Supporting information for

Mechanism of Formation of Highly Dispersed Metallic Ruthenium Particles on Ceria Support by Heating and Reduction

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Table S1. Comparison of EXAFS curve fitting results between REX2000 and Athena-Artemis suite

REX2000:

Entry	Sample	Shells	CN [a]	R [b] [0.1 nm]	ΔE_0 [c] [eV]	σ [d] [0.1 nm]	R_f [e]
1	Ru powder	Ru-Ru	12	2.68	0	0.06	
2	RuO_2	Ru-O	6.0	1.97	0	0.06	
	Ru/CeO_2						
3	Entry 1 in Table 1	Ru-O	5.9	2.05	-0.7	0.061	0.00
4	Entry 8 in Table 1	Ru-O	5.9	1.95	-3.7	0.079	0.01
5	Entry 9 in Table 1	Ru-O	6.0	1.96	-3.2	0.064	0.02
6	Entry 21 in Table 1	Ru-Ru	7.1	2.67	0.8	0.078	0.00
7	Entry 1 in Table 2	Ru-O	6.0	2.04	0.1	0.058	0.00
8	Entry 8 in Table 2	Ru-O	5.9	2.00	0.6	0.106	0.00
9	Entry 9 in Table 2	Ru-O	5.9	2.06	0.6	0.086	0.00
10	Entry 24 in Table 2	Ru-Ru	4.0	2.62	-1.4	0.096	0.01
	Ru/SiO_2						
11	Entry 1 in Table 3	Ru-O	5.8	2.05	-0.8	0.060	0.00
12	Entry 8 in Table 3	Ru-O	6.0	2.02	1.7	0.098	0.00
13	Entry 10 in Table 3	Ru–O	6.0	2.04	1.7	0.085	0.00
14	Entry 26 in Table 3	Ru-Ru	8.0	2.65	-1.7	0.084	0.00

[a] Coordination number. [b] Bond distance. [c] Difference in the origin of photoelectron energy between the reference and the sample. [d] σ = Debye-Waller factor. [e] Residual factor. Fourier filtering range: 0.120-0.199 nm (Entries 2-5, 7-9, 11-13), 0.169-0.288 nm (Entries 1, 6, 10, 14).

Athena-Artemis:

Entry	Sample	Shells	CN [a]	R [b] [0.1 nm]	ΔE_0 [c] [eV]	σ^2 [d] [(0.1 nm)^2]	σ [0.1 nm]	R_f [e]	S_0^2 [f]
1	Ru powder	Ru-Ru	12	2.68	-3.8	0.005	0.067	0.00	0.80
2	RuO_2	Ru-O	6.0	1.98	7.3	0.003	0.052	0.02	0.74
	Ru/CeO_2								
3	Entry 1 in Table 1	Ru-O	4.4 (± 2.1)	2.07 (± 0.03)	5.9	0.001	0.028	0.01	0.74
4	Entry 8 in Table 1	Ru-O	6.1 (± 3.3)	1.98 (± 0.04)	2.8	0.006	0.078	0.01	0.74
5	Entry 9 in Table 1	Ru-O	6.7 (± 3.8)	1.99 (± 0.04)	4.1	0.005	0.070	0.01	0.74
6	Entry 21 in Table 1	Ru-Ru	8.3 (± 2.4)	2.67 (± 0.01)	4.1	0.008	0.090	0.02	0.80
7	Entry 1 in Table 2	Ru-O	4.5 (± 1.9)	2.07 (± 0.02)	5.3	0.001	0.031	0.01	0.74
8	Entry 8 in Table 2	Ru-O	3.9 (± 1.7)	2.03 (± 0.03)	7.7	0.008	0.089	0.01	0.74
9	Entry 9 in Table 2	Ru-O	3.4 (± 1.0)	2.09 (± 0.02)	3.7	0.002	0.047	0.00	0.74
10	Entry 24 in Table 2	Ru-Ru	5.1 (± 2.2)	2.61 (± 0.02)	-7.7	0.011	0.103	0.05	0.80
	Ru/SiO_2								
11	Entry 1 in Table 3	Ru-O	4.3 (± 2.0)	2.07 (± 0.02)	7.9	0.001	0.023	0.01	0.74
12	Entry 8 in Table 3	Ru-O	3.8 (± 2.3)	2.06 (± 0.04)	9.8	0.005	0.072	0.02	0.74
13	Entry 10 in Table 3	Ru-O	4.0 (± 1.7)	2.08 (± 0.03)	6.6	0.004	0.060	0.01	0.74
14	Entry 26 in Table 3	Ru-Ru	8.1 (± 2.6)	2.65 (± 0.01)	1.1	0.009	0.095	0.03	0.80

[a] Coordination number. [b] Bond distance. [c] Difference in the origin of photoelectron energy between the reference and the sample. [d] σ = Debye-Waller factor. [e] Residual factor. [f] Passive electron reduction factor. This parameter was fixed in Entries 3-14. Fourier filtering range: 0.120-0.199 nm (Entries 2-5, 7-9, 11-13), 0.169-0.288 nm (Entries 1, 6, 10, 14).

Table S2. Curve fitting results of *in situ* Ru *K*-edge EXAFS of Ru/CeO_2 during calcination in air and reduction.

Entry	Gas	Time [min]	Temp. [a] [K]	Shells	CN [b]	R [c] [0.1 nm]	ΔE_0 [d] [eV]	σ [e] [0.1 nm]	R_f [f] [%]	CN*$_{Ru-Ru}$ [g]
1	Air	1	303.6 - 311.0	Ru-O	5.9	2.05	-0.7	0.061	0.12	
1’				Ru-O	5.9	2.05	0.0	0.063	8.47	
				Ru-Ru	0.9	2.48	31.2	0.056		
1’’				Ru-O	5.8	2.05	-0.2	0.052	23.15	
				Ru-Ce	1.1	3.98	70.4	0.200		
2		2	313.4 - 321.8	Ru-O	6.0	2.05	-0.1	0.061	0.39	
3		3	326.3 - 334.2	Ru-O	5.9	2.05	-0.2	0.061	0.24	
4		4	337.8 - 344.2	Ru-O	6.0	2.05	-0.1	0.060	0.42	
5		5	347.2 - 352.7	Ru-O	5.9	2.05	-0.2	0.062	0.28	
6		6	355.3 - 360.3	Ru-O	5.9	2.05	-0.4	0.063	0.32	
7		7	363.4 - 368.6	Ru-O	5.9	2.05	-0.2	0.063	0.42	
8		8	373.6 - 379.3	Ru-O	5.9	2.05	-0.1	0.064	0.39	
9		9	383.5 - 389.7	Ru-O	5.9	2.05	0.0	0.064	0.35	
10		10	393.5 - 400.0	Ru-O	5.9	2.05	0.0	0.065	0.34	
11		11	403.5 - 410.1	Ru-O	5.9	2.05	0.5	0.065	0.43	
12		12	413.5 - 420.0	Ru-O	6.0	2.05	0.1	0.068	0.46	
13		13	423.4 - 429.6	Ru-O	5.9	2.05	0.0	0.066	0.66	
14		14	433.5 - 439.4	Ru-O	5.9	2.05	-0.4	0.069	0.49	
15		15	443.5 - 449.4	Ru-O	5.9	2.05	-0.2	0.070	0.37	
16		16	453.5 - 459.5	Ru-O	6.0	2.05	1.0	0.071	0.63	
17		17	463.5 - 469.6	Ru-O	6.0	2.05	1.1	0.072	0.63	
18		18	473.5 - 479.6	Ru-O	5.9	2.05	1.1	0.073	0.73	
19		19	483.5 - 489.6	Ru-O	5.9	2.05	1.2	0.074	0.87	
20		20	493.5 - 499.7	Ru-O	5.8	2.05	1.8	0.075	0.96	
21		21	503.4 - 509.6	Ru-O	5.8	2.05	1.7	0.076	0.87	
22		22	513.9 - 521.5	Ru-O	6.0	2.04	1.2	0.085	1.58	
23		23	525.0 - 530.7	Ru-O	5.8	2.04	1.7	0.085	1.46	
24		24	533.5 - 538.4	Ru-O	5.8	2.05	3.4	0.085	1.76	
25		25	543.4 - 548.8	Ru-O	6.0	2.04	2.3	0.095	1.54	
26		26	553.4 - 559.3	Ru-O	5.9	2.04	1.7	0.100	1.90	
27		27	563.4 - 569.9	Ru-O	6.0	2.04	3.4	0.100	1.55	
28		28	573.6 - 578.7	Ru-O	5.6	2.02	1.9	0.100	1.96	

