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TPR-TPD-TPO studies on CGO/NiO and CGO/CuO ceramics obtained from freeze-dried precursors

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ABSTRACT

Nanocrystalline powders of $\text{Ce}_{0.99}\text{Gd}_{0.01}\text{O}_{2-\delta}$ have been obtained at a very low temperature (400°C) by a freeze-drying precursor method. Afterwards, ethanol solution of Ni or Cu nitrates were added to gadolinia doped ceria (CGO) by incipient wetness impregnation and then calcined in air at 650°C in order to obtain CGO/NiO and CGO/CuO series of SOFC anode materials. The resulting materials were characterized by X-ray Diffraction, N_2 adsorption-desorption (BET), Temperature Programmed Reduction (TPR), Temperature Programmed Desorption (TPD) and Temperature Programmed Oxidation (TPO) techniques. TPR showed wide overlapped peaks which are associated to the different reduction stages; firstly the reduction of highly dispersed metal oxide species took place and then the metal oxide bulk reduction process. After reduction of the CGO-metal powders, the metallic oxides were no longer present (as indicated by the presence of Ni or Cu), and the fluorite CGO solid solution remained stable. He-TPD tests showed that the series CGO/NiO adsorbed CO species on the material surface while CGO/CuO did not. O_2 -TPO analysis showed that C deposition occurred during the CO-TPR on CGO/NiO samples but this did not occur for the CGO/CuO series.

Keywords: Ceria; NiO; CuO; Freeze drying; SOFC; TPR; TPD; TPO.

I. INTRODUCTION

Solid oxide fuel cells (SOFCs) are a very promising technology for power generation, because they are thermodynamically more efficient than competing heat-engine power plants and produce lower emissions of NO_x , CO_2 and unreacted hydrocarbons compared to other conventional generators. Classical systems of this type involve the employment of thin yttria stabilized zirconia (YSZ) electrolytes with an anode based on YSZ-Ni cermets and operate at relatively high temperature (800°C-1000°C) [1,2].

Anode materials for application in solid oxide fuel cells (SOFCs) have requirements such as good electrochemical activity to oxidize fuels, high electronic conductivity, appropriate thermal expansion coefficient and compatibility with other components of SOFCs [2-4]. For intermediate temperature SOFC (IT-SOFC) applications, however, the activity of YSZ-Ni anode is relatively low due to the low ionic conductivity of YSZ at low temperatures. Cerium gadolinium oxide (CGO) presents higher ionic conductivity than YSZ over the temperature range of 300°C-700°C [5,6].

Nanocrystalline ceria powders have received great attention lately. They have been shown to exhibit higher catalytic activity, improved redox properties and a higher ionic conductivity in comparison with those of microcrystalline CeO_2 [7]. When pure CeO_2 is treated at high temperatures and under a reducing atmosphere, a removal of oxygen from the material takes place due to a partial reduction of Ce^{4+} to Ce^{3+} . This leads to the production of an oxygen-deficient nonstoichiometric CeO_{2-y} phase with $0 < y < 0.5$. This phase retains the same fluorite crystal structure as CeO_2 , facilitating the rapid and complete refilling of every oxygen vacancy upon exposure to oxygen, which eventually leads to recovery of CeO_2 [8-10].

CGO impregnated with either Ni or Cu has been suggested to be a suitable anode for both low and intermediate-temperature SOFCs [11-13]. In such composites, either Ni or Cu acts as a catalyst for the oxidation of fuels and provides electronic conduction, while CGO acts as support for the metal (Ni, Cu or a mixture of both) and retards agglomeration under operating conditions. At the same time, these composites extend gas-CGO-metal triple-phase boundary

(TPB) into the anode [11,12]. The electrochemical reaction for the hydrogen oxidation is directly related to the length of TPB. Large TPB's can be obtained from homogeneous and fine grains. That means that the performance of the anode depends on its microstructure and this is strongly dependent on the synthesis method [13,14]. However, the use of nanomaterials could lead to some disadvantages such as strong agglomeration tendency of particles, low green density, sintering inhibition and high powder reactivity [15].

