Electronic Supplementary Information

Structural, physical and chemical properties of nanostructured nickel-substituted ceria oxides under reducing and oxidizing conditions

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Figure S1. Synchrotron XRD patterns recorded at 500 ºC in different atmospheric conditions (empty circles) with the Rietveld-fitted pattern (red line) and the difference plot for nanostructured CeNi05.

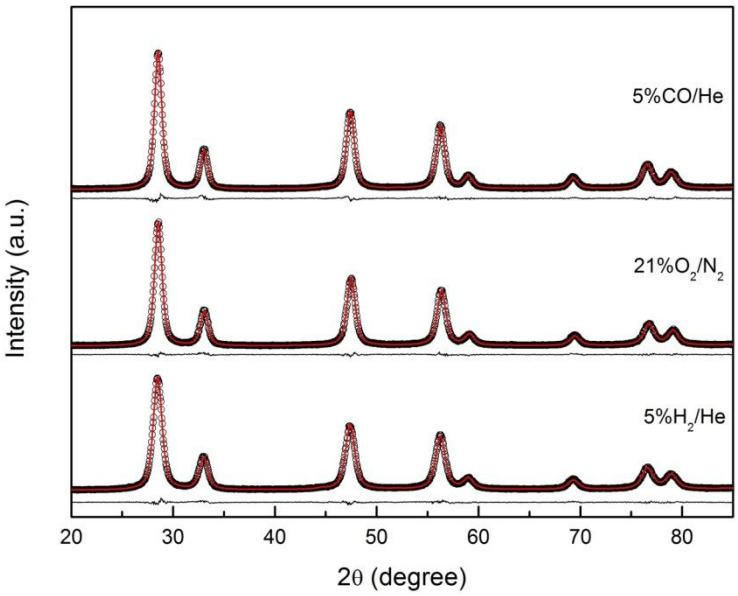

Table S1. Structural parameters and standard Rietveld agreement factors for CeNi05 at different temperatures under reducing/oxidizing condition. Before and after thermal treatments, the crystallite average size was 7.1 nm and 10 nm, respectively.

Atmosphere	5%H_2/He	Air*	5%CO/He
T (ºC)	500	500	500
a (Å)	5.4466(1)	5.4379(1)	5.4494(3)
V (Å^3)	161.583(3)	160.800(2)	161.822(3)
R_p	4.29	3.99	4.79
R_{wp}	6.08	5.73	6.52
R_e	4.36	4.53	4.34
χ^2	1.95	1.60	2.26
%CeNiO	100	100	100
%NiO	0	0	0
%Ni	0	0	0

*Air corresponds to synthetic air (21% O_2/N_2).

Figure S2. Synchrotron XRD patterns recorded at 500ºCin different atmospheric conditions (empty circles) with the Rietveld-fitted pattern (red line) and the difference plot for nanostructured CeNi10.

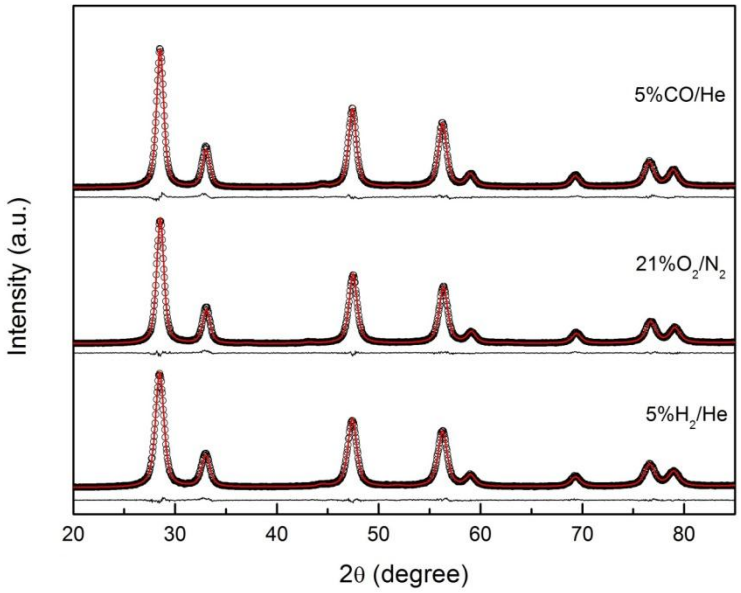

Table S2. Structural parameters and standard Rietveld agreement factors for CeNi10 at different temperatures under reducing/oxidizing condition. Before and after thermal treatments, the crystallite average size was 5.9 nm and 10 nm, respectively.

