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# SYNTHESIS AND CHARACTERIZATION OF Ni/GDC CERMET CATALYSTS FOR HYDROGEN PRODUCTION

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In this study we developed novel materials based on Ni supported on  $Ce_{0.8}Gd_{0.2}O_{2-\delta}$  (GDC), to be used in the  $H_2$  production technology. GDC as catalyst carrier is known to limit the coke formation in  $H_2$  production processes. However, previous studies dealing with the catalytic reforming of methane over Ni/GDC materials (Ni loading  $\sim 10\%$ ) show important structural limitations, such as the high particle size of the Ni particles ( $\sim 30$  nm), and their low specific surface area ( $\sim 20$ - $40$   $m^2/g$ ). In this work we developed novel Ni/GDC cermet (ceramic-metal) materials by the Weak Acid Resin (WAR) method. This synthesis procedure allows to prepare Ni/GDC materials in one step. In addition, in order to enhance the surface area of these materials, Ni was partially dissolved. The whole procedure led to catalysts with high metal loadings ( $\geq 10\%$ ), small Ni nanoparticles ( $< 10$  nm), and high surface areas ( $> 70$   $m^2/g$ ), exhibiting therefore promising properties in view of their further utilization for the  $H_2$  production technology.

## 1. Scope

$H_2$  is considered as the most promising energy carrier and it is expected to have a key role in future energy systems, such as fuel cells, for the production of clean electrical energy. Among the different  $H_2$  production processes, special interest lies in the catalytic reforming of methane, as the main component of natural gas.

In this sense, **Ni supported  $Ce_{0.8}Gd_{0.2}O_{2-\delta}$  (GDC) materials are known to efficiently catalyze  $H_2$  production** by catalytic reforming of methane. Ni/GDC catalysts present a **high resistance to coke deposition**<sup>1</sup> compared to conventional industrial materials (e.g. Ni supported on  $\gamma$ - $Al_2O_3$ ). This is due to metal/support interactions between Ni and GDC, since carbon species deposited on Ni sites can be oxidized by oxygen supplied by GDC. Up to now, **Ni/GDC materials are mostly prepared by impregnation** of Ni over a GDC support. By using this method, the final concentration of Ni is difficult to adjust properly and, more importantly, it gives rise to a non-homogeneous dispersion of metallic nanoparticles onto the GDC carrier. Hence, this preparation method usually results in Ni/GDC materials with **big Ni particles ( $\sim 30$  nm) and low specific surface area ( $20$ - $40$   $m^2/g$ )** when high Ni loadings are required ( $\sim 10\%$  Ni)<sup>1</sup>. The improvement of these structural properties will clearly enhance the activity of these catalysts towards the production of  $H_2$ .

In order to overcome these drawbacks, in this study we developed novel Ni/GDC catalysts by the so-called Weak Acid Resin (WAR) method<sup>2, 3, 4</sup>, followed by a partial dissolution of Ni to enhance the BET surface area. We have demonstrated that the whole procedure allows to produce porous materials with a very homogeneous distribution of the different phases at the nano-metric scale. Hence, catalysts with high metal loadings ( $\geq 10\%$ ), small Ni nanoparticles ( $< 10$  nm), and high specific surface areas ( $> 70$   $m^2/g$ ), where obtained in this study, exhibiting promising structural properties in view of their utilization for  $H_2$  production.

## 2. Experimental

Catalysts were prepared by the WAR method<sup>2, 3, 4</sup>: Briefly, several batches of acrylic resin microspheres (with ability to exchange  $NH_4^+$  ions) with a 630-800  $\mu m$  diameter distribution were placed in a beaker, together with a solution containing the ionic species that we need to fix ( $Ce^{3+}$ ,  $Gd^{3+}$  and  $Ni^{2+}$ ). The ionic exchange was performed during 24 hours to achieve the equilibrium. After exchange, the samples were dried and calcined for 1 hour at 750  $^\circ C$ , so that the acrylic skeleton of the resin was oxidized into  $CO_2$ . This way, the resulting material was a solid mixture of Ni, Ce and Gd oxides.

In order to enhance the specific surface area of these materials, NiO was selectively dissolved in a  $HNO_3$  solution at 90  $^\circ C$ <sup>4</sup>.