29		38	573.2	-	573.2	Ru-O	5.4	1.98	-0.8	0.100	1.99	
30		48	573.2	-	573.2	Ru-O	5.7	1.97	-1.2	0.100	1.98	
31		58	573.2	-	573.2	Ru-O	5.9	1.96	-2.0	0.090	0.51	
32		68	573.2	-	573.2	Ru-O	5.9	1.96	-3.3	0.082	0.19	
33		78	573.2	-	573.2	Ru-O	6.0	1.96	-2.0	0.082	0.47	
34		88	573.2	-	573.2	Ru-O	5.9	1.95	-3.7	0.079	1.45	
35	H_2+He (2:1)	123	313.8	-	322.1	Ru-O	6.0	1.96	-3.2	0.064	1.70	
36		124	326.1	-	333.0	Ru-O	5.9	1.96	-3.0	0.070	1.56	
37		125	335.9	-	341.5	Ru-O	6.0	1.97	-2.9	0.072	1.29	
38		126	344.2	-	349.1	Ru-O	6.0	1.98	-3.3	0.073	1.00	
39		127	353.4	-	358.7	Ru-O	6.0	1.98	-3.4	0.074	0.80	
40		128	363.4	-	369.4	Ru-O	6.0	1.98	-3.2	0.076	0.89	
41		129	373.4	-	379.7	Ru-O	6.0	1.98	-3.3	0.077	0.76	
42		130	383.4	-	389.8	Ru-O	5.8	2.00	-2.0	0.083	1.00	
43		131	393.5	-	399.9	Ru-O	5.2	2.02	-1.2	0.084	1.94	3.0
						Ru-Ru	0.4	2.64	-4.6	0.100		
44		132	403.4	-	409.8	Ru-O	4.6	2.02	-1.4	0.083	2.00	5.7
						Ru-Ru	1.3	2.65	-2.8	0.100		
45		133	413.5	-	419.7	Ru-O	3.4	2.02	-0.7	0.080	1.97	6.5
						Ru-Ru	2.8	2.66	-1.2	0.088		
46		134	423.6	-	430.0	Ru-O	1.4	2.02	-1.0	0.071	1.11	6.6
						Ru-Ru	5.0	2.67	0.6	0.076		
47		135	433.4	-	439.4	Ru-O	0.5	2.03	0.4	0.068	1.15	6.8
						Ru-Ru	6.2	2.67	0.8	0.075		
48		136	443.6	-	449.5	Ru-Ru	7.0	2.67	0.0	0.075	0.14	
49		137	453.4	-	459.5	Ru-Ru	7.1	2.67	0.3	0.076	0.15	
50		138	463.5	-	469.5	Ru-Ru	7.0	2.67	0.4	0.076	0.16	
51		139	473.5	-	479.5	Ru-Ru	7.1	2.67	0.4	0.077	0.17	
52		140	483.4	-	489.5	Ru-Ru	7.0	2.67	0.6	0.077	0.19	
53		141	493.4	-	499.6	Ru-Ru	7.0	2.67	0.4	0.078	0.18	
54		142	503.4	-	509.6	Ru-Ru	7.0	2.67	0.0	0.078	0.16	
55		143	513.2	-	518.2	Ru-Ru	7.0	2.67	0.6	0.078	0.18	
56		144	513.1	-	513.1	Ru-Ru	7.1	2.67	0.9	0.078	0.22	
57		145	513.1	-	513.1	Ru-Ru	7.1	2.67	0.6	0.078	0.18	
58		146	513.1	-	513.1	Ru-Ru	7.1	2.67	0.3	0.078	0.17	

59	147	513.1	-	513.1	Ru-Ru	7.1	2.67	0.7	0.078	0.19
60	148	513.1	-	513.1	Ru-Ru	7.1	2.67	0.5	0.078	0.22
61	149	513.1	-	513.1	Ru-Ru	7.1	2.67	0.8	0.078	0.17

[a] Average temperature. [b] Coordination number. [c] Bond distance. [d] Difference in the origin of photoelectron energy between the reference and the sample. [e] Debye-Waller factor. [f] Residual factor. [g] $CN_{Ru\text{-}Ru}/(1\text{-}CN_{Ru\text{-}O}/6)$. Fourier filtering range: 0.120-0.199 nm (Entries 1-42), 0.120-0.288 nm (Entries 43-47), 0.169-0.288 nm (Entries 48-61). Gas flow rate: Air (0, static), H_2+He (15 mL/min). Ru: 5 wt%. Each measurement took about 1 min. Entries marked in blue were included in Table 1. Entries marked in gray were fitting results with Ru-Ru or Ru-Ce bond in addition to Ru-O bond (Fourier filtering range: 0.120-0.338 nm). Theoretical functions for the Ru-Ce bond was calculated using the FEFF8.2 program.[S1]

(S1) Ankudinov, A. L.; Ravel, B.; Rehr, J. J.; Conradson, S. D. Real-space multiple-scattering calculation and interpretation of x-ray-absorption near-edge structure. *Phys. Rev. B* **1998**, *58*, 7565.

Table S3. Curve fitting results of *in situ* Ru *K*-edge EXAFS of Ru/CeO_2 during heating in N_2 and reduction.

Entry	Gas	Time [min]	Temp. [a] [K]	Shells	CN [b]	R [c] [0.1 nm]	ΔE_0 [d] [eV]	σ [e] [0.1 nm]	R_f [f] [%]	CN*$_{Ru-Ru}$ [g]
1	N_2	1	303.3 - 310.7	Ru-O	6.0	2.05	0.0	0.063	0.19	
2		2	316.1 - 323.9	Ru-O	5.9	2.05	-0.9	0.064	0.19	
3		3	328.3 - 333.3	Ru-O	6.0	2.05	-0.9	0.065	0.35	
4		4	336.5 - 343.1	Ru-O	5.9	2.05	-0.3	0.064	0.28	
5		5	344.5 - 349.9	Ru-O	6.0	2.05	1.0	0.063	0.29	
6		6	353.2 - 360.0	Ru-O	5.9	2.05	0.1	0.063	0.32	
7		7	363.3 - 370.1	Ru-O	6.0	2.05	1.2	0.064	0.38	
8		8	373.5 - 379.8	Ru-O	5.9	2.05	0.2	0.065	0.31	
9		9	383.2 - 389.9	Ru-O	6.0	2.05	-0.1	0.067	0.49	
10		10	393.3 - 399.8	Ru-O	6.0	2.05	1.1	0.068	0.35	
11		11	403.2 - 409.9	Ru-O	5.8	2.05	1.1	0.066	0.46	
12		12	413.3 - 420.0	Ru-O	5.8	2.05	0.6	0.069	0.30	
13		13	423.4 - 429.9	Ru-O	5.8	2.05	0.5	0.069	0.46	
14		14	433.4 - 439.8	Ru-O	5.9	2.05	1.1	0.071	0.45	
15		15	443.3 - 449.9	Ru-O	5.8	2.05	1.2	0.073	0.45	
16		16	453.2 - 459.7	Ru-O	5.9	2.05	1.2	0.075	0.56	
17		17	463.3 - 470.0	Ru-O	6.0	2.05	1.4	0.078	0.92	
18		18	473.3 - 480.0	Ru-O	6.0	2.05	1.9	0.080	1.01	
19		19	483.3 - 489.8	Ru-O	5.9	2.05	1.8	0.084	0.79	
20		20	493.2 - 499.9	Ru-O	5.8	2.05	2.3	0.086	0.98	
21		21	503.3 - 509.9	Ru-O	5.9	2.05	1.9	0.093	0.75	
22		22	513.3 - 520.1	Ru-O	5.9	2.05	2.3	0.096	0.50	
23		23	523.4 - 530.0	Ru-O	5.8	2.05	3.1	0.099	0.56	
24		24	533.4 - 540.1	Ru-O	5.9	2.04	2.9	0.100	0.70	
25		25	543.3 - 550.1	Ru-O	5.8	2.04	3.0	0.100	1.71	
26		26	553.4 - 560.0	Ru-O	5.9	2.04	3.7	0.100	1.64	
27		27	563.2 - 569.8	Ru-O	5.8	2.03	3.7	0.100	1.76	
28		28	573.2 - 578.2	Ru-O	5.8	2.03	3.9	0.103	0.45	
29		38	573.2 - 573.2	Ru-O	5.7	2.03	2.9	0.104	0.71	
30		48	573.2 - 573.2	Ru-O	5.7	2.02	2.2	0.107	0.39	
31		58	573.2 - 573.2	Ru-O	6.0	2.01	1.5	0.104	0.27	
32		68	573.2 - 573.2	Ru-O	5.7	2.01	1.0	0.106	0.29	

