Supporting Information

Formation, dynamics, and long-term stability of Mn- and Fe-promoted Rh/SiO_2 catalysts in CO hydrogenation

Phil Preikschas,*[,a] Julia Bauer,[a] Kristian Knemeyer,[a] Raoul Naumann d'Alnoncourt,*[,a] Ralph Kraehnert,[a] and Frank Rosowski [a,b]

[a] BasCat, UniCat BASF JointLab, Technische Universität Berlin, Hardenbergstraße 36, Sekr. EW-K01, 10623 Berlin
[b] BASF SE, Process Research and Chemical Engineering, Heterogeneous Catalysis, Carl-Bosch-Straße 38, 67056 Ludwigshafen

Corresponding Authors
*Email: r.naumann@bascat.tu-berlin.de, p.preikschas@bascat.tu-berlin.de

Table of Contents

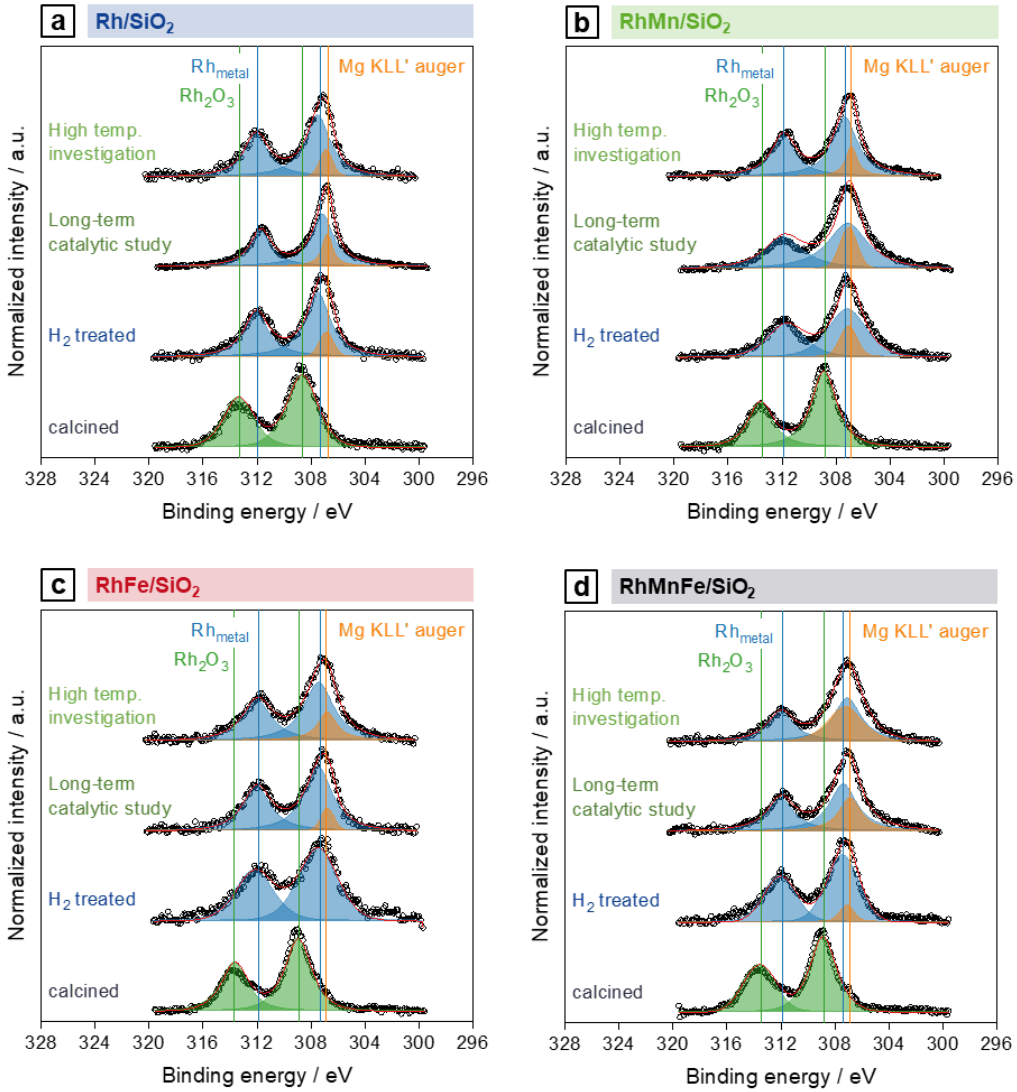

Figure S1. Rh 3d XP spectra of (a) Rh/SiO_2, (b) $RhMn/SiO_2$, (c) $RhFe/SiO_2$, and (d) $RhMnFe/SiO_2$ in four different states: calcined, reduced, after long-term catalytic study, and after high temperature stability investigation.

Table S1. Binding energy shifts of promoted and pure Rh/SiO_2 after different treatments.

Sample	Treatment	Binding energy (eV)		
		Rh 3d 5/2	**Mn 2p 3/2**	**Fe 2p 3/2**
Rh/SiO_2	calcination	308.6	-	-
	reduction	307.4	-	-
	high temperature	307.4	-	-
	long-term study	307.1	-	-
$RhMn/SiO_2$	calcination	308.8	641.6	-
	reduction	306.9	641.9	-
	high temperature	307.3	642.3	-
	long-term study	307.3	642.3	-
$RhFe/SiO_2$	calcination	308.9	-	710.7
	reduction	307.4	-	710.3
	high temperature	307.4	-	710.5
	long-term study	307.3	-	710.3
$RhMnFe/SiO_2$	calcination	308.9	641.5	710.6
	reduction	307.4	641.9	710.4
	high temperature	307.3	642.0	710.7
	long-term study	307.0	642.2	710.5

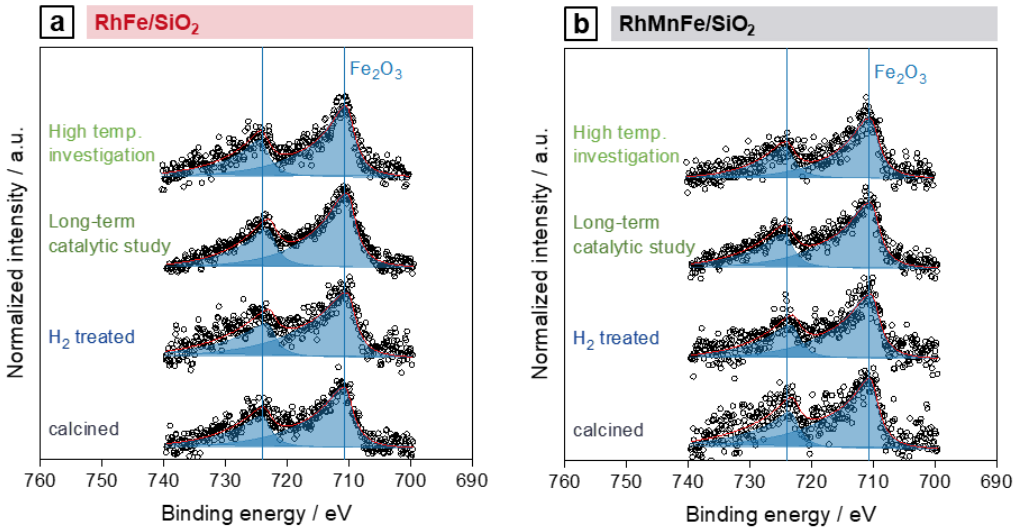

Figure S2. Fe 2p XP spectra of (a) $RhFe/SiO_2$ and (b) $RhMnFe/SiO_2$ in four different states: calcined, reduced, after long-term catalytic study, and high temperature stability investigation.

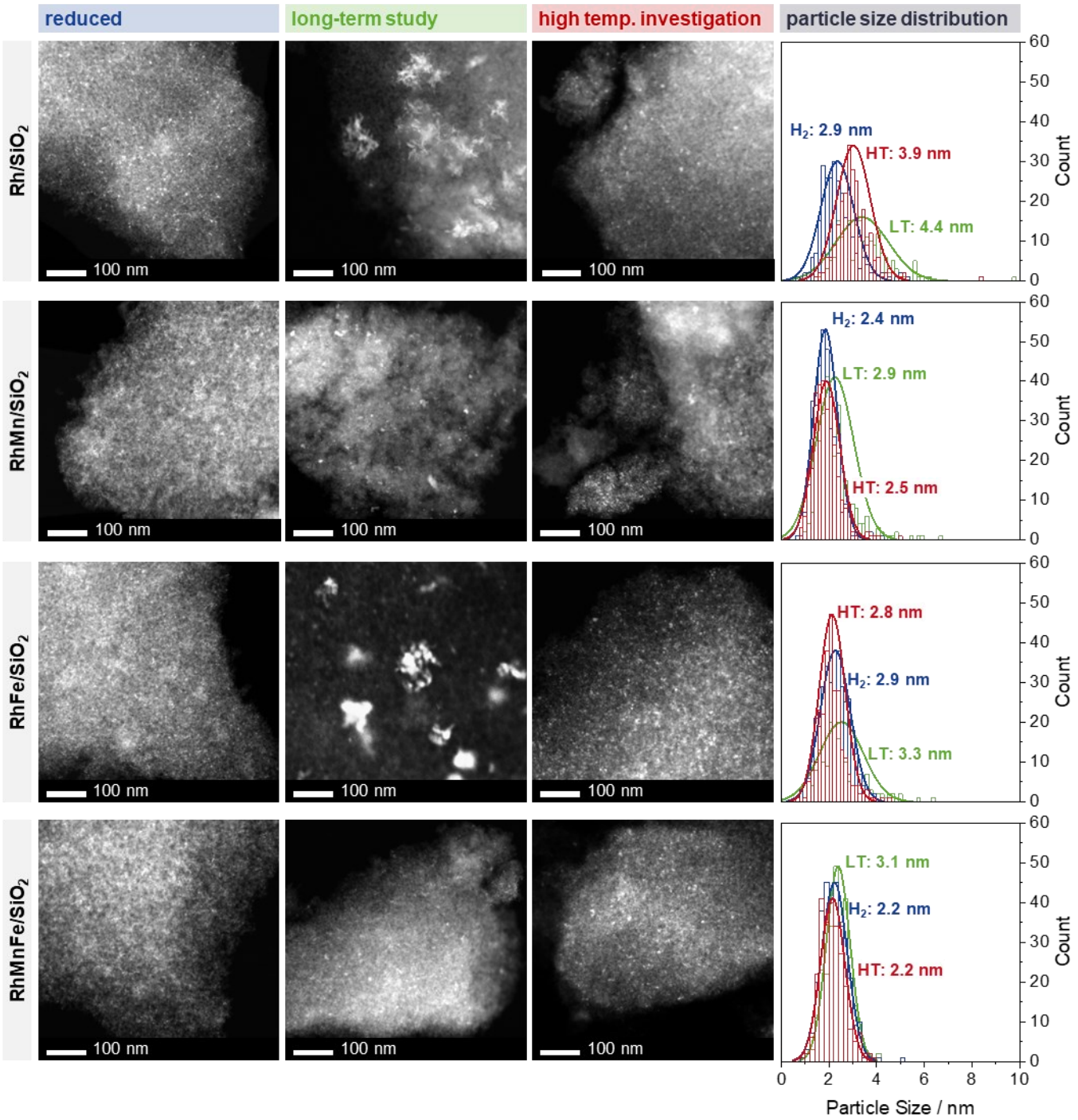

Figure S3. Overview HAADF-STEM images of Rh/SiO_2, $RhMn/SiO_2$, $RhFe/SiO_2$, and $RhMnFe/SiO_2$ and corresponding particle size distributions.

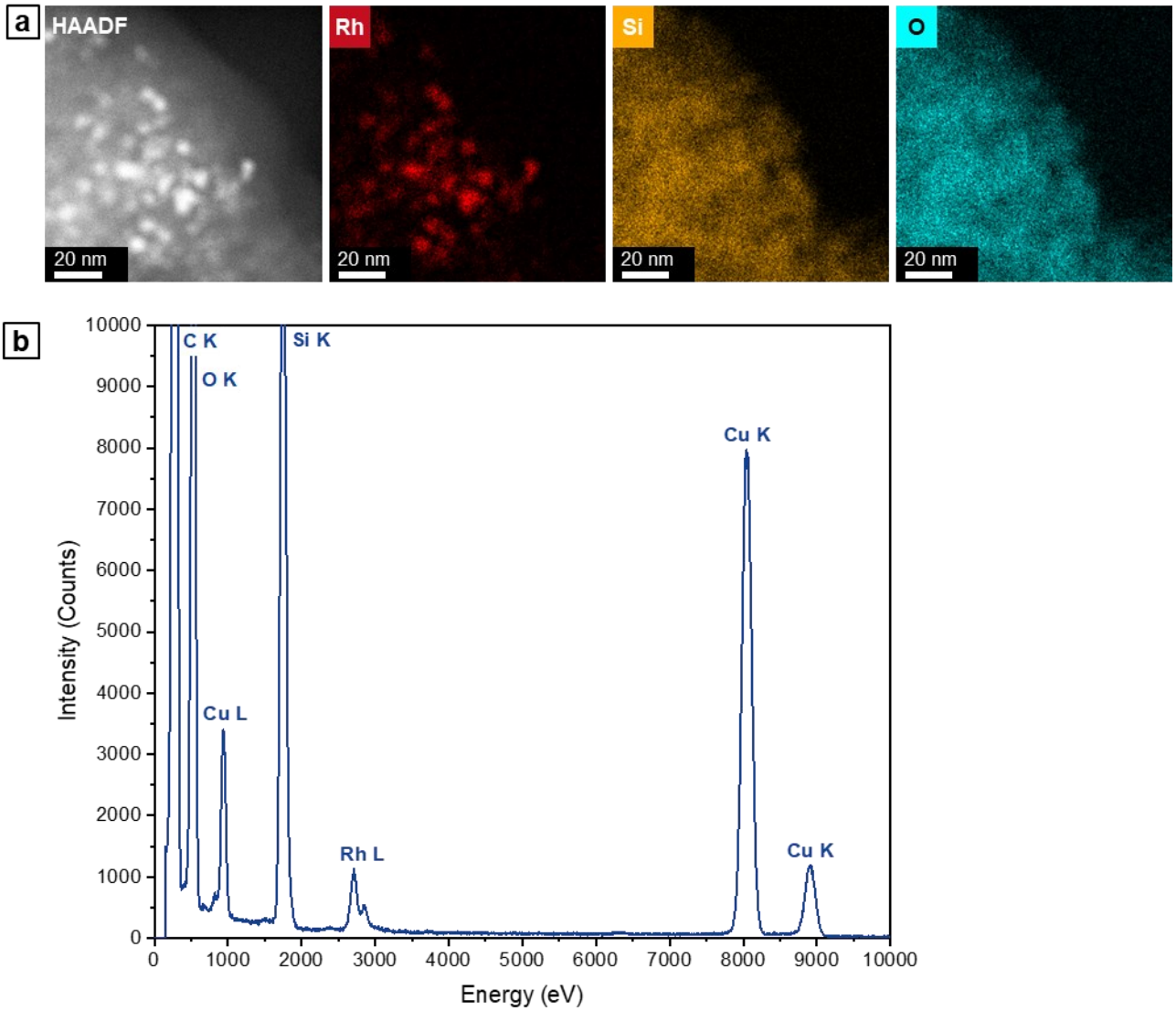

Figure S4. STEM-EDX analysis of reduced Rh/SiO_2 catalyst: (a) HAADF micrograph, single-element maps (Rh L, Si K, O K), and (b) corresponding EDX spectrum.

