Supporting Information

Nanoceria-promoted low Pd-Ni Catalyst for the Synthesis of Secondary Amines from Aliphatic Alcohols and Ammonia

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FIGURE CAPTIONS

Figure S1. Effect of a pre-reduction step and of the presence of H_2 (5 bar) during the reaction on the catalytic performance of 0.5Pd-0.5Ni/CeO_2-HS for the amination reaction of OL with NH_3. In parentheses, carbon balance. Reaction conditions: OL- 6.3 mmol, NH_3/OL- 5.0-6.1, Cat- 150-170 mg (0.074-0.079 mol%Pd and 0.18-0.20 mol%Ni with respect to OL), H_2- 0-5 bar, T- 180 ^oC, Time- 2 h, rpm- 600.

Figure S2. Catalytic performance of (A) yPd-xNi/CeO_2-HS_PR and (B) (xNi-yPd)/CeO_2-HS_PR (pre-reduced) catalysts based on x= 0.5 wt%Ni and y = 0.1-2.0 wt% Pd in the amination reaction of OL with NH_3. In parentheses, carbon balance. Reaction conditions: OL- 6.3 mmol, NH_3/OL- 5.2-7.5, Cat- 130-150 mg (0.021-0.38 mol%Pd and 0.15-0.22 mol%Ni with respect to OL), H_2- 5 bar, T- 180 ^oC, Time- 2 h, rpm- 600.

Figure S3. Catalytic performance of 0.5Pd-0.5Ni/CeO_2_PR (pre-reduced) as a function of the catalyst loading in the amination reaction of OL with NH_3. In parentheses, carbon balance. Reaction conditions: OL- 6.3 mmol, NH_3/OL- 4.0-7.0, H_2- 5 bar, T- 180 ^oC, Time- 2 h, rpm- 600.

Figure S4. XRD patterns of 0.5Ni/CeO_2-HS, 0.5Pd/CeO_2-HS, 0.5Ni-0.5Pd/CeO_2-HS, (0.5Pd-0.5Ni)/CeO_2-HS, 0.5Pd-0.5Ni/CeO_2-HS and the parent CeO_2-HS pre-calcined at 300 ^oC. For comparison, the XRD pattern of the spent 0.5Pd-0.5Ni/CeO_2-HS is also included.

Figure S5. STEM-EDX-SDD micrographs of Ce, O, Ni and Pd of a 0.5Pd-0.5Ni/CeO_2-HS debris.

Figure S6. FT-IR spectra of 0.5Pd/CeO_2-HS, 0.5Ni/CeO_2-HS, 0.5Ni-0.5Pd/CeO_2-HS, (0.5Pd-0.5Ni)/CeO_2-HS, 0.5Pd-0.5Ni/CeO_2-HS and the parent CeO_2-HS pre-calcined at 300 ^oC.

Figure S7. XPS spectra of (A) Ce3d and (B) O1s core levels of (a) 0.5Pd/CeO_2-HS, (b) 0.5Ni/CeO_2-HS, (c) 0.5Ni-0.5Pd/CeO_2-HS, (d) (0.5Pd-0.5Ni)/CeO_2-HS and (e) 0.5Pd-0.5Ni/CeO_2-HS.

Figure S8. XPS spectra of Ni2p core level of (a) 0.5Ni/CeO_2-HS, (b) 0.5Ni-0.5Pd/CeO_2-HS, (c) (0.5Pd-0.5Ni)/CeO_2-HS and (d) 0.5Pd-0.5Ni/CeO_2-HS.

Figure S9. (A) H_2-TPR profiles in the temperature range 50-300 ^oC for 0.5Ni/CeO_2-HS, 2Pd/CeO_2-HS, 2Pd-0.5Ni/CeO_2-HS, (2Pd-0.5Ni)/CeO_2-HS and 0.5Ni-2Pd/CeO_2-HS (unreduced); (B) H_2-TPR profiles in the temperature range 50-900 ^oC for the parent CeO_2-HS pre-calcined at 300 ^oC.

Figure S10. H_2-TPD profiles in the temperature range 50-300 ^oC for bimetallic (A) 2Pd-0.5Ni/CeO_2-HS, (B) (2Pd-0.5Ni)/CeO_2-HS and (C) 0.5Ni-2Pd/CeO_2-HS (unreduced). The blue and orange distributions correspond to the metal and ceria phases, respectively.

Figure S11. H_2-TPD profiles for the fresh and spent 0.5Pd-0.5Ni/CeO_2-HS after 4 catalytic runs with further calcination at 400 ^oC for 2 h.

Figure S12. XPS spectra of the Pd3d core level of the (a) fresh and (b) spent 0.5Pd-0.5Ni/CeO_2-HS after 4 catalytic runs with further calcination at 400 ^oC for 2 h. Reaction conditions as in Figure S2.

Figure S13. TG profiles of the fresh (dashed curve) and spent (straight curve) 0.5Pd-0.5Ni/CeO_2-HS after 4 catalytic runs. Reaction conditions as in Figure S2.

TABLE CAPTIONS

Table S1. Free energies of reaction, ΔG^o ($J.mol^{-1}$), as a function of the temperature in the liquid and gas phase for reactions R1-R13 in the main text.

Table S2. Summary of results for 2wt%Pd catalysts prepared over different supports in the direct amination reaction of OL with NH_3[a].

Table S3. Comparison of Pd-Ni/CeO_2-HS catalysts based on low Ni and Pd loading (0.5 wt% Ni, 0.1-0.5 wt%Pd) in the direct amination reaction of OL with NH_3[a].

Table S4. Comparison of Pd-Ni/Al_2O_3_PR (pre-reduced) catalysts in the direct amination reaction of OL with NH_3[a].

Table S5. Effect of the temperature on the catalytic performance of 0.5Pd-0.5Ni/CeO_2-HS_PR (pre-reduced) in the direct amination reaction of OL with NH_3[a].

Table S6. Effect of the catalyst loading on the catalytic performance of 0.5Pd-0.5Ni/CeO_2-HS_PR (pre-reduced) in the direct amination reaction of OL with NH_3[a].

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Table S8. Main properties of Pd-Ni/CeO_2-HS catalysts based on 2 wt%Pd

Table S9. Results for band deconvolution of Ce3d XPS spectra measured on 0.5Pd/CeO_2-HS, 0.5Ni/CeO_2-HS, 0.5Ni-0.5Pd/CeO_2-HS, (0.5Pd-0.5Ni)/CeO_2-HS and 0.5Pd-0.5Ni/CeO_2-HS. In parentheses, standard deviation for the BE.

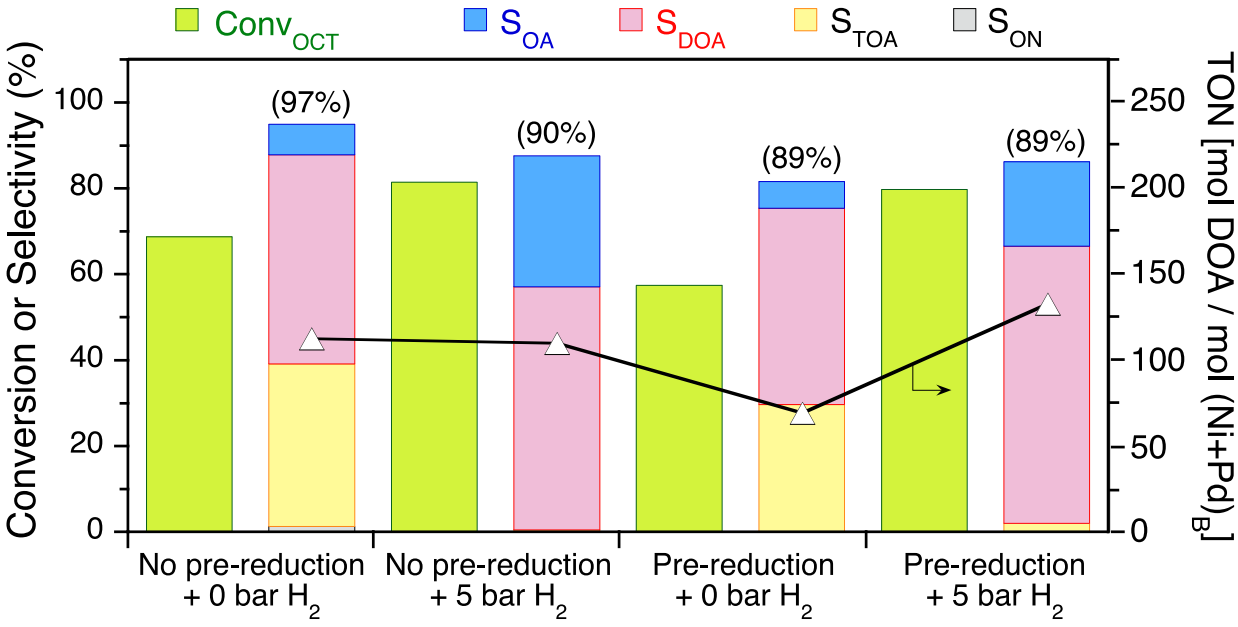
Table S10. Results for band deconvolution of O1s XPS spectra measured on 0.5Pd/CeO_2-HS, 0.5Ni/CeO_2-HS, 0.5Ni-0.5Pd/CeO_2-HS, (0.5Pd-0.5Ni)/CeO_2-HS and 0.5Pd-0.5Ni/CeO_2-HS. In parentheses, standard deviation for the BE.

Table S11. Results for band deconvolution of Ni2p XPS spectra measured on 0.5Ni/CeO_2-HS, 0.5Ni-0.5Pd/CeO_2-HS, (0.5Pd-0.5Ni)/CeO_2-HS and 0.5Pd-0.5Ni/CeO_2-HS. For comparison, the XPS spectrum of the spent 0.5Pd-0.5Ni/CeO_2-HS is also included. In parentheses, standard deviation for the BE.