33		78	573.2	-	573.2	Ru-O	5.9	2.02	3.0	0.106	0.38	
34		88	573.2	-	573.2	Ru-O	5.9	2.00	0.6	0.106	0.22	
35	H_2+He (2:1)	123	313.0	-	321.9	Ru-O	6.0	2.06	0.7	0.087	0.28	
36		124	325.0	-	331.8	Ru-O	6.0	2.07	1.1	0.092	0.15	
37		125	334.3	-	340.6	Ru-O	5.9	2.07	1.8	0.090	0.53	
38		126	343.0	-	349.0	Ru-O	5.1	2.05	-2.5	0.100	0.97	3.8
						Ru-Ru	0.5	2.61	-5.0	0.060		
39		127	353.0	-	358.8	Ru-O	4.6	2.06	-0.1	0.093	0.59	3.8
						Ru-Ru	0.9	2.59	-6.7	0.074		
40		128	363.1	-	369.7	Ru-O	3.3	2.07	0.8	0.079	1.05	3.6
						Ru-Ru	1.6	2.62	-1.2	0.092		
41		129	373.1	-	380.0	Ru-O	2.6	2.06	-0.3	0.076	1.65	3.6
						Ru-Ru	2.1	2.63	1.7	0.097		
42		130	383.1	-	390.0	Ru-O	2.1	2.07	0.7	0.068	1.93	3.7
						Ru-Ru	2.3	2.63	-0.1	0.100		
43		131	393.1	-	399.9	Ru-O	1.2	2.08	1.7	0.069	2.94	3.4
						Ru-Ru	2.4	2.63	0.6	0.100		
44		132	403.1	-	410.4	Ru-O	0.9	2.09	3.6	0.061	3.45	3.6
						Ru-Ru	2.8	2.63	0.8	0.100		
45		133	413.0	-	419.6	Ru-O	0.7	2.09	3.7	0.060	3.41	3.5
						Ru-Ru	2.9	2.63	1.3	0.097		
46		134	423.1	-	429.8	Ru-O	0.5	2.09	3.4	0.060	3.59	3.9
						Ru-Ru	3.4	2.63	1.0	0.100		
47		135	433.0	-	439.4	Ru-Ru	3.8	2.61	-2.0	0.102	0.28	
47’						Ru-O	1.6	2.05	0.3	0.100	2.10	
						Ru-Ru	3.0	2.63	1.1	0.100		
48		136	443.2	-	450.0	Ru-Ru	3.9	2.61	-1.3	0.100	0.31	
49		137	453.0	-	459.7	Ru-Ru	4.1	2.61	-1.0	0.100	0.23	
50		138	463.0	-	469.6	Ru-Ru	4.1	2.61	-1.3	0.100	0.29	
50’						Ru-O	1.2	2.04	-1.0	0.100	3.14	
						Ru-Ru	3.3	2.63	1.1	0.100		
51		139	473.0	-	479.4	Ru-Ru	4.0	2.61	-1.2	0.100	0.52	
52		140	483.2	-	489.6	Ru-Ru	4.0	2.61	-1.4	0.098	0.49	
53		141	493.1	-	499.5	Ru-Ru	4.1	2.62	-0.6	0.098	1.00	
53’						Ru-O	1.1	2.05	3.6	0.100	1.49	

					Ru-Ru	4.3	2.61	-0.8	0.098	
54	142	503.1	-	510.1	Ru-Ru	4.0	2.61	-1.7	0.098	0.61
55	143	513.0	-	518.5	Ru-Ru	4.1	2.61	-2.3	0.098	0.71
56	144	513.1	-	513.1	Ru-Ru	4.0	2.61	-1.3	0.096	1.85
57	145	513.1	-	513.1	Ru-Ru	4.1	2.61	-1.9	0.095	1.65
57’					Ru-O	1.0	2.06	6.1	0.100	1.89
					Ru-Ru	4.9	2.62	-0.8	0.100	
58	146	513.1	-	513.1	Ru-Ru	4.1	2.61	-1.4	0.096	1.65
59	147	513.1	-	513.1	Ru-Ru	4.1	2.61	-2.2	0.096	1.63
60	148	513.1	-	513.1	Ru-Ru	4.0	2.61	-2.4	0.096	1.92
61	149	513.1	-	513.1	Ru-Ru	4.0	2.62	-1.4	0.096	1.48
61’					Ru–O	0.9	2.08	8.0	0.100	1.62
					Ru–Ru	4.9	2.62	-0.7	0.098	

[a] Average temperature. [b] Coordination number. [c] Bond distance. [d] Difference in the origin of photoelectron energy between the reference and the sample. [e] Debye-Waller factor. [f] Residual factor. [g] $CN_{Ru\text{-}Ru}/(1\text{-}CN_{Ru\text{-}O}/6)$. Fourier filtering range: 0.120-0.199 nm (Entries 1-37), 0.120-0.288 nm (Entries 37-46, 47’, 50’, 53’, 57’, 61’), 0.200-0.288 nm (Entries 47-61). Gas flow rate: N_2 (100 mL/min), H_2+He (15 mL/min). Ru: 5 wt%. Each measurement took about 1 min. Entries marked in blue were included in Table 2. Entries marked in gray were fitting results with Ru-O bond in addition to Ru-Ru bond (Fourier filtering range: 0.120-0.288 nm).

Table S4 Curve fitting results of *in situ* Ru *K*-edge EXAFS of Ru/SiO_2 during heating in He and reduction.

Entry	Gas	Time [min]	Temp. [a] [K]	Shells	CN [b]	R [c] [0.1 nm]	ΔE_0 [d] [eV]	σ [e] [0.1 nm]	R_f [f] [%]	$CN^*_{Ru\text{-}Ru}$ [g]
1	He	1	r.t. - r.t.	Ru-O	5.9	2.05	-1.1	0.060	0.68	
2		2	308.2 - 315.5	Ru-O	5.8	2.05	-0.8	0.060	0.14	
3		3	317.6 - 325.8	Ru-O	5.9	2.05	-0.3	0.060	0.57	
4		4	327.9 - 335.7	Ru-O	5.9	2.05	-0.3	0.060	0.56	
5		5	338.5 - 345.7	Ru-O	5.8	2.05	-0.2	0.060	0.52	
6		6	349.0 - 356.4	Ru-O	5.7	2.05	-0.9	0.060	0.43	
7		7	359.4 - 366.8	Ru-O	5.7	2.05	-0.2	0.060	0.52	
8		8	370.0 - 377.3	Ru-O	5.7	2.05	-0.9	0.062	0.63	
9		9	380.4 - 387.8	Ru-O	5.8	2.05	-0.6	0.063	0.59	
10		10	390.8 - 398.2	Ru-O	5.9	2.05	-0.1	0.064	0.69	
11		11	401.3 - 408.8	Ru-O	5.9	2.05	-0.2	0.065	0.70	
12		12	411.9 - 419.4	Ru-O	5.9	2.05	-0.2	0.066	0.71	
13		13	422.3 - 429.8	Ru-O	5.8	2.05	-0.9	0.068	0.58	
14		14	432.9 - 440.2	Ru-O	5.9	2.05	-0.1	0.069	0.97	
15		15	443.3 - 450.8	Ru-O	5.7	2.05	-0.9	0.070	0.36	
16		16	453.8 - 461.4	Ru-O	5.8	2.05	0.1	0.070	0.87	
17		17	464.4 - 472.0	Ru-O	5.7	2.05	0.0	0.072	0.62	
18		18	474.8 - 482.2	Ru-O	5.8	2.05	0.0	0.073	0.72	
19		19	485.3 - 492.7	Ru-O	5.7	2.05	0.1	0.075	0.64	
20		20	495.8 - 503.2	Ru-O	5.8	2.05	1.2	0.077	0.76	
21		21	506.2 - 513.6	Ru-O	5.8	2.05	1.1	0.079	1.26	
22		22	516.8 - 524.3	Ru-O	5.7	2.05	1.8	0.081	0.81	
23		23	527.4 - 534.7	Ru-O	5.7	2.05	1.2	0.085	0.70	
24		24	537.7 - 545.1	Ru-O	5.8	2.05	1.8	0.088	1.14	
25		25	548.2 - 555.6	Ru-O	5.8	2.05	1.8	0.090	1.00	
26		26	558.6 - 566.0	Ru-O	5.9	2.05	2.0	0.091	1.88	
27		27	569.1 - 573.2	Ru-O	5.8	2.05	1.8	0.096	1.19	
28		28	573.2 - 573.2	Ru-O	6.0	2.04	2.2	0.095	1.64	
29		29	573.2 - 573.2	Ru-O	6.0	2.04	1.7	0.099	1.33	
30		30	573.2 - 573.2	Ru-O	6.0	2.04	1.2	0.099	1.87	
31		31	573.2 - 573.2	Ru-O	5.8	2.04	1.2	0.100	0.61	
32		32	573.2 - 573.2	Ru-O	6.0	2.04	1.8	0.100	1.23	