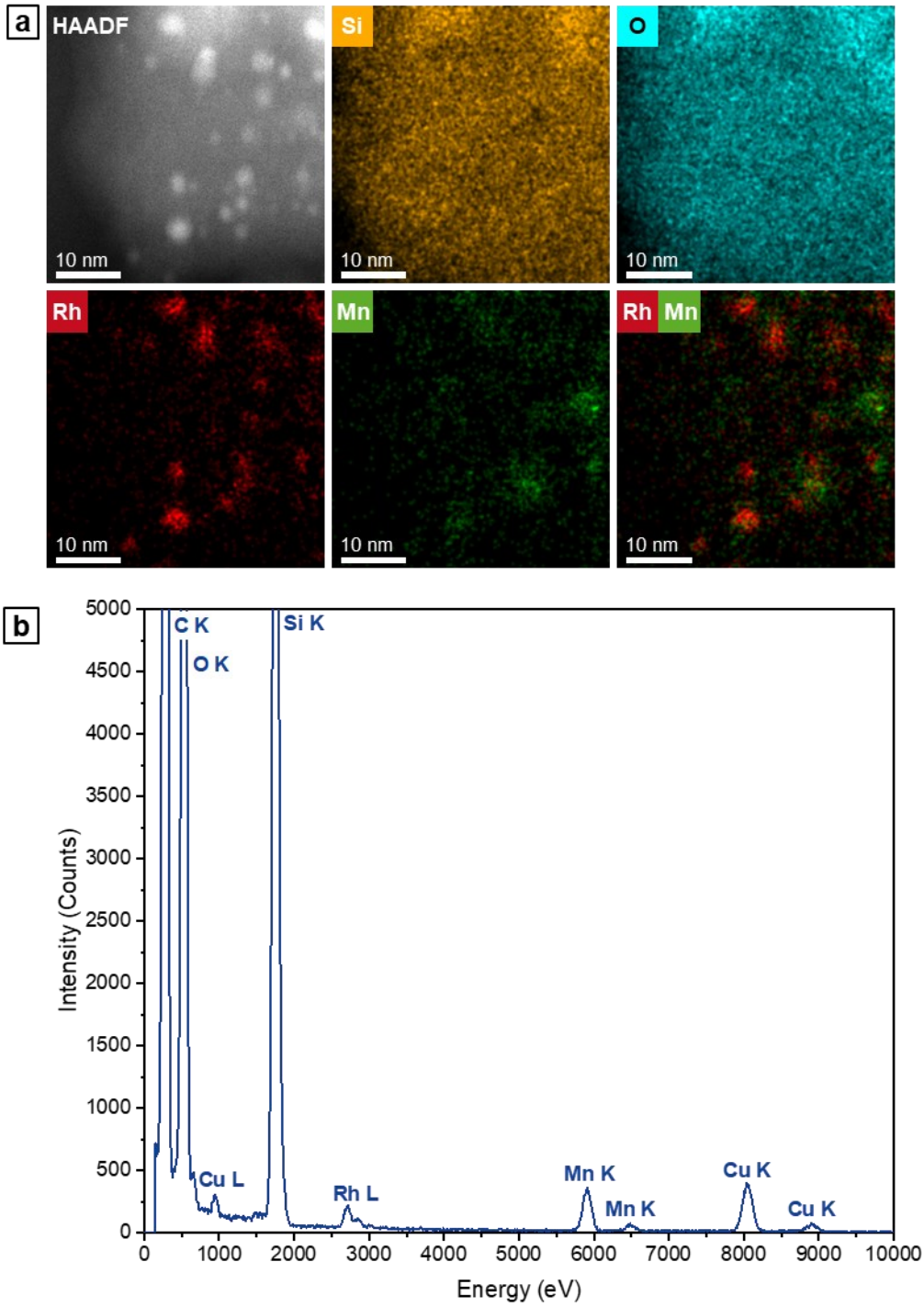

Figure S5. STEM-EDX analysis of reduced RhMn/SiO_2 catalyst: (a) HAADF micrograph, single-element maps (Rh L, Si K, O K, Mn K), superimposed map of Rh L and Mn K, and (b) corresponding EDX spectrum.

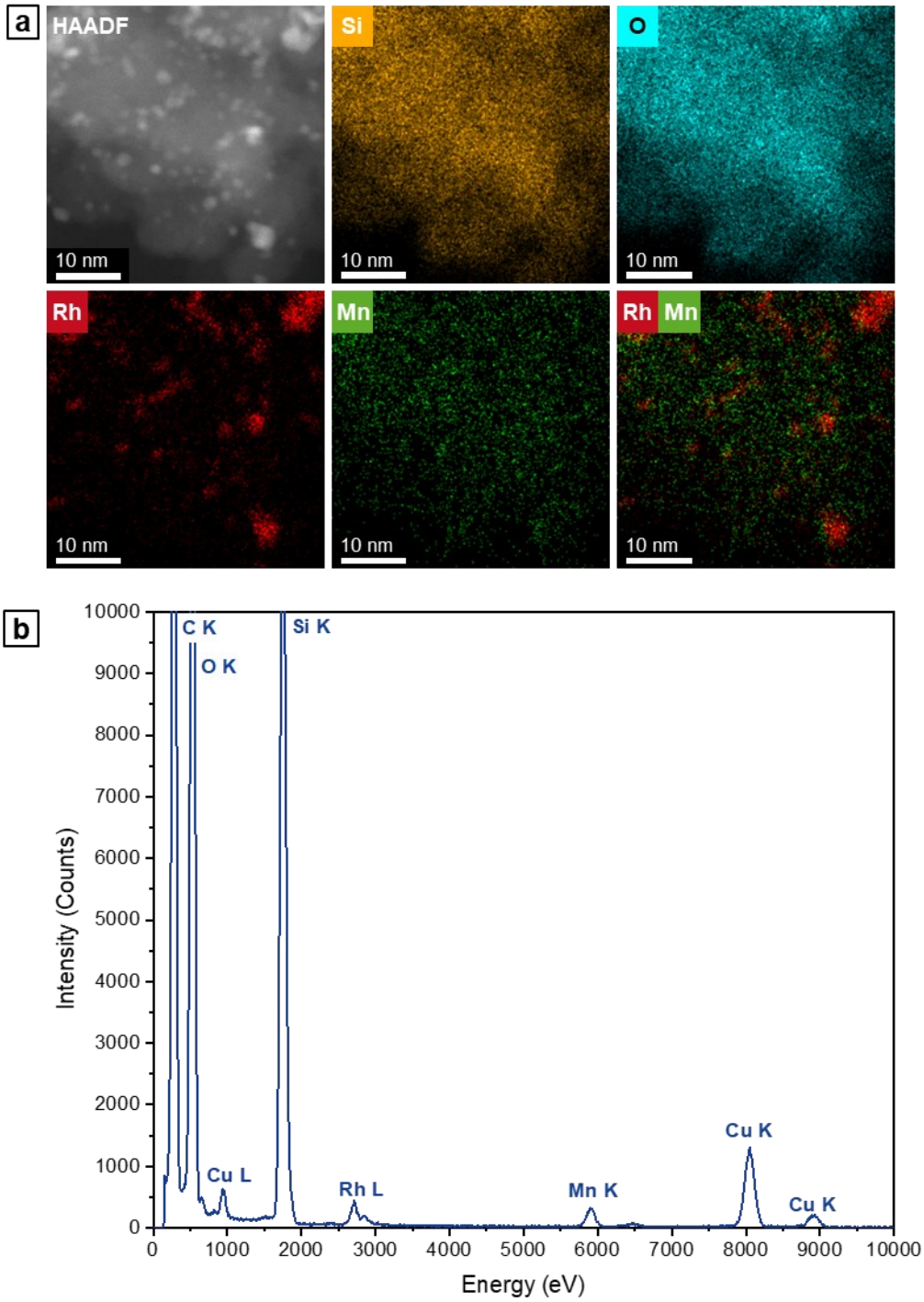

Figure S6. STEM-EDX analysis of RhMn/SiO_2 catalyst after long-term catalytic study: (a) HAADF micrograph, single-element maps (Rh L, Si K, O K, Mn K), superimposed map of Rh L and Mn K, and (b) corresponding EDX spectrum.

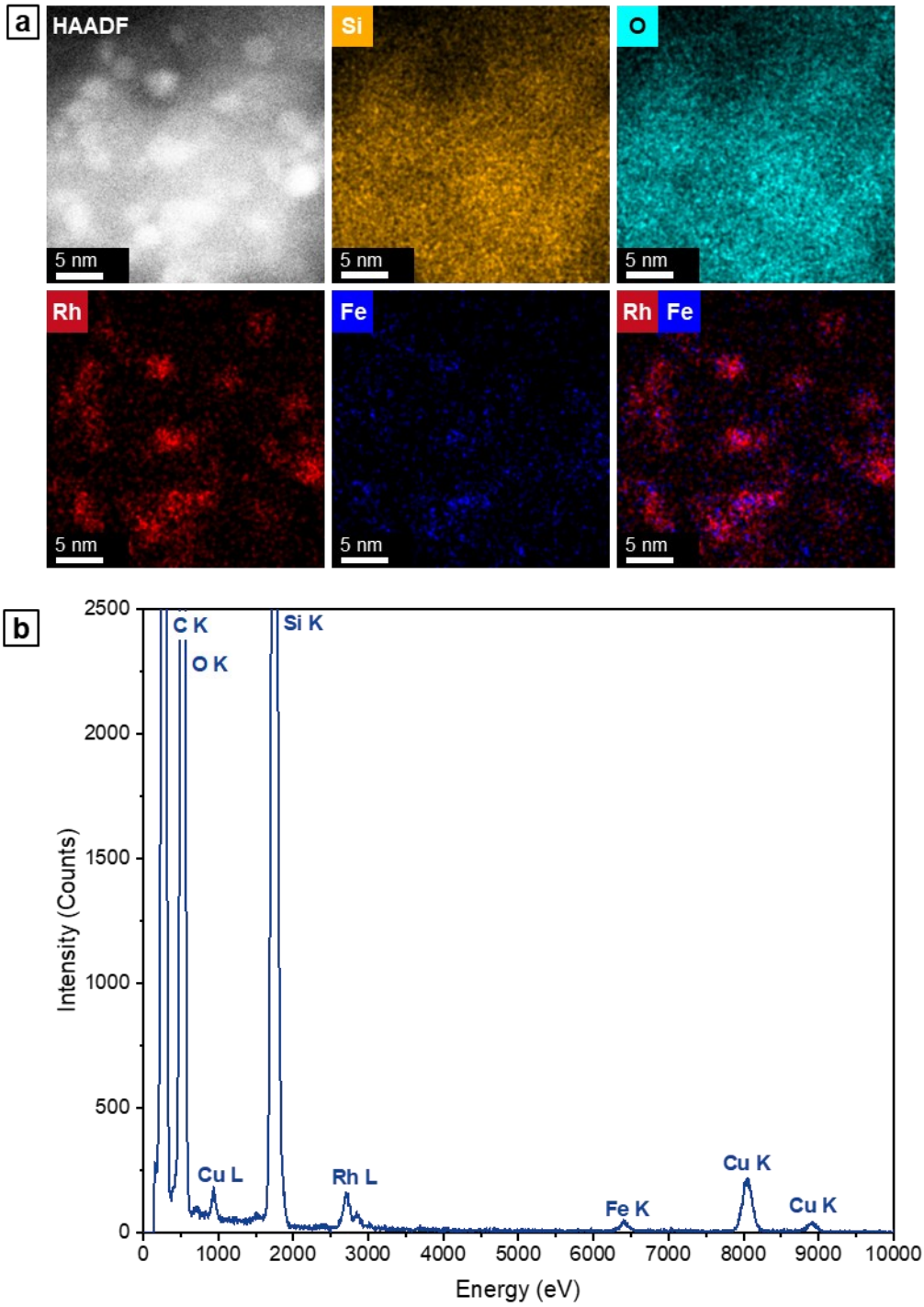

Figure S7. STEM-EDX analysis of reduced RhFe/SiO_2 catalyst: (a) HAADF micrograph, single-element maps (Rh L, Si K, O K, Fe K), superimposed map of Rh L and Fe K, and (b) corresponding EDX spectrum.