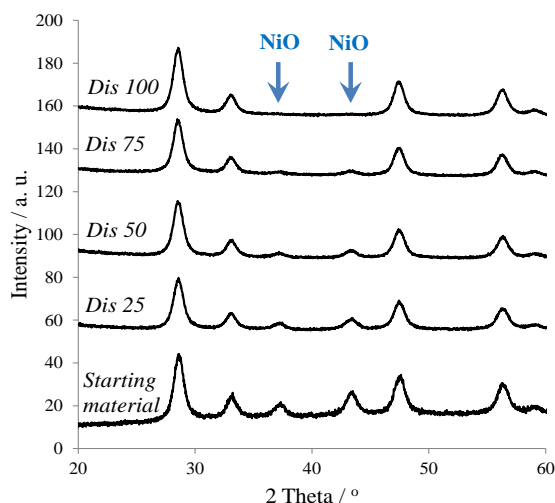
All samples were characterized by ICP-AES, BET, XRD and TEM, among other techniques. In addition, they will be tested for the catalytic steam reforming of methane, and compared with the state of the art Ni/ $\gamma$ - $Al_2O_3$  catalysts.

### 3. Results and discussion

Among all the samples prepared by the WAR method, we will discuss the results obtained over samples with high Ni loadings, so that the partial Ni dissolution leads to a significant modification of their structural properties. For instance, after ionic exchange and the subsequent calcination treatment, a sample was obtained with a **Ni loading of 37.3 % (Table 1, starting material)**, and a **Ce/Gd ratio ~ 4**, as we verified by ICP-AES. It clearly demonstrates the high potential of the WAR method to develop **materials with high metal loading in one step**, contrary to the conventional impregnation process, in which the final concentration of Ni is very difficult to adjust properly and usually requires several steps. Using this catalyst as **starting material**, we performed several partial dissolutions of the NiO by using stoichiometric amounts of HNO<sub>3</sub> at 90 °C. This way, we prepared 4 samples in which 25, 50, 75 and 100 % of NiO was dissolved, and they were called Dis 25, Dis 50, Dis 75 and Dis 100 % respectively.

Figure 1 shows the XRD patterns of the starting material and the samples obtained after partial dissolution of NiO. All **XRD patterns** exhibit major peaks of a fluorite structure, corresponding to **Ce<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>2.8</sub>**. It could be attributed to the solid solution of CeO<sub>2</sub> and Gd<sub>2</sub>O<sub>3</sub>, which usually takes place at calcination temperatures above 600 °C<sup>2</sup>. With regards to the NiO, a broad peak at 43.3 ° could be observed. As NiO was dissolved (decreasing therefore the Ni content in the samples, Table 1), the NiO peak intensity decreased. In addition, **NiO crystallite size** was calculated by Scherrer formula, being around **7 nm for the starting material**, and **decreasing below this value for the samples after partial dissolution**.

On the other hand, Table 1 shows the specific surface areas of the materials developed. It could be clearly observed that the specific surface area dramatically increased as the partial dissolution of NiO increased. It is worth noting that, for the sample called **Dis 75** (in which 75 % of the NiO present in the starting material was selectively dissolved), regardless the **high metal loading ~16 % w/w**, the surface area was higher than **70 m<sup>2</sup>/g**, and according to the **XRD (Fig 1) the NiO crystallite size was lower than 5 nm**. Hence, it seems that this synthesis procedure leads to a significant dispersion of Ni on the GDC matrix, and to high specific surface areas. Therefore, this material shows very promising properties in comparison with similar materials reported in literature<sup>1</sup> (for a loading ~10 % w/w Ni, surface area ~20 m<sup>2</sup>/g, NiO particle size ~30 nm).



**Fig 1.** XRD patterns of the starting Ni/GDC materials and the materials obtained after partial dissolution of NiO

**Table 1.** BET, BJH and ICP-AES results for the starting Ni/GDC materials and the materials obtained after partial dissolution of NiO

	BET Surface Area / m <sup>2</sup> g <sup>-1</sup>	BJH Pore Size / ångström (Å)	Ni loading % w/w
Starting material	25.2475	147,31	37,30
Dis25	33.5770	157,99	32,68
Dis50	49.5493	125,69	22,99
Dis75	72.5213	102,48	15,94
Dis100	105.6123	84,87	2,12

### 4. Conclusions

Novel Ni/GDC materials with advanced structural properties have been developed in this study following a new synthesis procedure which involved: a) ionic exchange in one step, and b) the partial dissolution of NiO to enhance the material specific surface area. The novel materials exhibit very interesting properties in view of their application to catalytic reforming of methane for hydrogen production.

### References

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