsic oxygen vacancies produced to maintain the electroneutrality when Ce\(^{4+}\) ions are replaced by La\(^{3+}\) ions. On the other hand, the band at \(\approx 610\) cm\(^{-1}\) is related to intrinsic oxygen vacancies, generated by the presence of Ce\(^{3+}\) ions.[30,31] These two bands are differentiated in some spectra such as the corresponding to the spent catalyst with 1% Ni (Ni\(_{0.01}\)/Ce\(_{0.9}\)La\(_{0.1}\)). In fresh samples, another component related to the formation of some NiO has to be considered (at around 520 cm\(^{-1}\)).[32]

The band between 520 and 610 cm\(^{-1}\) in the fresh prepared samples increases with Ni loading. This result is not related to the creation of oxygen vacancies by Ni incorporation into the La doped-ceria support, since Rietveld refinements (see Figure S2, Supporting Information) from XRD data for both samples with 4 and 10% Ni do not reveal an inclusion of Ni into the fluorite matrix.[13] The intensity of this band increases because the intensity of the peak corresponding to NiO (signal at \(\approx 520\) cm\(^{-1}\)) increase with Ni loading.[32]

2.7. Structural Properties by Raman Spectroscopy

Raman spectroscopy is a method that can provide information about oxygen vacancies in the fluorite structure of ceria. Also, it enables us to gain supplementary information on oxygen vacancies of the studied catalysts. The main peak of pure ceria is present at 466 cm\(^{-1}\) in F2g vibrational mode. In this mode, only oxygen atoms can turn around the cerium ions Ce\(^{4+}\); this mode corresponds to the symmetrical stretching mode (vs (Ce–O)) of the CeO\(_x\) vibrational unit, in the cubic fluorite lattice of ceria, being very sensitive to any disturbance in the symmetry of the oxygen sublattice, including changes in the oxygen stoichiometry of cerium dioxide.[27]
The spectra obtained in the catalysts after reaction also revealed an increase in the relative intensity of the maximum of the band placed between 520 and 610 cm\(^{-1}\) (related to the maximum intensity at 465 cm\(^{-1}\), main CeO\(_2\) Raman band) in comparison to the fresh counterparts (Table S2, Supporting Information). In these samples, the contribution of NiO is null or negligible, therefore the increase of the relative intensity while Ni loading increases is explained by the formation of oxygen vacancies by reduction of Ce\(^{4+}\) to Ce\(^{3+}\), also reported in literature for similar catalysts.\[^{34}\] This fact would be supported by the role of metallic nickel during reaction promoting ceria reduction and in agreement with the results obtained by TPR analyses\[^{35}\] since extrinsic oxygen vacancies derived by the La-doping are the same (same proportion of La in all the catalysts, Ce\(_{0.9}\)La\(_{0.1}\)O\(_{2-\delta}\)). As observed in the relative intensities of the bands at 520–610 cm\(^{-1}/465\) cm\(^{-1}\) for the fresh and the spent catalysts (Figure 7), the difference between both values for each catalyst remains large while Ni loading increases. Rietveld refinements from laboratory XRD data reveal a conspicuous contraction of the unit cell of the spent Ni\(_{0.04}/\)Ce\(_{0.9}\)La\(_{0.1}\) and Ni\(_{0.1}/\)Ce\(_{0.9}\)La\(_{0.1}\) catalysts when they are compared to the unit cell of the fresh counterparts (see Figure 8; Figures S2, S3, Supporting Information). These results support the formation of new oxygen vacancies derived from the formation of Ce\(^{3+}\) during the catalytic reaction.

Furthermore, bands at 1350 and 1580 cm\(^{-1}\), associated with the presence of disordered and graphitic carbon species, are only observed in the spent sample with 1% molar of Ni. This result is in accordance with the deactivation observed during the catalytic test of this sample, pointing out that a very small amount of Ni promotes the formation of carbon by the Boudouard reaction (2CO \(\rightleftharpoons\) CO\(_2\) + C), decreasing the selectivity to the RWGS reaction.

2.8. Surface Chemical Analysis by XPS

By way of example, XPS spectra of Ni 2p, Ce 3d, and La 3d core-levels for a representative catalyst (Ni\(_{0.07}/\)Ce\(_{0.9}\)La\(_{0.1}\) after reaction) are depicted in Figure S6, Supporting Information. Binding energies (BE) for Ni 2p3/2 core level are quite overlapped with La 3d3/2 core level.