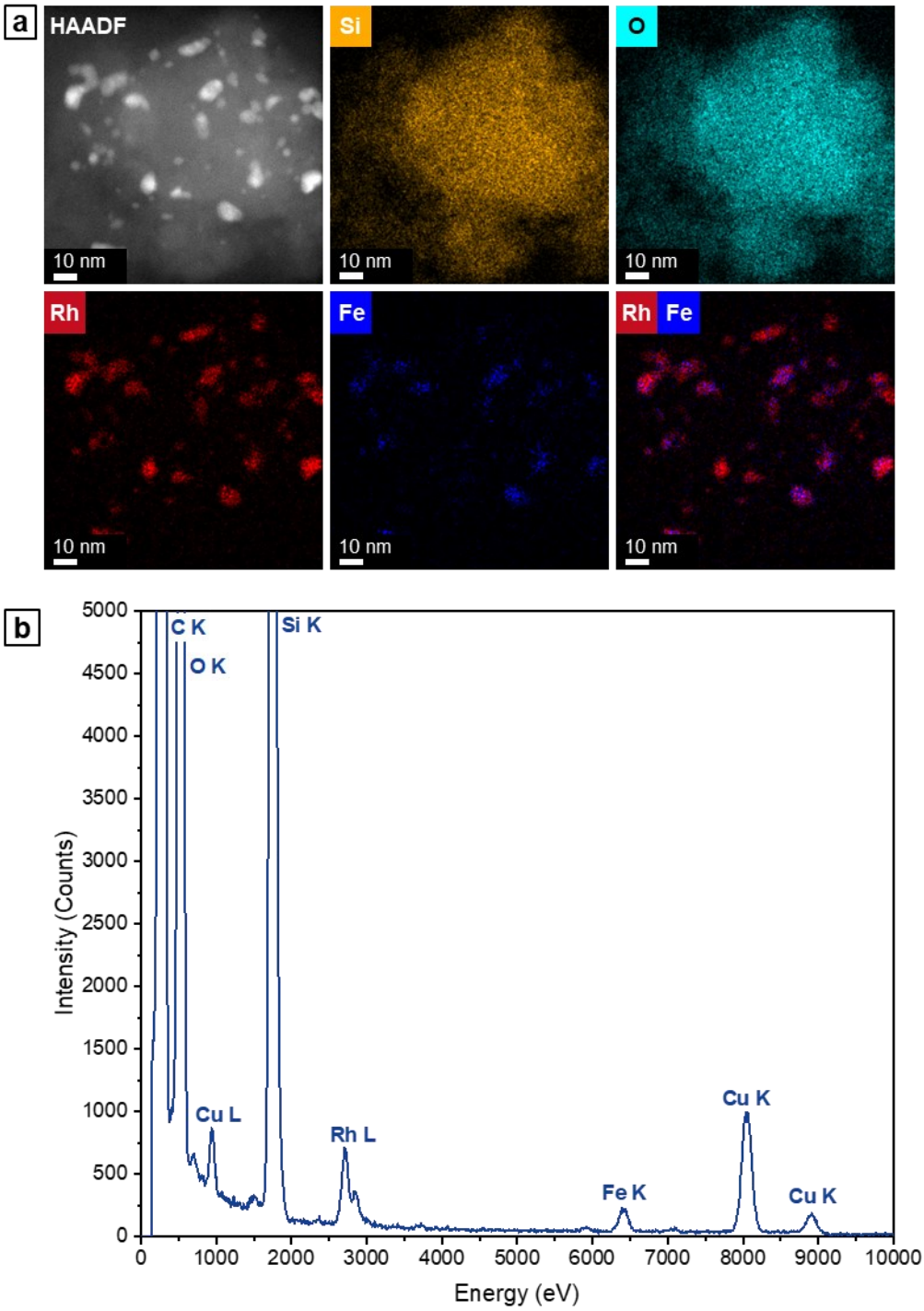

Figure S8. STEM-EDX analysis of $RhFe/SiO_2$ catalyst after long-term catalytic study: (a) HAADF micrograph, single-element maps (Rh L, Si K, O K, Fe K), superimposed map of Rh L and Fe K, and (b) corresponding EDX spectrum.

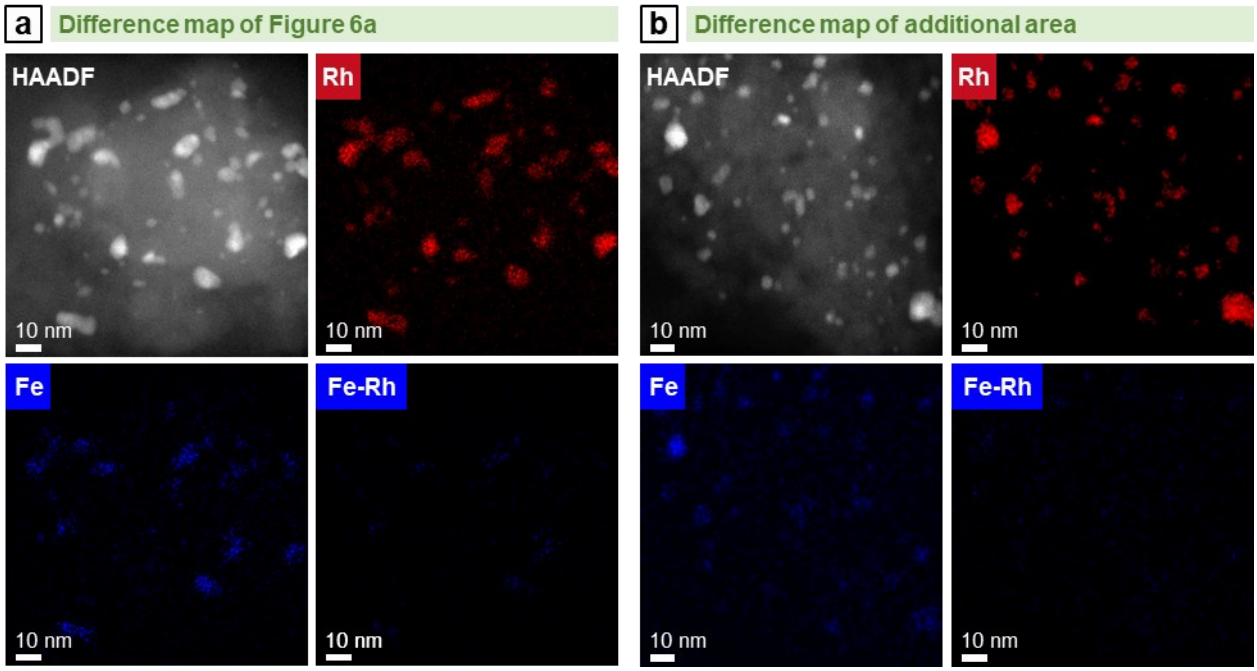

Figure S9. STEM-EDX mapping of RhFe/SiO_2 after long-term catalytic study (54 bar, max. 260 °C; 530 h on stream) within two different domains. Rh L and Fe K EDX signals were used. For additional single-element maps and corresponding EDX spectrum of (a) see Figure S8 and (b) see Figure S10.

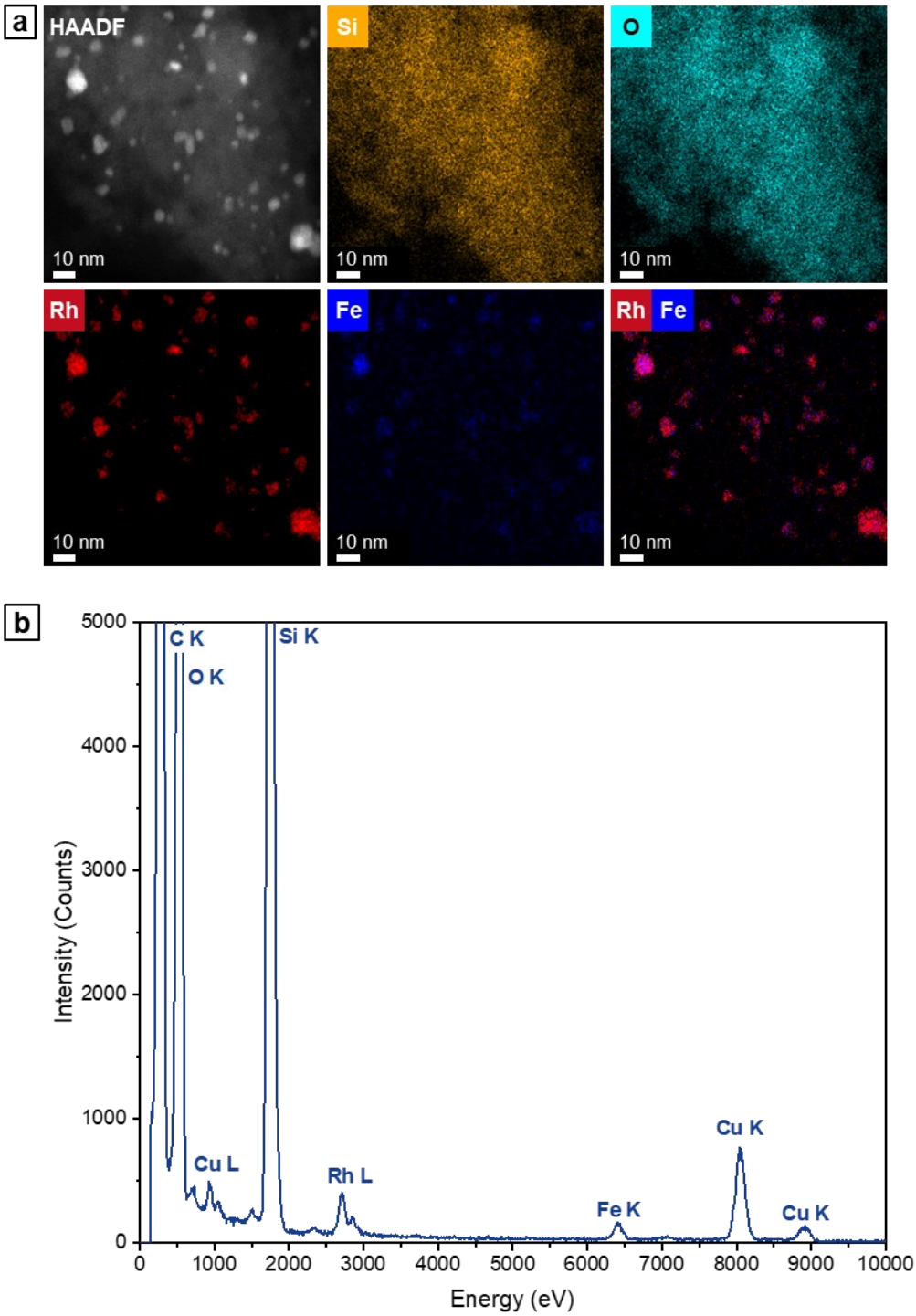

Figure S10. Additional STEM-EDX analysis of RhFe/SiO_2 catalyst after long-term catalytic study: (a) HAADF micrograph, single-element maps (Rh L, Si K, O K, Fe K), superimposed map of Rh L and Fe K, and (b) corresponding EDX spectrum.

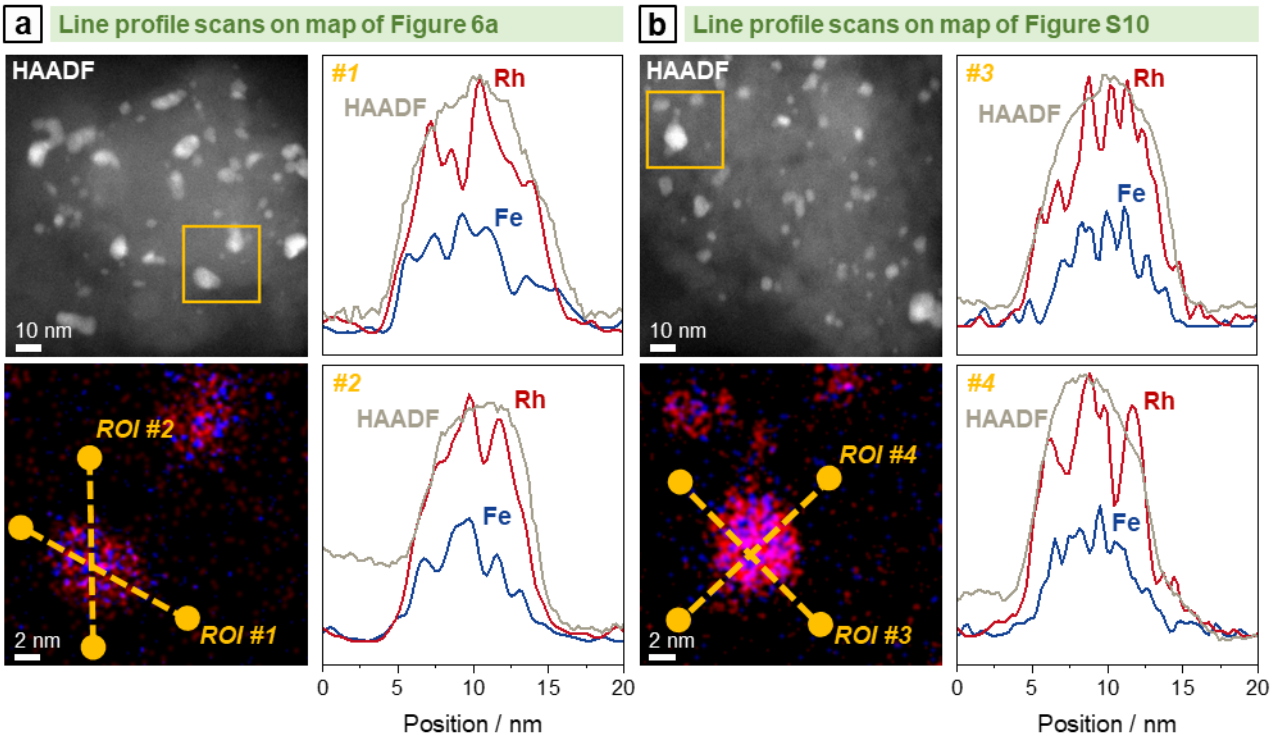

Figure S11. Additional STEM-EDX line profile analysis of $RhFe/SiO_2$ catalyst after long-term catalytic study from two different domains. For additional single-element maps and corresponding EDX spectrum of (a) see Figure S8 and (b) see Figure S10.

