Supporting Information

CeO_2-supported Ni and Co catalysts prepared by solution combustion method for H_2 production from glycerol: The effect of fuel/oxidizer ratio and oxygen excess

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Chemical equations used to obtain NiO–CeO_2

Total valency of glycine: $C_2H_5NO_2 = 4·2 + 1·5 – 2·2 = +9$

Total valency of urea: $(NH_2)_2CO = 1·4 + 4 – 2 = +6$

Total valency of oxidizers: $Ce(NO_3)_3 = 3 – 2·3·3 = –15$; $Ni(NO_3)_2 = 2 – 2·3·2 = –10$; $Co(NO_3)_2 = 2 – 2·3·2 = –10$; $NH_4NO_3 = 1·4 – 2·3 = –2$

<u>With glycine</u>

1) *<u>φ=0.72:</u>* $2Ce(NO_3)_3(aq) + 2Ni(NO_3)_2(aq) + 4C_2H_5NO_2 = 2(NiO·CeO_2) + 7N_2 + 8CO_2 + 3O_2 + (10H_2O)$

2) *<u>φ=1:</u>* $36Ce(NO_3)_3(aq) + 36Ni(NO_3)_2(aq) + 100C_2H_5NO_2 + 9O_2 = 36(NiO·CeO_2) + 140N_2 + 200CO_2 + (250H_2O)$

3) *<u>φ=1.25:</u>* $280Ce(NO_3)_3(aq) + 280Ni(NO_3)_2(aq) + 972C_2H_5NO_2 + 507O_2 = 280(NiO·CeO_2) + 1186N_2 + 1944CO_2 + (2430H_2O)$

4) *<u>φ=1.4:</u>* $1040Ce(NO_3)_3(aq) + 1040Ni(NO_3)_2(aq) + 4044C_2H_5NO_2 + 2859O_2 = 1040(NiO·CeO_2) + 4622N_2 + 8088CO_2 + (10110H_2O)$

5) *<u>φ=1.5:</u>* $24Ce(NO_3)_3(aq) + 24Ni(NO_3)_2(aq) + 100C_2H_5NO_2 + 81O_2 = 24(NiO·CeO_2) + 110N_2 + 200CO_2 + (250H_2O)$

6) *φ=2:* $18Ce(NO_3)_3(aq) + 18Ni(NO_3)_2(aq) + 100C_2H_5NO_2 + 117O_2 = 18(NiO\cdot CeO_2) + 95N_2 + 200CO_2 + (250H_2O)$

7) *φ=2.5:* $140Ce(NO_3)_3(aq) + 140Ni(NO_3)_2(aq) + 972C_2H_5NO_2 + 1347O_2 = 140(NiO\cdot CeO_2) + 836N_2 + 1944CO_2 + (2430H_2O)$

With glycine and NH_4NO_3

8) *φ=1.6:* $72Ce(NO_3)_3(aq) + 72Ni(NO_3)_2(aq) + 400C_2H_5NO_2 + 222NH_4NO_3 + 357O_2 = 72(NiO\cdot CeO_2) + 602N_2 + 800CO_2 + (1444H_2O)$

9) *φ=2.22:* $350Ce(NO_3)_3(aq) + 350Ni(NO_3)_2(aq) + 2430C_2H_5NO_2 + 539NH_4NO_3 + 3098O_2 = 350(NiO\cdot CeO_2) + 2629N_2 + 4860CO_2 + (7153H_2O)$

With urea

10) *φ=1:* $12Ce(NO_3)_3(aq) + 12Ni(NO_3)_2(aq) + 50(NH_2)_2CO + 3O_2 = 12(NiO\cdot CeO_2) + 80N_2 + 50CO_2 + (100H_2O)$

11) *φ=2:* $12Ce(NO_3)_3(aq) + 12Ni(NO_3)_2(aq) + 100(NH_2)_2CO + 78O_2 = 12(NiO\cdot CeO_2) + 130N_2 + 100CO_2 + (200H_2O)$