3. Conclusion

In this study, the influence of Ni loading on supported catalysts based on Ni\(_y/(\text{Ce})_{1-y}\)La\(_{0.1}\)O\(_{2-\delta}\)(\(y = 0.01, 0.04, 0.07,\) and 0.1) over the magnetic, structural, and morphologic properties were examined, as well as their catalytic behavior for the RWGS reaction. The catalysts were prepared by SCS, producing, under certain conditions, highly macroporous and crystalline materials based on metallic nickel polycrystalline nanoparticles supported on La-doped ceria, with a certain proportion of extrinsic oxygen vacancies derived from the inclusion of La ions into the ceria fluorite matrix. This simple method is able to produce nickel nanoparticles with a precise Ni particle size, depending on the Ni amount introduced in the preparation. Except for the catalyst with the smaller Ni loading (1% Ni), which deactivates quickly during reaction by carbon formation, the other compositions are very active for the RWGS reaction per unit mass of catalyst. The creation of new oxygen vacancies by Ce\(^{3+}\) formation during reaction...
the reaction is promoted by nickel sites, increasing with Ni loading.

### 4. Experimental Section

Cermets (Ni)$_x$(Ce$_{0.9}$La$_{0.1}$O$_{1.95}$)$_{1-x}$ ($x = 0.01; 0.04; 0.07, and 0.1$, with 0.35%, 1.49%, 2.51%, and 3.65% in weight, respectively) (coded Ni$_{0.01}$/Ce$_{0.9}$La$_{0.1}$, Ni$_{0.04}$/Ce$_{0.9}$La$_{0.1}$, Ni$_{0.07}$/Ce$_{0.9}$La$_{0.1}$, and Ni$_{0.1}$/Ce$_{0.9}$La$_{0.1}$, respectively) were prepared by the SCS method. Stoichiometric amounts of the corresponding nitrates were dissolved in distilled water, and then a certain amount of glycine was added. The mixture was heated on a hot plate up to 310°C. Once most of water was evaporated, a viscous gel was produced. Then a self-igniting process was triggered, leading, in a single step, to a finely particulate powder consisting of nickel metal particles supported on the corresponding doped-ceria mixed oxide.

The nature of the resulting powder after the SCS was assessed by laboratory XRD in a Bruker-AXS D8 diffractometer (40 kV, 30 mA), with Cu Kα radiation ($\lambda = 1.5418$ Å). SXRD experiments were carried out in transmission mode on the BL04-MSPD beamline of the ALBA synchrotron (Barcelona, Spain) using the highest angular resolution mode as provided by the MAD setup. The Ce$_{0.9}$La$_{0.1}$O$_{2.4}$ $\delta$%Ni cermet was sealed in a 0.7 mm diameter quartz capillary that was rotating during acquisition time to increase powder averaging. The beam energy was 28 keV ($\lambda = 0.4416$ Å), selected to optimize absorption. After a room temperature pattern, a high-temperature acquisition at 800°C was collected. The analysis of SXRD and laboratory XRD data was performed by the Rietveld method,[39] using the FullProf Suite.[39] The diffraction peak shape was defined with a pseudo-Voight function; a linear interpolation between points devoid of reflections was considered as background. The final refinement included the scale factor, zero-point shift, width and asymmetry parameters, unit-cell parameters, atomic positions, and isotropic displacement factors. No regions were excluded from the refinements.

Magnetic measurements were obtained by a SQUID magnetometer from Quantum Design (MPMS-5S, San Diego, USA) in a temperature range from 1.8 up to 800 K and a range of applied magnetic fields up to 5 T. The high temperature measurements (400–800 K) were performed with the specific furnace option for the MPMS-5S, which request a different sample holder able to work at high temperatures. In this case, a quartz container was used, which implied a very different background signal with respect to the low temperature measurements.

Specific surface areas were determined by the BET method from the nitrogen adsorption isotherms recorded at 196°C using a Micromeritics ASAP 2420 automatic instrument. The total pore volume, total pore area, and pore size distribution were determined using mercury porosimetry (Micromeritics AutoPore IV 9510).

Microstructural characterization of the catalysts was evaluated using a 200 kV field emission transmission electron microscope (Titan/STEM JEOL 2100F) equipped with an EDS (X-Max80 detector. Oxford Instruments). TEM samples were carefully prepared suspending particles in ethanol and dispersing them for 10 min, using an ultrasonication bath. One drop of the suspension was deposited on a commercial copper TEM grid.