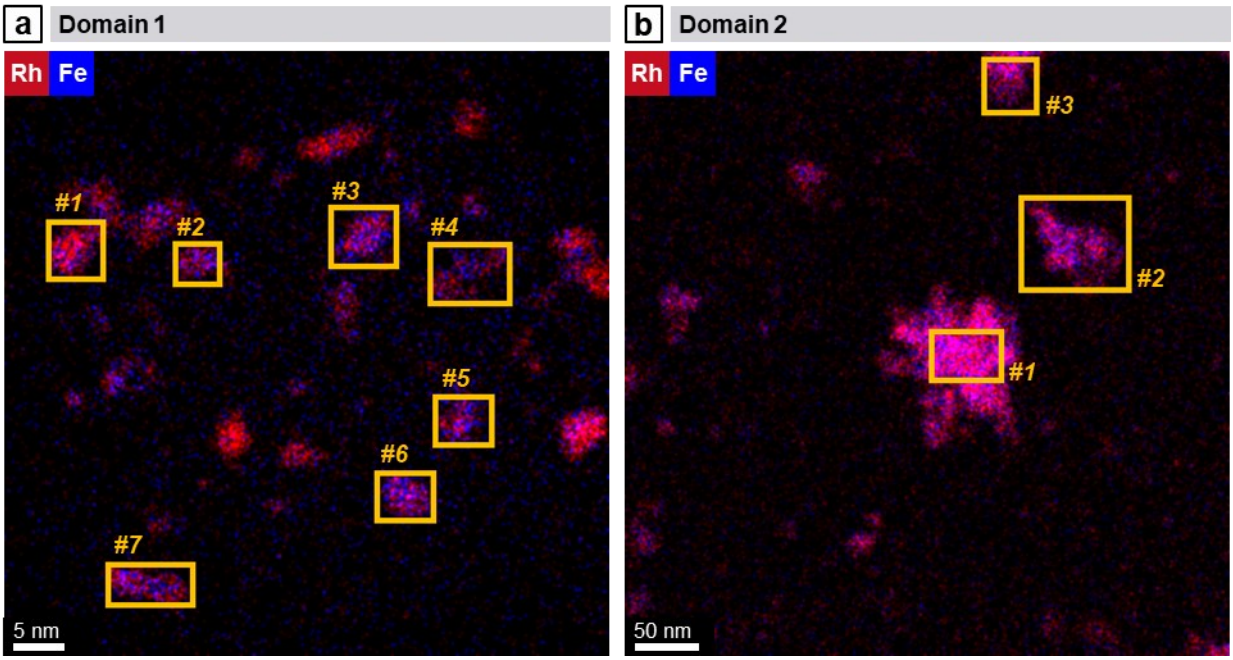

Figure S12. STEM-EDX area-selective analysis of $RhFe/SiO_2$ after long-term catalytic study. Investigated areas are highlighted in yellow. Corresponding elemental compositions area provided in Table S2.

Table S2. Elemental composition of Rh and Fe containing particles and aggregates from STEM area-selective analysis.

Area	Composition / atom-%				Rh:Fe ratio
	Si	O	Rh	Fe	
Domain 1	31 ± 7	67 ± 9	1.5 ± 0.3	0.5 ± 0.1	3.00
Area #1	19 ± 4	48 ± 7	28 ± 5	4.9 ± 0.9	5.71
Area #2	30 ± 7	63 ± 8	4.4 ± 0.9	2.0 ± 0.4	2.20
Area #3	29 ± 7	66 ± 8	3.0 ± 0.6	1.6 ± 0.3	1.88
Area #4	30 ± 7	67 ± 8	2.6 ± 0.5	0.8 ± 0.2	3.25
Area #5	30 ± 7	65 ± 8	3.5 ± 0.7	1.4 ± 0.3	2.50
Area #6	28 ± 6	60 ± 7	8.6 ± 1.5	3.6 ± 0.6	2.39
Area #7	23 ± 5	52 ± 7	19 ± 3	6.0 ± 1.0	3.17
Domain 2	35 ± 8	64 ± 9	0.8 ± 0.2	0.4 ± 0.1	2.00
Area #1	28 ± 6	53 ± 6	11 ± 2	7.7 ± 1.3	1.42
Area #2	33 ± 8	62 ± 8	2.9 ± 0.5	2.1 ± 0.4	1.38
Area #3	29 ± 7	60 ± 7	6.1 ± 1.1	4.2 ± 0.7	1.45

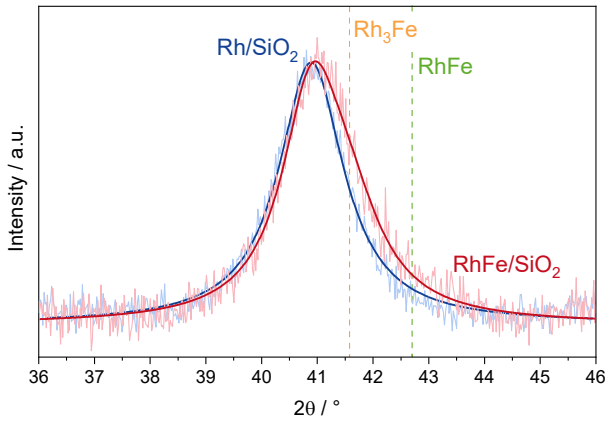

Figure S13. X-ray diffractograms after long-term catalytic study of Rh/SiO_2 (blue) and $RhFe/SiO_2$ (red) in the region of the (111) reflections. For the full X-ray diffractograms see Figure 1. RhFe reference (green; C25-1408) has been taken from ICDD database. Rh_3Fe reference (orange; 347421) has been calculated from Open Quantum Materials Database (OQMD).

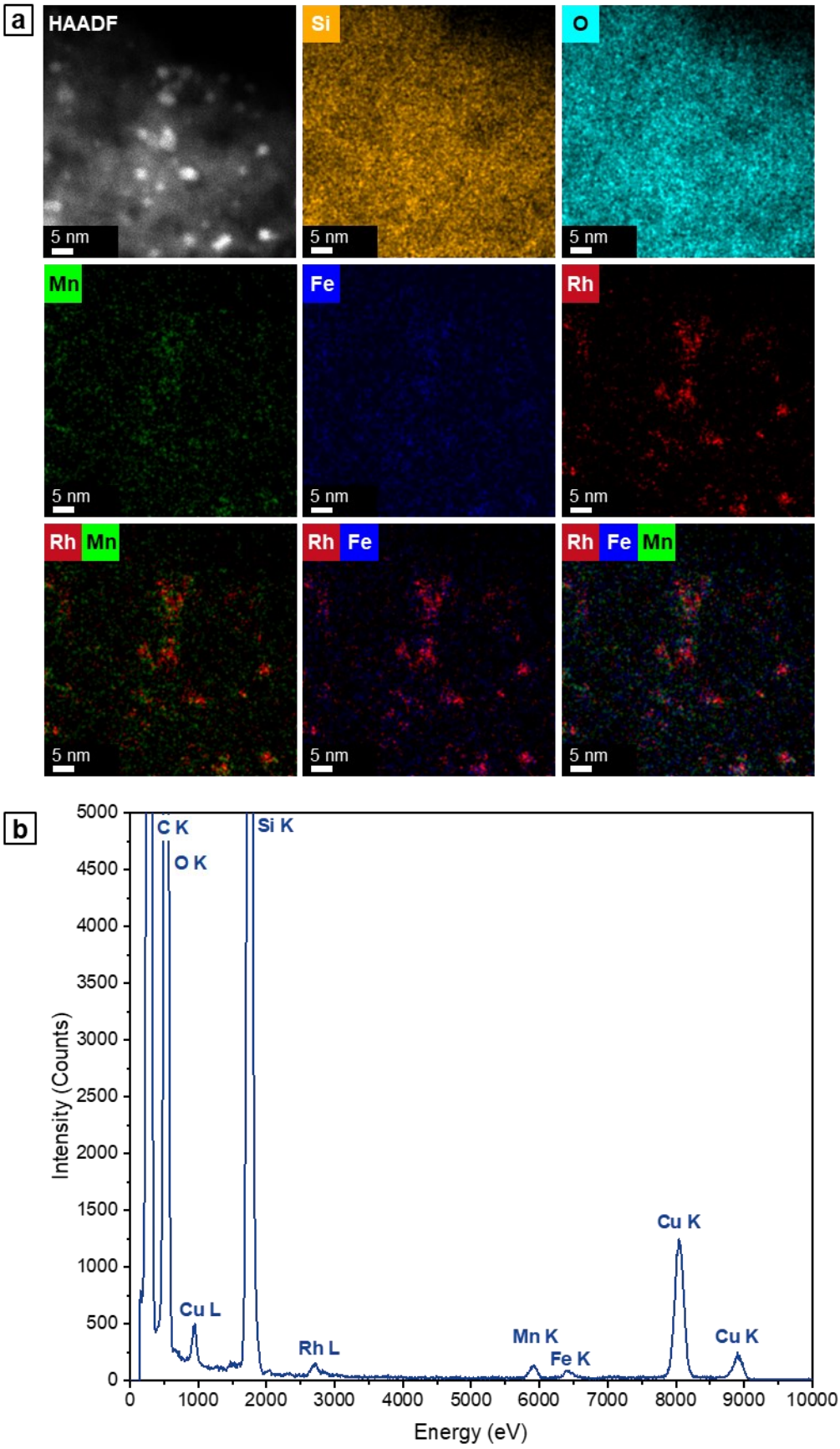

Figure S14. STEM-EDX analysis of reduced RhMnFe/SiO_2 catalyst: (a) HAADF micrograph, single-element maps (Rh L, Si K, O K, Fe K, Mn K), superimposed maps of Rh L, Mn K, and Fe K, and (b) corresponding EDX spectrum.

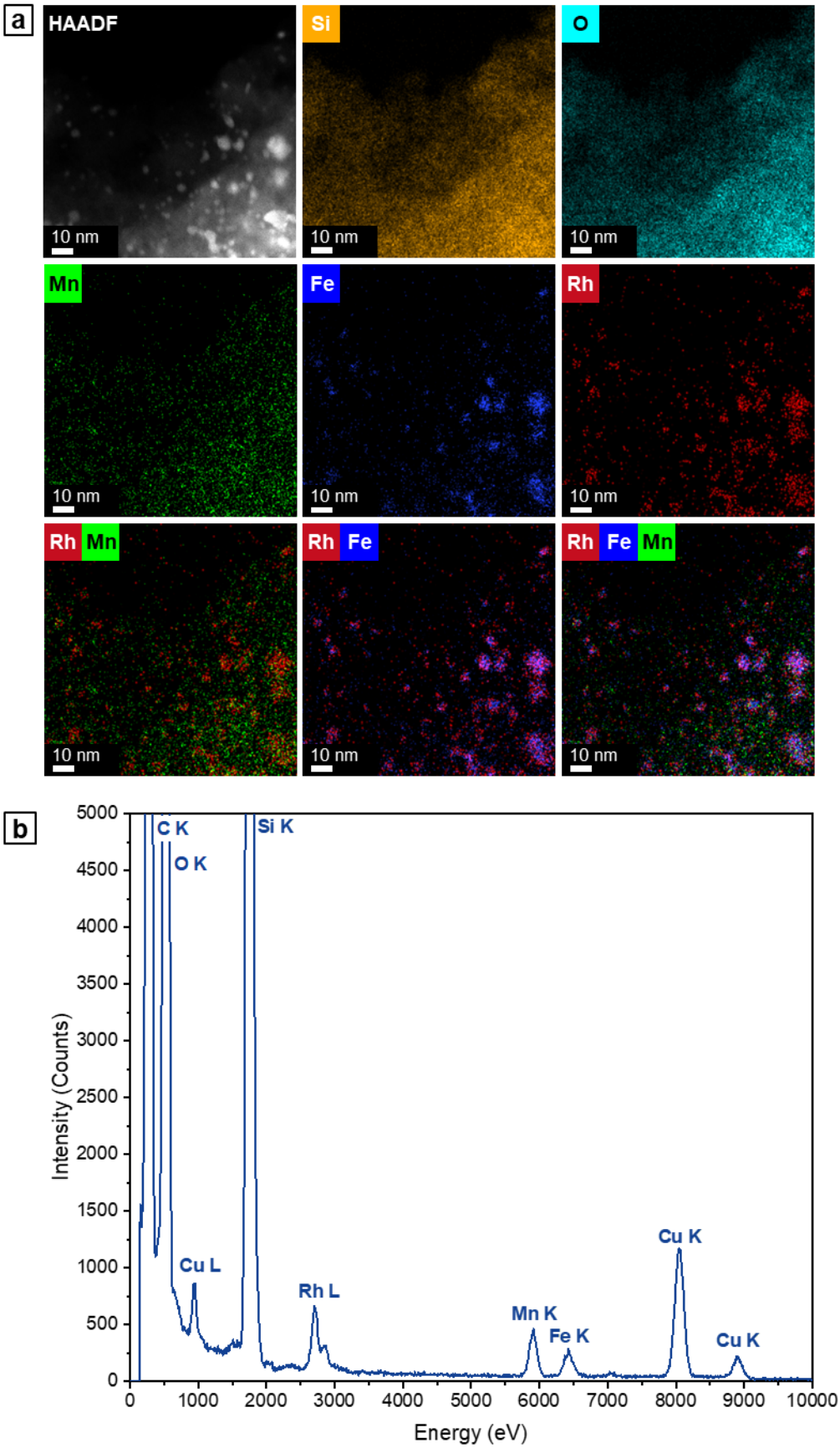

Figure S15. STEM-EDX analysis of RhMnFe/SiO_2 catalyst after long-term catalytic study: (a) HAADF micrograph, single-element maps (Rh L, Si K, O K, Fe K, Mn K), superimposed maps of Rh L, Mn K, and Fe K, and (b) corresponding EDX spectrum.

