Experimental report

03/02/2022

Proposal:	**5-23-746**	**Council:**	4/2020

Title: Unraveling the role of oxygen vacancies in high-performance catalystsbased on Ni/CeO2 for CO2 reductionto CO with hydrogen

Research area: Chemistry

This proposal is a new proposal

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Samples: Niy(Ce1-xLxO2-x/2)1-y (L: Lanthanide)

Instrument	Requested days	Allocated days	From	To
D2B	3	3	12/03/2021	15/03/2021

Abstract:

Carbon dioxide (CO2) has been attributed to be one of the main sources of the greenhouse effect. Nowadays, there are increasing attempts to consider it as a resource rather than a waste. Conversion of CO2 into CO by catalytic reduction with hydrogen (reverse water gas shift reaction (rWGS, CO2 + H2 \ CO + H2O) has been recognized as one of the most promising processes for CO2 valorization. We have succeeded in the development of catalysts based on Niy(Ce1-xLxO2-x/2)1-y (L: Lanthanide) cermets with high efficiency for the rWGS reaction. These cermet materials consist of a lanthande-doped-CeO2 matrix with supported Ni nanoparticles. The presence of oxygen vacancies in the matrix is essential for the catalytic process. These phases can be perfectly fitted in the structural model of a cubic fluorite for the ceria support. In this proposal we aim to investigate the crystal structure features at RT, including the evolution of the oxygen vacancies with rare-earth nature and the doping level, with respect to a catalyst based on non-doped CeO2. We ask for 3 days of beam time at D2B diffractometer, for 12 samples ((Ni)0.10(Ce1-xLxO2-d)0.90) (x= 0, 0.05, 0.1 and 0.2 for L= La, Pr, Nd).

CO_2 emissions are the main source of the greenhouse effect. Nowadays, there are increasing attempts to consider it as a resource rather than a waste, since large amounts of low cost and relatively pure CO_2 will be available from plants for carbon sequestration and storage. The conversion of CO_2 into useful chemicals (that effectively reduce its emissions) such as bulk chemicals and fuels, is a process in two steps.

The first and essential stage is the reduction of CO_2 to CO with H_2, or reverse water gas shift reaction (rWGS: $CO_2 + H_2 \rightleftarrows CO + H_2O$), using green H_2. This reaction is endothermic, being thermodynamically favored at high reaction temperatures (600-700 °C) and in excess of H_2. Lower temperatures will favor methanation reaction and carbon formation by Boudouard reaction. Therefore, the use of an efficient catalyst under these conditions is imperative. Some lab-scale catalysts based on RE-doped ceria-supported nickel (prepared by Solution Combustion Synthesis, *SCS*) have shown excellent performance in terms of activity, selectivity, and stability for rWGS reaction. Several studies suggest that the active site is related to the interface between metallic particles (that activate the dissociation of H_2) and a reducible oxide support, with oxygen vacancies, increased by doping with rare earths, which promote the adsorption of CO_2.

In order to perform a precise study about the influence of RE proportion as ceria dopant on the catalytic behavior, avoiding modifications in the dispersion of active phases by some uncontrollable porosity obtained by the *SCS*, another synthesis method has been used. Thus, we have succeeded in the preparation of a series of samples based on NiO supported on bare CeO_2 or doped with different proportions of La by a sol-gel method (trisodium citrate/cations = 3 (molar)): $NiO_{0.1}/(CeO_2)_{0.9}$; $NiO_{0.1}/(Ce_{0.95}La_{0.05}O_x)_{0.9}$; $NiO_{0.1}/(Ce_{0.9}La_{0.1}O_x)_{0.9}$ and $NiO_{0.1}/(Ce_{0.8}La_{0.2}O_x)_{0.9}$. Metallic nickel will be formed during the activation under a reducing atmosphere before the RWGS reaction.

Good quality neutron powder diffraction (NPD) patterns were collected for $(Ce_{1-x}La_xO_{2-\delta})$:$NiO_{0.1}$ (x= 0, 0.05, 0.10, 0.20) cermets at the high-resolution D2B neutron diffractometer of ILL (Grenoble-France), with the high-flux mode and a counting time of 2 h. The samples were contained in 8 mm dia. vanadium holders. A wavelength of 1.594 Å was selected from a Ge monochromator; the measurement temperature was 295 K. The patterns were refined by the Rietveld method, using the FULLPROF refinement program. A pseudo-Voigt function was chosen to generate the line shape of the diffraction peaks. No regions were excluded in the refinement. In the final run the following parameters were refined from the high-resolution D2B data: scale factor, background coefficients, zero-point error, unit-cell parameters, pseudo-Voigt corrected for asymmetry parameters, positional coordinates, and isotropic for the metals and oxygen atoms. The coherent scattering lengths for Ce, La, Ni and O atoms were 4.84, 8.24, 10.30, and 5.803 *fm*, respectively.

