Research Article

Ni-Catalysts Supported on Gd-Doped Ceria for Solid Oxide Fuel Cells in Methane Steam Reforming

The anode materials used in solid oxide fuel cells at intermediate temperature (IT-SOFC) consist of a mixture of nickel and cerium oxide doped with rare earth, forming a composite with a conductor metal and a ceramic with ionic conductivity. Nickel catalysts supported on gadolinium-doped ceria were prepared in this work in order to obtain materials with catalytic properties suitable for their use as anodes in IT-SOFC. The catalysts were evaluated in steam reforming of methane. It was noted that gadolinium caused an increase in the metal-support interaction and in the resistance to sintering of metal particles. Although the carbon content is not reduced, the carbon deposited in the 30CG10 catalyst is more reactive due to its amorphous nature, and it can therefore be regenerated at temperatures lower than 400 °C.

Keywords: Anode catalysts, Gadolinium-doped ceria, Steam reforming

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1 Introduction

The development of new technologies for power generation has become the subject of many scientific studies worldwide. The solid oxide fuel cells (SOFC) are promising as a clean and efficient means for the direct conversion of chemical energy into electricity, providing significant benefits to the environment. When operating at intermediate temperatures (IT-SOFC) between 550 and 750 °C, these devices have attracted much interest because they offer several advantages, such as better thermal compatibility among the components, less power consumption, and lower cost of acquisition and operation. However, the use of lower temperatures leads to a decrease in the cell efficiency and, to overcome these difficulties, it is essential to properly select the components and structure of the anode [1–3]. Although this selection is usually based on the electronic and ionic conductivities of the material rather than its catalytic properties, there is a consensus that the catalytic properties of the anode in IT-SOFC play an important role in the overall performance of the cells. These materials must be catalytically active for the oxidation of hydrocarbons and must have high conductivity [4].

Ceria is noted for its ability to resist carbon deposition and to catalyze the combustion of carbon [5]. As a result, it has been investigated as an anode material (or a constituent of composite anodes) for IT-SOFC using fuels such as syngas, methanol, and methane [6, 7].

Among the materials studied, ceria doped with rare earth metals is a promising material because it displays higher ion conductivities at low temperatures [5]. In particular, good performance was obtained with CeO2-5Sm2O3 anodes by several authors [5, 7, 8].

Ramirez-Cabrera et al. [9] have studied the effects of the calcination atmosphere on gadolinium- and niobium-doped ceria over the reactivity of methane. The samples of Nb-doped ceria were synthesized using hydroxide co-precipitation from aqueous cerium nitrate and niobium chloride solutions, and the Gd-doped ceria sample was supplied by Rhodia. Doped and undoped cerias exhibit significant reactivity with methane to produce syngas. Carbon deposition by methane cracking at 900 °C is extremely slow on doped and undoped cerias. Although Nb-doped cerias were more capable of oxidizing carbon deposits at lower temperatures than pure ceria or Gd-doped ceria, doping with Gd has little effect on the reaction rate, whereas doping with Nb considerably slows down the rate. Moreover, Hennings et al. [10] have studied Gd-doped cerias prepared with the glycine-nitrate combustion process for being used as a catalyst support in the steam reforming of natural gas. The material has no microporosity and a low specific surface area, which appears to be a disadvantage of the chosen preparation method.
Nickel is a desirable metal because it is not as expensive as Pt or Rh. Ni catalysts with ceria-based supports have been demonstrated to be active in partial oxidation, dry reforming and steam reforming of methane, with stable behavior, high methane conversions, and hydrogen yields approaching those of thermodynamic equilibrium [11–14]. By enhancing the support reducibility in Ni/ceria catalysts, their catalytic activity was promoted because the availability of the surface lattice oxygen was increased, enhancing its participation in the formation of CO and H₂ [12–14].

In order to obtain nickel catalysts with catalytic properties suitable for being used as anodes in IT-SOFC, in this work, supports of Ce and Ce doped with Gd were prepared, by co-precipitation of cerium nitrate and gadolium nitrate following the sol-gel method. The catalytic properties in the methane reforming reaction (since methane is the main component of natural gas) were evaluated, in the range from 600 to 750 °C, using different H₂/O/C ratios. Due to the importance of catalytic stability, the resistance to sintering and carbon deposition during the reaction were also analyzed.