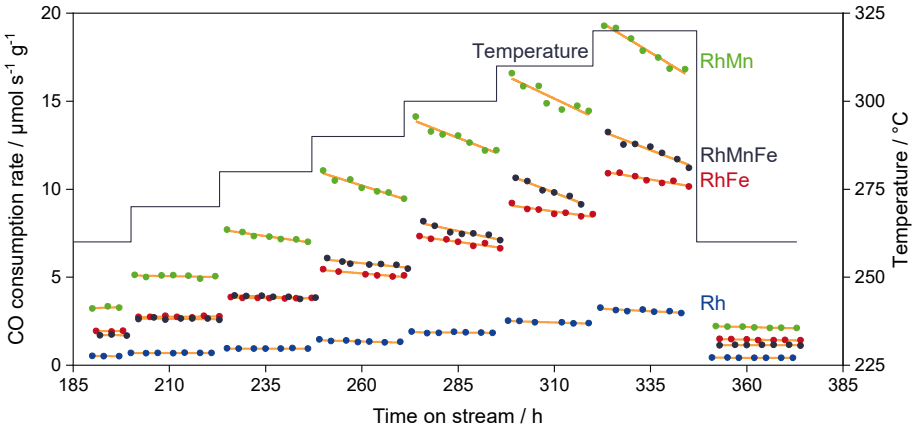

Figure S16. Linear regression for all four catalyst and each temperature step. Fit curves are highlighted in orange. Corresponding activity loss rates are given in Table S3.

Table S3. Activity loss rates from linear regression analysis at different temperatures.

Step	Temperature (°C)	Activity loss rate (µmol/s/g_{cal}/h_{TOS})			
		Rh	RhMn	RhFe	RhMn
1	260	0.00	0.01	0.00	0.00
2	270	0.00	0.00	0.00	0.00
3	280	0.00	-0.03	0.00	-0.01
4	290	-0.01	-0.07	-0.02	-0.02
5	300	0.00	-0.09	-0.03	-0.05
6	310	-0.01	-0.10	-0.03	-0.08
7	320	-0.01	-0.13	-0.04	-0.08
8	260	0.00	-0.01	0.00	0.00

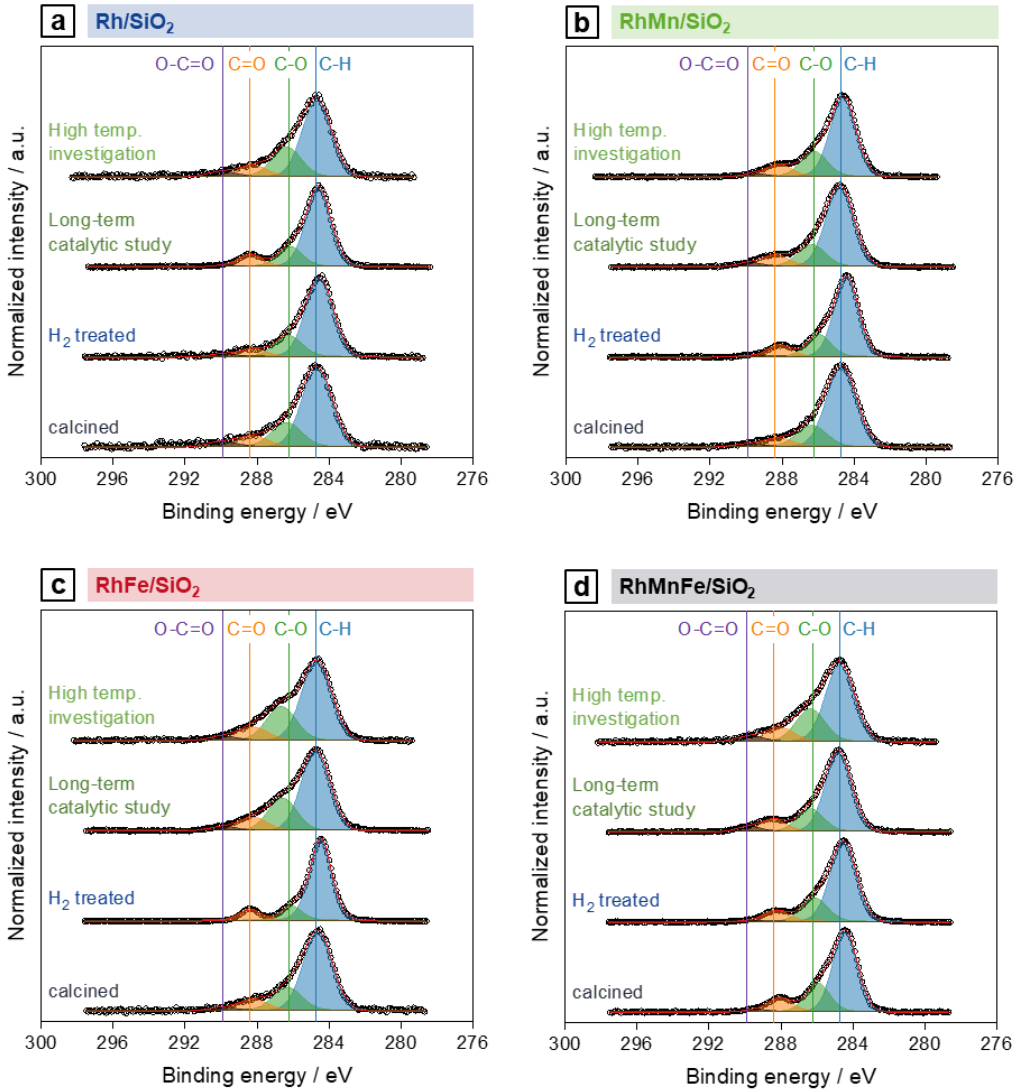

Figure S17. C 1s XP spectra of (a) Rh/SiO_2, (b) $RhMn/SiO_2$, (c) $RhFe/SiO_2$, and (d) $RhMnFe/SiO_2$ in four different states: calcined, reduced, after long-term catalytic study, and after high temperature stability investigation.

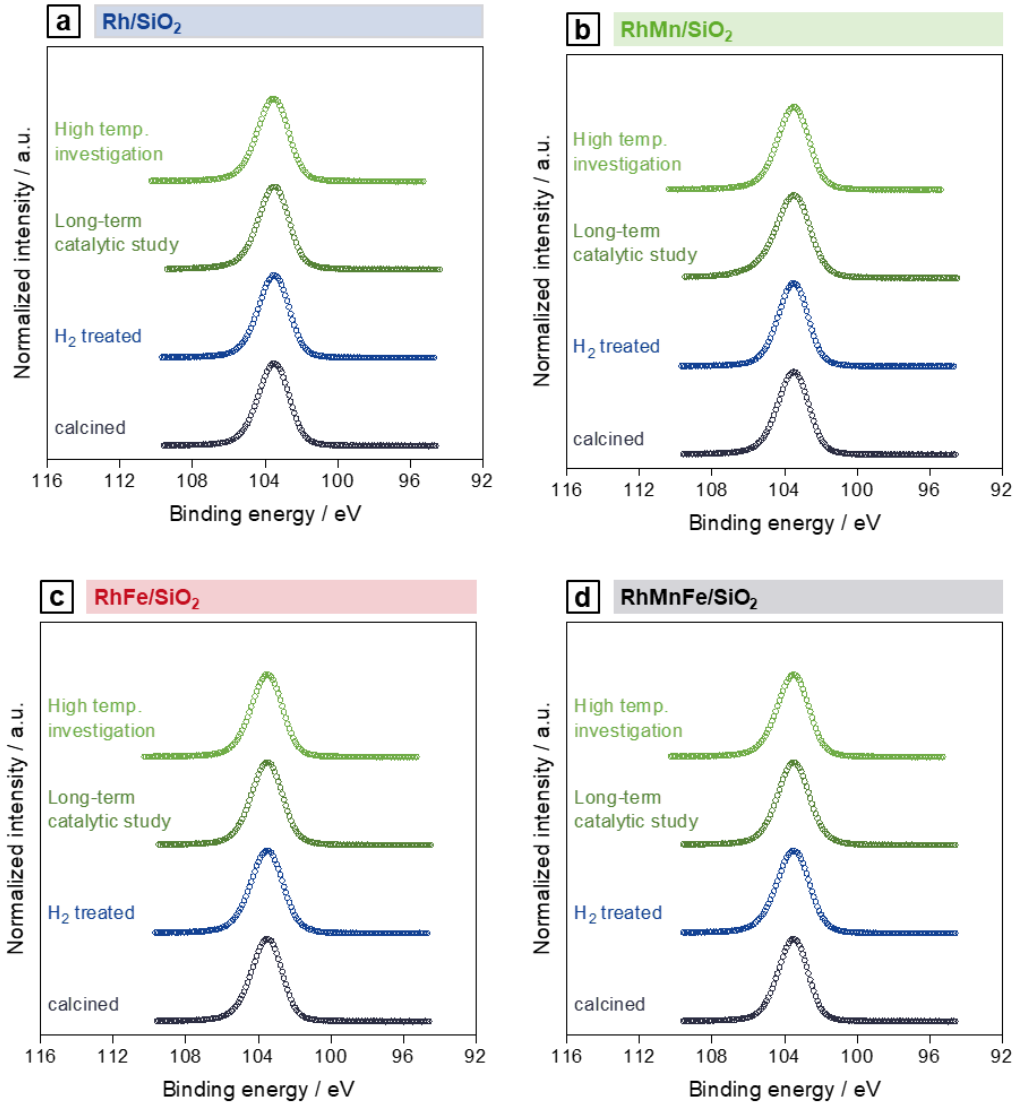

Figure S18. Si 2p XP spectra of (a) Rh/SiO_2, (b) $RhMn/SiO_2$, (c) $RhFe/SiO_2$, and (d) $RhMnFe/SiO_2$ in four different states: calcined, reduced, after long-term catalytic study, and after high temperature stability investigation.

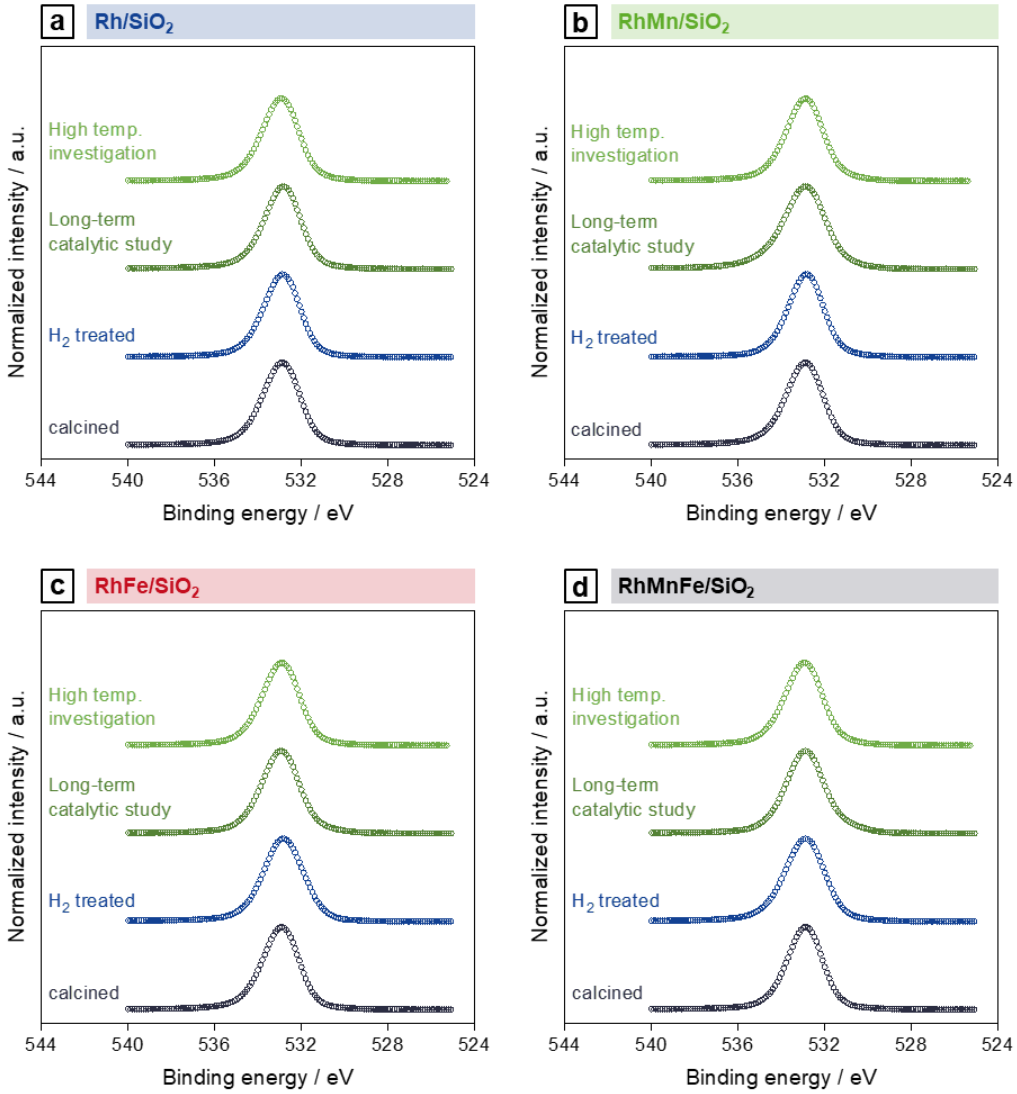

Figure S19. O 1s XP spectra of (a) Rh/SiO_2, (b) $RhMn/SiO_2$, (c) $RhFe/SiO_2$, and (d) $RhMnFe/SiO_2$ in four different states: calcined, reduced, after long-term catalytic study, and after high temperature stability investigation.