Table S12. Results for band deconvolution of Pd3d XPS spectra measured on 0.5Pd/CeO_2-HS, 0.5Ni/CeO_2-HS, 0.5Ni-0.5Pd/CeO_2-HS, (0.5Pd-0.5Ni)/CeO_2-HS and 0.5Pd-0.5Ni/CeO_2-HS. In parentheses, standard deviation for the BE.

Table S13. Reducibility and reversible H_2 storage capacity of Pd-Ni/CeO_2-HS catalysts based on 2 wt%Pd.

Table S14. Results for band deconvolution for H_2-TPD profiles measured on the different catalytic formulation. In parentheses, standard deviation for the band temperature. For simplification, the term "CeO_2-HS" referring to the support has been removed from the catalyst label.



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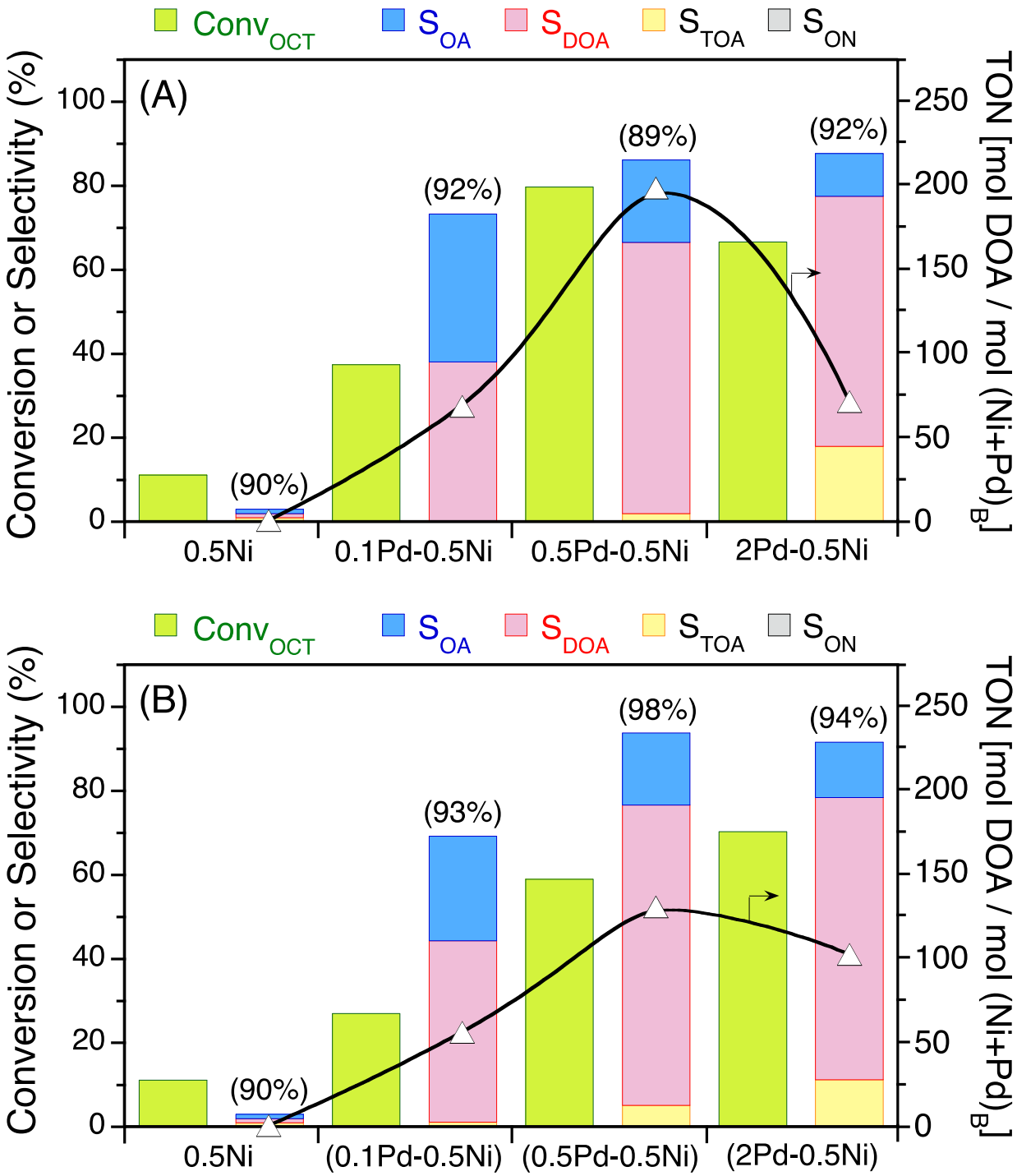
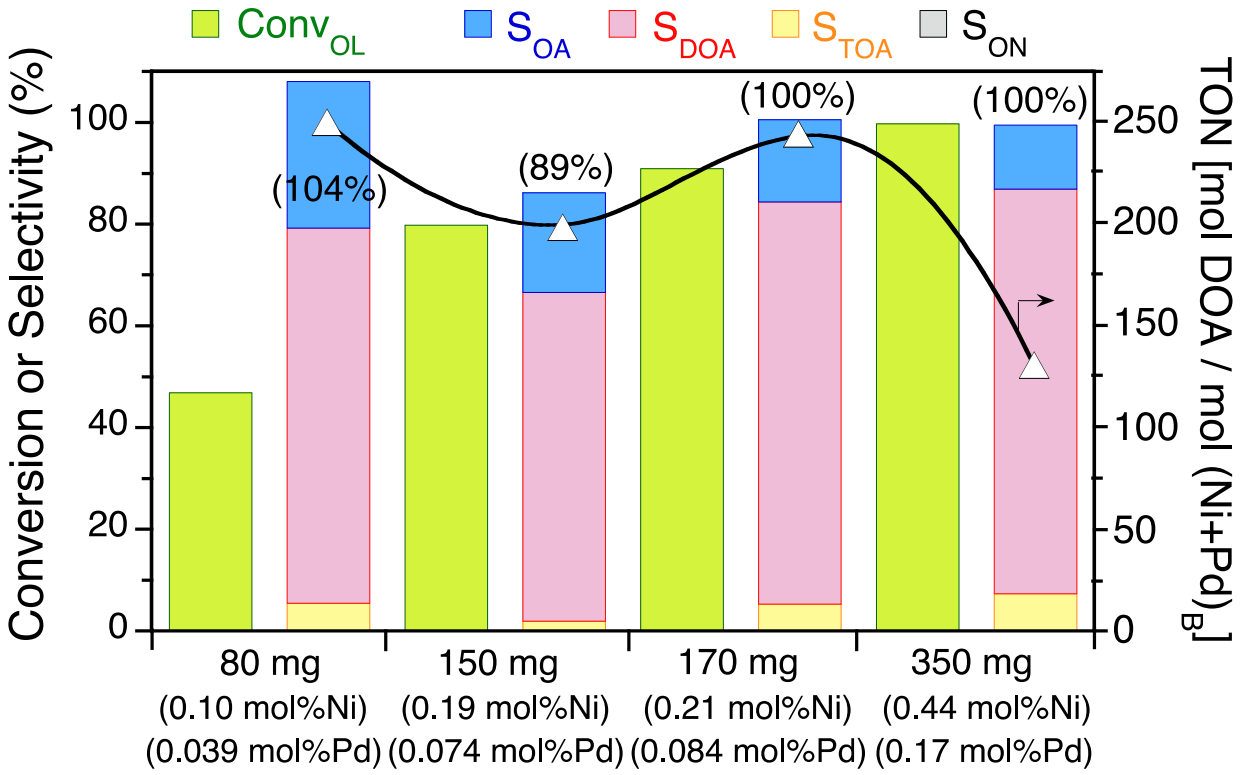


Figure S2. Catalytic performance of (A) yPd-xNi/CeO_2-HS_PR and (B) (xNi-yPd)/CeO_2-HS_PR (pre-reduced) catalysts based on x= 0.5 wt% Ni and y = 0.1-2.0 wt% Pd in the amination reaction of OL with NH_3. In parentheses, carbon balance. Reaction conditions: OL- 6.3 mmol, NH_3/OL- 5.2-7.5, Cat- 130-150 mg (0.021-0.38 mol%Pd and 0.15-0.22 mol%Ni with respect to OL), H_2- 5 bar, T- 180 ^oC, Time- 2 h, rpm- 600.