12) *φ=3:* $12Ce(NO_3)_3(aq) + 12Ni(NO_3)_2(aq) + 150(NH_2)_2CO + 153O_2 = 12(NiO\cdot CeO_2) + 180N_2 + 150CO_2 + (300H_2O)$

Chemical equations used to obtain CoO–CeO_2

With glycine

13) *φ=1:* $36Ce(NO_3)_3(aq) + 36Co(NO_3)_2(aq) + 100C_2H_5NO_2 + 9O_2 = 36(CoO\cdot CeO_2) + 140N_2 + 200CO_2 + (250H_2O)$

14) *φ=1.5:* $24Ce(NO_3)_3(aq) + 24Co(NO_3)_2(aq) + 100C_2H_5NO_2 + 81O_2 = 24(CoO\cdot CeO_2) + 110N_2 + 200CO_2 + (250H_2O)$

15) *φ=2:* $18Ce(NO_3)_3(aq) + 18Co(NO_3)_2(aq) + 100C_2H_5NO_2 + 117O_2 = 18(CoO\cdot CeO_2) + 95N_2 + 200CO_2 + (250H_2O)$

Table S1. Data on the phase composition and crystallinity of the synthesized Ce–Ni–O systems.

N	n(AN)/ n(MeN)	φ	Phase composition according Rietveld/Corrected[4], wt%			Ni, wt% (TGA[5])	Am. NiO[6], wt%	D (CeO_2), nm	a (CeO_2), Å	D (NiO), nm	D (Ni), nm
			CeO_2	NiO	Ni						
Fuel – glycine											
1	–	0.72	79/67	21/33	0	0	12	6.5	5.4190	6.4	–
2[1]	–	1	71/67	24/32	5/1	1.4	8	35.2	5.4112	29.1	18.7
3-1[1]	–	1.25	70/67	30/33	0	0	3	29.9	5.4105	25.9	–
3-2[1,2]			72/67	8/24	20/9	8.9	16	26.8	5.4120	13.0	17.0
4-1[2]	–	1.4	72/67	23/32	5/1	1.1	9	20.0	5.4154	13.4	13.1
4-2[1]			70/67	30/33	0	0	3	25.9	5.4111	22.1	–
5-1[1]	–	1.5	72/67	21/31	7/2	1.6	10	18.2	5.4149	9.8	8.9
5-2[1,3]			75/67	9/29	16/4	4.1	20	21.1	5.4141	7.7	14.3
6-1	–	2	73/67	27/33	0	0	6	7.0	5.4194	6.1	–
6-2[3]			79/67	0/29	21/4	3.6	29	9.5	5.4185	–	4.8
7	–	2.5	74/67	26/33	0	0	7	4.5	5.4188	4.7	–
8[1]	1.54	1.6	70/67	23/32	7/1	0.5	9	28.8	5.4099	21.1	3.9
9-1	0.77	2.22	73/67	27/33	0	0	6	8.8	5.4189	6.7	–
9-2[3]			81/67	0/32	19/1	1.1	32	10.2	5.4178	–	3.5
Fuel – urea											
10[3]	–	1	77/67	23/33	0/0	0	10	6.6	5.4093	17.0	–
11[1,3]	–	2	71/67	11/21	18/12	11.7	10	33.3	5.4110	11.2	25.7
12[1,3]	–	3	71/67	19/no data	10/no data	No data	No data	15.3	5.4133	10.4	7.6

Note: [1]the sample contains traces of the $CeNiO_3$ phase; [2]the sample left in the beaker; [3]immediately after the completion of the combustion process, the beaker was covered with a Petri dish to prevent oxidation of solid products; [4]taking into account amorphous nickel oxide and TGA results; [5]was calculated from the weight gain of the sample during heating, equal to the mass of oxygen involved in the oxidation of nickel according to the equation $2Ni + O_2 = 2NiO$; [6]the amount of amorphous NiO is equal to the difference between the total amount (according to stoichiometry, no more than 33 wt%) and crystalline (determined by the Rietveld method); n(AN) is the number of moles of ammonium nitrate; n(MeN) is the number of moles of cerium and nickel nitrates; φ is the fuel-to-oxidizer ratio; the ratio of weighted (R_{wp}) and expected (R_e) R-factors was 0.97–1.12, which characterizes goodness of fit (if the square value is equal to one or constant, the refinement procedure is completed).