Atmosphere	5%H_2/He	Air*	5%CO/He
T (ºC)	500	500	500
a (Å)	5.4455(1)	5.4390(3)	5.4484(3)
V (Å^3)	161.478(5)	160.900(4)	161.490(4)
R_p	4.16	4.12	4.87
R_{wp}	5.77	5.74	6.54
R_e	4.38	4.54	4.35
χ^2	1.74	1.60	2.26
%CeNiO	97.8(3)	97.8(4)	96.5(5)
%NiO	0	2.2(3)	0
%Ni	2.2(2)	0	3.5(5)

*Air corresponds to synthetic air (21% O_2/N_2).

Figure S3. Synchrotron XRD patterns recorded at 500ºCin different atmospheric conditions (empty circles) with the Rietveld-fitted pattern (red line) and the difference plot for nanostructured **CeNi20**.

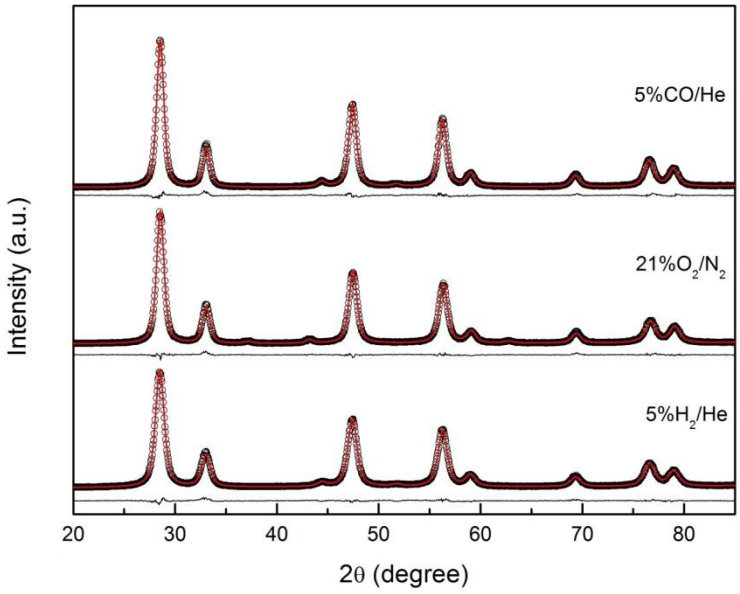

Table S3. Structural parameters and standard Rietveld agreement factors for CeNi20 at different temperatures under reducing/oxidizing condition. Before and after thermal treatments, the crystallite average size was 5.0 nm and 9.8 nm, respectively.

Atmosphere	5%H_2/He	Air*	5%CO/He
T (ºC)	500	500	500
a (Å)	5.4498(1)	5.4453(2)	5.4527(1)
V (Å^3)	161.868(5)	161.463(5)	162.120(5)
R_p	4.18	4.12	4.84
R_{wp}	5.85	5.80	6.67
R_e	4.28	4.41	4.21
χ^2	1.87	1.73	2.28
%CeNiO	95.8(3)	94.2(4)	94.3(4)
%NiO	0	5.8(3)	1.5(7)
%Ni	4.2(2)	0	4.2(3)

*Air corresponds to synthetic air (21% O_2/N_2).

Figure S4. Nitrogen adsorption isotherms of the as-prepared (solid circles) and calcined (open squares) powders.