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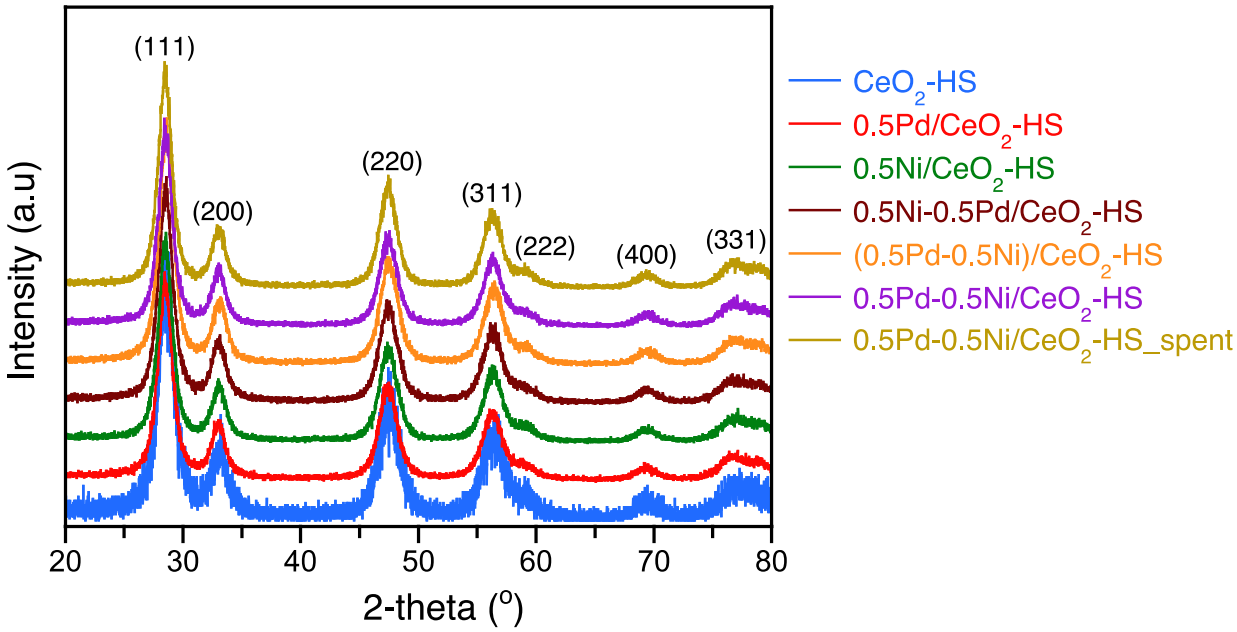

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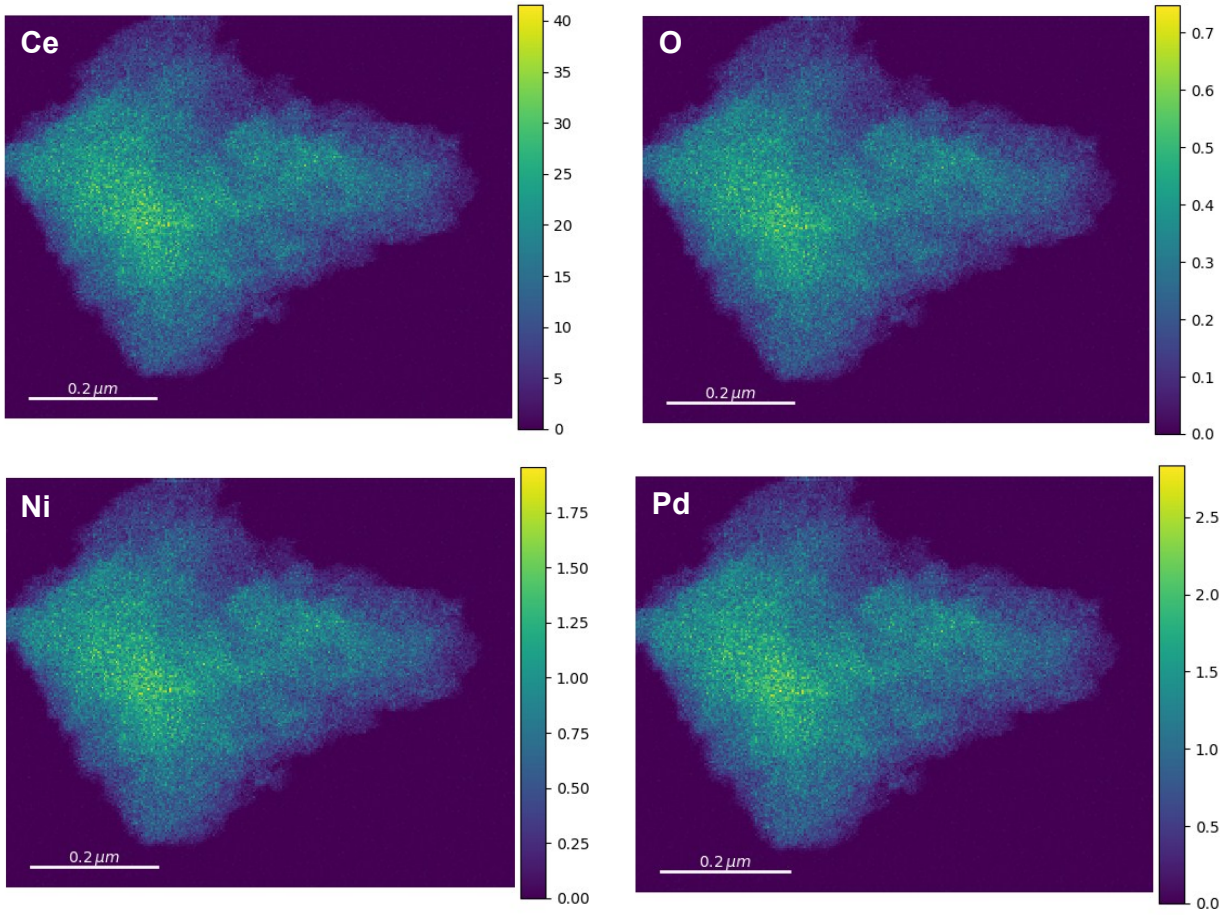

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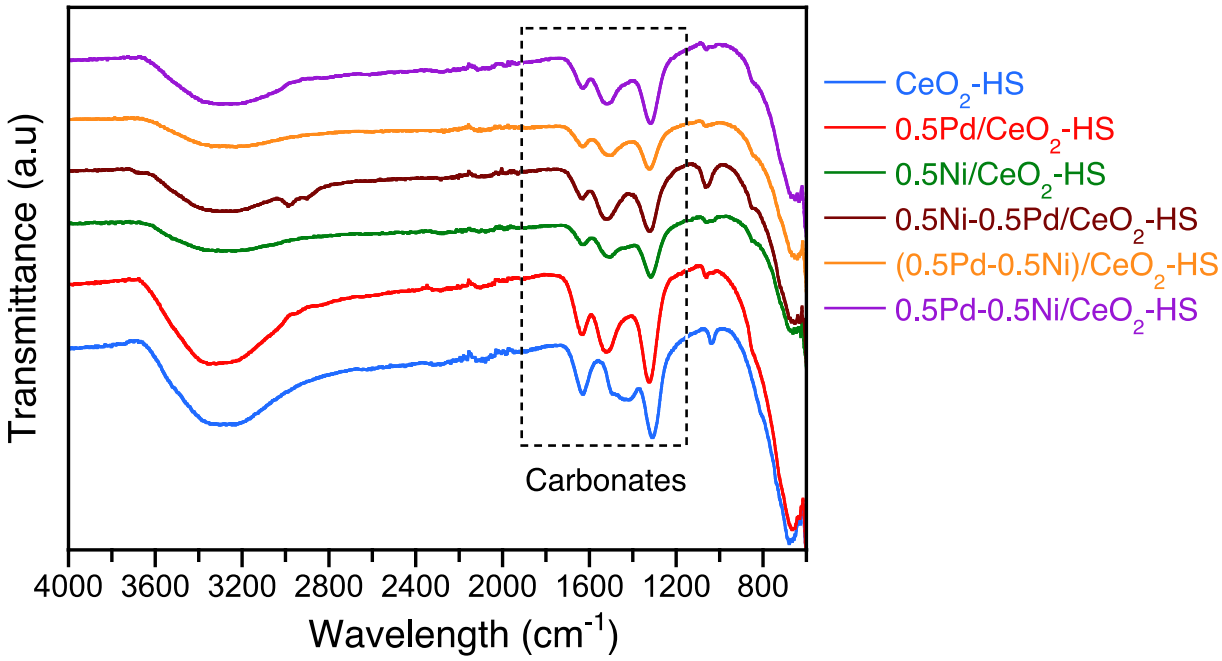
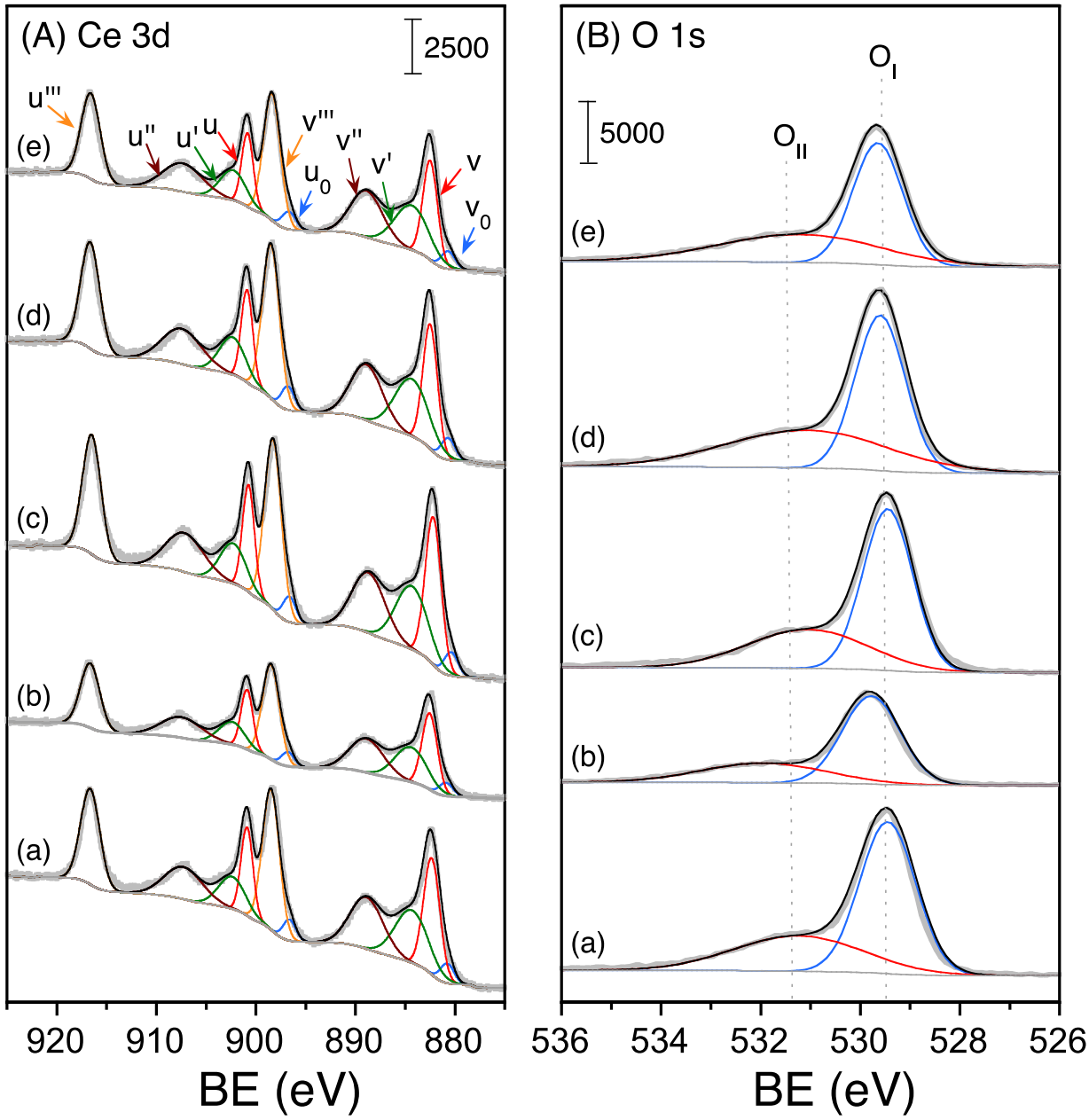