33	33	573.2	-	573.2	Ru-O	6.0	2.04	2.3	0.099	1.06
34	34	573.2	-	573.2	Ru-O	6.0	2.04	2.3	0.100	0.91
35	35	573.2	-	573.2	Ru-O	5.8	2.04	1.2	0.100	0.54
36	36	573.2	-	573.2	Ru-O	6.0	2.04	2.5	0.100	1.47
37	37	573.2	-	573.2	Ru-O	5.7	2.04	1.8	0.100	0.31
38	38	573.2	-	573.2	Ru-O	5.8	2.04	2.3	0.100	0.42
39	39	573.2	-	573.2	Ru-O	5.6	2.04	1.9	0.100	0.30
40	40	573.2	-	573.2	Ru-O	5.7	2.04	1.8	0.100	0.31
41	41	573.2	-	573.2	Ru-O	5.9	2.04	2.2	0.100	0.75
42	42	573.2	-	573.2	Ru-O	5.7	2.03	1.2	0.100	0.46
43	43	573.2	-	573.2	Ru-O	5.5	2.03	1.8	0.100	0.37
44	44	573.2	-	573.2	Ru-O	5.9	2.04	1.7	0.100	0.68
45	45	573.2	-	573.2	Ru-O	6.0	2.04	2.3	0.100	1.07
46	46	573.2	-	573.2	Ru-O	5.7	2.03	1.2	0.100	0.43
47	47	573.2	-	573.2	Ru-O	5.8	2.03	1.8	0.100	0.43
48	48	573.2	-	573.2	Ru-O	5.8	2.03	1.6	0.100	0.44
49	49	573.2	-	573.2	Ru-O	5.8	2.03	1.3	0.100	0.55
50	50	573.2	-	573.2	Ru-O	5.8	2.03	1.2	0.100	0.54
51	51	573.2	-	573.2	Ru-O	5.7	2.03	1.2	0.100	0.37
52	52	573.2	-	573.2	Ru-O	5.8	2.03	1.1	0.100	0.73
53	53	573.2	-	573.2	Ru-O	5.9	2.03	1.8	0.100	0.62
54	54	573.2	-	573.2	Ru-O	5.7	2.03	1.4	0.100	1.15
55	55	573.2	-	573.2	Ru-O	5.7	2.03	1.0	0.100	0.34
56	56	573.2	-	573.2	Ru-O	5.8	2.03	1.2	0.100	0.72
57	57	573.2	-	573.2	Ru-O	5.7	2.03	1.1	0.100	0.38
58	58	573.2	-	573.2	Ru-O	5.8	2.03	1.0	0.100	0.82
59	59	573.2	-	573.2	Ru-O	5.7	2.03	1.2	0.100	0.36
60	60	573.2	-	573.2	Ru-O	5.9	2.03	1.7	0.100	0.52
61	61	573.2	-	573.2	Ru-O	5.7	2.03	1.2	0.100	0.33
62	62	573.2	-	573.2	Ru-O	5.6	2.03	0.6	0.100	0.32
63	63	573.2	-	573.2	Ru-O	5.8	2.03	1.2	0.100	1.39
64	64	573.2	-	573.2	Ru-O	5.7	2.03	1.1	0.100	0.34
65	65	573.2	-	573.2	Ru-O	5.7	2.03	1.1	0.100	0.35
66	66	573.2	-	573.2	Ru-O	5.7	2.03	1.2	0.100	0.38
67	67	573.2	-	573.2	Ru-O	5.7	2.03	1.5	0.098	0.52

68		68	573.2	-	573.2	Ru-O	5.6	2.03	1.1	0.100	0.40	
69		69	573.2	-	573.2	Ru-O	5.9	2.03	1.8	0.100	0.57	
70		70	573.2	-	573.2	Ru-O	5.8	2.03	1.1	0.100	0.46	
71		71	573.2	-	573.2	Ru-O	5.8	2.03	1.1	0.100	0.39	
72		72	573.2	-	573.2	Ru-O	5.6	2.02	1.1	0.100	0.41	
73		73	573.2	-	573.2	Ru-O	5.8	2.03	1.0	0.100	0.43	
74		74	573.2	-	573.2	Ru-O	5.8	2.02	1.2	0.100	0.46	
75		75	573.2	-	573.2	Ru-O	5.7	2.03	1.0	0.100	0.40	
76		76	573.2	-	573.2	Ru-O	5.8	2.02	1.2	0.100	0.42	
77		77	573.2	-	573.2	Ru-O	5.9	2.02	1.1	0.100	0.43	
78		78	573.2	-	573.2	Ru-O	5.8	2.02	1.1	0.100	0.45	
79		79	573.2	-	573.2	Ru-O	5.7	2.02	1.0	0.100	0.39	
80		80	573.2	-	573.2	Ru-O	5.8	2.02	1.1	0.099	0.42	
81		81	573.2	-	573.2	Ru-O	5.7	2.02	1.0	0.100	0.38	
82		82	573.2	-	573.2	Ru-O	5.6	2.02	1.0	0.100	0.44	
83		83	573.2	-	573.2	Ru-O	5.6	2.02	1.0	0.100	0.54	
84		84	573.2	-	573.2	Ru-O	5.7	2.02	1.1	0.100	0.45	
85		85	573.2	-	573.2	Ru-O	5.7	2.02	1.0	0.100	0.46	
86		86	573.2	-	573.2	Ru-O	5.8	2.02	1.1	0.100	0.52	
87		87	573.2	-	573.2	Ru-O	6.0	2.02	1.7	0.098	0.39	
88		107	r.t.	-	r.t.	Ru-O	6.0	2.02	1.2	0.090	0.46	
89	Air	108	r.t.	-	r.t.	Ru-O	6.0	2.02	1.2	0.091	0.47	
90	H_2+He (2:1)	113	r.t.	-	r.t.	Ru-O	6.0	2.03	-0.4	0.085	0.34	
91		114	306.7	-	314.4	Ru-O	6.0	2.04	1.7	0.085	0.20	
92		115	323.5	-	329.9	Ru-O	6.0	2.04	1.2	0.090	0.08	
93		116	334.5	-	342.0	Ru-O	5.9	2.04	0.6	0.090	1.25	
94		117	345.0	-	352.5	Ru-O	5.8	2.04	1.5	0.090	1.30	
95		118	355.6	-	362.9	Ru-O	5.0	2.03	-0.7	0.091	1.77	8.1
						Ru-Ru	1.4	2.65	-6.3	0.074		
96		119	366.0	-	373.3	Ru-O	4.3	2.03	-0.6	0.088	1.88	8.3
						Ru-Ru	2.4	2.65	-5.4	0.073		
97		120	376.3	-	383.7	Ru-O	3.8	2.03	-0.8	0.085	1.59	8.2
						Ru-Ru	3.0	2.65	-5.2	0.074		
98		121	386.8	-	394.3	Ru-O	3.5	2.03	-1.0	0.085	1.33	8.3
						Ru-Ru	3.5	2.65	-4.6	0.076		