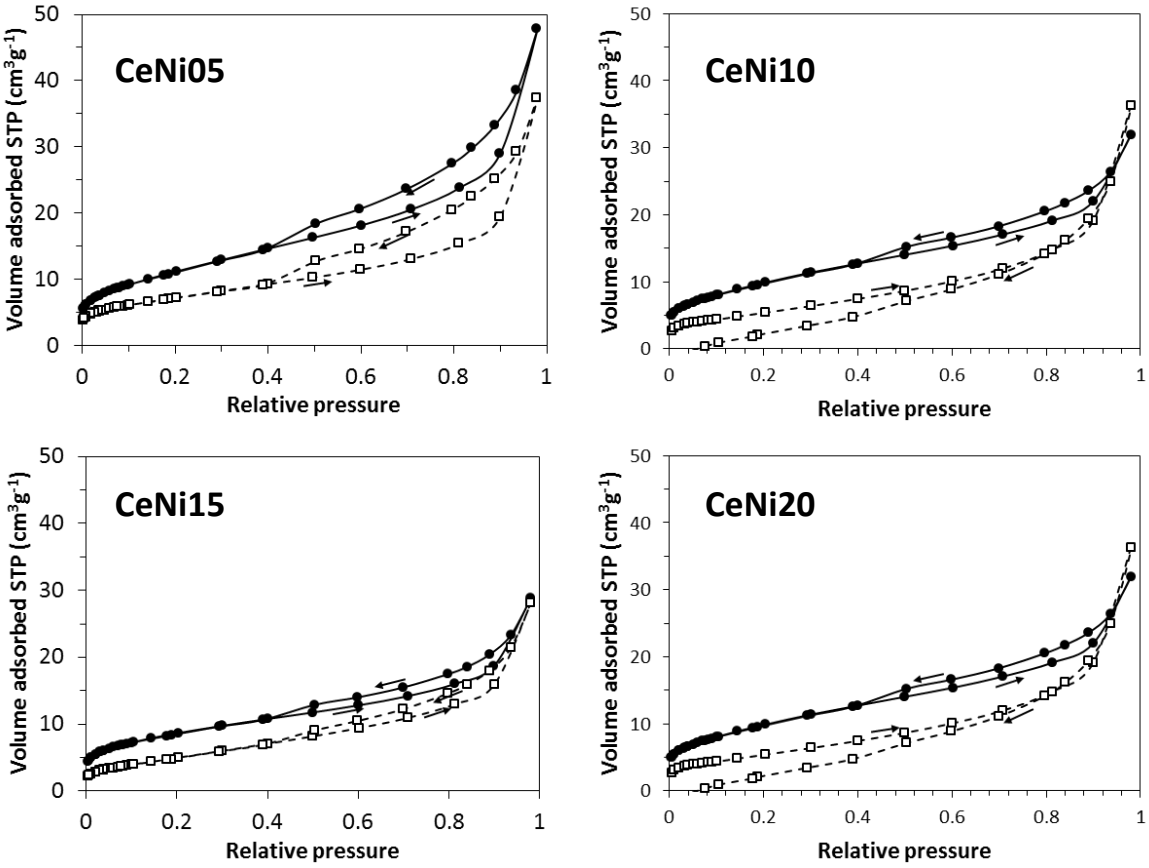

Figure S5. Normalized XANES spectra at the Ce L_3-edge for CeNi05 a) at room temperature in air and at 500 ºC under b) 5% H_2/He; c) 21% O_2/N_2 and d) 5% CO/He, showing the experimental data (empty circles), four Gaussian peaks (A–D),one arctangent function obtained by least-squares fitting and the sum of all five functions (continuous line).

