Supplementary Materials

Propane dehydrogenation on Co-N-C/SiO_2 catalyst: the role of single-atom active sites

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Table of contents

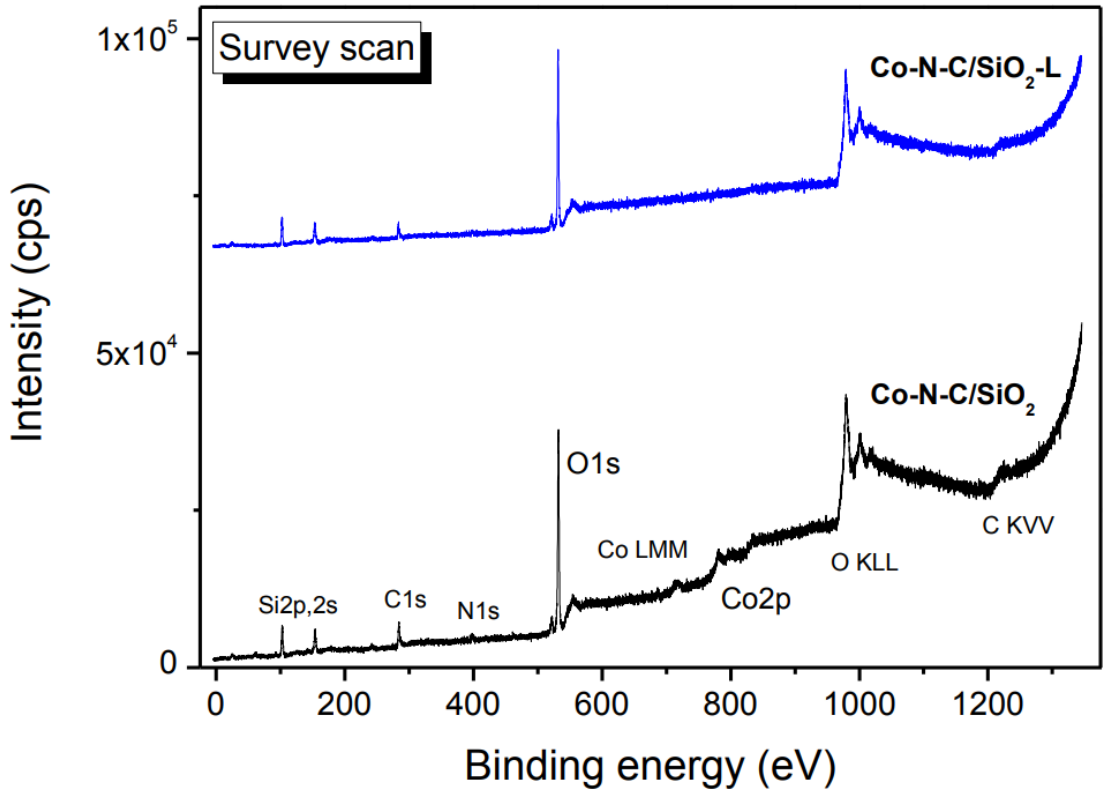


Figure S1. Survey XPS of the samples.

Table S1. The XPS-derived chemical composition of the samples (%).

Sample	**C**	**N**	**O**	**Co**	**Si**
Co-N-C/SiO_2	20.8	2.6	49.2	2.0	25.5
Co-N-C/SiO_2-L	20.9	2.3	50.2	0.3	26.3

Table S2. The XPS-derived atomic fractions of elements in the samples.

Sample	**Co/N**	**Co/Si**	**N/Si**	**O/Si**
Co-N-C/SiO_2	0.75	0.08	0.10	1.93
Co-N-C/SiO_2-L	0.13	0.01	0.09	1.91