2 Experimental

2.1 Catalyst Preparation

Cerium oxide support was prepared by the hydrolysis of cerium nitrate (Ce(NO₃)₃·6H₂O) with ammonium hydroxide. An aqueous solution of 25 vol % of the precipitating agent was added to the precursor salt aqueous solution (0.75 M). The solution temperature during precipitation was maintained at 60 ± 5 °C. The gel was kept under stirring at the same temperature for 4 h. The final pH was adjusted to 10. The supports of cerium doped with gadolinium (10 and 20 mol %) were obtained following the same procedure: 100 mL of 0.75 M cerium nitrate solution and 100 mL of 0.075 or 0.15 M gadolinium nitrate solution were used. In this case, the two solutions of cerium and gadolinium nitrate were mixed and then precipitated with ammonium hydroxide. The precursors of the support obtained were dried for 12 h at 120 °C, and, subsequently, they were calcined at 500 °C (heating rate of 10 °C min⁻¹) during 2 h under a flow of synthetic air (100 mL min⁻¹). Pure cerium oxide and cerium oxide doped with 10 and 20 mol % gadolinium were designated as C, CG10, and CG20, respectively.

The supports obtained were impregnated with aqueous solutions of nickel nitrate (30 wt %) using a volume of solution of 1.5 mL per gram of support. The system was kept under stirring for 6 h at 80 °C. These materials were dried in an oven for 12 h at 120 °C (with a heating rate of 10 °C min⁻¹). Then the samples were calcined at 450 °C (with a heating rate of 10 °C min⁻¹) for 2 h under a flow of synthetic air (100 mL min⁻¹). The catalyst containing 30 wt % of nickel supported on pure ceria and doped with 10 and 20 mol % gadolinium were designated as 30C, 30CG10, and 30CG20, respectively.

2.2 Catalyst Characterization

The specific surface areas were measured using the Micromeritics AccuSorb 2100E nitrogen adsorption equipment. The experiments were conducted at −196 °C, employing 200 mg of sample previously degassed at 200 °C under vacuum for 2 h.

Structural characterization of the catalysts was performed by the X-ray diffraction (XRD) technique on Philips PW 1740 equipment using CuKα radiation, under a current of 30 mA and voltages of 40 kV, and a continuous scan angle 2θ from 20° to 100° with steps of 0.05° at 1 s per step was selected.

The temperature-programmed reduction (TPR) tests were performed in conventional dynamic equipment, using a feed gas with an H₂/N₂ ratio of 1:9 and a heating rate of 10 °C min⁻¹ from room temperature to 800 °C. Hydrogen chemisorption measurements were carried out in dynamic equipment with a thermal conductivity detector. Samples were reduced in an H₂ flow at 700 °C during 1 h, cooled in H₂ down to 400 °C, flushed with Ar for 2 h at 400 °C and then cooled down to room temperature in an Ar flow. Hydrogen pulses were then injected up to saturation. Dispersions were estimated from the hydrogen amount consumed, assuming an adsorption stoichiometry H/Ni = 1.

The supports were characterized using laser Raman spectroscopy (LRS) in a LabRAM HR UV 800 (Horiba/Jobin-Yvon) instrument, with a He-Ne laser (λ = 632 nm), a charge-coupled device and an Olympus microscope, model BX41. The measurements of the samples, diluted in KBr, were taken with 100 × magnification and the scattered light was collected through a confocal hole of 100 mm.

2.3 Carbon Deposit Characterization

Carbon deposits were characterized by temperature-programmed oxidation (TPO), measuring the weight variation as a function of the temperature in a thermogravimetric instrument (Shimadzu TGA 50). Post-reaction samples of 10 mg were used with an air flow of 40 mL min⁻¹ and a heating rate of 10 °C min⁻¹, from room temperature to 850 °C.