99	122	397.3	-	404.7	Ru-O	3.1	2.03	-0.9	0.086	1.31	8.3
					Ru-Ru	4.0	2.65	-4.2	0.077		
100	123	407.9	-	415.6	Ru-O	2.6	2.02	-1.2	0.082	0.96	8.4
					Ru-Ru	4.8	2.65	-3.6	0.077		
101	124	418.3	-	425.7	Ru-O	2.1	2.02	-1.1	0.081	0.90	8.3
					Ru-Ru	5.4	2.65	-3.3	0.076		
102	125	428.8	-	436.3	Ru-O	1.6	2.01	-2.5	0.078	0.82	8.2
					Ru-Ru	6.0	2.65	-3.3	0.079		
103	126	439.2	-	446.6	Ru-O	1.2	2.01	-2.3	0.075	1.07	8.2
					Ru-Ru	6.6	2.65	-2.7	0.083		
104	127	449.9	-	457.2	Ru-O	0.6	2.01	-2.4	0.065	0.86	8.1
					Ru-Ru	7.3	2.65	-2.6	0.082		
105	128	460.2	-	467.7	Ru-O	0.2	2.01	-1.6	0.063	1.15	8.0
					Ru-Ru	7.7	2.65	-1.8	0.084		
106	129	470.5	-	478.0	Ru-Ru	8.0	2.65	-1.8	0.084	0.97	
107	130	481.1	-	488.6	Ru-Ru	8.0	2.65	-1.4	0.085	0.43	
108	131	491.6	-	499.1	Ru-Ru	8.1	2.65	-1.9	0.084	0.33	
109	132	502.1	-	509.9	Ru-Ru	8.1	2.65	-1.1	0.085	0.30	
110	133	513.2	-	513.2	Ru-Ru	8.1	2.65	-1.3	0.085	0.26	
111	134	513.2	-	513.2	Ru-Ru	8.0	2.65	-1.8	0.086	0.34	
112	135	513.2	-	513.2	Ru-Ru	8.1	2.65	-1.8	0.085	0.26	
113	136	513.2	-	513.2	Ru-Ru	8.0	2.65	-1.5	0.084	0.29	
114	137	513.2	-	513.2	Ru-Ru	8.1	2.65	-1.3	0.085	0.25	
115	138	513.2	-	513.2	Ru-Ru	8.0	2.65	-1.6	0.084	0.28	
116	139	513.2	-	513.2	Ru-Ru	8.0	2.65	-1.7	0.084	0.25	
117	140	513.2	-	513.2	Ru-Ru	8.1	2.65	-1.5	0.084	0.26	
118	141	513.2	-	513.2	Ru-Ru	8.1	2.65	-1.4	0.085	0.25	
119	142	513.2	-	513.2	Ru-Ru	8.1	2.65	-1.8	0.084	0.23	
120	143	513.2	-	513.2	Ru-Ru	8.0	2.65	-1.4	0.084	0.25	
121	144	513.2	-	513.2	Ru-Ru	8.0	2.65	-1.0	0.084	0.22	
122	145	513.2	-	513.2	Ru-Ru	8.0	2.65	-1.3	0.084	0.24	
123	146	513.2	-	513.2	Ru-Ru	8.0	2.65	-1.3	0.084	0.24	
124	147	513.2	-	513.2	Ru-Ru	8.1	2.65	-1.3	0.084	0.23	
125	148	513.2	-	513.2	Ru-Ru	8.0	2.65	-1.7	0.084	0.26	
126	149	513.2	-	513.2	Ru-Ru	8.1	2.65	-1.6	0.084	0.25	

127	150	513.2	-	513.2	Ru-Ru	8.0	2.65	-1.7	0.084	0.25
128	170	r.t.	-	r.t.	Ru-Ru	8.0	2.65	-0.9	0.069	0.16

[a] Temperature. [b] Coordination number. [c] Bond distance. [d] Difference in the origin of photoelectron energy between the reference and the sample. [e] Debye-Waller factor. [f] Residual factor. [g] $CN_{Ru-Ru}/(1-CN_{Ru-O}/6)$. Fourier filtering range: 0.120-0.199 nm (Entries 1-94), 0.120-0.288 nm (Entries 95-106), 0.169-0.288 nm (Entries 107-128). Ru: 5 wt%. Gas flow rate: He (100 mL/min), Air (0, static), H_2+He (15 mL/min). Entries marked in blue were included in Table 3.

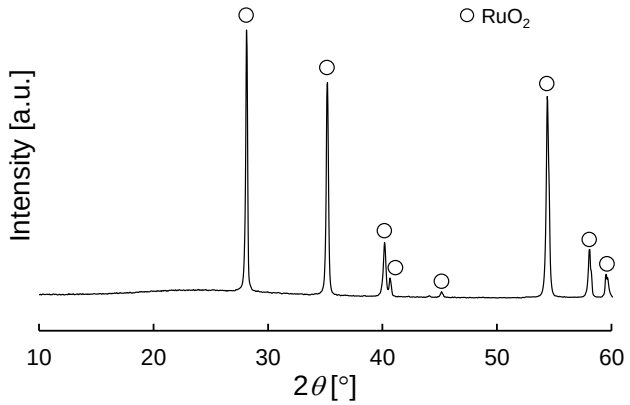

Figure S1 XRD pattern of RuO_2 as reference.

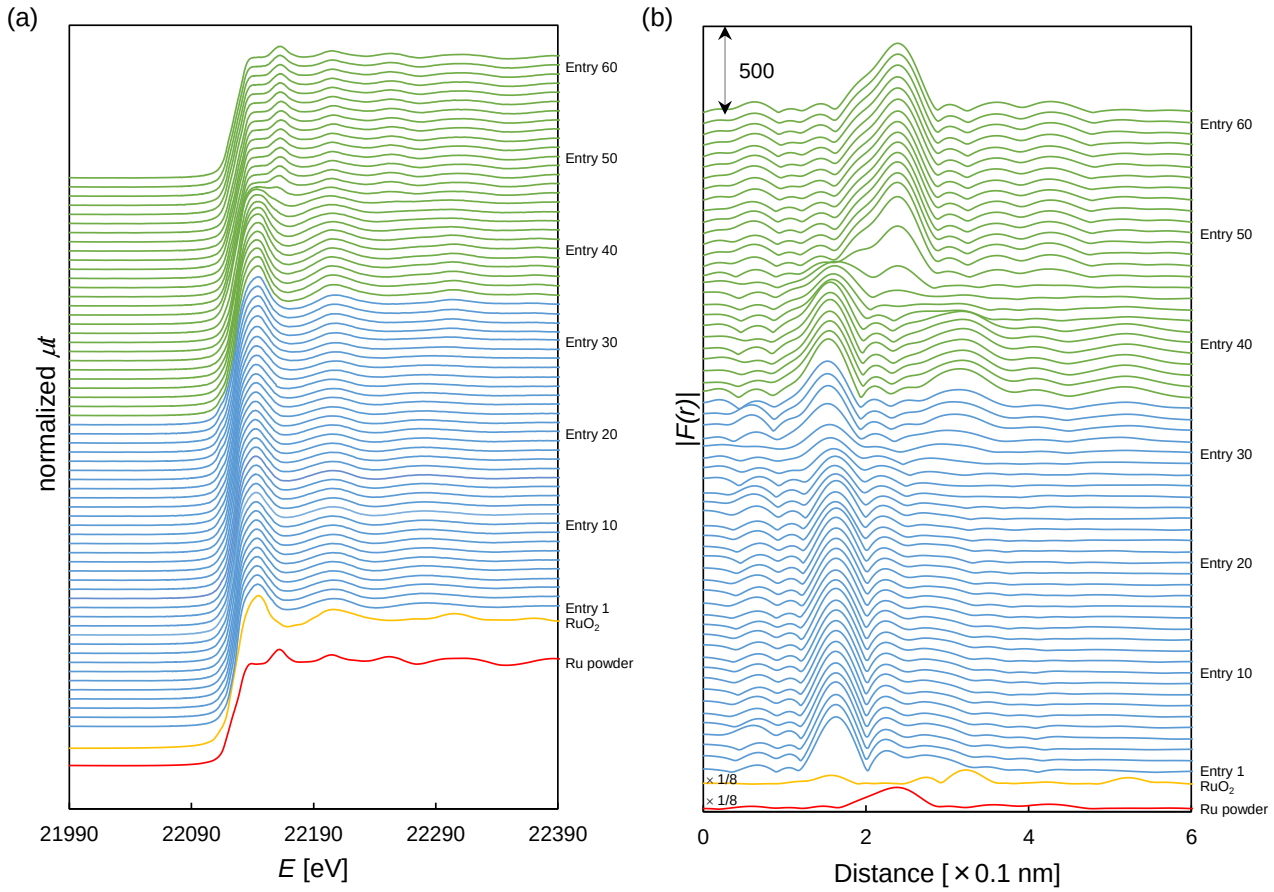

Figure S2. All the obtained results of Ru *K*-edge XANES and EXAFS analysis of Ru/CeO_2 during calcination in air and reduction. (a) XANES spectra. (b) Fourier transform of k^3-weighted EXAFS. FT range: 30-120 nm^{-1}. The filtering range is listed in Table S2.