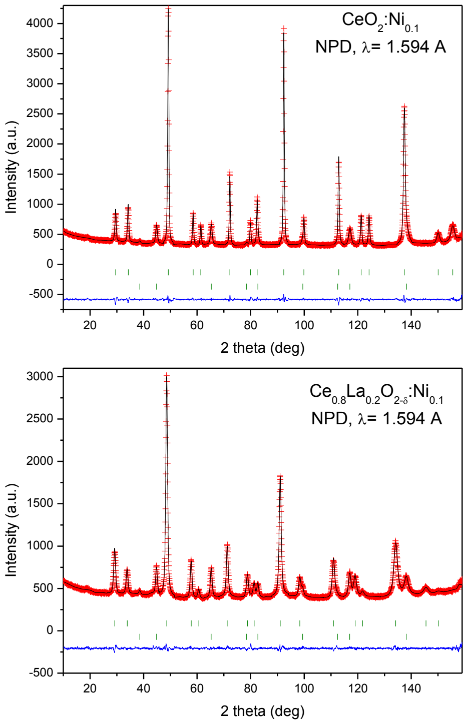

Figure 1. Room temperature NPD patterns after the Rietveld refinements of $CeO_2:Ni_{0.1}$ and $(Ce_{0.9}La_{0.1}O_2)_{:}$ $Ni_{0.1}$

Neutron diffraction experiments (NPD) were performed in order to identify the evolution of the oxygen vacancies induced by the La^{3+}-doping at the Ce^{4+} structural sites of the fluorite matrix of composition $Ce_{1-x}La_xO_{2-\delta}$. The determination of the O positions in oxide networks is difficult by X-ray diffraction given the weak scattering factor for O^{2-} ions; therefore, neutron diffraction measurements are essential. Our neutron data allowed us the access to a wide region of the reciprocal space enabling the successful refinement of the occupancy factors for O atoms, minimizing the correlation with the displacement factors.

The NPD diagrams are perfectly indexed in the cubic Fm-3m cubic space group; no impurities or additional reflections that could have indicated a departure from this symmetry were observed. As a second phase, metal Ni was included in the refinement, defined in the space group Fm-3m with a= 3.5223 Å.

Fig. 1 shows the goodness of the neutron fits, illustrated for both end members, x= 0 and x= 0.2. The presence of Ni is essential in the performance of the cermet as catalysts; despite the relatively low amount present in the cermet (not visible from the DRX patterns), the large scattering factor of Ni for neutrons (b= 10.30 *fm*) allowed us to confirm its presence, as a metal, in the cermet composition.

Fig. 2a shows the variation of the unit-cell parameter ***a*** with the La contents; a regular expansion of the lattice is observed as the Ce is replaced by La, given the larger ionic radius of La^{3+} (1.16 Å) *vs* Ce^{4+} (0.97 Å) in eightfold coordination [R. Shannon, Acta Crystallographica Section A 32 (1976) 751-767]. The most significant conclusion of this study is the refined value of the oxygen contents, evolving with the La contents between the expected value of 2.0 for x= 0 to of 1.89(1) per formula unit, which agrees perfectly, within the standard deviations, with the expected amount from the La doping level of x= 0.2.

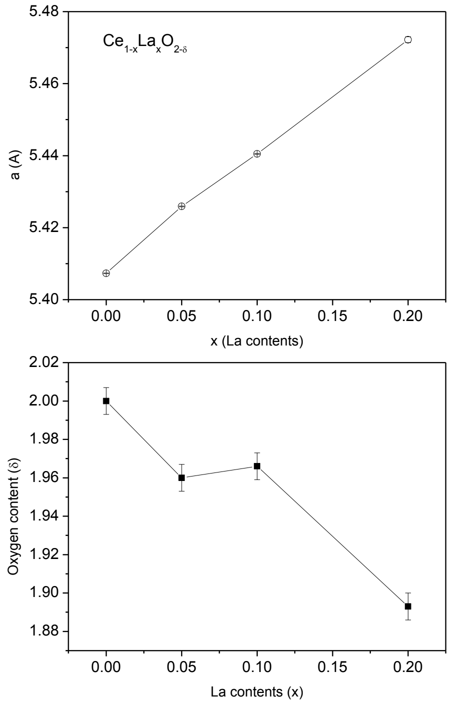

Figure 2. a) Variation of the unit-cell parameter with the La content, b) evolution of the oxygen contents with La doping the $Ce_{1-x}La_xO_{2-\delta}$ fluorite matrix.