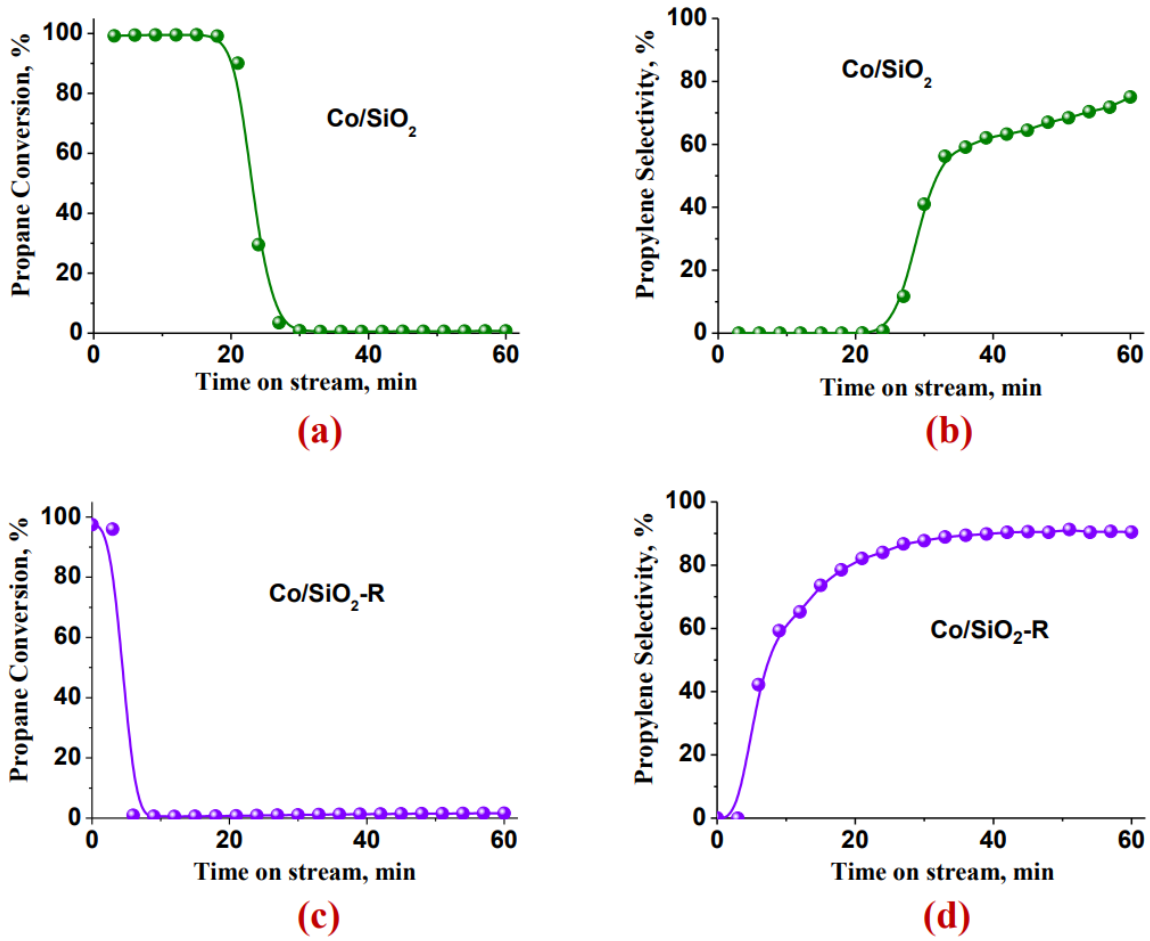


Figure S2. Propane conversions (**a**, **c**) and selectivities to propylene (**b, d**) as functions of time on stream over Co/SiO_2 and Co/SiO_2-R (a fresh sample of Co/SiO_2, reduced preliminarily in a 25 mL min^{-1} flow of H_2 at T = 600 °C for 4 h) at T = 600 °C and P = 1 atm. Gas mixture: 10 vol% propane, N_2 balance; GHSV = 7500 mL h^{-1} g_{cat}^{-1}.

