Silicon content after template removal

Due to the well-known negative effect of SiO₂ segregation impurities along the grain boundaries and surface on ionic conductivity and catalysis performance [1, 2, 3, 4], an analysis of the silica content after template removal have been carried out by Inductively Coupled Plasma and EDX. An iterative washing methodology was implemented in the methodology. Increasing the number of times where the mesoporous material is washed with the NaOH hot solution, the silica content remaining in the replica decreases (1 wash ~ 3.51 % Si, 2 washes ~ 1.6% Si, 4 washes ~ 1.3% Si). It was also found better to wash the replica several times with deionised pure water (1.16 % Si) than with a solution of H₂O:EtOH (50 % wt) (1.5 % Si). Although these values are over the typical levels of silicon impurities that affect the CGO properties (low-grade CGO powders typically contain silica impurities < 100 ppm), it is believed that keeping the high surface area contribute to minimize the portion of surface blocked by the impurity in the mesoporous case of study. Despite this, an iterative process of template removal is therefore strongly recommended.

Phase identification in mesoporous NiO-CGO composite

X-ray diffraction (XRD) patterns of the NiO-CGO mesoporous cermets show two single phases at the sintering temperatures: a cubic structure of NiO (JCPDS 47-1049) and a cubic fluorite structure of Ce₀.8Gd₀.2O₁.₉ (JCPDS database 75-0162). No parasitic phases were presented in any of the spectra (Figure S1).

Fig. S1  a) XRD pattern of NiO (KIT-6) mesoporous annealed at 600 °C; b) XRD pattern of the composite NiO (KIT-6)-CGO sintered at high temperature. Diffraction peaks are labelled according to the reflections corresponding to each phase.
N\textsubscript{2} adsorption-desorption experiments of mesoporous NiO calcined at 600°C

![N\textsubscript{2} adsorption-desorption isotherms and pore size distribution](image)

Fig S2 a) N\textsubscript{2} adsorption-desorption isotherms and b) pore size distribution calculated from the desorption branch using the BJH method, of the NiO mesoporous annealed at 600°C.

TEM-EELS analysis of typical NiO-CGO cermet

A mesoporous sample of NiO, infiltrated with CGO has been observed in scanning transmission electron microscope (STEM) and analyzed with electron energy-loss spectroscopy (EELS). Figure S3 show that most of the mesoporous particles appear mixed with smaller size nanoparticles embedded. EELS analysis confirms that the mesoporous is made of Ni, and that Ni and CGO are mixed on those mesoporous particles where the nanoparticles are found.
**Fig. S3.** Bright field STEM images, HAADF STEM images and EELS spectra (corresponding to the points marked with the arrows) of two typical mesoporous particles of NiO-CGO.

The energy window of the EEL detector is technically limited to 500 eV. Since the energy gap between the oxygen and Gd peaks is higher than 500 eV, they cannot be evaluated in a single spectrum at a time. Figure S4 shows the two spectra confirming the presence of O and Ce (Figure 2c) and Gd inside the mesoporous structure.

**Fig. S4** EELS spectra covering the electron energy loss of O, Ce and Gd inside a filled porous of the NiO nanoparticle showed in Figure 2b of the main manuscript.
Connectivity of CGO replica inside NiO

In order to check the good connectivity of CGO itself, the NiO backbone was removed after reduction to metallic Ni. An acid leaching in 2 M HNO$_3$ at 60 ºC was employed, although it etches both Ni and CGO since the CGO etch rate is lower. XRD confirmed that there is no Ni present after the etching (only CGO). Find below a TEM image of the Ni-CGO powder after being subjected to this acid leaching process. It can be seen that: i) good connectivity exists between the CGO particles; ii) the particle size is in the order of the porosity of the mesoporous NiO (the CGO penetrated inside the NiO); iii) a high porosity is maintained (not perfectly ordered probably due to the effects of the nitric acid etch on the CGO).

![TEM image of a CGO particle after nitric acid leaching of a Ni-CGO particle stabilized at high temperature.](image)

**Fig. S5** TEM image of a CGO particle after nitric acid leaching of a Ni-CGO particle stabilized at high temperature.
Microstructure of the mesostructured Ni-CGO composite compared to commercial Ni-CGO fabricated by tape casting

Fig. S6 Backscatter SEM image of a cross-section of commercial Ni-CGO fabricated by tape casting (FAE S.A.) compared to mesoporous Ni-CGO fabricated for this work. Please notice that both images are presented in the same scale.

Notes and references