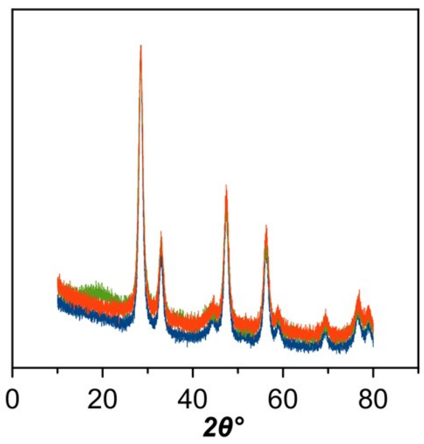

Figure S1. Reproduction of X-ray diffraction patterns of Ce–Ni oxide system obtained by glycine-nitrate combustion at φ=2 with a covering.

Table S2. The actual NiO content in Ce–Ni–O according to the EDX analysis.

φ	NiO, wt%
1.25	32.9
1.4	33.3
1.5*	32.8
2*	33.7

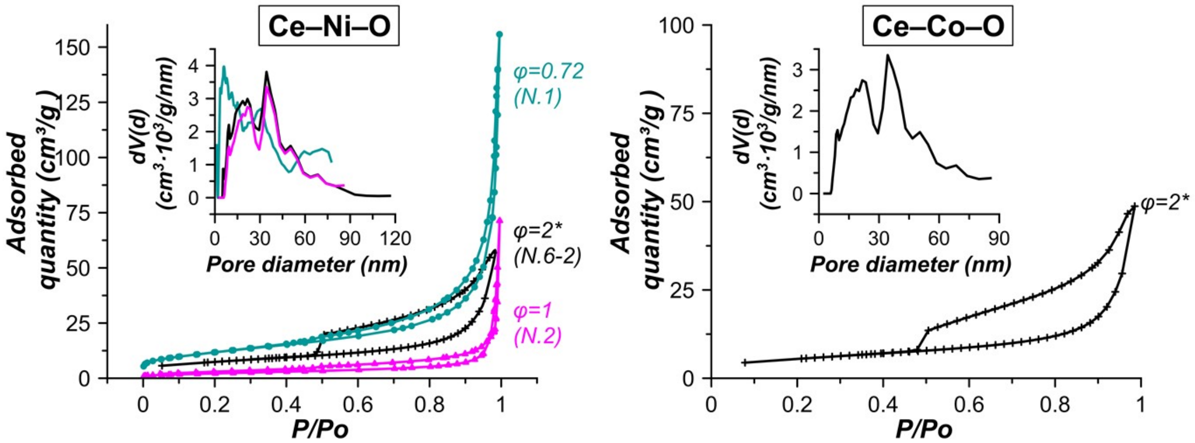

Figure S2. N_2 adsorption–desorption isotherms and the pore size distribution.

