Supporting Information

Synthesis and characterization of nickel-doped ceria nanoparticles with improved surface reducibility

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Supporting information 1: Synthesis and Characterization

1.1 Synthesis of Ni_{0.1}Ce_{0.9}O_{2-x} nanoparticles.

The synthesis of Ni_{0.1}Ce_{0.9}O_{2-x} nanoparticles is close to the synthesis method previously described by J.S. Elias *et al.* in ref [1] but is simplified since it takes place in 2 steps instead of 3 steps in [1]. Ce(III)L complex and Ce(III)Ni(II)-L binuclear complex have been prepared on one step separately. The bidentate Schiff-base complex was synthesized following click chemistry approach formerly described in ref. [2]. Initially the aforementioned Schiff-base complexes were mixed in a ratio of 8/1 and the the Ni_{0.1}Ce_{0.9}O_{2-x} nanoparticles have been obtained in a following step by pyrolysis of the mixture.

Preparation of Ce(III)-L complex: In a solution of 20 ml of methanol we added two equivalents of 2-hydroxy-3- methoxybenzaldehyde (0.30 g, 2 mmol), an equivalent of 1,3-diaminopropane (0.07 g, 1 mmol) and an equivalent of cerium (III) nitrate hexahydrate Ce (NO₃) 2.6 H₂O (0.406 g, 1 mmol), giving an yellow precipitate immediately, according to *scheme 1*. The yellow suspension was stirred at reflux for 4 hours before cooling down to room temperature. The crude product was filtered through a frit, washed with cold EtOH (3 x 20 mL) and dried under vacuum to give Ce(III)-L complex as a yellow powder with a yield one step synthesis of 94%. The purity is controlled by TLC plate and Rf = 11% eluent (CH₂Cl₂ / EtOH).



Scheme S1: Synthesis step of Ce^{III}-(N,N'-bis(3-methoxysalicylidene)-propylene-1,3-diamine)

Preparation of Ce(III)Ni (II)-L binuclear complex: In a three-necked flask we mixed two equivalent of 2-hydroxy-3-methoxybenzaldehyde (4 g , 26.31 mmol), an equivalent of 1,3-diaminopropane (1.05 g, 15 mmol) and an equivalent of Nickel(II) tetrahydrate Ni (OCOCH₃)₂. 4H₂O (3.33 g, 13.5 mmol) in a solution of 50 ml of methanol. The green solution was refluxed at 80 °C for 9 h and after cooling down at room temperature an equivalent of cerium(III) nitrate hexahydrate Ce (NO₃)₂. 6H₂O (5.48 g 13.5 mmol) previously dissolved in 5 ml of methanol, was included to the solution. Consequently the mixture was stirred for 10 minutes and then allowed to crystallize at room temperature, according to *scheme 2*. The yellow-green crystals were obtained after reducing the volume of the solution to 20 ml and subsequently they were filtered and washed by methanol (3 * 20 ml). The synthesis yield of the Ce(III)Ni(II)-L binuclear complex was 57%, and its purity was controlled by TLC plate and the Rf = 20% eluent (CH₂Cl₂ / EtOH 8.5 / 1.5).



Scheme S2: Synthesis step of Ni^{II}-Ce^{III} (N,N'-bis(3-methoxysalicylidene)-propylene-1,3-diamine)

Preparation of Ni_{0.1}**Ce**_{0.9}**O**_{2-x} **nanoparticles:** The Ni_{0.1}Ce_{0.9}O_{2-x} nanoparticles were prepared by a mixture of (0.092 g, 0.173 mmol) of Ce (III)-L and Ni (II) Ce (III)-L (0.440 g, 0.547 mmol) in 40 ml of oleylamine. The mixture was refluxed at 180 °C under argon for 4 hours, and the remaining dark brown product was isolated by centrifugation. The brown solutions were divided into fractions of 3.5 mL and flocculated with ethanol (30 mL each). Consequently the brown flocculent was isolated by centrifugation (4000 rpm for 20 min) and re-dispersed in hexane (5 mL fractions). Bulk precipitates were removed by centrifugation (3000 rpm for 3 min) and subsequent decanting of these solutions. This process was repeated two times to give brown hexanes solutions of Ni_{0.1}Ce_{0.9}O_{2-x}.

For characterization the solution was drop casted on a planar support and the protective organic cap layer was removed by calcination in air at 400°C for 1 hour, which produces bare $Ni_{0.1}Ce_{0.9}O_{2-x}$ nanoparticles.