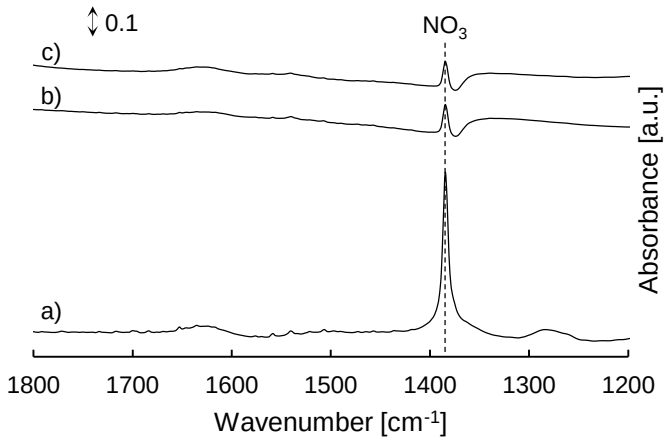

Figure S3. FT-IR spectra of Ru/CeO_2 catalysts. a) Ru/CeO_2, dried after impregnation, b) Ru/CeO_2-Air, c) Ru/CeO_2-N_2.

FT-IR measurements

Fourier transform infrared (FT-IR) spectra were recorded with a NICOLET6700 spectrometer (Thermo SCIENTIFIC) equipped with a liquid nitrogen-cooled Mercury-Cadmium-Telluride (MCT) detector (resolution = 4 cm^{-1}) in a transmission mode, using an in situ IR quartz cell with KBr windows. All samples (20 mg) were mixed with KBr (200 mg) and pressed into disks with 20 nm ϕ (120 mg). FT-IR spectra of adsorbed species were obtained by subtracting the background spectrum of air.

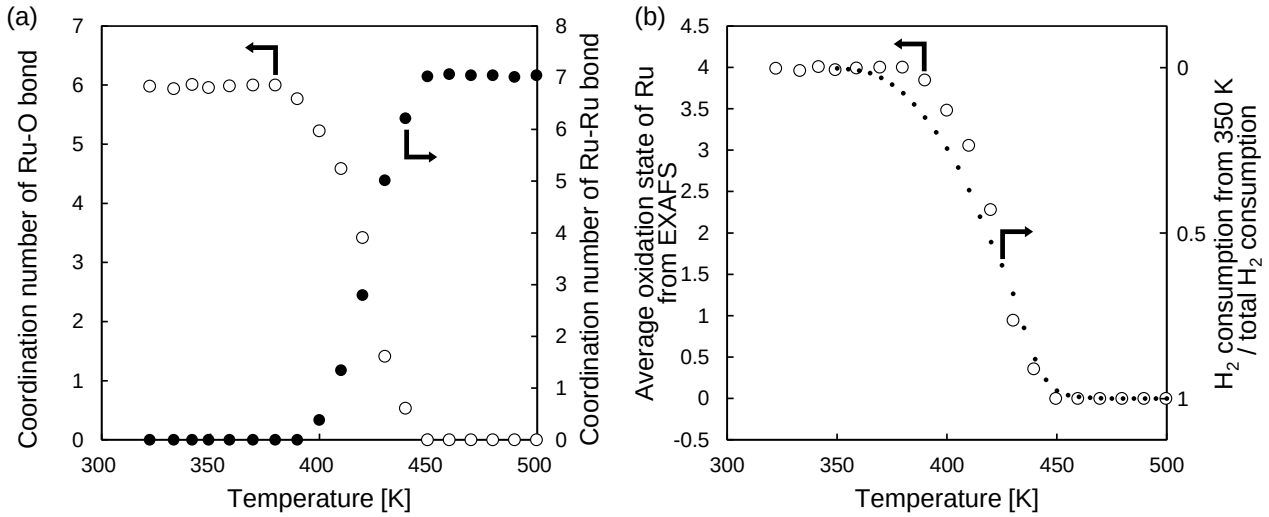

Figure S4. All the obtained results of Ru *K*-edge EXAFS analysis of Ru/CeO_2-Air during the reduction. (a) Coordination numbers from curve fitting of Ru *K*-edge EXAFS analysis during the reduction (Table S2). ○: Coordination number of Ru-O; ●: Coordination number of Ru-Ru. (b) Average valence of Ru as a function of reduction temperature. ○: From Ru *K*-edge EXAFS analysis (Table S2). The average valence of Ru was calculated by $4\times CN_{Ru\text{-}O}/6$. Dotted line: H_2 consumption in the H_2-TPR profile (Figure 3(a)).

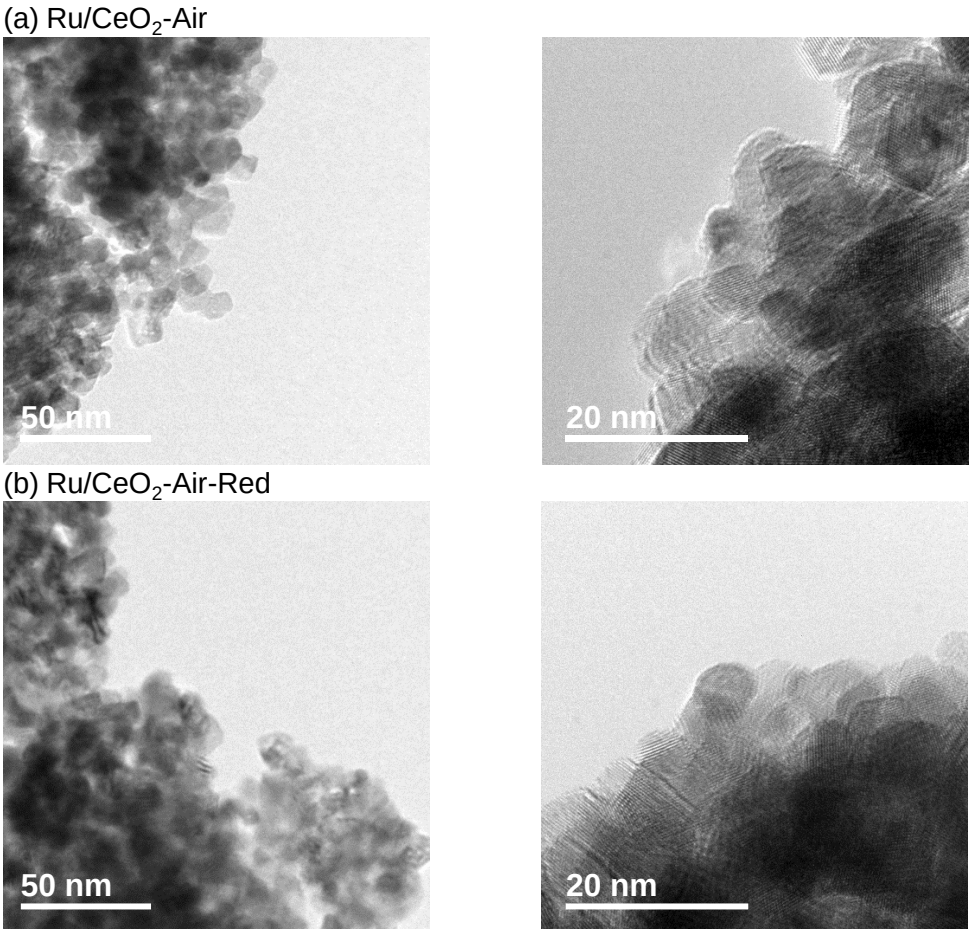

Figure S5. TEM images of (a) Ru/CeO_2-Air and (b) Ru/CeO_2-Air-Red.

TEM observation

Transmission electron microscope (TEM) images were obtained on JEOL JEM-2100F instrument. The samples were dispersed in *n*-hexane under supersonic waves and were dropped on Cu grids.