It is well known that precursor synthesis methods can improve properties of the materials by controlling the structure, morphology, reactivity and grain size of the obtained materials [16]. In this context, the synthesis of different materials using freeze-dried precursors has shown good results in SOFC applications [17-19].

One of the main objectives in this work is the study of the CuO role as alternative electrocatalyst to reduce the carbon deposition susceptibility of NiO. We have prepared submicrometric crystalline powders derived of CGO by freeze drying precursor method and impregnated with NiO or CuO using the corresponding metallic nitrates. We have also study their redox behavior in the presence of H₂, CO and O₂ gases. These composites were characterized by XRD, BET, SEM, TPR, TPO and TPD techniques.

II. EXPERIMENTAL

A) Powder Synthesis

Ce_{0.99}Gd_{0.01}O_{2-δ} polycrystalline powders were synthesized by a freeze-drying method, using Ce(NO₃)₃·6H₂O (99.9%, Aldrich) and Gd(NO₃)₃·6H₂O (99.9%, Aldrich) as reagents. These hydrated metal nitrates were previously studied by thermogravimetric analysis to determine the exact water content. Stoichiometric quantities of the reagents were individually dissolved in distilled water and mixed together. Then, ethylenediaminetetraacetic acid (EDTA) (99.7% Aldrich) was added as complexing agent in a 1:1 ligand to metal molar ratio to prevent precipitation. The pH of the solution, which was initially acidic, was adjusted to around 7-8 by adding aqueous ammonia. Droplets of the as-obtained solution were subsequently flash-frozen

by pouring them into liquid nitrogen. In this way, each frozen droplet retained the homogeneous cation distribution of the original solution. This flash cooling process rendered small ice crystals, which were dehydrated by vacuum sublimation in a freeze-dryer (HetoLyolab) for 3 days. The obtained amorphous and highly hygroscopic precursors were immediately calcined at 400°C for 2 hours in alumina crucibles to prevent rehydration and to remove the organic matter by combustion. Under these synthesis conditions, crystallization of $\text{Ce}_{0.99}\text{Gd}_{0.01}\text{O}_{2-\delta}$ (CGO) powders as a single phase was achieved.

CGO/MO materials preparation

Dopants were incorporated to the CGO polycrystalline powders by incipient wetness impregnation using the corresponding nitrates solved in ethanol (Aldrich) solution with the adequate concentration to get a nominal loading of 20, 40 and 60 weight% of Ni ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98.5%, Sigma-Aldrich), and 20, 40 and 60 weight% of Cu ($\text{C}_4\text{H}_6\text{CuO}_4$) $_3 \cdot \text{H}_2\text{O}$, 99%, Fluka). After impregnation the materials were dried overnight at 60°C and calcined at 650°C during 1 h in order to improve the surface diffusion of the doping phase and avoid it entering the ceria lattice [20]. Table 1 shows the synthesis conditions and codes of all samples.

B) Powder Characterization

In order to investigate the phase purity of the materials, room temperature X-ray diffraction patterns (XRD) were collected using a PANalytical X'Pert Pro automated diffractometer, equipped with a primary monochromator ($\text{Cu K}_{\alpha 1}$ radiation) and an X'Celerator detector. Scans were performed in 2 hours within the 2θ range (15–100°) with a 0.016° step. XRD phase identification was performed with X'Pert HighScore Plus v.2.0a software [21].

N_2 adsorption–desorption isotherms were collected with a Micromeritics Gemini V (USA) gas adsorption analyzer at 77 K, after degassing the samples at 150°C overnight in a Micromeritics Flow prep 060 system with nitrogen flux gas. The BET surface areas were calculated from the adsorption branch of the isotherm by the BJH method.

C) Temperature Programmed measurements

Temperature-Programmed Reduction (H_2 -TPR) profiles were obtained with an AUTOCHEM II 2920, Automated Catalyst Characterisation System (Micromeritics, USA). For the H_2 -TPR analysis, the sample was exposed to a flow of a reducing gas (5vol.% H_2 -Ar balance), while the temperature was linearly increased at a constant rate. By measurement of thermal conductivity of input and output gas flows the reduction profile of the sample, which constitutes a “fingerprint” of its reducibility was possible to obtain.