TPR experiments were carried out in an automatic Micromeritics TPD/TPR 2900. The catalyst was pre-treated under helium at 110°C for 15 min. The TPR profile was recorded by heating the sample at 110°C in helium for 15 min and then from room temperature to 850°C at a rate of 10°C min$^{-1}$ under a H$_2$/Ar (10% v/v) flow, maintaining this temperature for 15 min.

Photoelectron spectra were recorded on a SPECS GmbH electron spectrometer equipped with a hemispherical electron analyzer, using a Mg-Kα ($hv = 1253.6$ eV, 1 eV = $1.605 \times 10^{-19}$ J) X-ray source (200 W, 12 kV). After degassing at 10$^{-6}$ mbar, the samples were transferred to the ion-pumped analysis chamber, where the residual pressure was kept below 4 $\times$ 10$^{-9}$ mbar during data acquisition. All BE were referenced to the C 1s signal as an internal standard at 284.8 eV from carbon contamination of the samples to correct the charging effects. Peak
intensities were estimated by calculating the integral of each peak after subtracting an S-shaped background and fitting the experimental peak to a combination of Lorentzian/Gaussian lines of variable proportions. Atomic surface contents were estimated from the areas of the peaks, corrected using the corresponding sensitivity factors.

CO yield and CO selectivity were determined according to Equations (1) and (2), respectively.

CO selectivity (%) = \( \frac{\text{CO molar flow outlet}}{\text{CO}_2 \text{ molar flow inlet} - \text{CO}_2 \text{ molar flow outlet}} \times 100 \)  

CO yield(%) = \( \frac{\text{CO molar flow outlet}}{\text{CO}_2 \text{ molar flow inlet}} \times 100 \)

Raman spectra were recorded with a Renishaw in Via Raman Microscope spectrometer equipped with a laser beam emitting at 532 nm, at 100 mW output power. The photons scattered by the sample were dispersed by a 1800 lines per mm grating monochromator and simultaneously collected on a CCD camera; the collection optic was set at 50x objective.

The reverse water-gas shift reaction was performed with a continuous flow fixed-bed quartz tubular reactor (4 mm, inner diameter) under atmospheric pressure. The catalyst (sieved between 50 and 100 µm) was activated under the reactive feed up to 700 °C at atmospheric pressure. The catalyst (sieved between 50 and 100 µm) was chosen in order to increase the conversion of CO \(_2\). The reaction stream was analyzed on line by gas chromatography (HP 6890), equipped with a column Carboxen 1010 PLOT (SUPELCO®) and with a thermal conductivity detector. Nitrogen was used as an inert standard for quantification. The catalysts were tested for 6 h.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
C.A.-G. acknowledges financial support given by the Spanish Ministry of Economy and Competitiveness (ENE2016-74889-C4-3-R). J.A.A. and J.L.M. acknowledge financial support given by the Spanish Ministry of Economy and Competitiveness (MAT2017-84496-R).

Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

Keywords
catalysts, CeO\(_2\), lanthanide, magnetism, nickel, reverse water gas shift reaction

Received: February 3, 2021
Revised: April 19, 2021
Published online:

[1] G. Centi, S. Perathoner, Catal. Today 2009, 148, 191.
[2] Y. Qi, Y. Zhu, D. Chen, Green Chem. 2020, 1, 131.
[3] S. Qin, C. W. Hu, H. Q. Yang, Z. S. Su, J. Phys. Chem. A 2005, 109, 6498.
[4] E. L. Fornero, D. L. Chiavassa, A. L. Bonivardi, M. A. Baltanás, J. CO2 Util. 2017, 22, 289.
[5] J. Schumann, M. Eichelbaum, T. Lunkenbein, N. Thomas, M. C. Alvarez-Galvan, R. Schlögl, M. Behrens, ACS Catal. 2015, 5, 3620.
[6] C. Álvarez Galván, J. Schumann, M. Behrens, J. L. G. Fierro, R. Schlögl, E. Frei, Appl. Catal., B 2016, 195, 104.
[7] W. Wang, S. Wang, X. Ma, J. Gong, Chem. Soc. Rev. 2011, 40, 3703.
[8] L. Wang, S. Zhang, Y. Liu, J. Rare Earths 2008, 26, 66.
[9] L. Wang, H. Liu, Y. Chen, R. Zhang, S. Yang, Chem. Lett. 2013, 42, 682.
[10] D. Tibiletti, A. Goguet, F. C. Meunier, J. P. Breen, R. Burch, Chem. Commun. 2004, 1636.
[11] M. Tahir, Int. J. Hydrog. Energy 2017, 42, 28309.
[12] B. Tahir, M. Tahir, N. A. S. Amin, Appl. Catal., B 2019, 248, 167.
[13] L. Wang, H. Liu, Y. Chen, S. Yang, J. Rare Earths 2013, 31, 969.
[14] M. C. Álvarez-Galvan, M. Dapena Osypina, J. A. Alonso-Alonso, L. Troncoso Aguilera, V. Cascos Jimenez, J. L. Campos-Martin, J. L. García Fierro, H. Falcon Richen, ES1641.1265 BIS 2017, ES2674434.
[15] B. Legendre, M. Sghaier, J. Theram. Anal. Calorim. 2011, 105, 141.
[16] X. He, W. Zhong, C. T. Au, Y. Du, Nanoscale Res. Lett. 2013, 8, 446.
[17] V. L. Parola, G. Pantaleo, A. M. Venezia, Catalysts 2018, 8, 220.
[18] H. S. Roh, K. W. Jun, W. S. Dong, J. S. Chang, S. E. Park, Y. I. Joe, J. Mol. Catal. A: Chem. 2002, 181, 137.
[19] L. Pino, A. Vita, F. Cipiti, M. Lagana, V. Recupero, Appl. Catal., B 2011, 104, 64.
[20] S. Zhang, J. Lee, D. H. Kim, T. Kim, Catal. Sci. Technol. 2020, 10, 2339.
[21] M. Li, A. C. van Veen, Appl. Catal., B 2018, 237, 641.
[22] F. J. Lin, R. Delmelle, T. Vinodkumar, B. M. Reddy, A. Wokaun, A. Alkheit, Catal. Sci. Technol. 2015, 5, 3336.
[23] C. Álvarez-Galvan, H. Falcon, V. Cascos, L. Troncoso, S. Perez-Ferreras, M. Capel-Sanchez, J. M. Campos-Martin, J. A. Alonso, J. L. G. Fierro, Int. J. Hydrog. Energy 2018, 43, 16384.
[24] S. Specchia, G. Ercolino, S. Karimi, C. Italiano, A. Vita, Int. J. Hydrog. Energy 2017, 26, 166.
[25] S. V. Taranchand, J. Singh, C. Nayak, D. Bhattacharyya, N. Kaurav, S. Jha, G. Okram, J. Phys. Chem. C 2016, 120, 28354.
[26] M. D. Porosoff, B. Yan, J. G. Chen, Energy Environ. Sci. 2016, 9, 62.
[27] N. Kainbayev, M. Siubas, D. Virbuskas, Z. Rutkuniene, K. Bockute, S. Bolegenova, G. L. Kainbayet, Coatings 2020, 10, 432.
[28] F. L. Liang, Y. Yu, W. Zhou, X. Y. Xu, Z. H. Zhu, J. Mater. Chem. A 2015, 3, 634.
[29] F. Esch, S. Fabris, L. Zhou, T. Montini, C. Africh, P. Fornasiero, G. Comelli, R. Rosei, Science 2005, 309, 752.
[30] A. Singhania, A. N. Bhaskarwar, Int. J. Hydrog. Energy. 2018, 43, 4818.
[31] D. D. He, H. S. Hao, D. K. Chen, J. P. Liu, J. Yu, J. C. Lu, F. Liu, F. G. P. Wan, S. F. He, Y. M. Luo, Catal. Today 2017, 281, 559.
[32] A. Löfberg, J. Guerrero-Caballero, T. Kane, A. Rubbens, L. Jawiowski-Duhamel, Appl. Catal., B 2017, 212, 159.
[33] C. Tang, J. Li, X. Yao, J. Sun, Y. Cao, L. Zhang, F. Gao, Y. Deng, L. Dong, Appl. Catal., A 2015, 494, 77.
[34] D. D. Chen, Q. H. Ma, L. F. Wei, N. X. Li, Q. H. Shen, W. Tian, J. C. Zhou, J. Y. Long, J. Anal. Appl. Pyrolysis 2018, 130, 169.
[35] M. A. Ocsachoche, J. I. Eugenio Russman, B. Iriogoyen, D. Gazzoli, M. G. González, Mater. Chem. Phys. 2016, 172, 69.
[36] H. M. Rietveld, J. Appl. Crystallogr. 1969, 2, 65.
[37] J. Rodríguez-Carvajal, Phys. B 1993, 192, 55.