Figure S6. FT-IR spectra of 0.5Pd/CeO_2-HS, 0.5Ni/CeO_2-HS, 0.5Ni-0.5Pd/CeO_2-HS, (0.5Pd-0.5Ni)/CeO_2-HS, 0.5Pd-0.5Ni/CeO_2-HS and the parent CeO_2-HS pre-calcined at 300 ^oC.



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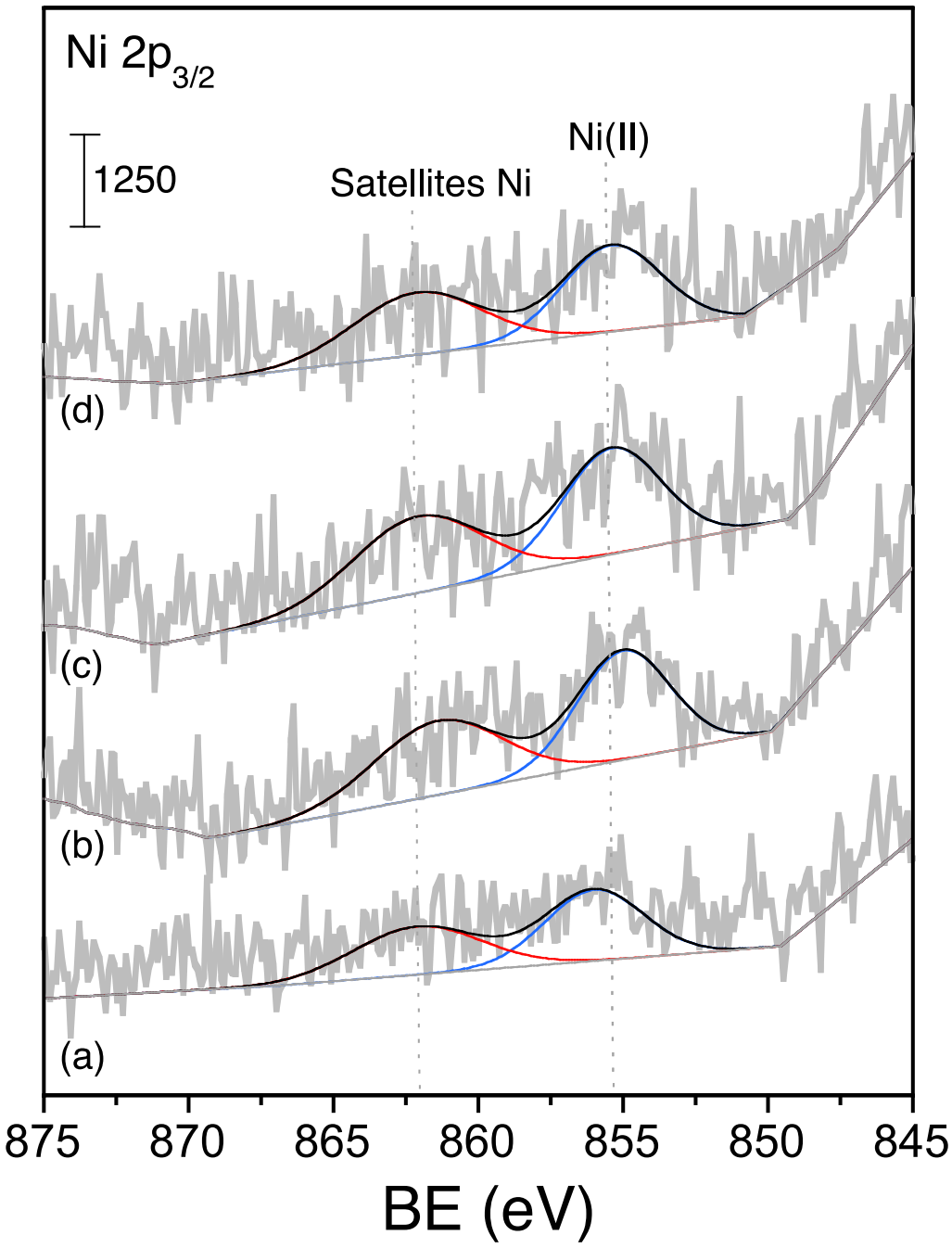