The samples were loaded on top of wool glass in a quartz tube in an electric furnace. 80 mg of catalyst was always used in order to achieve reproducible and comparable results in the temperature-programmed tests. All samples were pre-treated by heating in a helium atmosphere at 350°C for one hour before the H_2 -TPR tests in order to remove possible contaminants. After cooling to room temperature, the reduction process using 5 vol.% H_2/Ar gas mixture was carried out (20 mL min^{-1} , volumetric flowrate are given at NTP) in the temperature range of 25°C - 900°C at a heating rate of $10^\circ\text{C min}^{-1}$. Hydrogen consumption was monitored using an in-situ thermal conductivity detector (TCD). A cryogenic trap, consisting of a gel formed by adding liquid nitrogen to isopropyl alcohol in a dewar flask, was used to prevent water from entering the detector. The TPR results reveal the temperatures at which the reduction of the species in the series CGO/NiO and CGO/CuO take place.

CO-TPR, He-TPD and O_2 -TPO consecutive tests were performed using a fully automated and programmable gas supply microreactor gas-analysis system (CATLAB, Hidden Analytical, UK) at 1 atm. The outlet from the microreactor was fed into a soft ionisation quadrupole mass spectrometer (QMS) via a heated capillary line for continuous online analysis (QIC-20 model).

In this case, the samples (80 mgs) were also loaded on top of wool glass in a quartz tube in an electric furnace. All samples were pre-treated in a helium atmosphere at room temperature until signal stabilisation in order to remove volatile contaminants. Then, reduction process using 5 vol.% CO/He gas mixture was carried out (20 mL min^{-1}) in the temperature range of 25°C - 950°C at a heating rate of $10^\circ\text{C min}^{-1}$. After room temperature cooling He-TPD was performed heating at 950°C with a ramp of $10^\circ\text{C min}^{-1}$ flowing helium gas (20 mL min^{-1}). Afterwards, O_2 -

TPO was carried out by heating from room temperature to 950°C with a flow of 5vol.% O₂/He (20 mL min⁻¹). The output gases were monitored using the integrated mass spectrometer.

III. RESULTS AND DISCUSSION

XRD studies

In the XRD patterns shown in Fig. 1 we can observe that CGO/NiO composites are achieved as a mixture of two well-differentiated phases (CGO and NiO). The XRD pattern of CGO-40Ni sample, obtained after the freeze-drying and wetness impregnation synthesis method presents a small peak around 38° (2θ), corresponding to an unidentified impurity. However, no impurities were detected in the other two compositions. As NiO content increases, the intensity in the patterns of NiO phase also increases as was expected. On the other hand, CGO/CuO composites (Fig. 1b) were confirmed by XRD as a mixture of two well-differentiated phases (CGO and CuO) with no additional impurities detected.

XRD patterns of the studied samples after TPR tests

XRD profiles for CGO/Ni and CGO/Cu samples after TPR tests in different compositions are shown in Fig. 2. The materials underwent strong changes in composition due to the complete reduction of the NiO. These patterns showed only CGO and Ni phases, the Bragg peaks corresponding to NiO disappearing completely (Fig. 2a). As observed, when Ni content increases in the composite, the Bragg peak of the Ni phase increases in intensity as was expected. Similar results were found for CGO/CuO (Fig. 2b). Neither secondary phases nor impurities were detected.

As aforementioned, after a TPR analysis the complete reduction of the metallic phase in the composites is observed with reduction from NiO to Ni and from CuO to Cu. When samples are reoxidized again, the previous phases of CGO/NiO and CGO/CuO oxide mixtures are recovered. Following a reduction-oxidation-reduction cycle the complete reduced phase was recovered confirming the stability of the studied samples (Fig. 3a and 3b).

On the other hand, SEM micrographs before (Fig. 4a) and after (Fig. 4b) the CGO-40Ni sample CO-TPR tests are shown. The sample presents agglomerates of well distributed CGO and Ni. No changes in the morphology of the powders are observed after reduction of the material. Similar results were found for CGO-60Cu sample (Fig. 4c,4d).