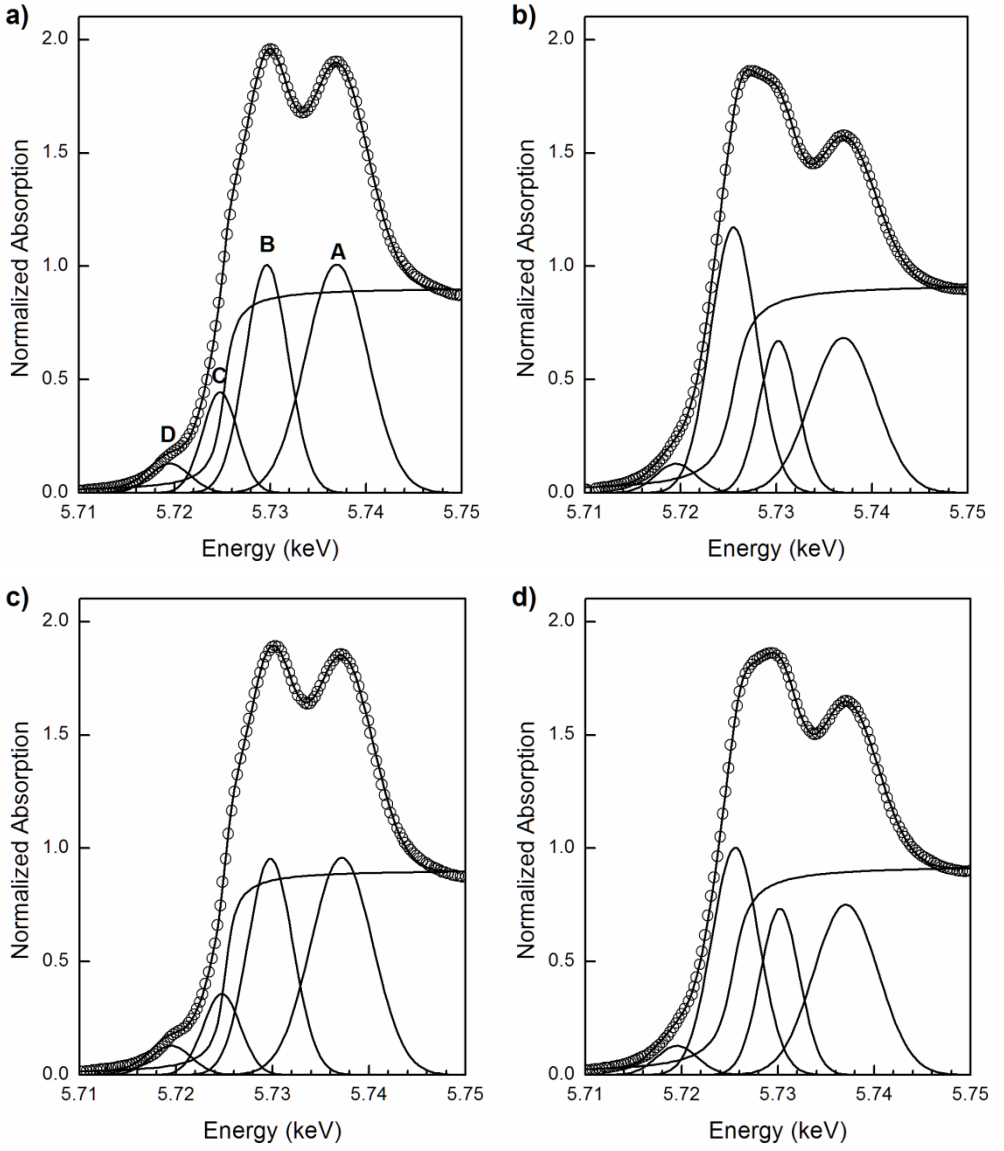

Figure S6. Normalized XANES spectra at the Ce L_3-edge for CeNi20 a) at room temperature in air and at 500 ºC under b) 5% H_2/He; c) 21% O_2/N_2 and d) 5% CO/He, showing the experimental data (empty circles), four Gaussian peaks (A–D),one arctangent function obtained by least-squares fitting and the sum of all five functions (continuous line).