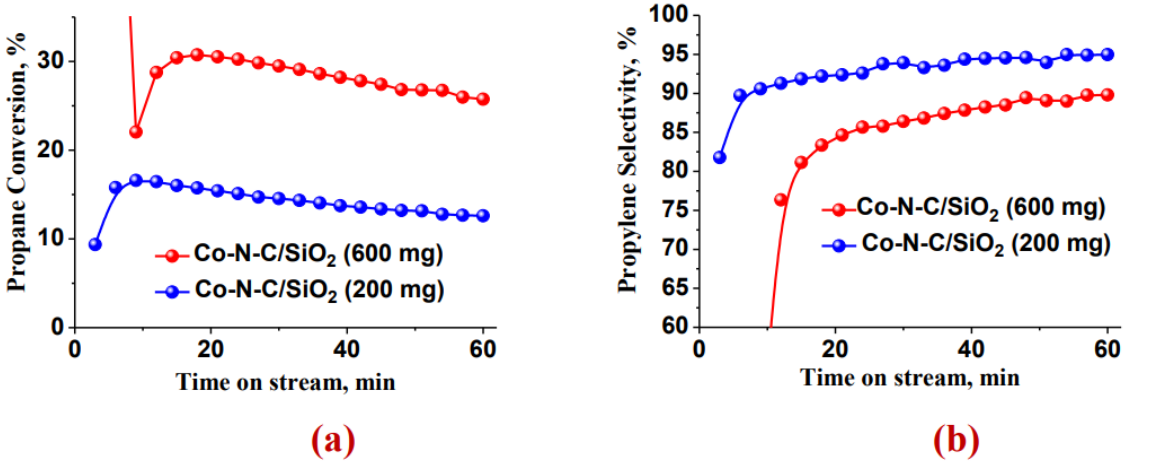
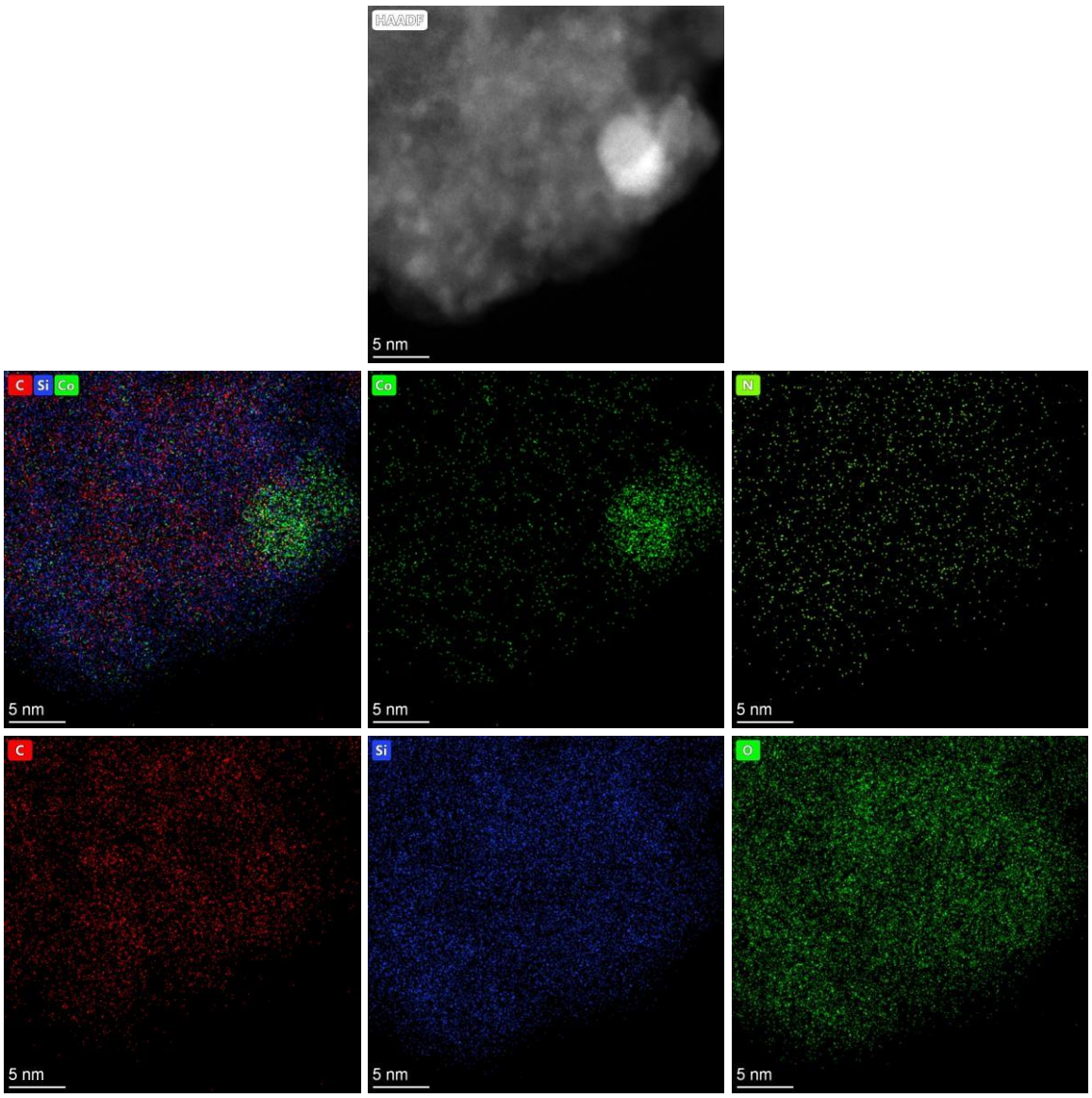
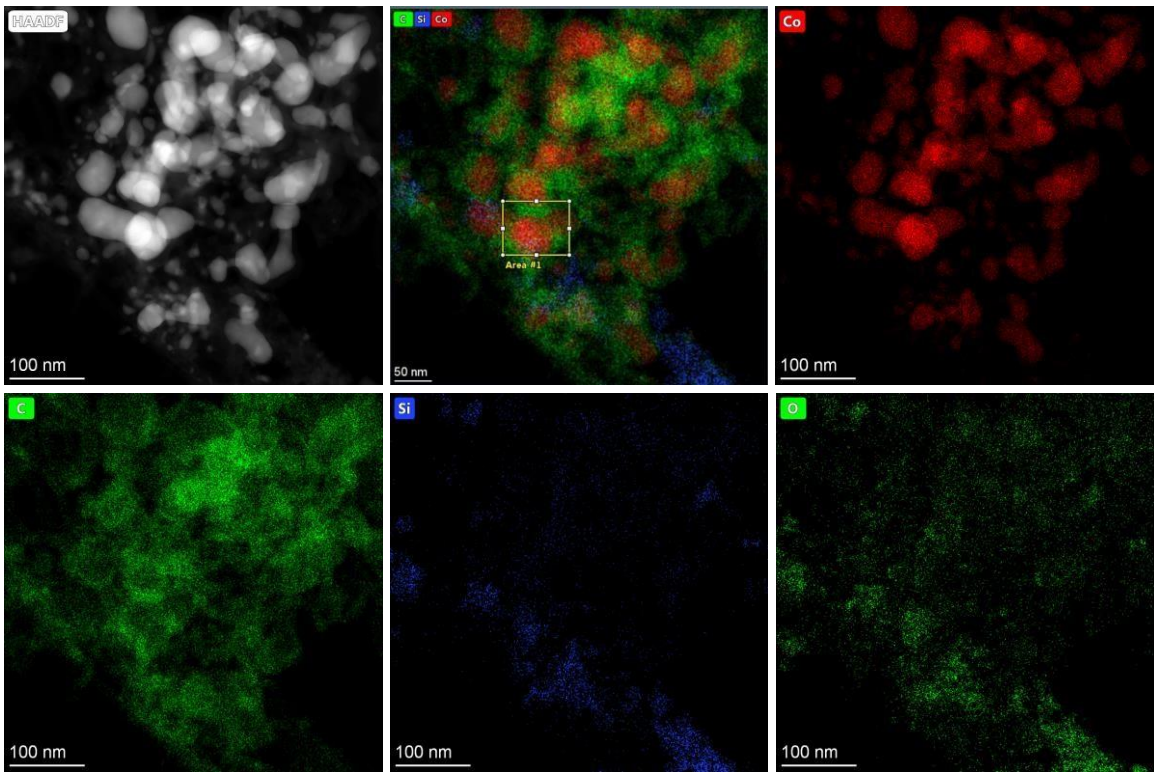