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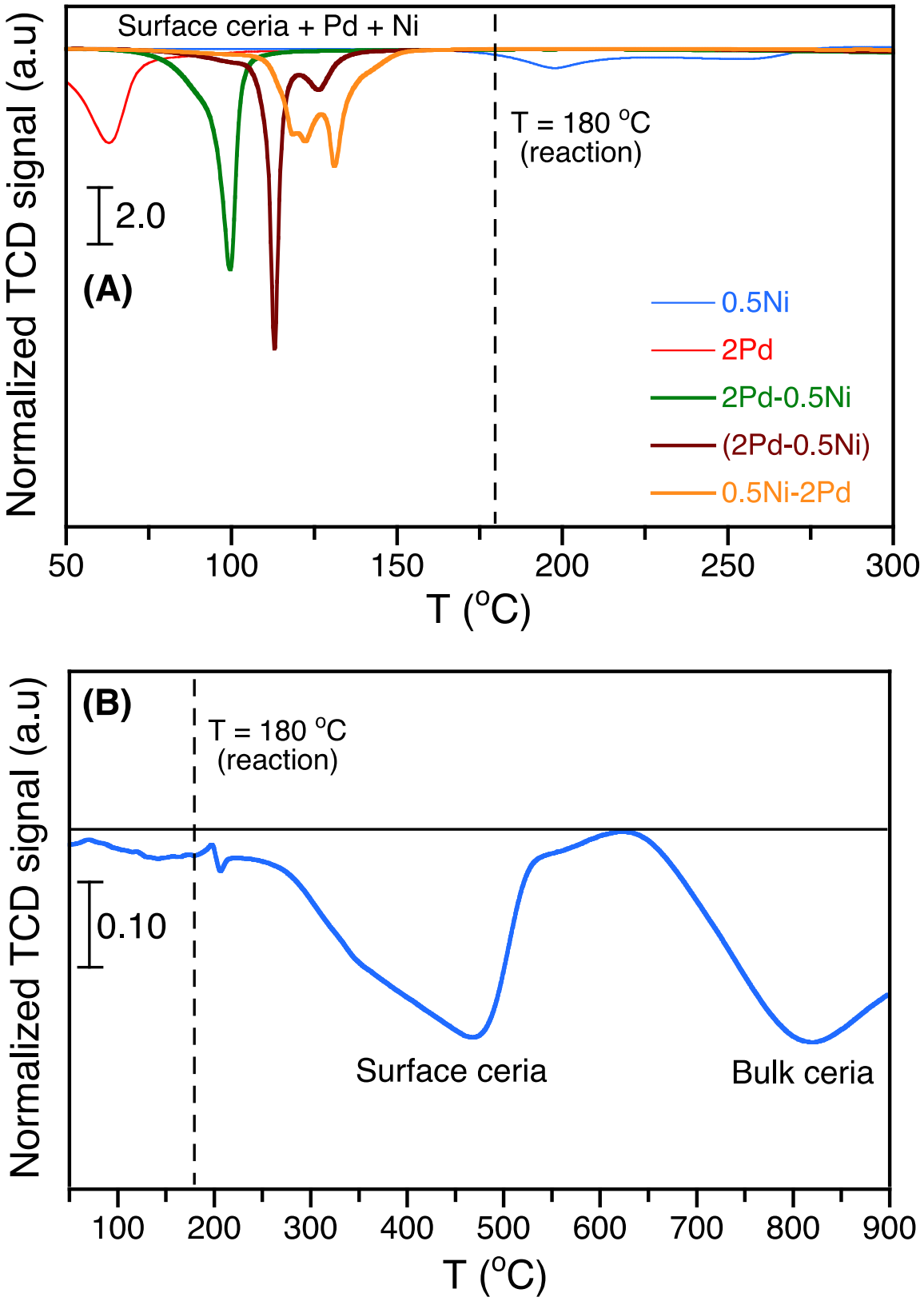
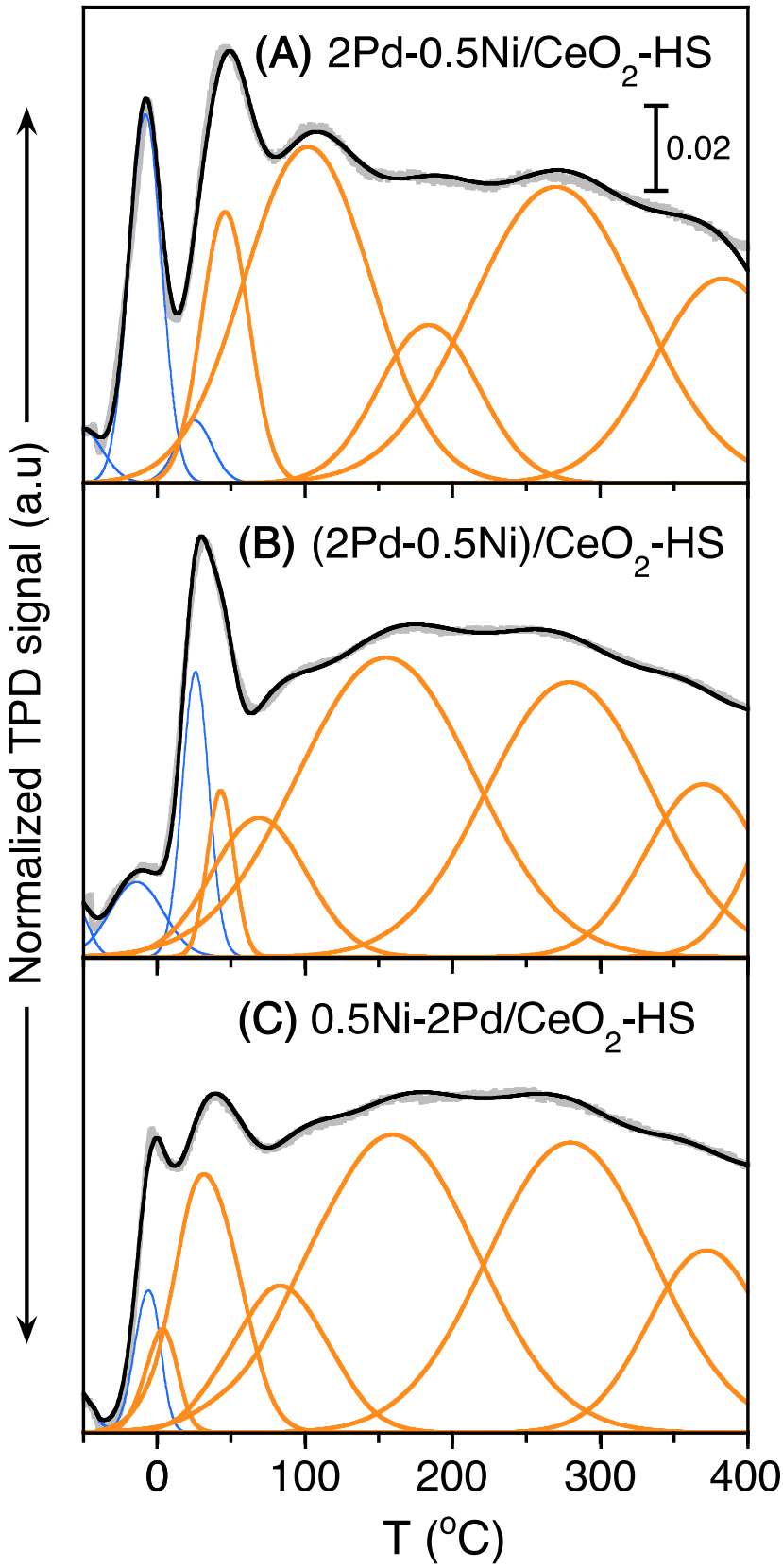


Figure S9. (A) H_2-TPR profiles in the temperature range 50-300 °C for 0.5Ni/CeO_2-HS, 2Pd/CeO_2-HS, 2Pd-0.5Ni/CeO_2-HS, (2Pd-0.5Ni)/CeO_2-HS and 0.5Ni-2Pd/CeO_2-HS (unreduced); (B) H_2-TPR profiles in the temperature range 50-900 °C for the parent CeO_2-HS pre-calcined at 300 °C.



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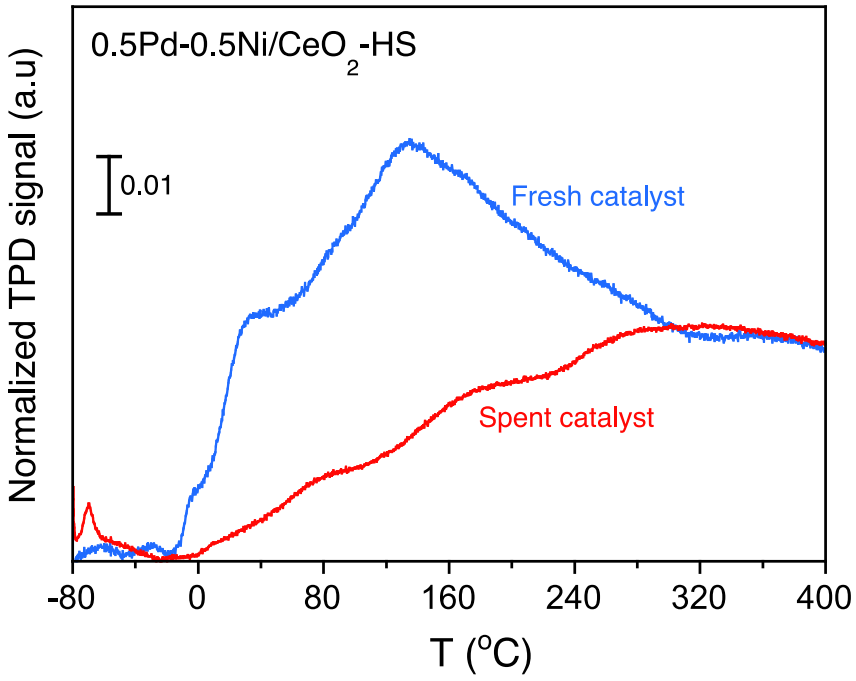
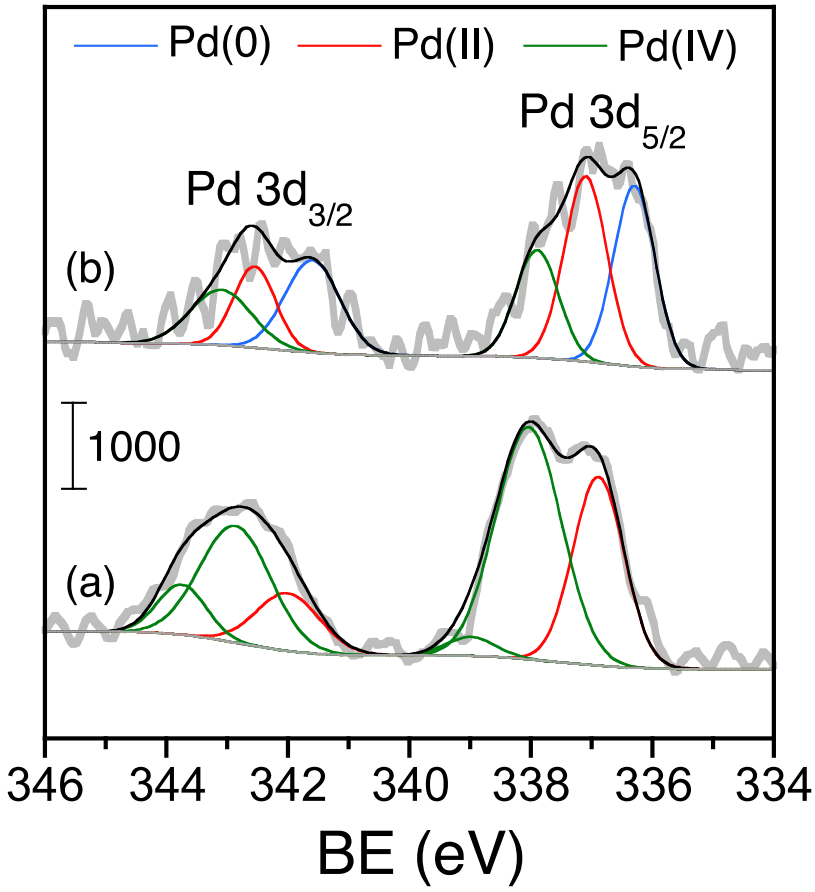


Figure S11. H_2-TPD profiles for the fresh and spent 0.5Pd-0.5Ni/CeO_2-HS after 4 catalytic runs with further calcination at 400 °C for 2 h.