We have also observed that the higher metal content is, the lower the value of BET surface is both for Ni and Cu samples (Table 1).

Reduction Behaviour

H₂-TPR results of the studied samples

Fig. 5 shows H₂-TPR hydrogen consumption curves of CGO/Ni samples in different compositions (20%, 40% and 60% w/w Ni). The three composites showed similar behaviour with four peaks assigned to four reduction processes. Around 260°C a small peak is observed, this process could be ascribed to a reduction of some impurities not well eliminated during the synthesis due to the rather low calcination temperature. At low temperatures (between 300°C and 400°C) NiO to Ni reduction processes take place. These peaks are ascribed as follows, the first one (~400°C) to the reduction of the surface NiO species (small size and well dispersed). The second peak observed (~500°C) is related to reduction of NiO species with higher interaction with the support [22,23]. However, Shan et al. have ascribed these overlapped peaks to the different steps in oxidation state of Ni, from Ni^{δ+} to Ni⁰ [24]. The other two peaks found between 750°C and 900°C correspond to the surface and bulk reduction of the CGO phase [25,26].

It can also be observed that as Ni content increases, larger peak areas are observed. A growth in the area of the second peak is also observed as Ni content increases and a slight shift of the peaks towards higher temperatures occurs.

As can be observed in the CO-TPR (Fig. 6), CGO-40Ni sample consumes a large amount of CO around 400°C and produces a slightly smaller amount of CO₂. Comparing the areas of

production and consumption we obtained a value of 63.5% from the following equation for the CGO-40Ni sample:

$$\frac{CO_2 \text{ mol Production Peak Area}}{CO \text{ mol Consumption Peak Area}} \times 100 = 63.5\%$$

This fact could be an indication of carbon deposition but a TPO test is necessary to confirm this hypothesis. Comparing H₂-TPR profiles in CGO/Ni samples with the CO-TPR ones (Fig. 6) we can see that reduction processes occur at similar temperatures for both, between 350°C and 650°C.

The He-TPD profile (Fig. 7) shows four peaks centred at 650°C, 775°C, 875°C and 950°C. They can be ascribed to different CO desorption processes from the previous reduction (CO-TPR), but we do not exclude a possible oxidation of deposited carbon, even if it is expected in a lower rate. A small production of CO₂ is observed in the O₂-TPO (Fig. 8) between 400°C and 600°C. The two TPO peaks are indicative of two different species of carbon deposited during CO-TPR test.

The CO balance during these processes lead to the following results:

Balance on CO-TPR

$$\left\{ \begin{array}{l} 100\% \text{ of CO} \\ \text{consumption} \end{array} \right\} - \left\{ \begin{array}{l} 63.5 \% \text{ of CO} \\ \text{oxidized as CO}_2 \end{array} \right\} = \left\{ \begin{array}{l} 37.5\% \\ \text{of retained CO} \end{array} \right\}$$

Balance on He-TPD

$$\left\{ \begin{array}{l} 37.5\% \\ \text{of retained CO} \end{array} \right\} - \left\{ \begin{array}{l} 14.2\% \text{ of removed CO} \\ \text{by desorption} \end{array} \right\} = \left\{ \begin{array}{l} 23.3 \% \\ \text{of remained CO} \end{array} \right\}$$

Balance on O₂-TPO

23.3% of remained CO - 19.8 % of CO oxidized as CO₂= 3.5 % of CO globally lost

$$\left\{ \begin{array}{l} 23.3\% \\ \text{of remained CO} \end{array} \right\} - \left\{ \begin{array}{l} 19.8\% \text{ of CO} \\ \text{oxidized as CO}_2 \end{array} \right\} = \left\{ \begin{array}{l} 3.5 \% \text{ of CO} \\ \text{missing} \end{array} \right\}$$

In summary, during the CO-TPR (Fig. 6) a 37.5% of CO was retained, and we recovered a 14.2% by desorption (Fig. 7) and a 19.8% by oxidation (Fig. 8), that is, it is globally missing a 3.5%. This low value could be due to the C loss during the different processes or due to the measurement uncertainty.