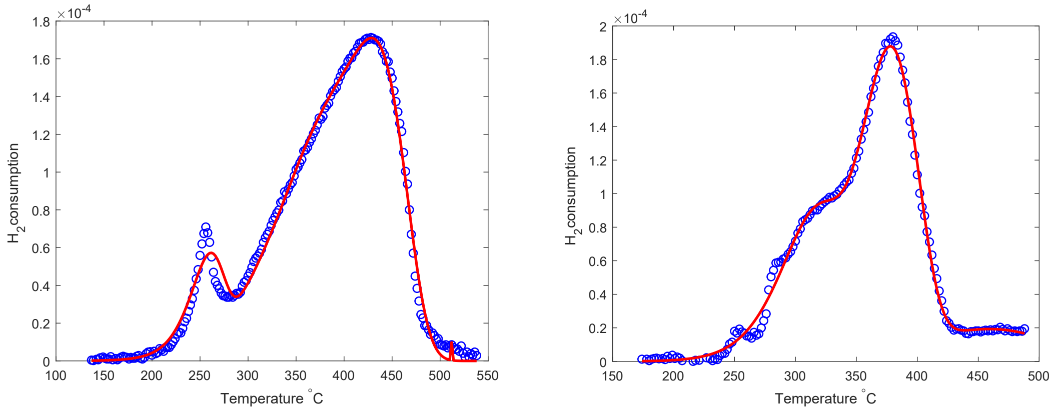

Figure S3. Modelling of TPR data for samples a) 1, b) 2 (coding of Table 1), where α, β, γ, ε peaks in Figure 8*a* correspond respectively to amorphous NiO, fine particles of nickel oxide, the same oxide strongly interacting with ceria (or large particles) and a solid solution of NiO. The values of parameters are given in Table S2.

Table S3. Values of parameters for TPR modelling. Data fitting done with ModEst software (Profmath OY).

Sample 1 (coding in Table 1)		
Parameter	Value	Error, %
$k^0{}_\alpha$*	0.092	1
$k^0{}_\beta$	0.041	1
$k^0{}_\gamma$	38	1
Eact, $_\alpha$**	129 kJ/mol	0.3
Eact, $_\beta$	71 kJ/mol	0.1
Eact, $_\gamma$	137 kJ/mol	0.3
f, $_\alpha$***	0.51	0.3
f, $_\beta$	0.41	0.1
f, $_\gamma$	0.08	1.1
Sample 2 (coding in Table 1)		
Parameter	Value	Error, %
$k^0{}_\alpha$*	0.084	>100
$k^0{}_\beta$	0.98	12.3
$k^0{}_\gamma$	0.134	>100
$k^0{}_\varepsilon$	0.0057	9.8
Eact, $_\alpha$**	149 kJ/mol	>100
Eact, $_\beta$	115 kJ/mol	2.1
Eact, $_\gamma$	139 kJ/mol	>100
Eact, $_\varepsilon$	73 kJ/mol	29
f, $_\alpha$***	0.49	>100
f, $_\beta$	0.21	15.8
f, $_\gamma$	0.15	>100
f, $_\varepsilon$	0.15	22

*Pre-exponential factor in temperature dependent reduction of the phase corresponding to α peak, etc, with the mean T of 400^{o}C.

**Activation energy in temperature dependent reduction of the phase corresponding to α peak, etc.

***Fraction of the phase corresponding to α peak, etc.

Table S4. H_2-TPR results.

Sample	*φ*	mmol H_2/g_{cat}	H_2/Ni or H_2/Co, mol/mol
Ce–Ni–O	0.72	6.0	1.3
	1	4.9	1.1
	1.5*	3.1	0.8
	2	6.1	1.4
	2*	4.9	1.2
Ce–Co–O	1*	5.1	1.2
	1.5*	5.0	1.2
	2*	5.7	1.6

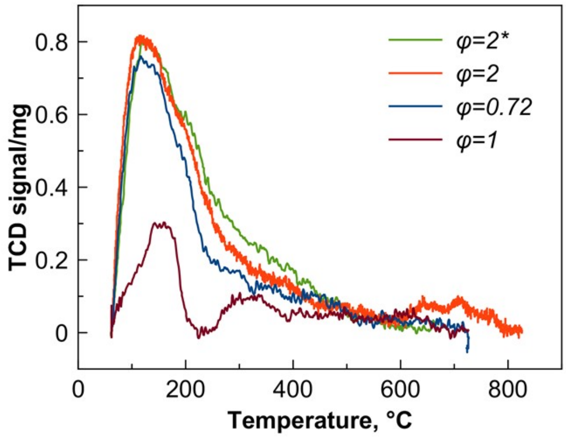

Figure S4. H_2-TPD spectra for Ce–Ni–O systems prepared at different φ.