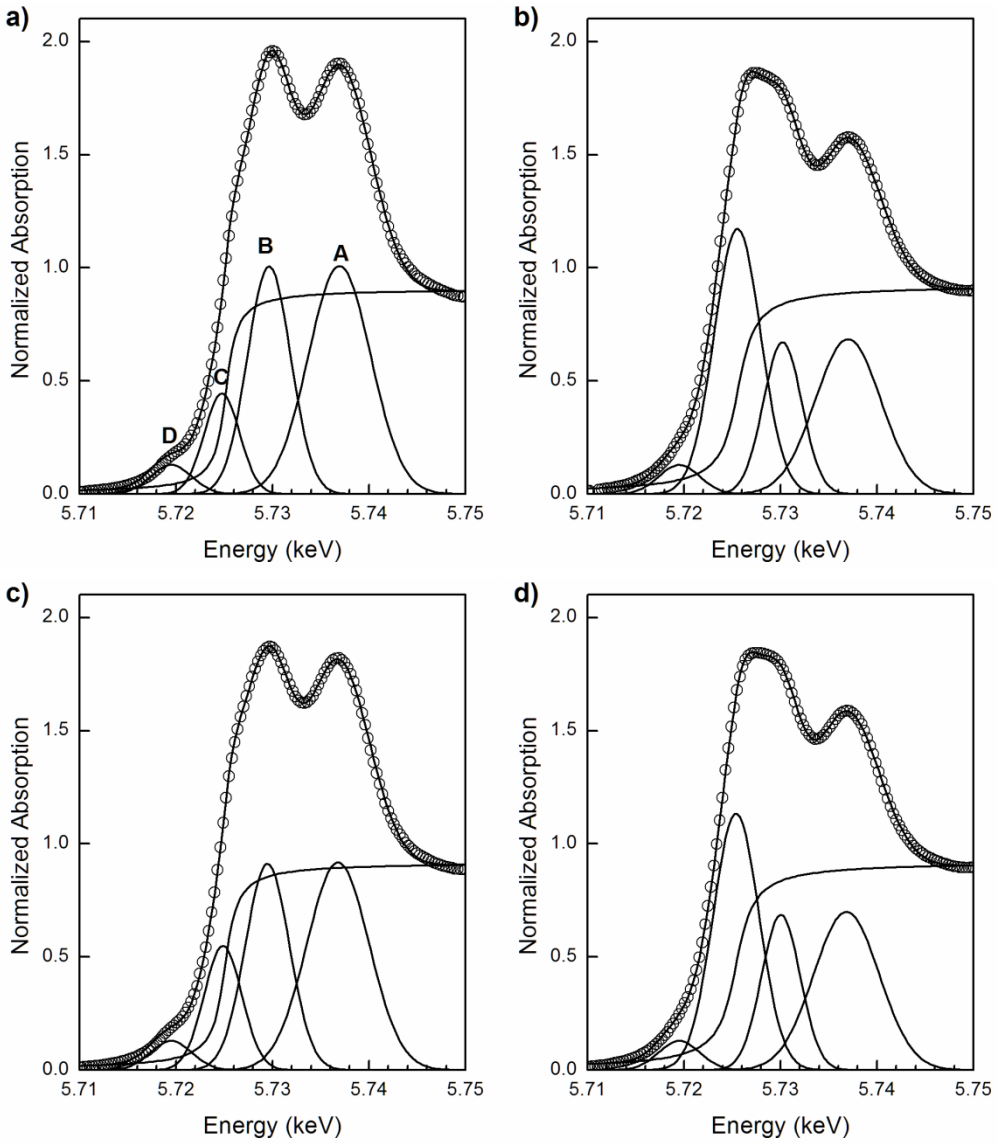

Table S4- Fraction of Ce present as Ce^{3+} in nanostructured CeNi05, CeNi10 and CeNi20 powders under reducing and oxidizing conditions at 500 ºC, estimated from Ce L_3-edge XANES spectra fit.

Sample	Atmosphere	$Ce^{3+}/(Ce^{4+}+Ce^{3+})$ % (*)
CeNi05	5% H_2/He	23.4
	21% O_2/N_2	-4.9
	5% CO/He	21.5
CeNi10	5% H_2/He	26.8
	21% O_2/N_2	-4.3
	5% CO/He	24.7
CeNi20	5% H_2/He	27.1
	21% O_2/N_2	1.2
	5% CO/He	25.5

(*) Values are calculated with respect to a standard material: pure, nanoparticulate ceria. Negative values indicate that the sample contained a smaller percentage of Ce^{3+} than this standard.