1.2 Synthesis of 10% Ni/CeO₂ using the co-precipitation method.

The 10% Ni-CeO₂ reference material was prepared by the co-precipitation method using metal nitrates. Specifically, in an aqueous solution containing the required amounts of Nickel(II) nitrate hexahydrate [Ni(NO₃)₂·3H₂O] (Sigma-Aldrich) and Cerium(III) nitrate hexahydrate [Ce(NO₃)₃·6H₂O (Sigma-Aldrich)], a 1 M NaOH solution was added dropwise. The co-precipitated mass was thoroughly washed, filtered and dried overnight at 110 °C followed by calcination at 400 °C for 1 hour in a furnace.

Supporting information 2: STEM images and FFT patterns of NiCe NPs



Figure S1. Left and middle: Typical bright field (BF) and annular dark field (ADF) STEM images of NiCe nanoparticles.

Supporting information 3: In situ XRD analysis during redox cycles

Data collection conditions:

Thermal stability of the two samples was determined by XRD under either $96\%N_2-4\%O_2$ or $96\%N_2-4\%H_2$ atmosphere at different temperatures along the profiles displayed in Figure S2. Temperaturecontrolled X-ray diffractograms were collected at 25 °C intervals between 25 and 400 °C (heating rate of 10 °C/min, temperature stabilisation for 20 min, cooling rate of 60°C/min). The sample was deposited on the sieve (pore size \emptyset 0.2mm) of the open sample holder cup, both made of glass ceramic Macor, thus allowing gas to flow through and eventually reacting with the sample. For CeO₂/NiO (10 mol%) powder sample, the diffractogram was collected at each temperature in the [20°-130°] scattering angle range with a 0.0131° step for a total acquisition time of 220 min. For Ni_{0.1}Ce_{0.9}O₂₋₁₂ drop casted sample, the diffractogram was collected at each temperature in the [20°- 65°] scattering angle range with a 0.0131° step for a total acquisition time of 155 min. The program FullProf was used for Le Bail refinements.



Sample : Ni_{0.1}Ce_{0.9}O_{2-x} drop-casted on quartz substrate

Raw drop casted sample does not contain any secondary phase (Figure S3, *left side*). Whatever the annealing temperature under diluted oxygen, the diffraction pattern remains similar to that of a ceria type compound. It suggests that a partial substitution of cerium by nickel occurs. When the sample is annealed under diluted hydrogen, no appearance of nickel metal as secondary phase is observed whatever the annealing temperature. The sample is then stable in reducing atmosphere up to 400°C. The diffraction patterns of the sample recorded under diluted hydrogen are similar to that recorded under diluted oxygen. Indeed, after being annealed at 400°C either under 96%N₂-4%O₂ or 96%N₂-4%H₂ atmosphere, cubic unit cell parameter of ceria at room temperature did not change (please refer to *Table 1 of the main text*).

Sample : powder Ni/CeO₂ (10mol%)

As shown by the diffractograms in Figure S3 (*right side*) the 10 mol% Ni/CeO₂ raw powder contains NiO as secondary phase (large (200) peak at around 43.3° in 2theta in agreement with the JCPDS card n° 01-071-1179). When this powder is annealed under diluted hydrogen, a reduction of NiO into Ni starts at 275°C (appearance of the (111) peak at around 44.5° in 2theta in agreement with the JCPDS card n° 00-004-0850). At 300°C, Ni is the only secondary phase present in the sample. When this powder is re-annealed under diluted oxygen after being reduced, the diffraction lines assigned to Ni start decreasing in intensity at around 275°C. A diffuse peak at around 43.3° in 2theta assigned to Ni O, appears only above 300 °C. At 400 °C, the oxidation is not yet complete and a large amount of Ni remains present. The cubic unit cell parameter of ceria found at room temperature did not change

after 400°C annealing either in 96% N_2 -4% O_2 or in 96% N_2 -4% H_2 atmosphere (please refer to *Table 1 of the main text*). This indicates that ceria structure remains stable in both environments at list in the temperature range between 25 and 400°C.



Figure S3. In situ XRD patterns of $Ni_{0.1}Ce_{0.9}O_{2-x}$ NPs (left) and 10%Ni/CeO₂ (middle) upon treatment up to 400 °C first in H₂ and then in O₂ atmospheres. For both samples, all Bragg peaks are singly indexed onto the CeO₂-like fluorite cubic subcell. An enlarged view of the 42-46 degrees region is also given at the right or the figure.

References

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