We have observed that the presence of Ni in the composite increases the hydrogen consumption compared with the pure CGO samples. However, the Ni gives rise to carbon deposition (when exposed to CO) which may limit the application of these materials as anodes in an IT-SOFC. Not all CO consumption is due to reduction of the NiO species and formation of CO₂ but some is adsorbed on the surface and some is deposited as C on the surface.

H₂-TPR curves of CGO/Cu samples are shown in Fig. 9. For these composites, there are four peaks associated with four different reduction processes. At low temperatures, between 150°C and 450°C, CuO to Cu reduction is expected. The asymmetric peak shape indicates that at least two different CuO species or processes coexist. These TPR peaks are usually ascribed as follows. The first maximum corresponds to the reduction of highly dispersed CuO species strongly interacting with ceria while the second maximum is assigned to the reduction of bulk CuO or larger CuO species [27-30]. However, other authors ascribed these overlapped peaks to Cu²⁺ to Cu¹⁺ reduction step and Cu¹⁺ to Cu⁰ reduction process [31,32]. As expected, H₂ consumption is proportional to the Cu loading due to the presence of more reducible species. It also can be observed that as Cu loading increases, a slight shift toward higher temperatures in reduction peaks occurs. Thus, the CGO-20Cu peak is centered at 260°C, the one of CGO-40Cu peak at 310°C and CGO-60Cu at 350°C. Hence, when Cu loading content increases the metal species are likely to be less dispersed on the ceria surface support. This shift to higher temperature also occurs for the CuO bulk reduction process.

Referring to the other two peaks observed, a consensus exists in ascribing them to Ce⁴⁺ to Ce³⁺ reduction processes: surface and bulk respectively [27,29]. In our case, the surface and bulk reduction processes take place centered at around 575°C and 875°C respectively. In addition, we observe that high loading content of Cu does not change the temperature of the

ceria position peaks significantly. Despite of the fact that it has been reported that a low loading of Cu on CGO (i.e. 5%) could give rise to an improvement in the CGO reduction behaviour [31], in our case with much higher loads of Cu (20, 40 and 60 w/w%), a such improvement was not observed. This is due the fact that increasing the copper loads for high values does not enhance the catalytic activity, because the maximum catalytic capacity of the copper in this system is probably over.

It is worthwhile mentioning that as Cu loading increases, the second H₂-TPR peak shows an increase in area. This fact seems to support those authors who ascribe this process to reduction of CuO bulk species [27,30] because when Cu loading content becomes higher there is a growth of CuO entities.

In general, the shape and position of the peaks in the TPR analysis vary with synthesis method, heat treatment conditions and TPR conditions. If one compares the H₂-TPR results (Fig. 9) with the CO-TPR ones (Fig. 10) we can deduce that reduction processes occur at higher temperatures for H₂-TPR, between 200°C and 400°C while the reduction process for CO-TPR occurs around 200°C and the peaks are narrower. These facts are important in catalytic applications such as the preferential oxidation of CO (COPROX) because differences in selectivity can be inferred knowing the positions of the reduction peaks for CO and H₂.

As can be observed in the CO-TPR (Fig. 10), the CGO-40Cu sample consumes a large amount of CO around 160°C and produces approximately the same amount of CO₂. That means that low carbon deposition is expected on the surface of the sample. Comparing the areas of production and consumption we obtained the following ratio for the CGO-40Cu sample:

$$\frac{CO_2 \text{ mol Production Peak Area}}{CO \text{ mol Consumption Peak Area}} \times 100 = 99.8\%$$

In addition, the He-TPD plot is featureless consistent with no CO adsorption on the sample during CO-TPR. Consequently, in the O₂-TPO no CO₂ production was observed, confirming that carbon deposition did not take place during CO-TPR.

Comparing CGO/Cu samples with CGO/Ni ones it can be observed that Cu doped samples present no carbon deposition while Ni doped ones do. In addition, we observe that the reduction process occurs at much more higher temperatures in Ni doped samples.

