DEVELOPMENT, CHARACTERIZATION AND CATALYTIC STUDY OF NOVEL NiO/GDC MATERIALS FOR HYDROGEN PRODUCTION

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Abstract: In this study we developed novel materials based on Ni supported on $Ce_{0.8}Gd_{0.2}O_{1.9\pm\delta}$ (GDC), for H_2 production via methane reforming, by the Weak Acid Resin (WAR) process. This procedure allows to prepare NiO/GDC materials from ion exchange resin templates, then calcined in air to give the oxide material. Moreover, the surface area of these materials was enhanced by NiO partial dissolution in aqueous-acid solution. The whole procedure led to catalysts with unique properties compared to other materials reported in literature, i.e., high metal loadings (≥ 10 %), small Ni nanoparticles (< 10 nm), and high specific surface areas (> 70 m^2/g).

1. Introduction

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

Ni supported $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (GDC) materials exhibit high resistance to coke deposition[1] compared to conventional industrial materials (e.g. Ni supported on γ-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 O^{2-} supplied by GDC. Up to now, Ni/GDC materials are mostly prepared by impregnation of Ni precursors over a GDC support. This method gives rise to a non-homogeneous dispersion of metallic nanoparticles onto the GDC matrix, resulting in Ni/GDC materials with big Ni particles (~ 30 nm) and low specific surface area (20-40 m^2/g) when high Ni loadings are required (~10 % Ni)[1].

In this study we developed, characterized and tested novel Ni/GDC catalysts by the Weak Acid Resin (WAR) method[2, 3, 4], followed by a partial dissolution of Ni to enhance the specific 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. Catalysts with high metal loadings (≥ 10 %), small Ni nanoparticles (< 10 nm), and high specific surface areas (> 70 m^2/g), where obtained in this study. The materials exhibit an unique performance for H_2 production via methane steam reforming.

2. Experimental

Catalysts were prepared by the WAR process[2, 3, 4]: Briefly, microspheres of polyacrylic ion exchange resin in the ammonium form were exchanged with Ce^{3+}, Gd^{3+} and Ni^{2} during 24 hours. After exchange, the samples were dried (110°C) and calcined in air (750 °C), so that the acrylic skeleton of the resin was fired into CO_2 and H_2O. The resulting material was an intimate mixture of NiO and Ce/Gd mixed oxide. To enhance the specific surface area of these materials, NiO was partially dissolved in a HNO_3 solution [4].

All samples were characterized by ICP-AES, BET, XRD and TEM-EDX, among other techniques. In addition, first tests were implemented to assess the ability of those materials for H_2 production via catalytic steam reforming of methane, compared with the state of the art Ni/γ-Al_2O_3 catalysts.

3. Results and discussion

First, a NiO/GDC catalyst was prepared by the above described WAR method. After simultaneous ionic exchange of Ce^{3+}, Gd^{3+} and Ni^{2+}, and the subsequent calcination treatment, a sample was obtained with a Ni loading of 37.3 wt% (Table 1, starting material), and a Ce/Gd ratio ~ 4, as we verified by ICP-AES.

Using this catalyst as starting material, we performed several partial dissolutions of the NiO by using stoichiometric amounts of HNO_3. This way, four samples were prepared 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 lines of a fluorite structure, corresponding to $Ce_{0.8}Gd_{0.2}O_{1.9-\delta}$ (GDC). It could be attributed to the solid solution of CeO_2 and Gd_2O_3 [2]. 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. NiO crystallite size was estimated by Scherrer formula, being around 7-10 nm for all samples.

As a representative example, Fig 2 shows the TEM measurements on the Dis 50 sample (50 % of the NiO present in the starting material was selectively dissolved). The presence of Ce, Gd, and Ni was confirmed by EDX analysis. EDX mappings of the different elements have clearly shown that the catalyst is very homogeneous, containing well dispersed NiO nanoparticles in the GDC matrix. In addition, both GDC and NiO nanoparticles exhibit a small particle size (6–10 nm).

Table 1 shows the specific surface areas of the materials developed. It could be observed that the SSA significantly increased as the partial dissolution of NiO increased. It is worth noting that, for sample Dis 50, regardless the resulting high metal loading ~23 % w/w, the specific surface area was 49 m^2/g, and according to XRD (Fig 1) and TEM (Fig 2) the NiO crystallite size was lower than 10 nm. Hence, it seems that this synthesis procedure leads to a significant dispersion of Ni on GDC, and to high specific surface areas. This material shows very promising properties in comparison with similar materials previously reported in literature[1]: for a loading ~10 % w/w Ni, SSA ~20 m^2/g, NiO particle size ~30 nm.

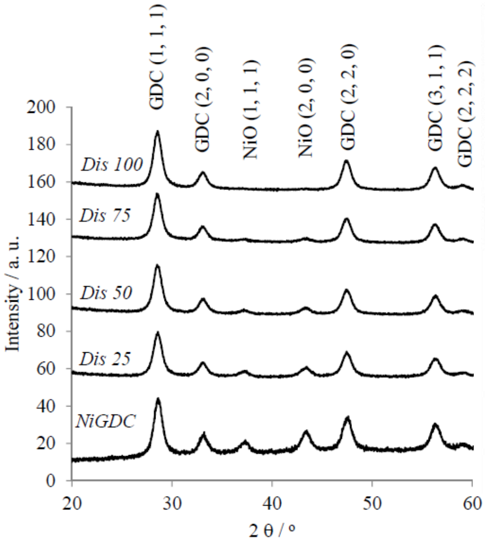

Figure 1. XRD patterns of the novel catalysts after the NiO partial dissolution

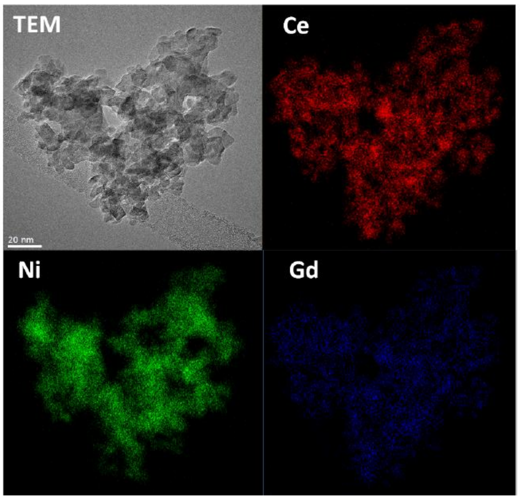

Figure 2. TEM image of catalyst Dis 50 (50% of Ni in starting material, was selectively dissolved), and EDX mapping of Ce, Ni, and Gd.

Table 1. Specific Surface Area and ICP-AES results for the starting Ni/GDC material and the materials obtained after partial dissolution of NiO

	SSA m^2 g^{-1}	Ni loading % wt
Start. Material Ni/GDC	25	37.3
Dis 25	33	32.7
Dis 50	49	23.0
Dis 75	72	15.9
Dis 100	105	2.1

4. Conclusions

Novel Ni/GDC materials with advanced and unique structural properties have been developed in this study following a new synthesis procedure which involved: a) ionic exchange of all metal cations in a once-through procedure followed by a thermal treatment in air, and b) the partial dissolution of NiO to enhance the material surface area. The novel materials exhibit unique properties compared to similar materials reported in literature, in view of their application to catalytic reforming of methane for H_2 production.

References

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