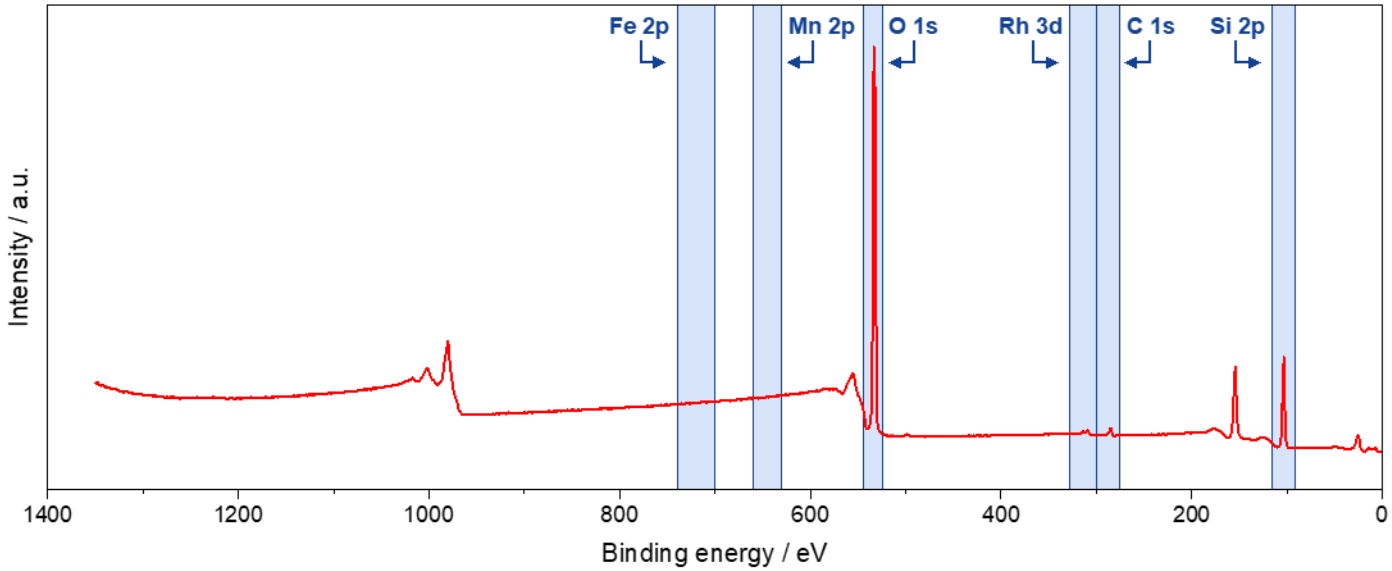

Figure S20. XP survey spectrum of calcined Rh/SiO_2 catalyst. Regions selected for high-resolution spectra are highlighted in blue.

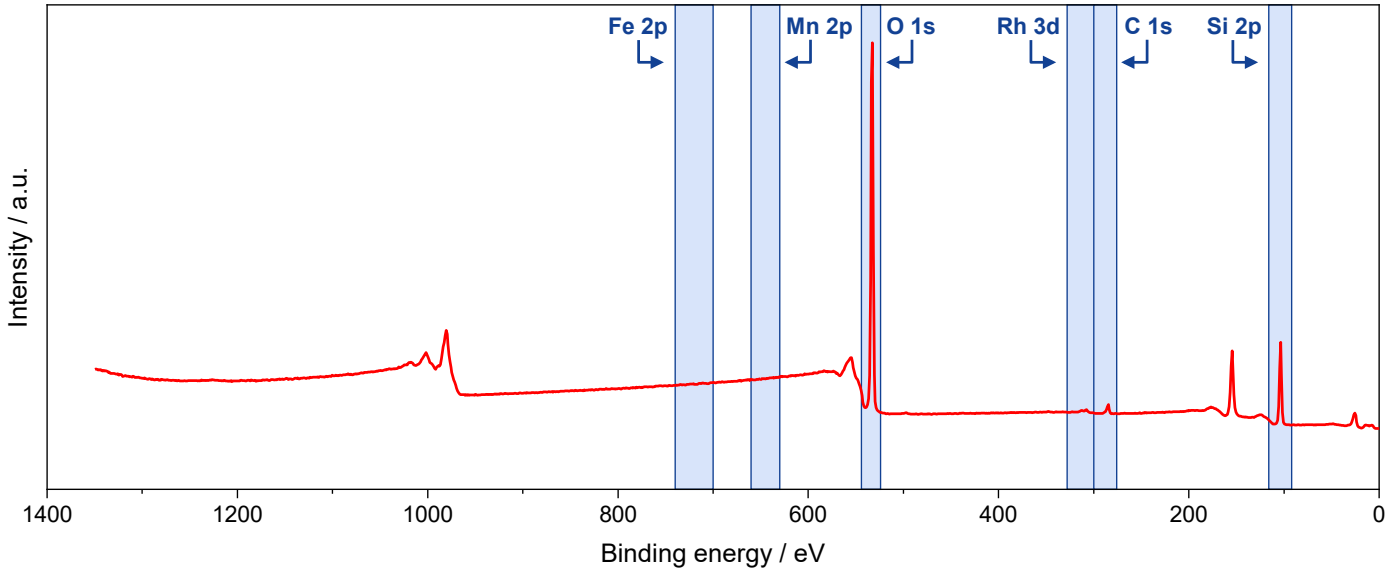

Figure S21. XP survey spectrum of reduced Rh/SiO_2 catalyst. Regions selected for high-resolution spectra are highlighted in blue.

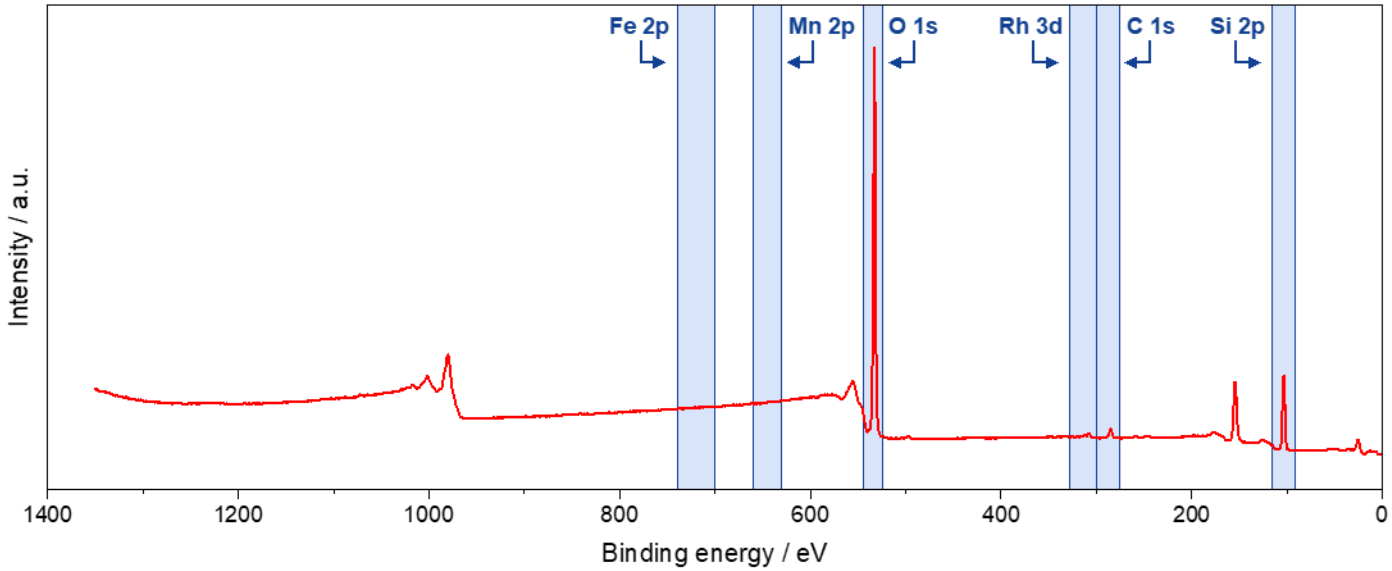

Figure S22. XP survey spectrum of Rh/SiO_2 catalyst after high temperature investigation. Regions selected for high-resolution spectra are highlighted in blue.

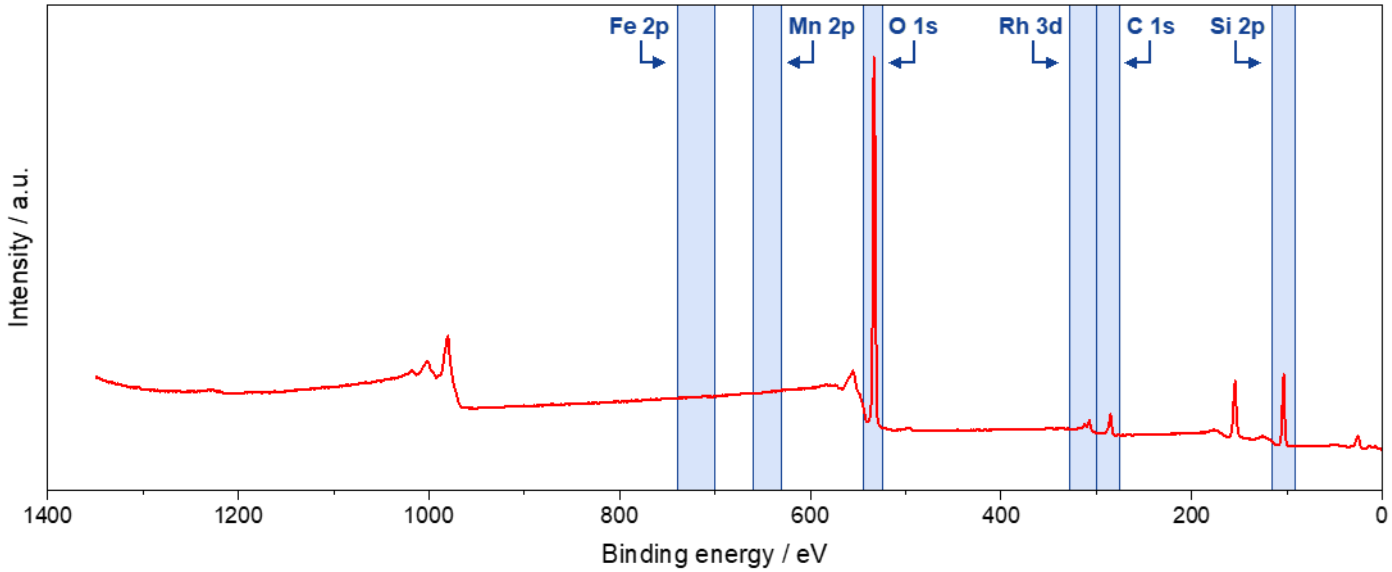

Figure S23. XP survey spectrum of Rh/SiO_2 catalyst after long-term study. Regions selected for high-resolution spectra are highlighted in blue.

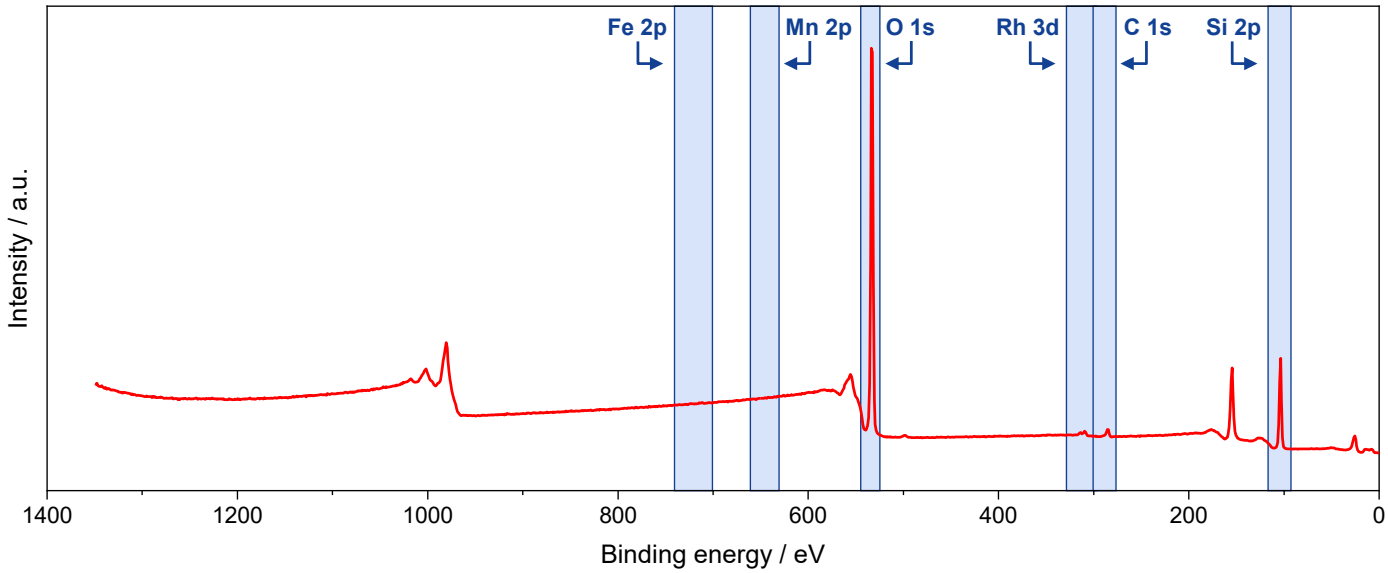

Figure S24. XP survey spectrum of calcined $RhMn/SiO_2$ catalyst. Regions selected for high-resolution spectra are highlighted in blue.

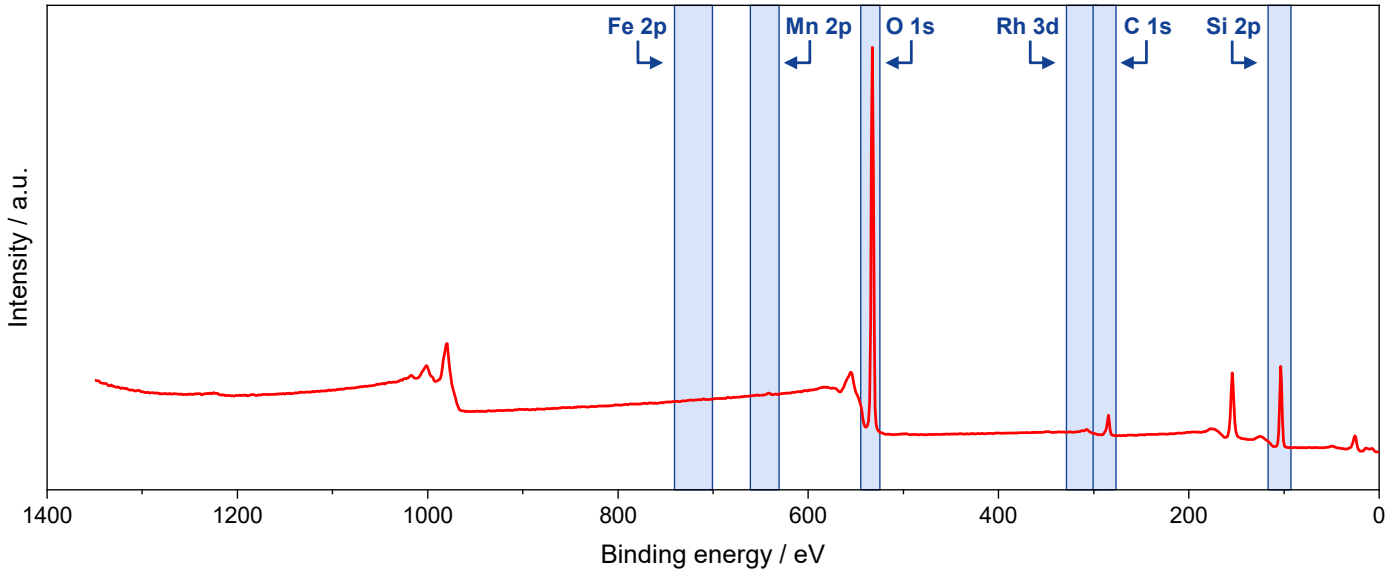

Figure S25. XP survey spectrum of reduced $RhMn/SiO_2$ catalyst. Regions selected for high-resolution spectra are highlighted in blue.