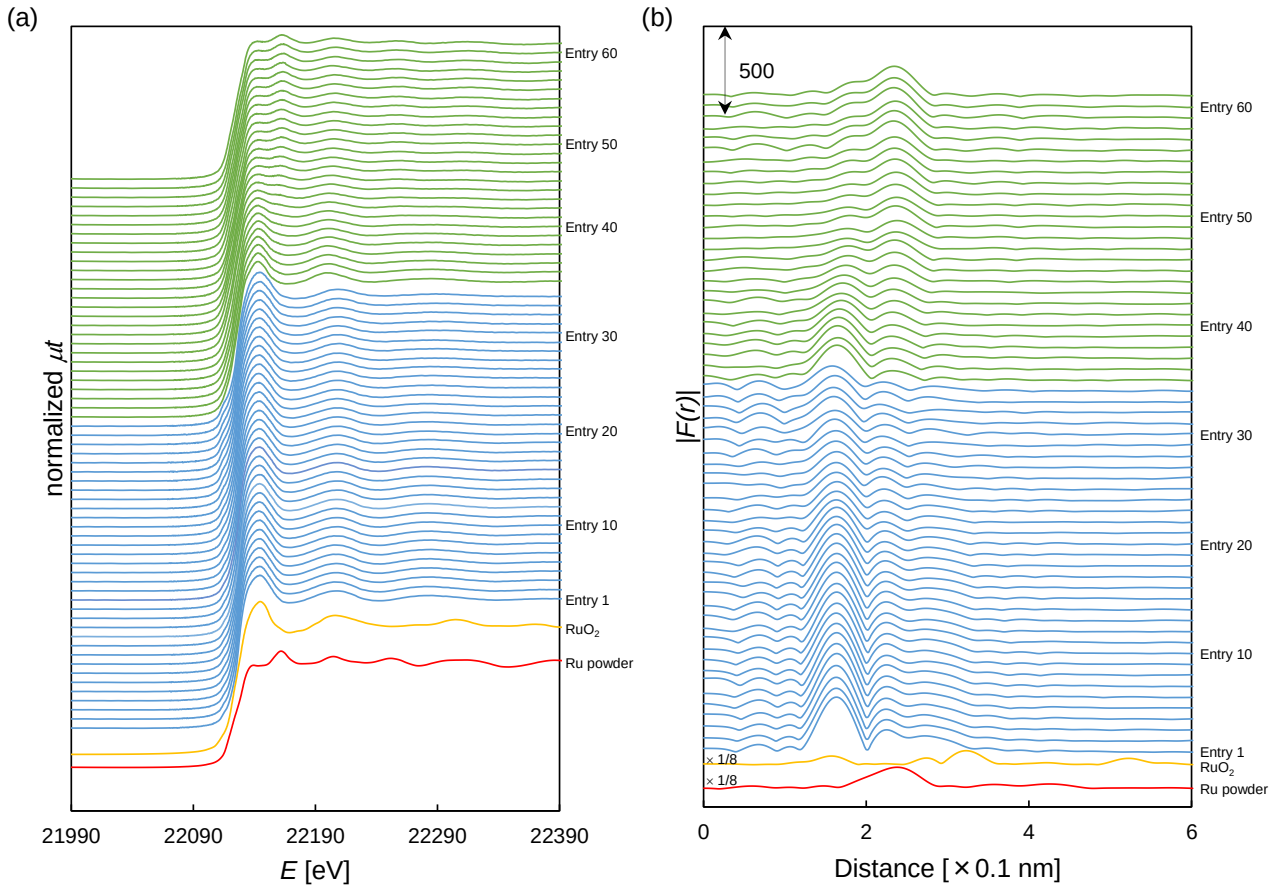

Figure S6. All the obtained results of Ru *K*-edge XANES and EXAFS analysis of Ru/CeO_2-N_2. (a) Ru *K*-edge XANES spectra. (b) Fourier transform of k^3-weighted Ru *K*-edge EXAFS. FT range: 30-120 nm^{-1}. The filtering range is listed in Table S3.

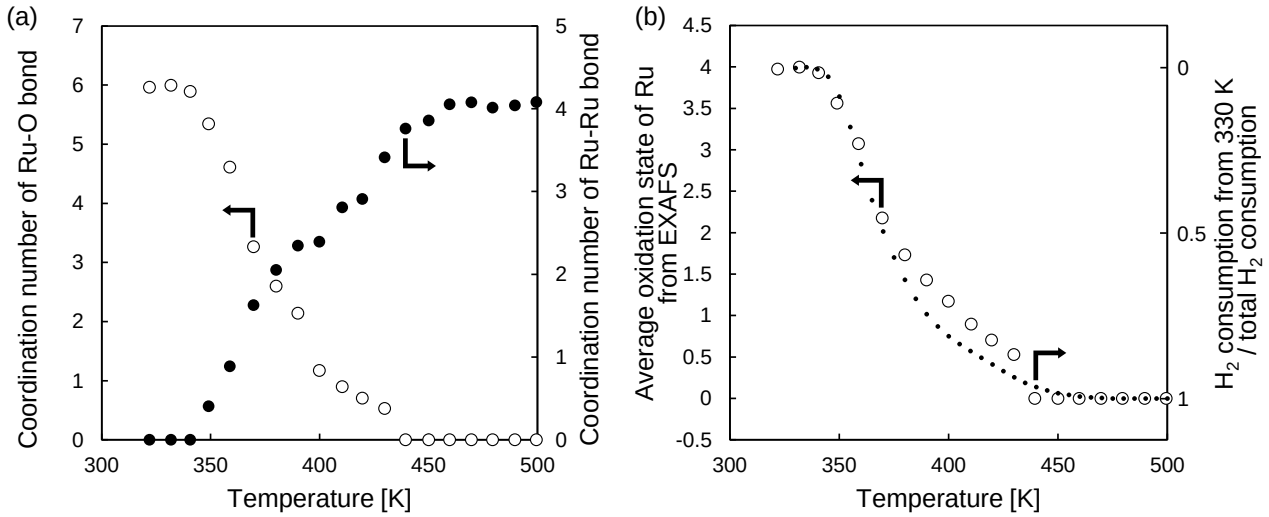

Figure S7. All the obtained results of Ru *K*-edge EXAFS analysis of Ru/CeO_2-N_2 during the reduction. (a) Coordination numbers from curve fitting of Ru *K*-edge EXAFS analysis (Table S3). ○: Coordination number of Ru-O; ●: Coordination number of Ru-Ru. (b) Average valence of Ru as a function of reduction temperature. ○: From Ru *K*-edge EXAFS analysis (Table S3). The average valence of Ru was calculated by $4 \times CN_{Ru\text{-}O}/6$. Dotted line: H_2 consumption in the H_2-TPR profile (Figure 5(a)).

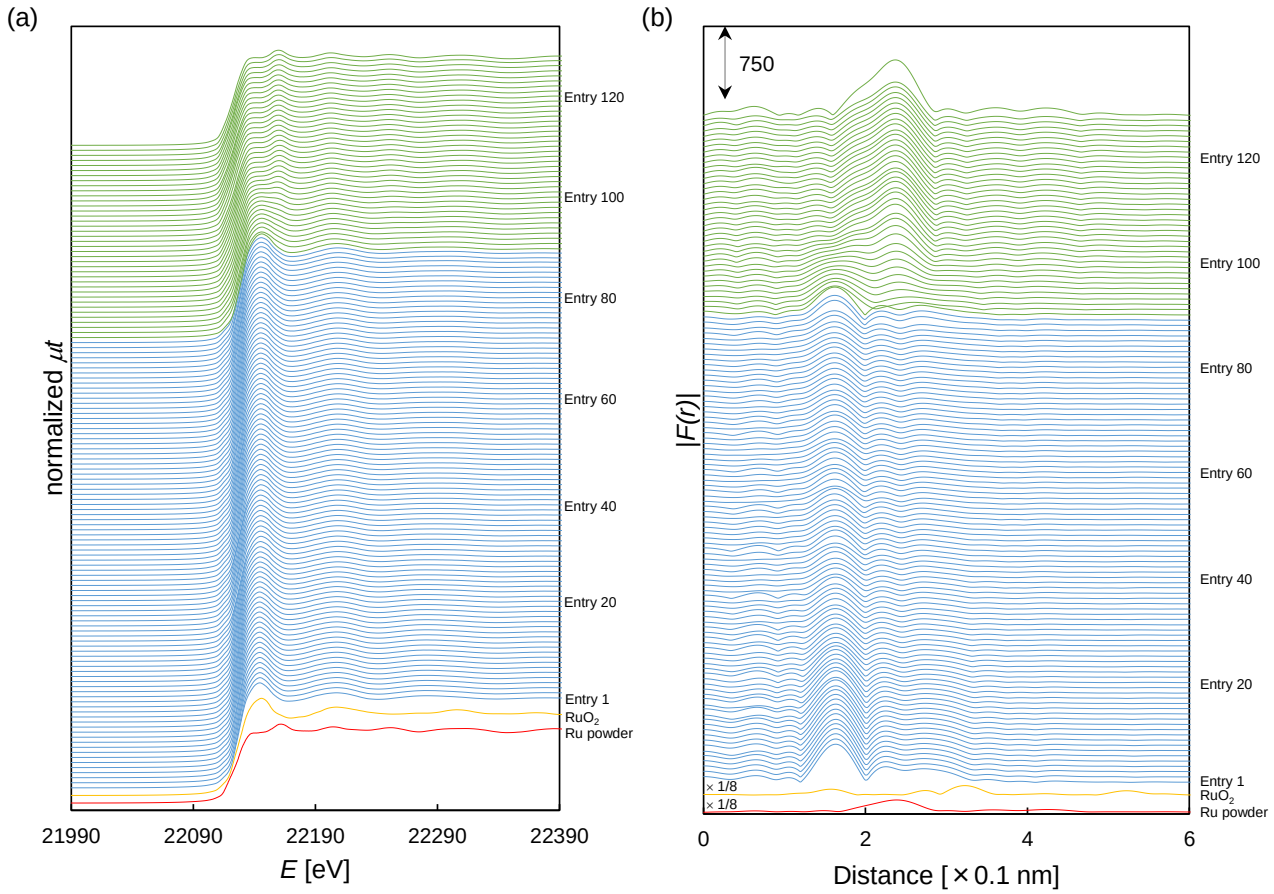

Figure S8. The detailed results of Ru *K*-edge XANES and EXAFS analysis of Ru/SiO_2. (a) Ru *K*-edge XANES spectra. (b) Fourier transform of k^3-weighted Ru *K*-edge EXAFS. FT range: 30-120 nm^{-1}. The filtering range is listed in Table S4.