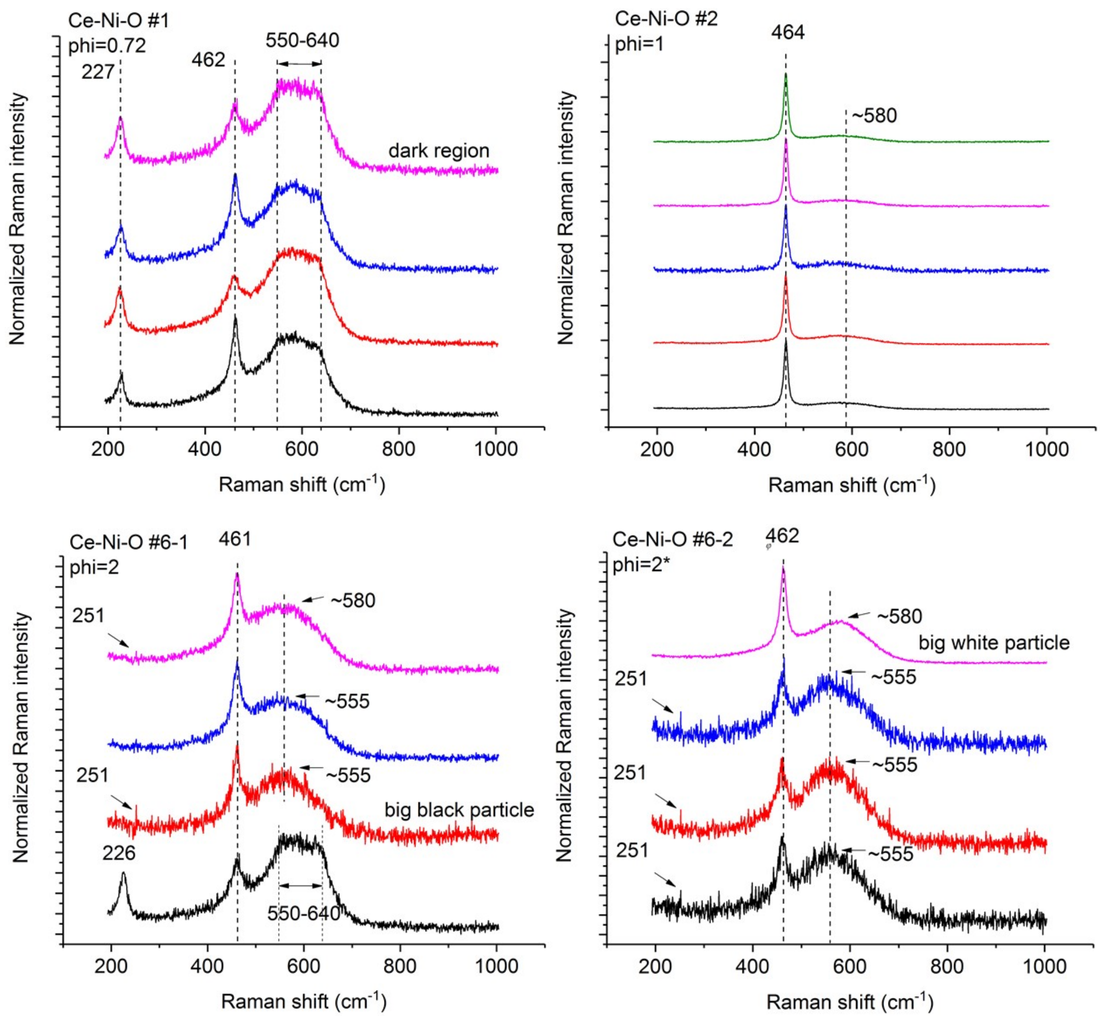

Figure S5. Raman spectra.