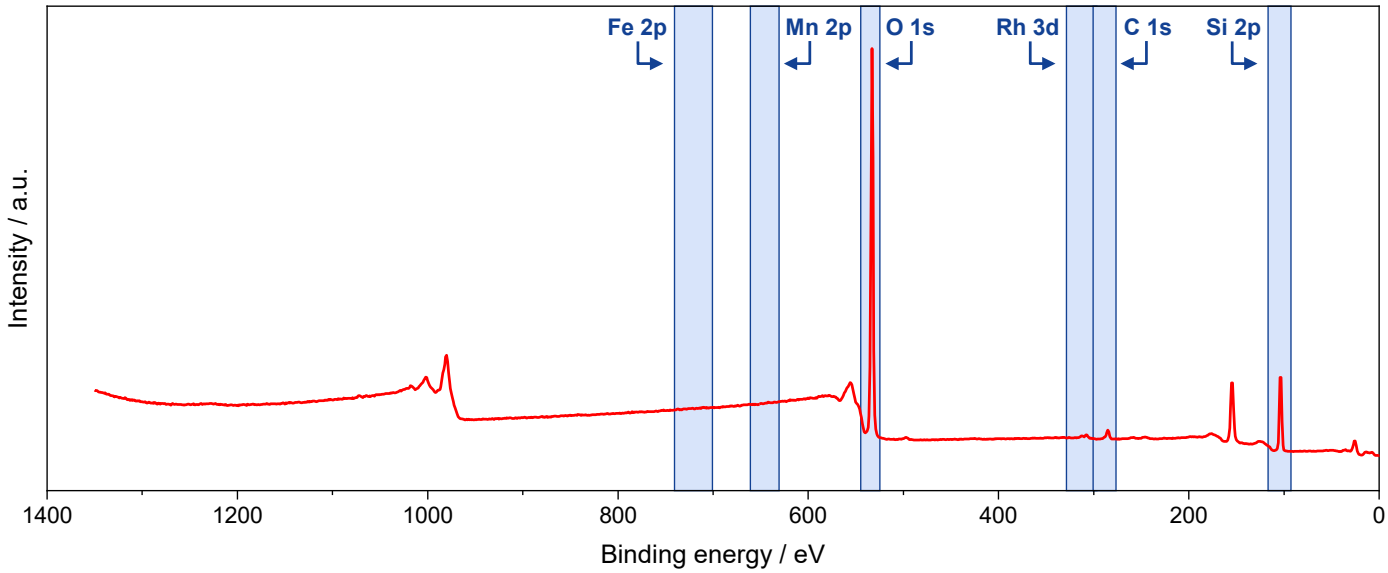

Figure S26. XP survey spectrum of $RhMn/SiO_2$ catalyst after high temperature investigation. Regions selected for high-resolution spectra are highlighted in blue.

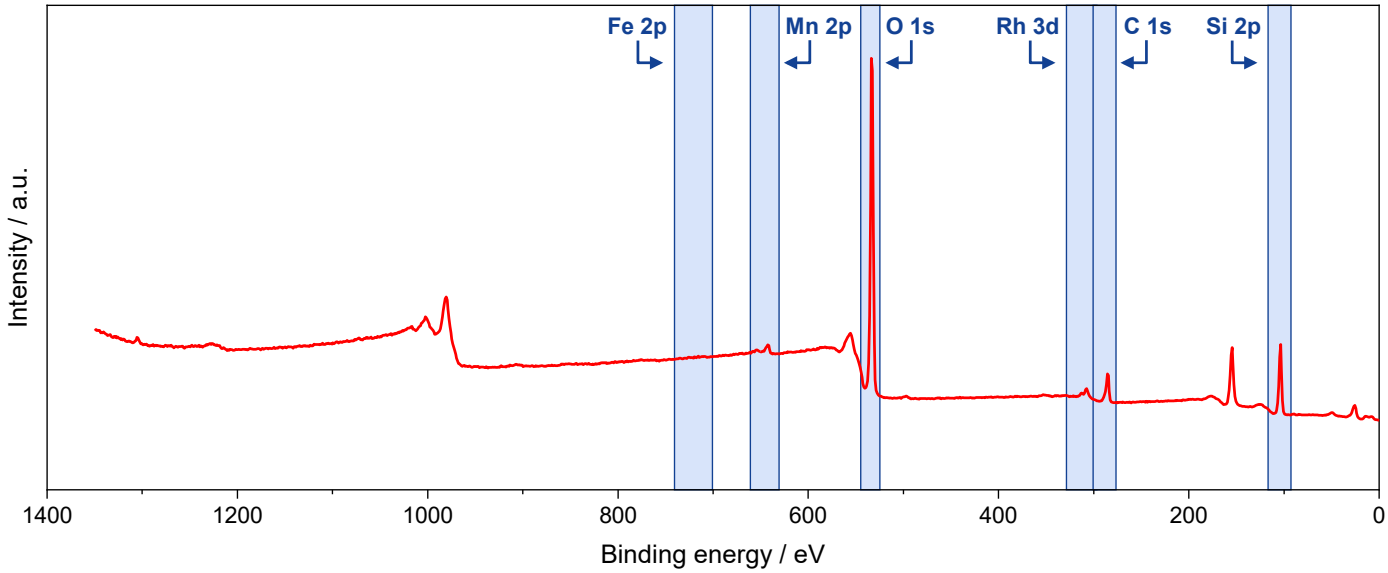

Figure S27. XP survey spectrum of $RhMn/SiO_2$ catalyst after long-term study. Regions selected for high-resolution spectra are highlighted in blue.

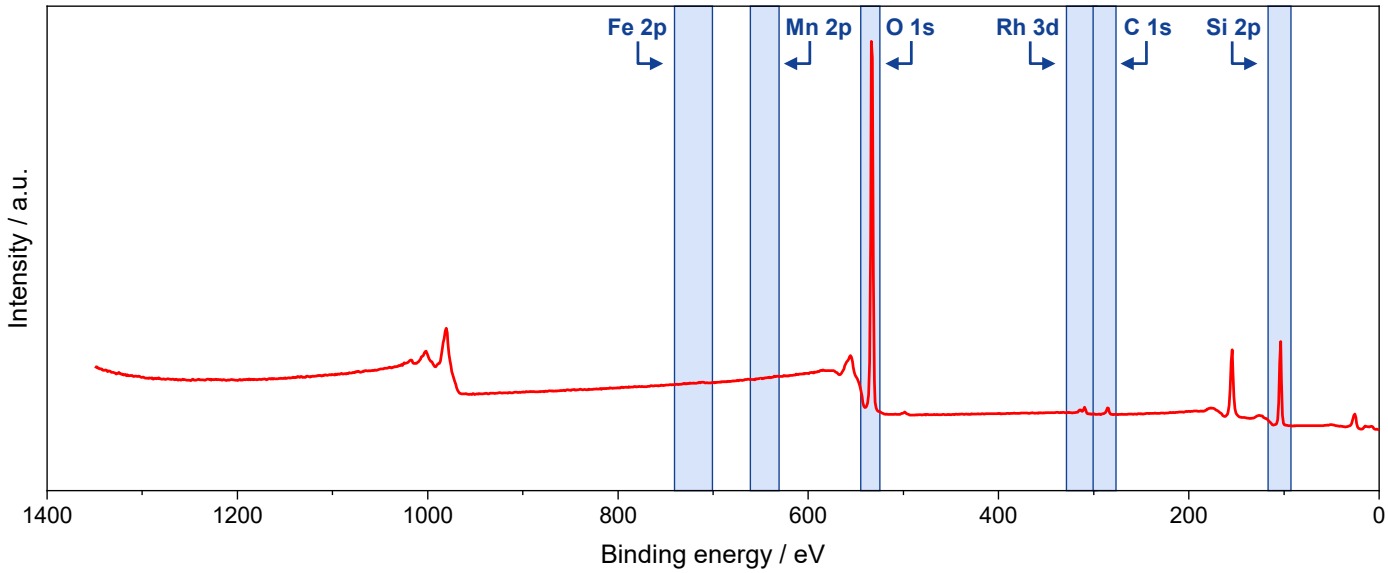

Figure S28. XP survey spectrum of calcined $RhFe/SiO_2$ catalyst. Regions selected for high-resolution spectra are highlighted in blue.

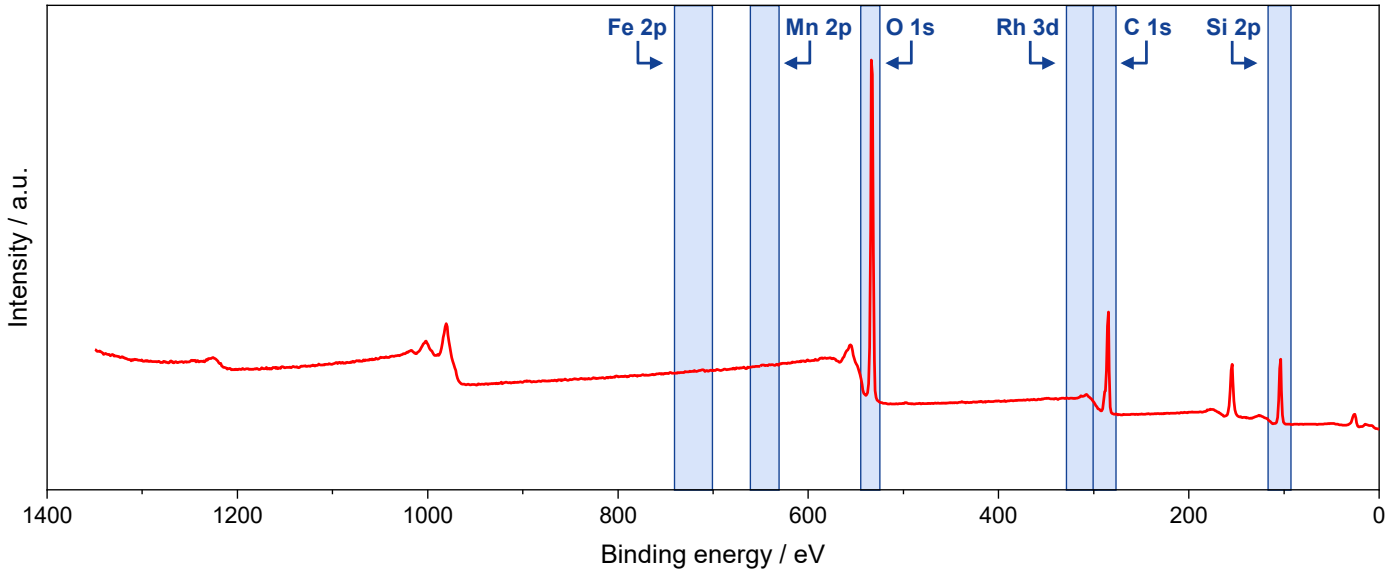

Figure S29. XP survey spectrum of reduced $RhFe/SiO_2$ catalyst. Regions selected for high-resolution spectra are highlighted in blue.

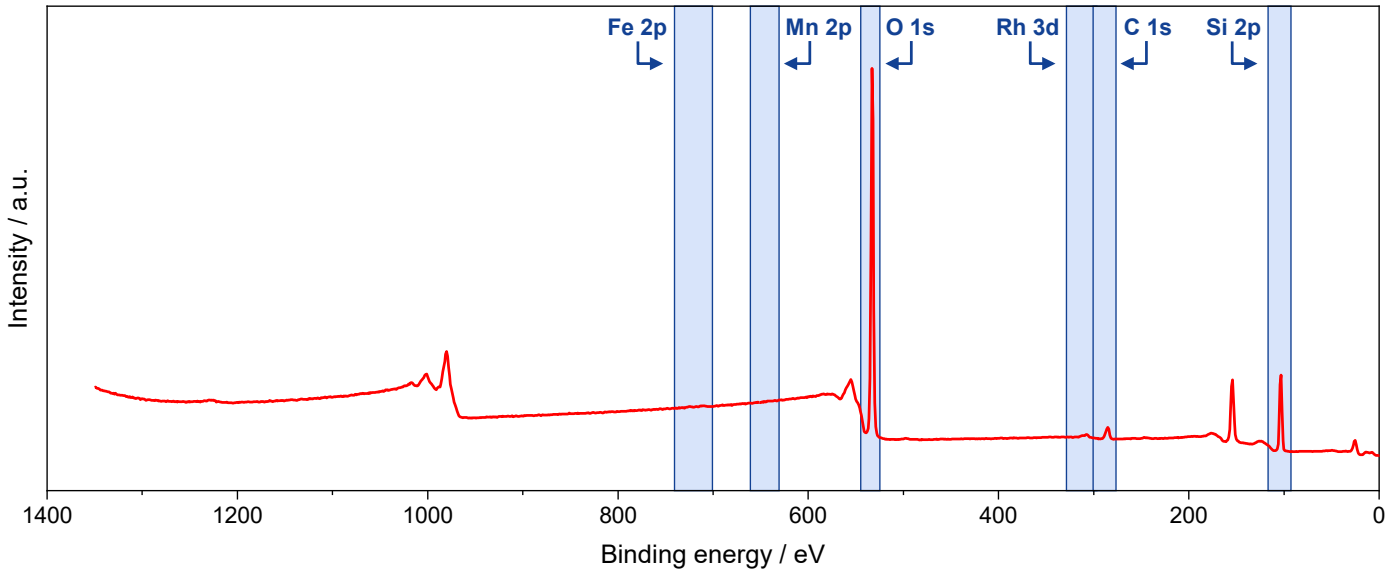

Figure S30. XP survey spectrum of $RhFe/SiO_2$ catalyst after high temperature investigation. Regions selected for high-resolution spectra are highlighted in blue.