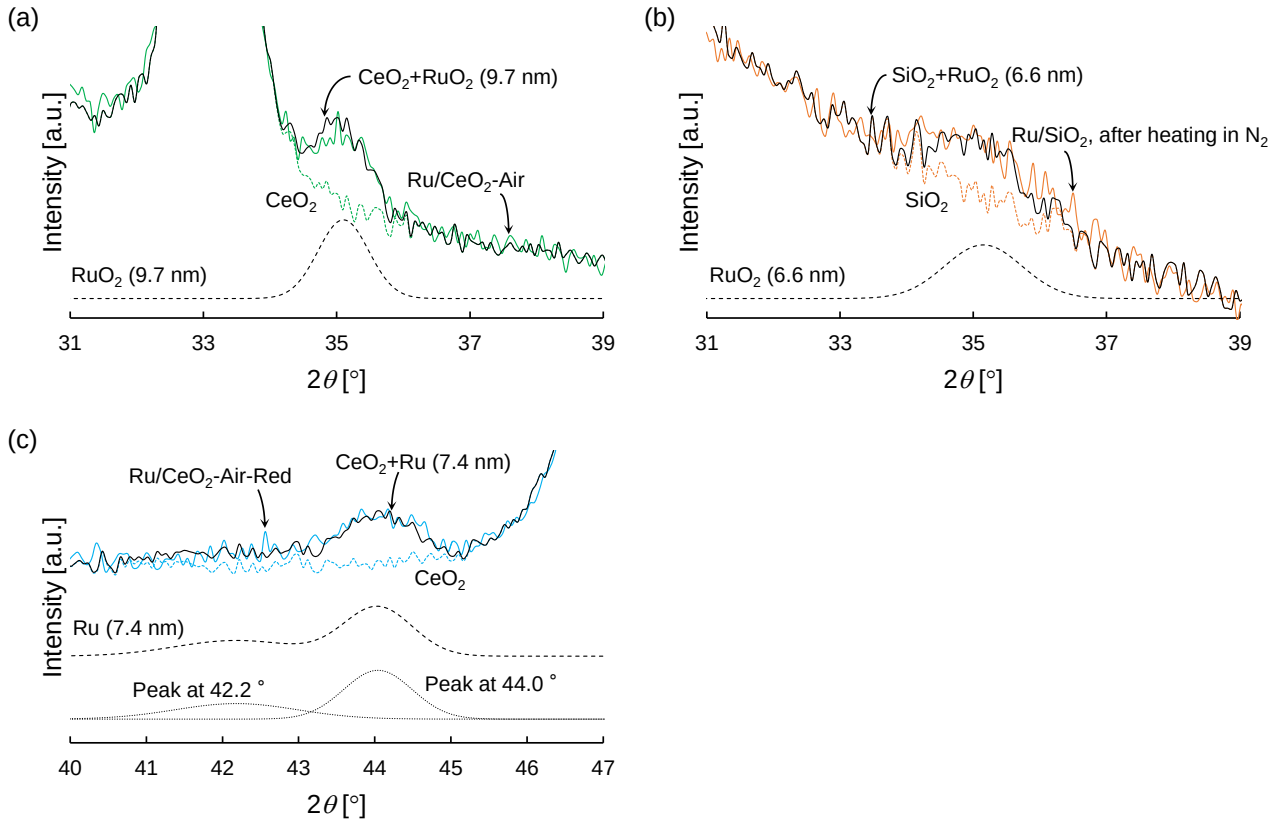

Figure S9. Curve fitting of XRD patterns of (a) Ru/CeO_2-Air, (b) Ru/SiO_2, after heating in N_2, and (c) Ru/CeO_2-Air-Red with support and RuO_2 phase.

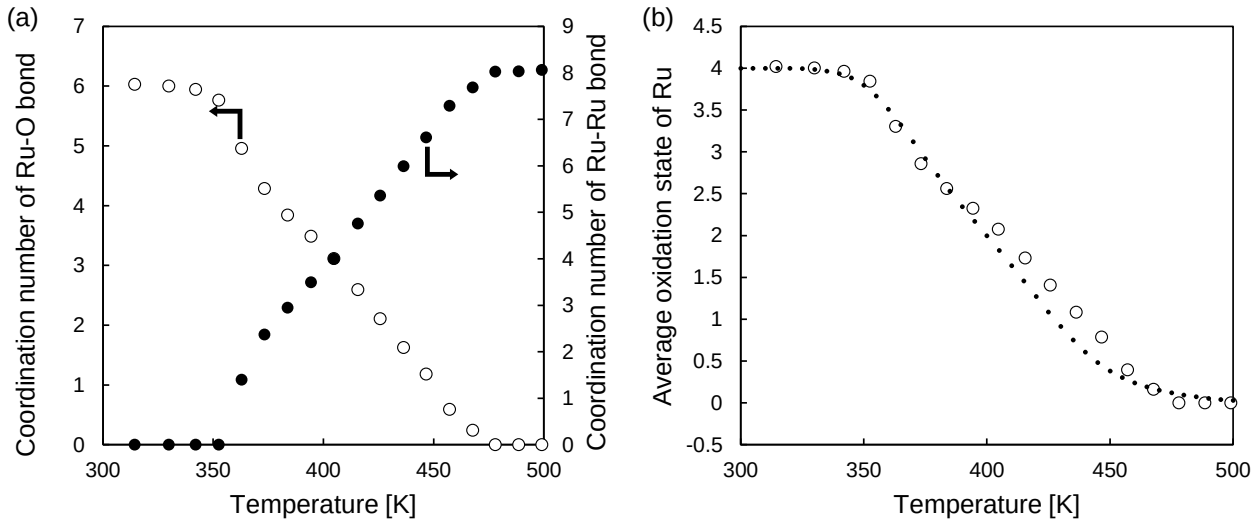

Figure S10. The detailed results of Ru *K*-edge EXAFS analysis of Ru/SiO_2 during the reduction. (a) Coordination numbers from curve fitting of Ru *K*-edge EXAFS analysis (Table S4). ○: Coordination number of Ru-O; ●: Coordination number of Ru-Ru. (b) Average valence of Ru as a function of reduction temperature. ○: From Ru *K*-edge EXAFS analysis (Table S4). The average valence of Ru was calculated by $4\times CN_{Ru\text{-}O}/6$. Dotted line: H_2 consumption in the H_2-TPR profile (Figure 8(a)).

Calculation of the number of Ru atoms in one particle. The number of Ru atoms in one RuO_2 and Ru particle of Ru/CeO_2-Air (9.7 nm) and Ru/CeO_2-Air-Red (7.4 nm) was calculated by eq. (S1) and eq. (S2), respectively as follows.

$$\frac{\frac{4}{3}\pi\times\left(\frac{9.7\times10^{-7}}{2}\,[\mathrm{cm}]\right)^3\times 6.77\,[\mathrm{g/cm^3}]}{133.07\,[\mathrm{g/mol}]}\times 6.02\times10^{23}\,[\mathrm{mol^{-1}}] = 1.46\times10^4 \approx 15000 \quad \text{(S1)}$$

$$\frac{\frac{4}{3}\pi\times\left(\frac{7.4\times10^{-7}}{2}\,[\mathrm{cm}]\right)^3\times 12.06\,[\mathrm{g/cm^3}]}{101.07\,[\mathrm{g/mol}]}\times 6.02\times10^{23}\,[\mathrm{mol^{-1}}] = 1.52\times10^4 \approx 15000 \quad \text{(S2)}$$