IV. CONCLUSIONS

Submicrometric powders of ceria-based materials were synthesized by a freeze-drying method. XRD measurements indicate that all ceria samples studied are achieved at low temperatures compared with the ceramic method. The fluorite phase is readily formed by heating at temperatures as low as 400°C. Suitable anode material powders of the series CGO/NiO and CGO/CuO composites are obtained by wetness impregnation method at 650°C.

TPR tests showed that the CGO/NiO composites studied in this work present good activity towards the oxidation of both H₂ and CO in the temperature range 300°C-600°C (with a maximum around 450°C). For CGO/CuO samples, the oxidation of H₂ takes place between 200°C-400°C, while the oxidation of CO takes place between 125°C-225°C. TPR data show two broad overlapping peaks corresponding to the following events. Thus, the reduction of the highly dispersed metal oxide takes place at lower temperatures followed by the reduction of the agglomerated metal oxide particles on the surface. He-TPD and O₂-TPO measurements revealed the existence of carbon deposition in CGO/NiO samples but no carbon deposition was found for CGO/CuO.

In conclusion, successful synthesis of CGO/NiO and CGO/CuO cermets was achieved and temperature programmed reactions (reduction, adsorption and oxidation) show promising results for the application of these materials as candidates for IT-SOFC or LT-SOFC anodes. The CGO/CuO sample was not susceptible to carbon formation in the presence of CO.

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Table 1. CeO₂ based material samples and compositions prepared by freeze-drying method and impregnated with nickel or copper.

List of Figures captions

Figure 1. XRD spectra of a) CGO/NiO and b) CGO/CuO samples in different compositions (synthesis conditions)

Figure 2. XRD pattern of anode materials after H₂-TPR for a) CGO/Ni and b) CGO/Cu samples

Figure 3. XRD patterns of a) CGO-NiO and b) CGO-CuO samples after H₂-TPR-oxidation-H₂-TPR cycle

Figure 4. SEM micrographs of CGO-40Ni powder sample a) before and b) after the temperature programmed tests and CGO-60Cu powder sample c) before and d) after the temperature programmed tests

Figure 5. H₂-TPR of CGO/Ni samples (one TPR run)

Figure 6. CO-TPR of CGO-40Ni sample

Figure 7. He-TPD of CGO-40Ni sample

Figure 8. O₂-TPO of CGO-40Ni sample

Figure 9. H₂-TPR of CGO/Cu samples (one TPR run)

Figure 10. CO-TPR of CGO-40Cu sample

Sample (w/w%)	Code	S_{BET} (m ² /g)
$\text{Ce}_{0.99}\text{Gd}_{0.01}\text{O}_{2-\delta}$	CGO	12.4
80% $\text{Ce}_{0.99}\text{Gd}_{0.01}\text{O}_{2-\delta}$ -20%Ni	CGO-20Ni	12.2
60% $\text{Ce}_{0.99}\text{Gd}_{0.01}\text{O}_{2-\delta}$ -40%Ni	CGO-40Ni	10.8
40% $\text{Ce}_{0.99}\text{Gd}_{0.01}\text{O}_{2-\delta}$ -60%Ni	CGO-60Ni	7.2
80% $\text{Ce}_{0.99}\text{Gd}_{0.01}\text{O}_{2-\delta}$ -20%Cu	CGO-20Cu	11.2
60% $\text{Ce}_{0.99}\text{Gd}_{0.01}\text{O}_{2-\delta}$ -40%Cu	CGO-40Cu	6.9
40% $\text{Ce}_{0.99}\text{Gd}_{0.01}\text{O}_{2-\delta}$ -60%Cu	CGO-60Cu	4.6

Table 1. CeO_2 based material samples and compositions prepared by freeze-drying method and impregnated with nickel or copper. All samples were calcinated at 650°C for 1 hour.

Figure 1. XRD spectra of a) CGO/NiO and b) CGO/CuO samples.

Figure 2. XRD patterns of anode materials after H_2 -TPR for a) CGO/Ni and b) CGO/Cu samples

Figure 3. XRD patterns of a) CGO-NiO and b) CGO-CuO samples after H₂-TPR-oxidation-H₂-TPR cycle.

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