TPO coupled with in situ LRS has been used as an effective qualitative analysis of carbon deposits on spent catalysts. This system is equipped with an in situ reaction chamber that can be heated up to more than 700 °C under flowing gases. Before each spectrum was acquired, the sample was placed in the in situ cell and then exposed to a continuous flow of a mixture of 5% air in argon while the temperature was increased at 10 °C min⁻¹, reproducing the conditions of the TPO. The heating was stopped at a given temperature and, to obtain the Raman spectrum, the sample was cooled down to room temperature under the same flow. To make meaningful comparisons, it is essential to acquire the spectra on the same spot of the sample every time this heating-cooling sequence is followed.
2.4 Catalytic Activity

The catalysts were evaluated in the reaction of steam reforming at atmospheric pressure using methane as the main component of natural gas. The experimental equipment used for the catalytic tests was a continuous-flow reactor equipped with mass flow controllers (Burkert Instruments) in each gaseous current (N₂, CH₄, and H₂), an electric furnace with temperature controller, and a quartz reactor with an internal diameter of 8 mm. A bed consisting of fresh powdered catalyst (15 mg) mixed with 150 mg α-alumina was loaded between quartz wool plugs.

The gas analysis was carried out by using a chromatograph connected to the experimental unit (Shimadzu, model CG 8A, equipped with a Hayesep D column). The reaction temperature increased in the range from 600 to 750 °C. The samples were previously reduced in situ from room temperature up to 750 °C (10 °C min⁻¹) for 1 h in pure H₂ flow (30 mL min⁻¹). Water was injected into the reactor by a HPLC pump (Waters 590). The evaporator was a stainless-steel tube of 6 mm in diameter, filled with quartz pellets heated by an electric furnace. The operating conditions with respect to total feed flow rate and average catalyst particle size were defined so as to eliminate intraphase and interphase transport resistances. The reagent mixture was employed in a 3:1 to 1:1 molar ratio of water vapor (0.05 and 0.018 mL min⁻¹) and methane (20 mL min⁻¹), diluted in nitrogen (120 mL min⁻¹). The experiments were conducted at 700 °C during 24 h to study the catalyst stability.

3 Results and Discussion

The specific surface areas and pore volumes of the supports are shown in Tab. 1. The addition of gadolinium did not change the surface area of the solids (≈60 m² g⁻¹), the differences being within the experimental error of the measurements. The pore volume also did not change significantly (≈0.25 mL g⁻¹). Tab. 1 also shows that all of the Ni catalysts had a similar metal dispersion of about 1.5%.

By analysis of the X-ray diffractograms, the cubic phase of cerium oxide (2θ = 28.52° and 47.42°) was identified in all cases (Fig. 1). By doping with gadolinium, the fluorite structure of ceria was conserved, suggesting the formation of a solid solution of oxides, in agreement with other studies [15, 16]. This can be attributed to the ionic radius of Gd³⁺ (1.053 Å), which is close to the ionic radius of Ce³⁺ (1.143 Å), allowing the formation of a solid solution of oxides [17]. In the XRD patterns of the catalysts, peaks relating to cerium oxide and nickel oxide (NiO, 2θ = 37.2° and 43.3°) were identified, suggesting no formation of a solid solution of nickel oxide and cerium oxide. No differences were observed between the interplanar spacings of the solids before and after incorporation of nickel.

Fig. 2 shows the TPR profiles of the samples. The event with a maximum at ~550 °C in the TPR profiles present in the supports C, CG10 and CG20 is related to the consumption of oxygen species (O²⁻ and/or O⁻) adsorbed on the solid, with the subsequent formation of non-stoichiometric oxides (CeₓOᵧ) [18]. This reduction peak can also be linked to the reduction of Ce⁴⁺ species to Ce³⁺ species on the surface of ceria [5]. According to the literature [19–21], above 600 °C, Ce⁴⁺ species are reduced to Ce³⁺ species in cerium oxide, leading to the formation of oxygen vacancies and increasing their diffusion in the material. The reduction in events that occur at elevated temperatures, usually above 900 °C, is

![Figure 1. X-ray diffractograms. (a) Supports; signals at 2θ = 28.52° ( ● ) and 2θ = 47.42° ( ● ) corresponding to the cubic phase of cerium oxide. (b) Catalysts; signal at 2θ = 37.2° ( ● ) and 2θ = 43.3° ( ○ ) corresponding to NiO.](image)

![Figure 2. TPR profiles of the supports and catalysts.](image)

<table>
<thead>
<tr>
<th>Table 1. Textural properties of the supports and catalysts.</th>
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<td>Support</td>
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<tr>
<td>C</td>
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<td>CG10</td>
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<td>CG20</td>
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a) Dispersion calculated from hydrogen chemisorption data.
related to the reduction of the solid interior (bulk) with the elimination of the O\(^{2-}\) anion reticule and the subsequent formation of cerium oxide, Ce\(_2\)O\(_3\) [19, 20, 22].