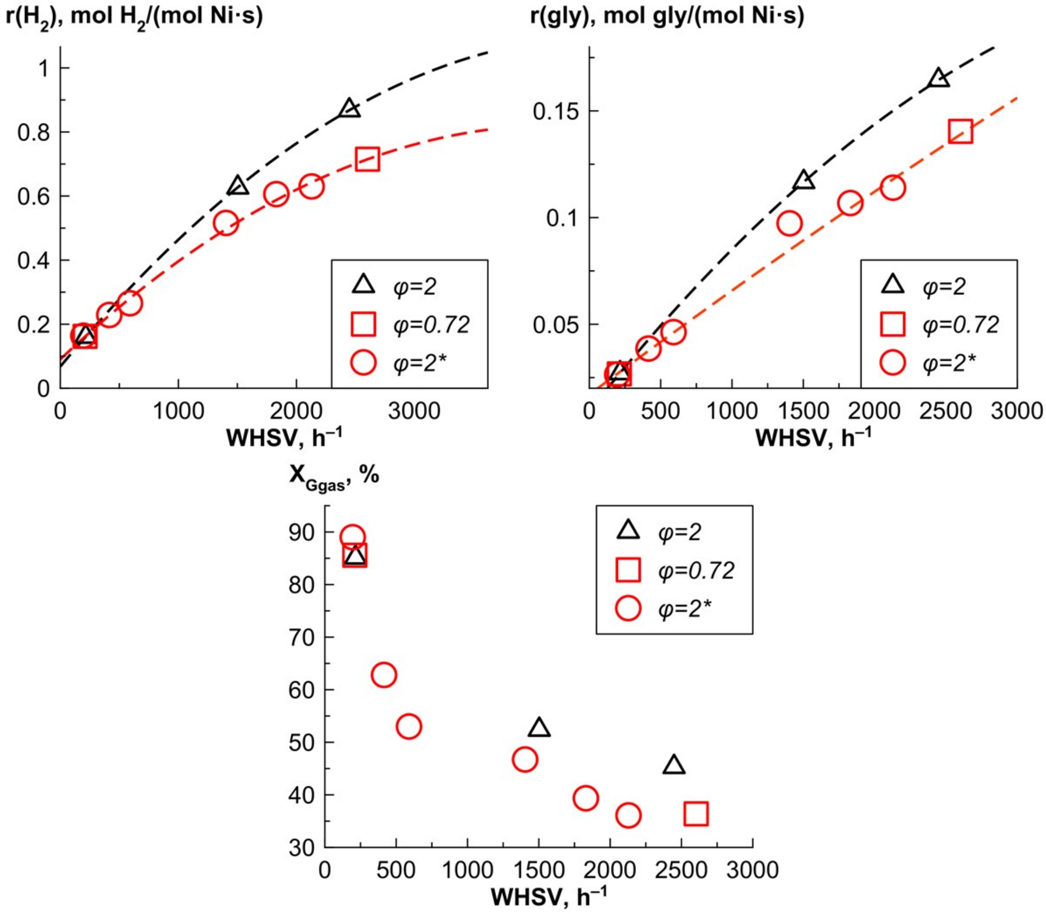

Figure S6. Dependence of the H_2 formation rate, glycerol (gly) transformation rate, and glycerol conversion into gaseous products on *WHSV* for the Ce–Ni–O systems obtained at various fuel-to-oxidizer ratios.