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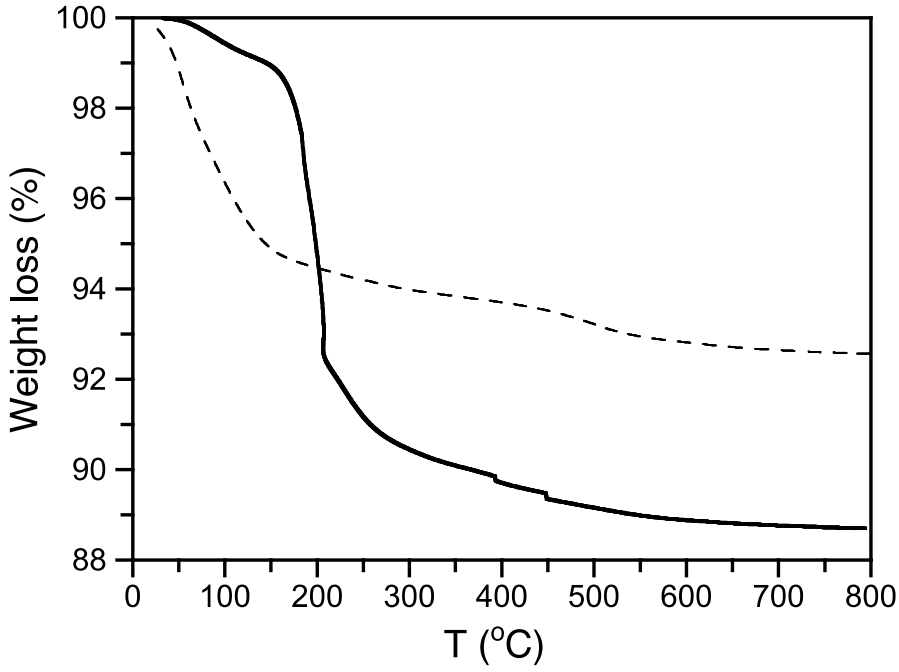

Figure S13. TG profiles of the fresh (dashed curve) and spent (straight curve) 0.5Pd-0.5Ni/CeO_2-HS after 4 catalytic runs. Reaction conditions as in Figure S2.

Table S1. Free energies of reaction, ΔG^o ($J.mol^{-1}$), as a function of the temperature in the liquid and gas phase for reactions R1-R13 in the main text.

	Liquid phase			Gas phase		
	150 °C	180 °C	210 °C	150 °C	180 °C	210 °C
R1	-12125	-12027	-11919	-5664	-5802	-5968
R2	13597	6537	-562	4062	246	-6748
R3	-10110	-12211	-14287	-41968	-48896	-55558
R4	-25166	-24382	-23594	-78405	-103480	-127948
R5	-32704	-31831	-30963	-23007	-22429	-21848
R6	-15057	-12171	-9307	29999	38541	46764
R7	-13041	-12355	-11676	-19778	-19385	-18974
R8	-20578	-19804	-19044	-17007	-16503	-16006
R9	-7537	-7449	-7368	-10722	-10640	-10574
R10	-38764	-30920	-23033	27200	31081	38069
R11	-46301	-38369	-30401	41435	45342	48523
R12	-35635	-31976	-28351	45349	50953	56177
R13	-61358	-50540	-39708	38949	44157	49020

Table S2. Summary of results for 2wt%Pd catalysts prepared over different supports in the direct amination reaction of OL with NH_3[a]

Entry	Catalyst	Ni loading (mol%)	Pd loading (mol%)	H_2 pressure (bar)	OL conv. (%)	Selectivity (%)				DOA yield (%)	TON (DOA)[b]	Carbon balance
						OA	DOA	TOA	ON			
1	$2Pd/SiO_2$	-	0.45	0	16	8.0	19	4.0	6.0	3.0	8.2	90
2	$2Pd/SiO_2$	-	0.45	5	2.0	47	29	2.0	0.0	0.6	1.6	100
3	$2Pd/Al_2O_3$	-	0.45	0	8.0	5.0	5.0	0.0	7.0	0.4	1.0	94
4	$2Pd/Al_2O_3$	-	0.45	5	3.0	51	39	2.0	0.0	1.3	3.7	100
5	2Pd/MgO	-	0.45	0	0.0	-	-	-	-	-	-	-
6	2Pd/MgO	-	0.45	5	6.0	27	69	4.0	0.0	3.8	11	100
7	$2Pd/CeO_2$-LS	-	0.45	0	0.0	-	-	-	-	-	-	-
8	$2Pd/CeO_2$-LS	-	0.45	5	1.0	-	-	-	-	-	-	-
9	$2Pd/CeO_2$-HS	-	0.32	0	70	8.0	52	37	1.4	36	112	100
10	$2Pd/CeO_2$-HS	-	0.32	5	78	3.0	45	10	0.0	35	110	68
11	$2Pd/CeO_2$-HS_PR[c]	-	0.30	0	52	3.5	40	46	1.5	21	69	95
12	$2Pd/CeO_2$-HS_PR[c]	-	0.28	5	72	5.3	51	13	0.0	35	132	78
13	$(2Pd\text{-}0.5Ni)/CeO_2$-HS_PR[c]	0.15	0.32	5	70	13	67	11	0.0	47	102	94
14	$2Pd\text{-}0.5Ni/CeO_2$-HS_PR[c]	0.18	0.38	5	67	10	60	18	0.0	40	71	92
15	$0.5Ni\text{-}2Pd/CeO_2$-HS_PR[c]	0.16	0.27	5	81	6.0	33	6.9	0.0	27	62	56
16	$0.5Ni/CeO_2$-HS_PR[d]	0.21	-	5	11	-	-	-	-	-	-	90
17	$5Ni/CeO_2$-HS_PR[d]	1.89	-	5	55	73	14	0	0.0	7.8	4.1	87
18	$20Ni/Al_2O_3$_PR[e]	12.4	-	5	92	42	49	1.4	0.0	45	3.6	94

[a] Reaction conditions: OL- 6.3 mmol, NH_3/OL - 4.6-8.0, Cat - 150 mg, T- 180 ^oC, Time- 2 h, rpm- 600. The nanoceria was calcined at 300 ^oC before impregnation

[b] TON_{DOA}: moles of DOA formed per mol of bulk metal (Pd, Ni or Pd+Ni) at 2 h

[c] The catalysts were pre-reduced at 180 °C for 0.5 h under 70% H_2/N_2 atmosphere at 40 mL(STP)/min with a heating ramp of 4 °C/min

[d] The catalysts were pre-reduced at 300 °C for 0.5 h under 70% H_2/N_2 atmosphere at 40 mL(STP)/min with a heating ramp of 4 °C/min

[e] Benchmark catalyst: pre-reduction at 550 °C for 1 h under 70% H_2/N_2 atmosphere at 40 mL(STP)/min with a heating ramp of 4 °C/min

Table S3. Comparison of Pd-Ni/CeO_2-HS catalysts based on low Ni and Pd loading (0.5 wt% Ni, 0.1-0.5 wt%Pd) in the direct amination reaction of OL with NH_3[a]

Entry	Catalyst	Pre-reduction	Ni loading (mol%)	Pd loading (mol%)	OL conv. (%)	Selectivity (%)				DOA yield (%)	TON_{DOA}[b]	Carbon balance
						OA	DOA	TOA	ON			
1	0.5Pd	Y	-	0.098	36	14	62	13	0.0	23	231	97
2	(0.1Pd-0.5Ni)	Y	0.19	0.021	27	25	43	1.2	0.0	12	56	93
3	0.1Pd-0.5Ni	Y	0.19	0.021	37	35	38	0.0	0.0	14	68	92
4	(0.5Pd-0.5Ni)	Y	0.22	0.099	59	17	72	5.2	0.0	42	130	98
5	0.5Pd-0.5Ni[c]	N	0.19	0.074	69	7.1	49	38	1.4	33	128	97
6	0.5Pd-0.5Ni[c]	Y	0.20	0.079	58	6.2	46	30	0.0	26	101	89
7	0.5Pd-0.5Ni	N	0.19	0.074	81	30	57	0.6	0.0	46	166	90
8	0.5Pd-0.5Ni	Y	0.19	0.074	80	20	65	2.0	0.0	52	198	89
9	0.5Ni-0.5Pd	Y	0.21	0.098	35	19	73	7.7	0.0	26	83	100
10	0.5Ni	Y	0.22	-	11	-	-	-	-	-	-	90

[a] Reaction conditions: Oct- 6.3 mmol, NH_3/Oct- 6.0-8.0, Cat- 120-150 mg, H_2- 5 bar; T- 180 ^oC, Time- 2 h, rpm- 600. The nanoceria was calcined at 300 ^oC before impregnation

[b] TON_{DOA}: moles of DOA formed per mol of bulk Ni and Pd at 2 h

[c] Experiments conducted with no H_2

Table S4. Comparison of Pd-Ni/Al_2O_3_PR (pre-reduced) catalysts in the direct amination reaction of OL with NH_3[a]

Entry	Catalyst	Cat. loading (mg)	Ni loading (mol%)	Pd loading (mol%)	OL conv. (%)	Selectivity (%)				DOA yield (%)	TON_{DOA}[b]	Carbon balance
						OA	DOA	TOA	ON			
1	(0.5Pd-0.5Ni)	120	0.16	0.073	1.2	28	2.7	0.0	62	0.03	0.2	92
2	0.5Pd-0.5Ni	140	0.19	0.086	6.3	56	42	3.0	0.0	2.5	17	120
3	0.5Ni	150	0.20	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-
4	5Ni	130	1.76	-	23	89	9.6	0.0	0.0	0.4	0.2	88

[a] Reaction conditions: OL- 6.3 mmol, NH_3/Oct- 6.0-8.0, Cat- 120-150 mg, H_2- 5 bar; T- 180 ^oC, Time- 2 h, rpm- 600.