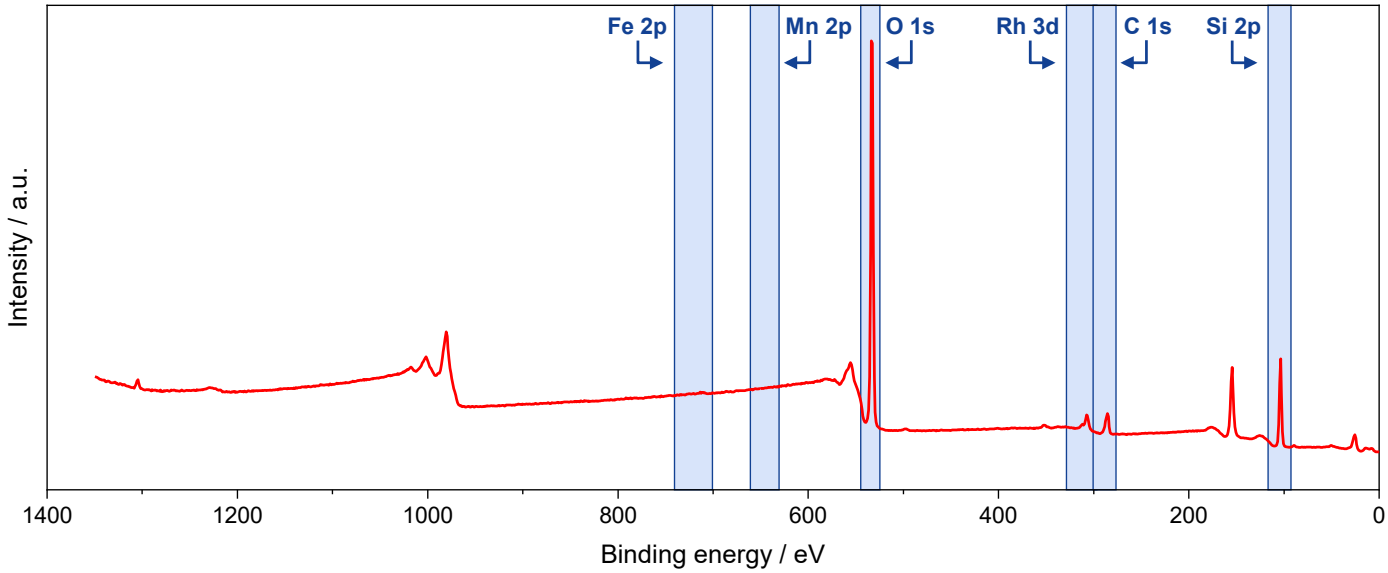

Figure S31. XP survey spectrum of $RhFe/SiO_2$ catalyst after long-term study. Regions selected for high-resolution spectra are highlighted in blue.

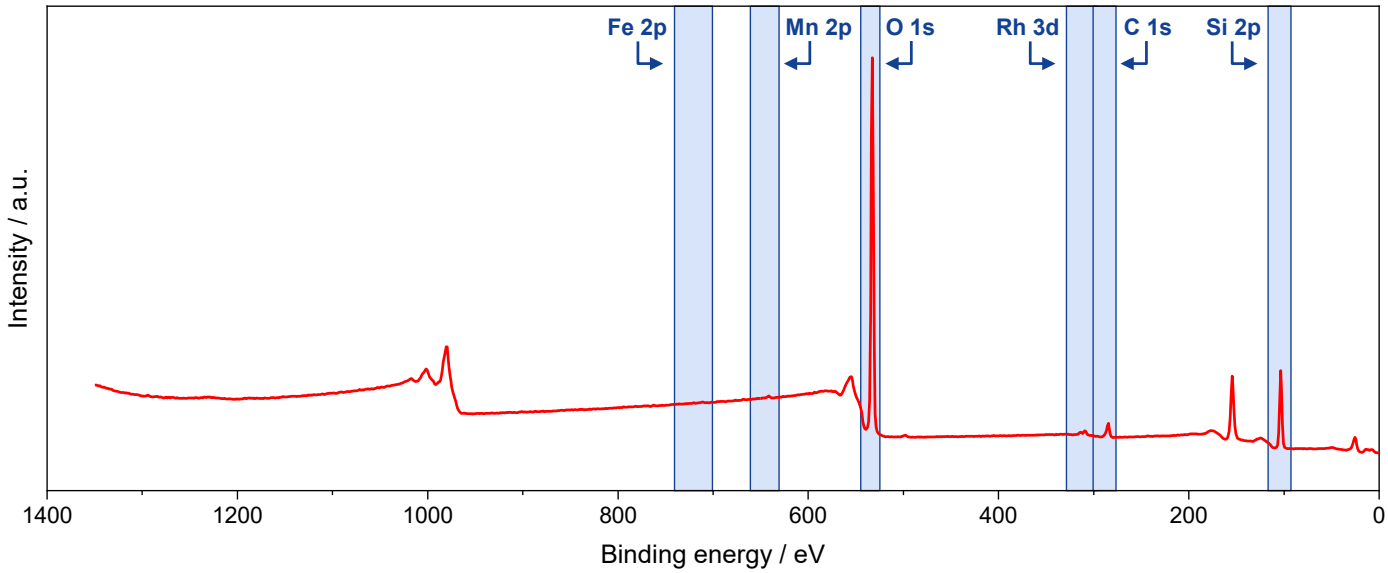

Figure S32. XP survey spectrum of calcined RhMnFe/SiO_2 catalyst. Regions selected for high-resolution spectra are highlighted in blue.

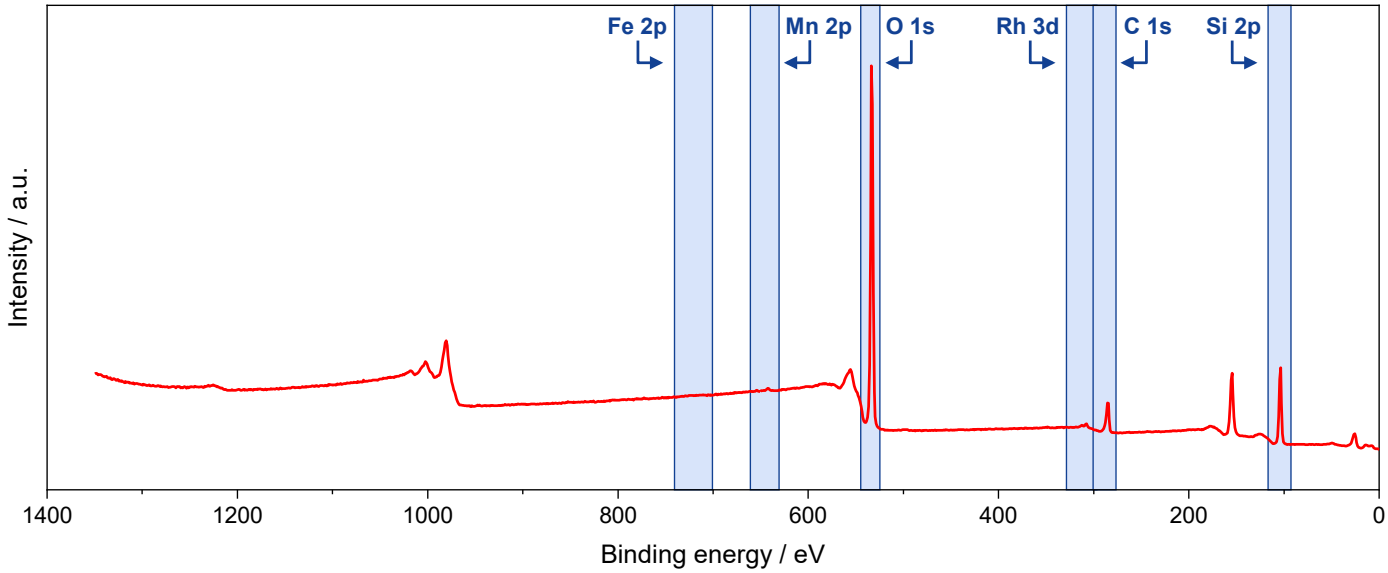

Figure S33. XP survey spectrum of reduced RhMnFe/SiO_2 catalyst. Regions selected for high-resolution spectra are highlighted in blue.

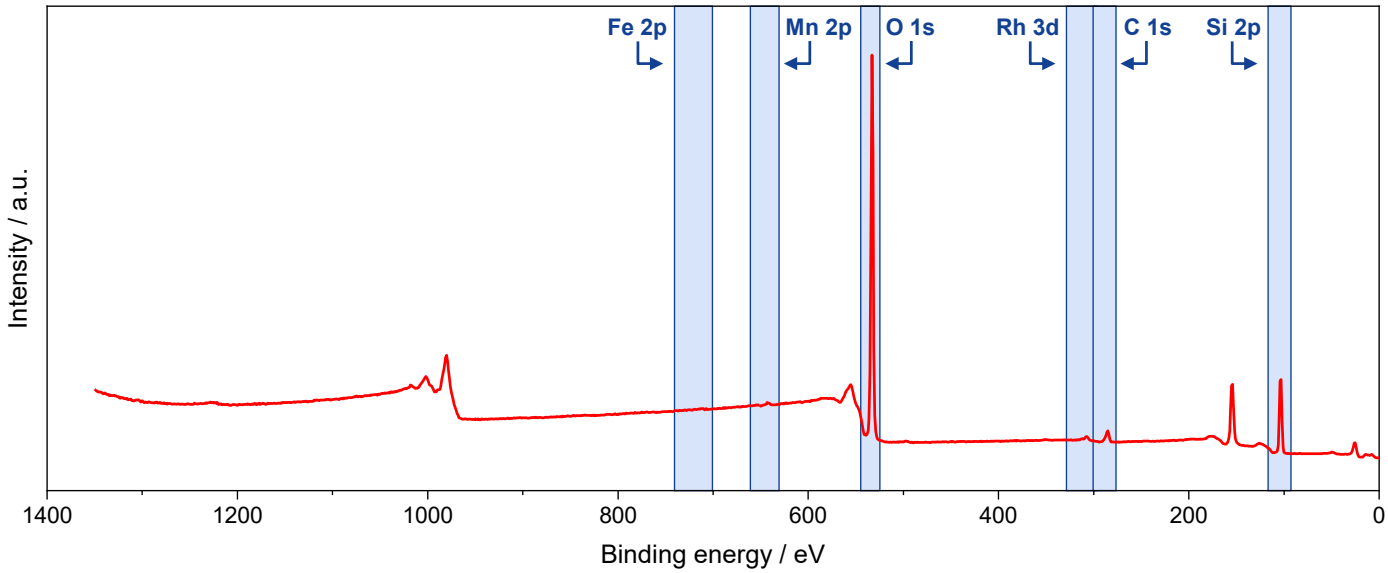

Figure S34. XP survey spectrum of RhMnFe/SiO_2 catalyst after high temperature investigation. Regions selected for high-resolution spectra are highlighted in blue.

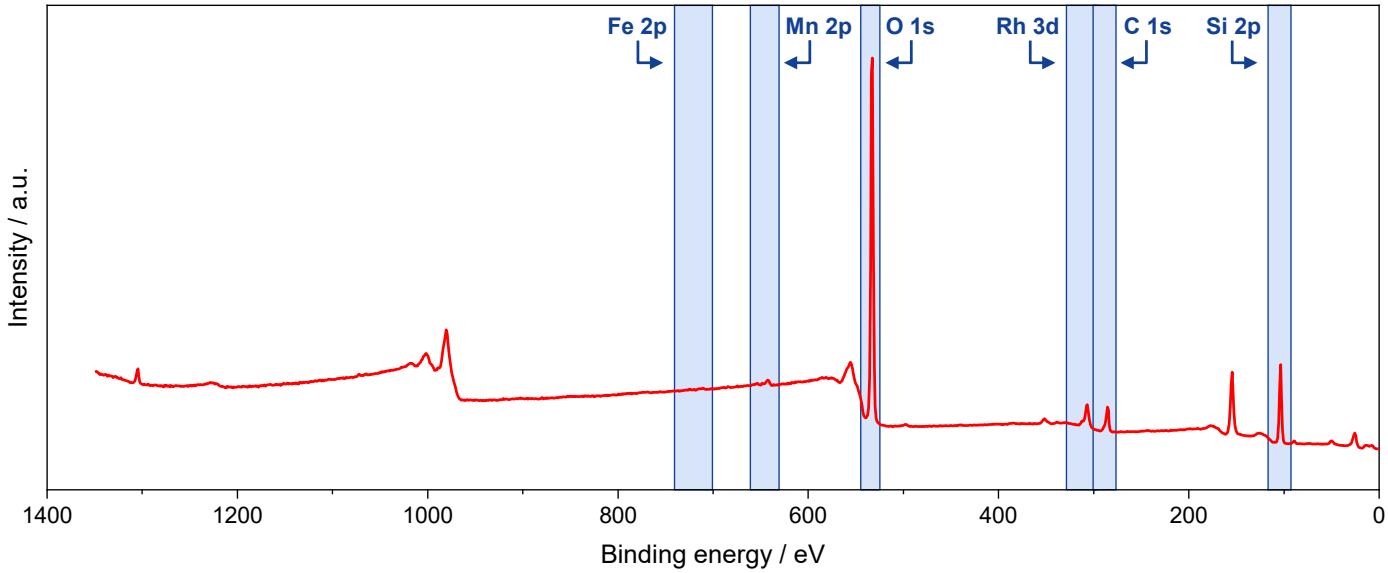

Figure S35. XP survey spectrum of RhMnFe/SiO_2 catalyst after long-term study. Regions selected for high-resolution spectra are highlighted in blue.