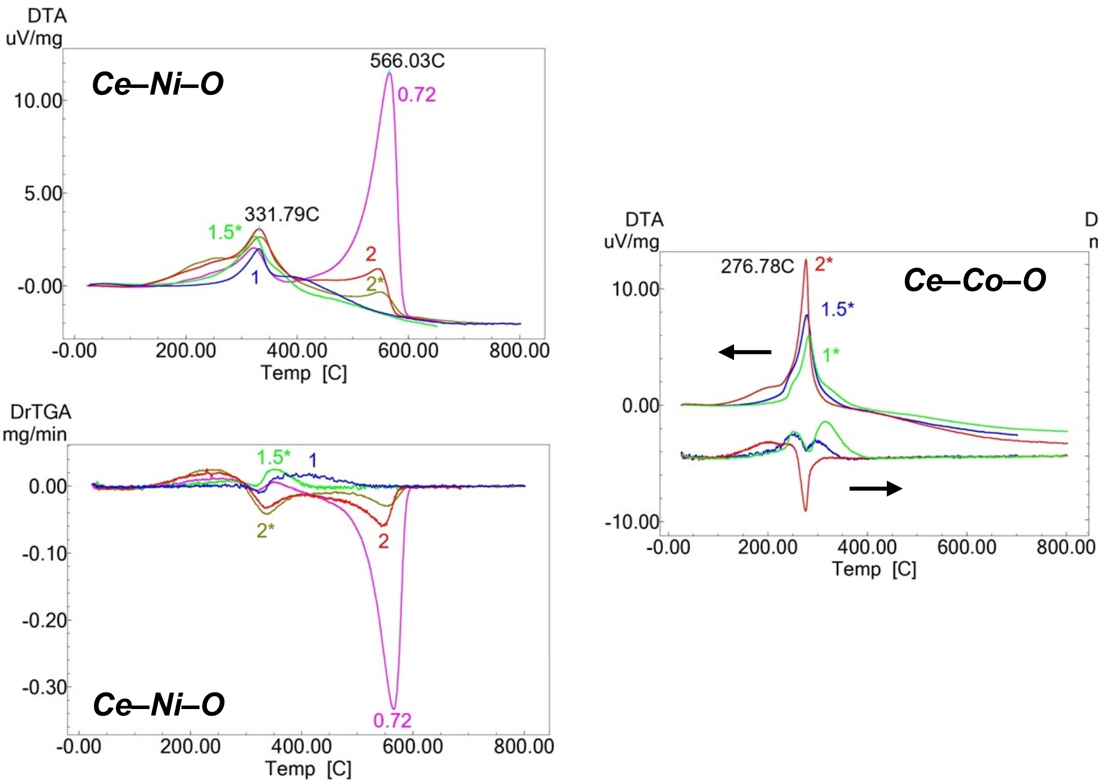

Figure S7. DTA and DTG curves for spent glycerol steam reforming catalysts. The numbers indicate the ratio of fuel-to-oxidizer.

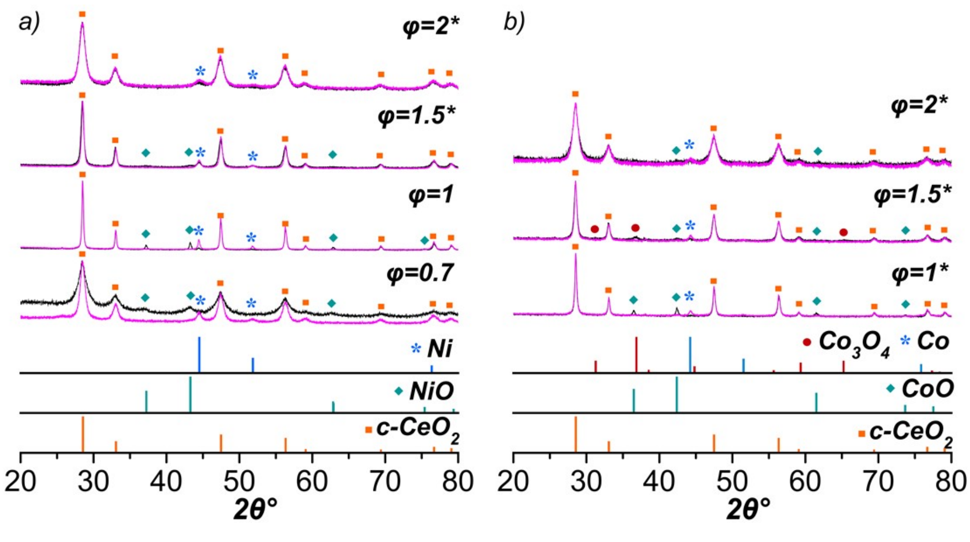

Figure S8. XRD patterns of the initial (black curves) and spent (pink curves) Ce–Ni–O (a), Ce–Co–O (b) systems obtained by the SCS method at various fuel-to-oxidizer ratios (φ) (obtained using a covering).