The TPR profile of sample 30C exhibited a strong reduction peak at 350 °C, with a shoulder at 380 °C, which is in accordance with other authors. The TPR profiles of the 30CG10 and 30CG20 samples show a displacement at 380 °C, indicating higher metal-support interaction. The TPR profiles of the catalysts are similar to each other, independently of the content of dopant. Also, the peaks in the region of 350–450 °C, type I in accordance with Mori et al. [23], are related to the reduction of NiO species that are located on the surface of the supports and which are weakly interacting with them.

The characteristic information obtained from visible Raman spectra was used to obtain the bulk properties of ceria. The Raman spectra of Gd-doped ceria were obtained under ambient conditions, with an excitation laser of 632 nm, as shown in Fig. 3. The CG10 sample shows an intense band at 455 cm\(^{-1}\), which corresponds to the Raman-active vibrational mode \(\nu_0\) of the fluorite-type structure. Sakar et al. [17] established that the D band observed at 580 cm\(^{-1}\) corresponds to the vibrational modes and is connected to the defect spaces related to the oxygen vacancies present in the structure [17, 23]. According to Nakajima et al. [24], the mode near 550 cm\(^{-1}\) is associated with oxygen vacancies induced by Gd\(^{3+}\) (extrinsic vacancies). Hence, it is expected that the ionic conductivity of these doped nanostructures should be higher compared to the pure ceria. Furthermore, Jadhav et al. [25] established that the absence of the vibrational mode at 360 cm\(^{-1}\) corresponding to the Gd\(_2\)O\(_3\) cubic phase confirms the formation of a solid solution.

Regarding the catalytic activity, all catalysts were active in steam reforming of methane between 600 and 750 °C, as shown in Fig. 4. It is observed that the sample 30C showed higher activity, regardless of the H\(_2\)O/C ratio in the reaction mixture. The effect of Gd causes a decrease in activity. With a H\(_2\)O/C ratio of 3:1 in the reaction mixture, a slight improvement was observed in the activities of the 30CG10 and 30CG20 catalysts.

Tab. 2 shows the values of the H\(_2\)/CO molar ratio obtained on the catalysts at different temperatures, with a molar ratio of H\(_2\)O/C of 3:1. A decrease in the H\(_2\)/CO ratio with increasing temperature indicates a smaller contribution of the water-gas shift reaction (WGS; CO + H\(_2\)O ↔ CO\(_2\) + H\(_2\)). Moreover, a greater H\(_2\)/CO ratio in the 30CG10 catalyst was observed, which might indicate that this catalyst favors the WGS reaction.

The catalytic stability results are shown in Fig. 5. The activity as a function of time is expressed as coefficient \(a_{CH_4}\) which expresses the ratio between methane conversion at time \(t\) divided by the initial methane conversion. It can be seen that

| Tab. 2. H\(_2\)/CO molar ratio obtained in steam reforming of methane as a function of the reaction temperature. |
|---|---|---|---|---|
| Catalyst | H\(_2\)/CO (molar ratio) |
|  | 600 °C | 650 °C | 700 °C | 750 °C |
| 30C (3:1) | 13 | 10 | 7 | 6 |
| 30CG10 (3:1) | 27 | 14 | 11 | 9 |
| 30CG20 (3:1) | 10 | 8 | – | 6 |

Figure 3. Raman spectra of Gd-doped ceria powder.

Figure 4. Conversion of methane as a function of temperature on the catalysts. (a) H\(_2\)O/C = 3:1, (b) H\(_2\)O/C = 1:1.
the highest stability at 700°C is reached with 30CG10, with a molar ratio of H₂O/C of 3:1.