[b] TON_{DOA}: moles of DOA formed per mol of bulk Ni and Pd at 2 h

Table S5. Effect of the temperature on the catalytic performance of 0.5Pd-0.5Ni/CeO_2-HS_PR (pre-reduced) in the direct amination reaction of OL with NH_3[a]

Entry	T (^oC)	Cat. loading (mg)	Ni loading (mol%)	Pd loading (mol%)	OL conv. (%)	Selectivity (%)				DOA yield (%)	TON_{DOA}[b]	Carbon balance (%)
						OA	DOA	TOA	ON			
1	120	150	0.19	0.074	<1.0	-	-	-	-	-	-	-
2	150	140	0.17	0.069	24	56	44	1.0	0.0	11	13	101
3	180	150	0.19	0.074	80	20	65	2.0	0.0	52	198	89
4	210	170	0.21	0.084	100	5.6	19	7.2	0.0	0.0	65	32

[a] Reaction conditions: Oct- 6.3 mmol, NH_3/- 4.0-5.8, Cat- 140-170 mg, H_2- 5 bar; Time- 2 h, rpm- 600. The nanoceria was calcined at 300 ^oC before impregnation

[b] TON_{DOA}: moles of DOA formed per mol of bulk Ni and Pd at 2 h

Table S6. Effect of the catalyst loading on the catalytic performance of 0.5Pd-0.5Ni/CeO_2-HS_PR (pre-reduced) in the direct amination reaction of OL with NH_3[a]

Entry	Cat. loading (mg)	Ni loading (mol%)	Pd loading (mol%)	OL conv. (%)	Selectivity (%)				DOA yield (%)	TON_{DOA}[b]	Carbon balance (%)
					OA	DOA	TOA	ON			
1	80	0.10	0.039	47	29	74	5.5	0.0	35	250	104
2	150	0.19	0.074	80	20	65	2.0	0.0	52	198	89
3	170	0.21	0.084	91	16	79	5.3	0.0	72	244	100
4	350	0.44	0.17	99	13	79	7.4	0.0	79	130	99

[a] Reaction conditions: OL- 6.3 mmol, NH_3/Oct- 4.0-7.0, H_2- 5 bar; T- 180 ^oC, Time- 2 h, rpm- 600. The nanoceria was calcined at 300 ^oC before impregnation

[b] TON_{DOA}: moles of DOA formed per mol of bulk Ni and Pd at 2 h

Table S7. Effect of the reaction time on the catalytic performance of 0.5Pd-0.5Ni/CeO_2-HS_PR (pre-reduced) in the direct amination reaction of OL with NH_3[a]

Entry	Time (h)	Cat. loading (mg)	Ni loading (mol%)	Pd loading (mol%)	OL conv. (%)	Selectivity (%)				DOA yield (%)	TON_{DOA}[b]	Carbon balance (%)
						OA	DOA	TOA	ON			
1	0.5	170	0.21	0.084	30	37	66	1.6	0.0	20	68	101
2	1	160	0.20	0.079	44	29	63	1.8	0.0	28	101	97
3	2	170	0.21	0.084	91	16	79	5.3	0.0	52	244	101
4	4	180	0.22	0.089	97	13	80	7.3	0.0	78	248	100
5	6	160	0.20	0.072	100	13	69	7.2	0.0	69	248	89

[a] Reaction conditions: OL- 6.3 mmol, NH_3/OL- 4.0-5.0, Cat- 160-180 mg, H_2- 5 bar; T- 180 ^oC, rpm- 600. The nanoceria was calcined at 300 ^oC before impregnation

[b] TON_{DOA}: moles of DOA formed per mol of bulk Ni and Pd at 2 h

Table S8. Main properties of Pd-Ni/CeO_2-HS catalysts based on 2 wt%Pd

Entry	Catalyst	CeO_2 particle size (nm) [b]	Textural properties [c]			Composition (bulk) [d]			Metal dispersion [e]	
			S_{BET} (m^2/g)	V_g (cm^3/g)	D_p (nm)	$(Ni/Ce)_b$ $x10^{-3}$ (-)	$(Pd/Ce)_b$ $x10^{-3}$ (-)	$(Ni/Pd)_b$ (-)	D_M (%)	$\overline{d}_{p,Ni-Pd}$ (nm)
1	2Pd/CeO_2-HS	6.3	173	0.17	3.5	0	23	0	48 (67)	2.8 (1.7)
2	2Pd/CeO_2-HS [a]	6.9	158	0.15	3.1	0	26	0	33 (-)	4.4 (-)
3	0.5Ni-2Pd/CeO_2-HS	6.1	184	0.16	3.1	13	23	0.56	26 (-)	5.6 (-)
4	(2Pd-0.5Ni)/CeO_2-HS	6.3	120	0.11	3.3	12	26	0.47	36 (-)	3.9 (-)
5	2Pd-0.5Ni/CeO_2-HS	6.6	194	0.16	3.1	13	27	0.48	44 (-)	3.1 (-)

[a] The nanoceria was pre-calcined at 500 ^oC instead of 300 ^oC before metal impregnation

[b] Measured from XRD using Scherrer equation applied to (111) reflection

[c] Measured by N_2 adsorption at -196 ^oC

[d] Measured by ICP-OES

[e] Measured from the H_2-TPD profiles in the range from -80 ^oC to 40 ^oC (bands I-III) after reduction at 180 ^oC for 0.5 h; in parentheses, values measured by CO pulse chemisorption after reduction at 180 ^oC for 0.5 h. The particle sizes were measured by assuming cubooctahedral shape (see SI).

Table S9. Results for band deconvolution of Ce3d XPS spectra measured on 0.5Pd/CeO_2-HS, 0.5Ni/CeO_2-HS, 0.5Ni-0.5Pd/CeO_2-HS, (0.5Pd-0.5Ni)/CeO_2-HS and 0.5Pd-0.5Ni/CeO_2-HS. In parentheses, standard deviation for the BE.

Entry	Catalyst		v_0	v	v'	v''	v'''	u_0	u	u'	u''	u'''
1	CeO_2-HS	BE (eV)	880.9 (0.7)	882.5 (0.8)	884.6 (1.7)	888.9 (1.7)	898.5 (0.8)	896.8 (0.6)	900.9 (0.6)	902.7 (1.5)	907.5 (1.8)	916.7 (1.0)
		%	2.0%	13%	15%	12%	18%	2.0%	7.9%	8.5%	9.1%	14%
2	0.5Pd/CeO_2-HS	BE (eV)	880.8 (0.7)	882.4 (0.8)	884.4 (1.6)	888.9 (1.6)	898.5 (0.8)	896.6 (0.6)	900.9 (0.6)	902.4 (1.4)	907.3 (1.9)	916.6 (1.0)
		%	2.1%	14%	13%	13%	18%	2.1%	8.0%	6.5%	9.2%	14%
3	0.5Ni/CeO_2-HS	BE (eV)	880.9 (0.7)	882.6 (0.8)	884.4 (1.6)	888.9 (1.7)	898.5 (0.8)	896.8 (0.6)	900.9 (0.6)	902.4 (1.3)	907.5 (2.0)	916.6 (1.0)
		%	2.1%	13%	13%	13%	18%	2.1%	8.0%	6.7%	9.4%	14%
4	0.5Ni-0.5Pd/CeO_2-HS	BE (eV)	880.4 (0.7)	882.2 (0.8)	884.4 (1.6)	888.7 (1.6)	898.3 (0.8)	896.6 (0.6)	900.8 (0.6)	902.3 (1.3)	907.4 (2.0)	916.6 (1.0)
		%	2.1%	15%	13%	12%	18%	2.1%	8.0%	6.6%	9.3%	14%
5	(0.5Pd-0.5Ni)/CeO_2-HS	BE (eV)	880.7 (0.7)	882.5 (0.7)	884.4 (1.7)	888.9 (1.6)	898.5 (0.8)	896.8 (0.6)	900.9 (0.6)	902.4 (1.3)	907.2 (1.9)	916.5 (0.9)
		%	2.2%	13%	14%	13%	18%	2.2%	7.5%	6.8%	9.7%	14%
6	0.5Pd-0.5Ni/CeO_2-HS	BE (eV)	880.7 (0.7)	882.5 (0.7)	884.4 (1.7)	888.9 (1.6)	898.4 (0.8)	896.7 (0.7)	900.8 (0.6)	902.3 (1.3)	907.4 (2.0)	916.6 (1.0)
		%	2.2%	13%	13%	13%	19%	2.2%	7.5%	6.8%	9.6%	14%
7	0.5Pd-0.5Ni/CeO_2-HS [a]	BE (eV)	879.8 (0.8)	881.8 (0.8)	884.0 (1.7)	888.4 (1.8)	898.2 (0.8)	896.5 (0.6)	900.6 (0.6)	902.4 (1.6)	907.1 (1.6)	916.4 (1.0)
		%	2.1%	13%	16%	12%	17%	2.1%	7.5%	9.7%	7.7%	13%

[a] Spent catalyst after 4 runs was recovered , washed by ethanol for 3 times and dried, calcined at 400 ^oC for 2 h

Table S10. Results for band deconvolution of O1s XPS spectra measured on 0.5Pd/CeO_2-HS, 0.5Ni/CeO_2-HS, 0.5Ni-0.5Pd/CeO_2-HS, (0.5Pd-0.5Ni)/CeO_2-HS and 0.5Pd-0.5Ni/CeO_2-HS. In parentheses, standard deviation for the BE

Entry	Catalyst		O1s		
			Band I	Band II	Band III
1	CeO_2-HS	BE (eV)	529.7 (0.6)	531.3 (1.2)	532.4 (0.3)
		%	65%	3.2%	32%
2	0.5Pd/CeO_2-HS	BE (eV)	529.4 (0.6)	531.2 (1.3)	-
		%	65%	35%	-
3	0.5Ni/CeO_2-HS	BE (eV)	529.8 (0.6)	-	532.0 (1.2)
		%	68%	-	32%
4	0.5Ni-0.5Pd/CeO_2-HS	BE (eV)	529.4 (0.5)	531.0 (1.2)	-
		%	63%	37%	-
5	(0.5Pd-0.5Ni)/CeO_2-HS	BE (eV)	529.6 (0.5)	531.1 (1.6)	-
		%	56%	44%	-
6	0.5Pd-0.5Ni/CeO_2-HS	BE (eV)	529.6 (0.5)	531.2 (1.6)	-
		%	57%	43%	-
7	0.5Pd-0.5Ni/CeO_2-HS [a]	BE (eV)	529.3 (0.5)	531.0 (1.4)	-
		%	56%	44%	-