It is known that Ni catalysts promote carbon or coke deposition, and the amount of carbon formed strongly depends on the H₂O/C ratio of the reaction mixture [26–29]. In Tab. 3, the carbon content determined by TPO/thermogravimetric analysis (TGA) is reported for some post-reaction samples. On sample 30C, the carbon content varies from 16 to 25 wt % when the H₂O/C ratio is reduced from 3:1 to 1. For 30CG10 and 30CG20, the results go in the same direction. In addition, it could be observed for H₂O/C = 1:1 that the 30CG10 and 30C post-reaction samples have the lower carbon content (16 wt %). However, 30CG20 exhibits greater stability (aCH₄ = 0.9) than 30C (aCH₄ = 0.6), which may indicate that the greater deactivation of 30C cannot be explained only by carbon deposition.

Table 3. Activity test results obtained after methane steam reforming at 700°C during 30h, and results obtained after the sintering process with steam and hydrogen at 800°C during 5 h.

<table>
<thead>
<tr>
<th>Activity (aCH₄) after</th>
<th>Activity (aCH₄) after</th>
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<td>CH₄ steam reforming</td>
<td>CH₄ steam reforming</td>
<td>CH₄ sintering with</td>
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<tr>
<td>700°C during 30h</td>
<td>800°C during 5 h</td>
<td>steam and hydrogen</td>
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<tr>
<td></td>
<td></td>
<td>800°C during 5 h</td>
</tr>
<tr>
<td>30C</td>
<td>0.8 (±0.1)</td>
<td>0.9</td>
</tr>
<tr>
<td>30C</td>
<td>0.8 (±0.1)</td>
<td>n.d.</td>
</tr>
<tr>
<td>30CG10</td>
<td>0.8 (±0.1)</td>
<td>0.9</td>
</tr>
<tr>
<td>30CG10</td>
<td>0.8 (±0.1)</td>
<td>n.d.</td>
</tr>
<tr>
<td>30CG20</td>
<td>0.8 (±0.1)</td>
<td>0.9</td>
</tr>
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n.d.: Not determined.

To evaluate the resistance to sintering of the metal particles, experiments were also carried out in which the samples were kept in contact with water steam and a hydrogen flow at 800°C for 5 h, and the activity was then measured under the methane steam reforming conditions at 700°C. It was observed that the 30CG10 and 30CG20 catalysts showed similar resistance to sintering, since both of them present an aCH₄ of 0.9 (Tab. 3). When these results are compared with those of sample 30C, which presents an aCH₄ of 0.3, the highest stability to sintering is noted for doped cerias (Tab. 3). This may be related to the higher metal-support interaction promoted by gadolinium, and should explain the stability results of Fig. 5. 30CG10 is more stable during the 20 h of reaction than 30C, due to the higher resistance to sintering.

Regarding the nature of the carbon deposits, the Raman spectra of the post-reaction samples did not show any significant differences in the carbon species formed in 30CG10 and 30CG20. The tangential-mode G-band appearing in the 1400–1700 cm⁻¹ region is related to the Raman-allowed phonon mode E₂g and involves out-of-plane intralayer displacement in the graphene structure. It provides information about the electronic properties and is a measure of the presence of ordered carbon. The so-called D-band at around 1350 cm⁻¹ is related to the presence of defects nanometer carbons [30]. The D- and D'-bands (Fig. 6) at 1345 and 1610 cm⁻¹, respectively, are assigned to amorphous carbon, and the G-band, 1580 cm⁻¹, corresponds to graphitic carbon [31].

In situ regeneration tests were performed on Fourier transform infrared Raman equipment with a continuous flow of a
mixture of 5% air in argon at 400 and 500°C (Fig. 6). The presence of gadolinium leads to carbon deposits with more reactive and less crystalline structure in the 30CG10 catalysts (carbon burning at a lower temperature (<400°C) than in the 30C catalyst (>400°C)). This observation is consistent with the greater presence of amorphous carbon, which would facilitate regeneration of the catalyst.

4 Conclusions

The presence of Gd on the ceria affects the catalytic properties of Ni, because 30CG20 and 30CG10 are not more active than 30C. The 30CG10 catalyst (ceria doped with 10% Gd) improves the H₂/CO ratio in the products and the stability on steam reforming at 700°C with a ratio of H₂O/C = 3:1 in the feeding.

The presence of gadolinium confers higher resistance to sintering of the metal particles, by promoting increased interaction between the metal and the support.

Although the carbon content is not reduced, the carbon deposited in the 30CG10 catalyst is more reactive due to its amorphous nature, and it can therefore be regenerated at temperatures lower than 400°C.

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