[a] Spent catalyst after 4 runs was recovered , washed by ethanol for 3 times and dried, calcined at 400 ^oC for 2 h

Table S11. Results for band deconvolution of Ni2p XPS spectra measured on 0.5Ni/CeO_2-HS, 0.5Ni-0.5Pd/CeO_2-HS, (0.5Pd-0.5Ni)/CeO_2-HS and 0.5Pd-0.5Ni/CeO_2-HS. For comparison, the XPS spectrum of the spent 0.5Pd-0.5Ni/CeO_2-HS is also included. In parentheses, standard deviation for the BE

Entry	Catalyst		$Ni2p_{1/2}$	
			Band I	Band II
1	0.5Ni/CeO_2-HS	BE (eV)	856.0 (1.7)	862.1 (2.2)
		%	53%	47%
2	0.5Ni-0.5Pd/CeO_2-HS	BE (eV)	855.0 (1.6)	861.4 (2.2)
		%	52%	48%
3	(0.5Pd-0.5Ni)/CeO_2-HS	BE (eV)	855.4 (1.7)	862.1 (2.2)
		%	52%	48%
4	0.5Pd-0.5Ni/CeO_2-HS	BE (eV)	855.4 (1.7)	862.1 (2.2)
		%	52%	48%
5	0.5Pd-0.5Ni/CeO_2-HS [a]	BE (eV)	855.2 (2.5)	862.1 (2.2)
		%	65%	35%

[a] Spent catalyst after 4 runs was recovered , washed by ethanol for 3 times and dried, calcined at 400 ^oC for 2 h

Table S12. Results for band deconvolution of Pd3d XPS spectra measured on 0.5Pd/CeO_2-HS, 0.5Ni/CeO_2-HS, 0.5Ni-0.5Pd/CeO_2-HS, (0.5Pd-0.5Ni)/CeO_2-HS and 0.5Pd-0.5Ni/CeO_2-HS. In parentheses, standard deviation for the BE

Entry	Catalyst		$Pd3d_{5/2}$				$Pd3d_{3/2}$			
			Band I (Pd^{2+})	Band II (Pd^{2+})	Band III (Pd^{4+})	Band IV (Pd^{4+})	Band V (Pd^{0})	Band VI (Pd^{2+})	Band VII (Pd^{4+})	Band VIII (Pd^{4+})
1	0.5Pd/CeO_2-HS	BE (eV)	-	336.6 (0.6)	337.9 (0.4)	338.8 (0.3)	-	342.0 (0.6)	343.1 (0.6)	344.1 (0.5)
		%	-	8.0%	48%	4.5%	-	6.0%	30%	3.3%
2	0.5Ni-0.5Pd/CeO_2-HS	BE (eV)	-	337.3 (0.6)	337.8 (0.5)	338.9 (0.4)	-	342.4 (0.3)	343.2 (0.4)	344.1 (0.2)
		%	-	7.1%	49%	6.1%	-	6.7%	28%	3.1%
3	(0.5Pd-0.5Ni)/CeO_2-HS	BE (eV)	-	336.7 (0.5)	338.0 (0.5)	339.2 (0.3)	-	342.0 (0.2)	343.2 (0.6)	344.4 (0.5)
		%	-	5.2%	54%	3.3%	-	2.6%	32%	2.6%
4	0.5Pd-0.5Ni/CeO_2-HS	BE (eV)	-	336.9 (0.4)	338.0 (0.5)	339.0 (0.4)	-	342.0 (0.5)	343.9 (0.6)	343.8 (0.4)
		%	-	24%	38%	2.3%	-	9.1%	20%	6.1%
5	0.5Pd-0.5Ni/CeO_2-HS [a]	BE (eV)	336.3 (0.3)	337.1 (0.4)	337.9 (0.4)	-	341.6 (0.4)	342.6 (0.3)	343.1 (0.5)	-
		%	37%	40%	23%	-	42%	29%	29%	-

[a] Spent catalyst after 4 runs was recovered , washed by ethanol for 3 times and dried, calcined at 400 ^{o}C for 2 h

Table S13. Reducibility and reversible H_2 storage capacity of Pd-Ni/CeO_2-HS catalysts based on 2 wt%Pd

Entry	Catalyst	Catalyst reducibility [b]			H_2 reversibility [c]					
		TPR bands (°C)	H_2 uptake (μmol/g)	Red (%)	TPD bands (2 most intense) (°C)	H_2 release (μmol/g)	Rev (%)	TPD bands (V-VI) (°C)	H_2 release (μmol/g)	Rev (%)
1	0.5Ni-2Pd/CeO_2-HS	122 / 131	1570	54	160 / 280	441	28	34 / 84	86	6.0
2	(2Pd-0.5Ni)/CeO_2-HS	113	1230	42	155 / 279	457	37	43 / 69	55	4.5
3	2Pd-0.5Ni/CeO_2-HS	99	1260	43	102 / 270	494	39	46 / 102	174	11
4	2Pd/CeO_2-HS	69	1530	53	151 / 268	318	21	70 / 86	75	4.9
5	2Pd/CeO_2-HS [a]	48	1000	34	142 / 279	430	43	46 / 73	44	4.4

[a] The nanoceria was pre-calcined at 500 °C instead of 300 °C before metal impregnation

[b] Measured from the H_2-TPR profiles in the temperature range from 30 °C to 200 °C under H_2 flow (40 mL(STP)/min); the reducibility (red) was measured from the H_2 uptake using Eq 2

[c] Measured from the H_2-TPD profiles in the temperature range from 40 °C to 400 °C after reduction at 180 °C for 30 min using a heating ramp of 10 °C.min^{-1} except for 0.5Ni/CeO2-HS, which was reduced at 300 °C for 5 min using a heating ramp of 10 °C.min^{-1}; the H_2 reversibility (rev) was measured from the desorbed H_2 amount using Eq 3

Table S14. Results for band deconvolution for H_2-TPD profiles measured on the different catalytic formulation. In parentheses, standard deviation for the band temperature. For simplification, the term "CeO_2-HS" referring to the support has been removed from the catalyst label

Entry	Catalyst		H_2 desorption form metal				H_2 backspillover (metal-nanoceria)					
			Band I	Band II	Band III	Band IV	Band V	Band VI	Band VII	Band VIII	Band IX	Band X
1	0.5Ni	T (°C)	-51 (31)	-	-	28 (19)	-	103 (25)	166 (39)	286 (105)	-	450 (40)
		µmol/g	1.3	-	-	7.6	-	13	12	368	-	21
2	0.5Pd	T (°C)	-	-	4.0 (8)	20 (8)	73 (16)	128 (67)	199 (79)	284 (41)	374 (50)	-
		µmol/g	-	-	8.3	13	27	133	139	60	97	-
3	0.5Ni-0.5Pd	T (°C)	-65 (25)	-1.0 (8)	4.0 (8)	23 (18)	64 (33)	-	155 (52)	262 (45)	370 (72)	-
		µmol/g	3.5	4.4	2.7	32	55	-	128	57	84	-
4	(0.5Pd-0.5Ni)	T (°C)	-57 (18)	-4.0 (3)	-	16 (11)	40 (17)	90 (28)	168 (51)	269 (45)	376 (74)	-
		µmol/g	2.6	3.3	-	9.3	43	46	154	66	139	-
5	0.5Pd-0.5Ni	T (°C)	-50 (24)	-	3.3 (8)	31 (14)	55 (20)	134 (62)	-	249 (44)	379 (81)	-
		µmol/g	1.6	-	1.8	9.5	6.6	168	-	44	97	-
6	0.5Pd-0.5Ni [a]	T (°C)	-69 (20)	-	-	23 (18)	56 (19)	89 (28)	147 (29)	194 (43)	285 (51)	420 (88)
		µmol/g	2.3	-	-	2.5	2.8	13	12	34	52	79
7	0.5Ni-2Pd	T (°C)	-59 (14)	-6.0 (8)	3.5 (11)	-	34 (22)	84 (32)	160 (57)	280 (56)	372 (39)	435 (32)
		µmol/g	5.4	10	10	-	52	43	155	148	63	34
8	(2Pd-0.5Ni)	T (°C)	-55 (8)	-14 (18)	-	26 (9)	43 (9)	69 (32)	155 (60)	279 (56)	370 (39)	435 (32)
		µmol/g	4.0	12	-	24	14	41	166	142	61	33
9	2Pd-0.5Ni	T (°C)	-51 (14)	-8 (11)	-	25 (12)	46 (16)	102 (43)	184 (34)	270 (57)	383 (46)	-
		µmol/g	6.8	37	-	6.9	40	133	50	156	80	-
10	2Pd	T (°C)	-49 (13)	-2.0 (12)	-	24 (13)	38 (20)	86 (27)	151 (41)	268 (80)	-	405 (50)
		µmol/g	2.9	15	-	15	35	39	81	137	-	26
11	2Pd [b]	T (°C)	-58 (10)	-21 (12)	-	26 (11)	46 (10)	73 (24)	142 (64)	279 (69)	297 (17)	439 (110)
		µmol/g	5.4	5.8	-	13	13	21	172	126	3.8	105

[a] Spent catalyst after 4 runs was recovered , washed by ethanol for 3 times, dried and calcined at 400 °C for 2 h

[b] The nanoceria was pre-calcined at 500 °C instead of 300 °C before metal impregnation