Figure S3. Propane conversion (**a**) and selectivity to propylene (**b**) as functions of time on stream over Co-N-C/SiO_2 (for the increased catalyst loading) at T = 600 °C and P = 1 atm. Gas mixture: 10 vol% propane, N_2 balance; GHSV = 2500 and 7500 mL h^{-1} g_{cat}^{-1}, for a 200 and 600 mg catalyst loadings, respectively.



Z	Element	Family	Atomic Fraction (%)	Atomic Error (%)	Mass Fraction (%)	Mass Error (%)	Fit error (%)
6	C	K	25.26	4.65	15.73	1.68	0.23
7	N	K	0.00	0.02	0.00	0.02	0.00
8	O	K	45.58	12.39	37.81	8.58	0.98
14	Si	K	26.67	7.10	38.84	8.55	0.68
27	Co	K	2.49	0.57	7.62	1.30	0.97

Figure S4. HAADF, EDX-STEM mixed C/Si/Co and separate Co, N, C, Si and O mapping images for a typical area of spent Co-N-C/SiO_2 catalyst (after 1 h of operation), with atomic and mass fraction analysis.



Z	Element	Family	Atomic Fraction (%)	Atomic Error (%)	Mass Fraction (%)	Mass Error (%)	Fit error (%)
6	C	K	71.26	8.47	36.31	2.93	0.30
7	N	K	1.04	0.28	0.62	0.15	12.52
8	O	K	3.10	0.72	2.10	0.45	1.21
14	Si	K	0.42	0.10	0.50	0.11	4.14
27	Co	K	24.18	4.32	60.47	9.43	0.28

Figure S5. HAADF, EDX-STEM mixed C/Si/Co and separate Co, C, Si and O mapping images for the spent Co-N-C/SiO_2 catalyst (after 1 h of operation) for the area of increased content of "oversized" Co nanoparticles, with atomic and mass fraction analysis.

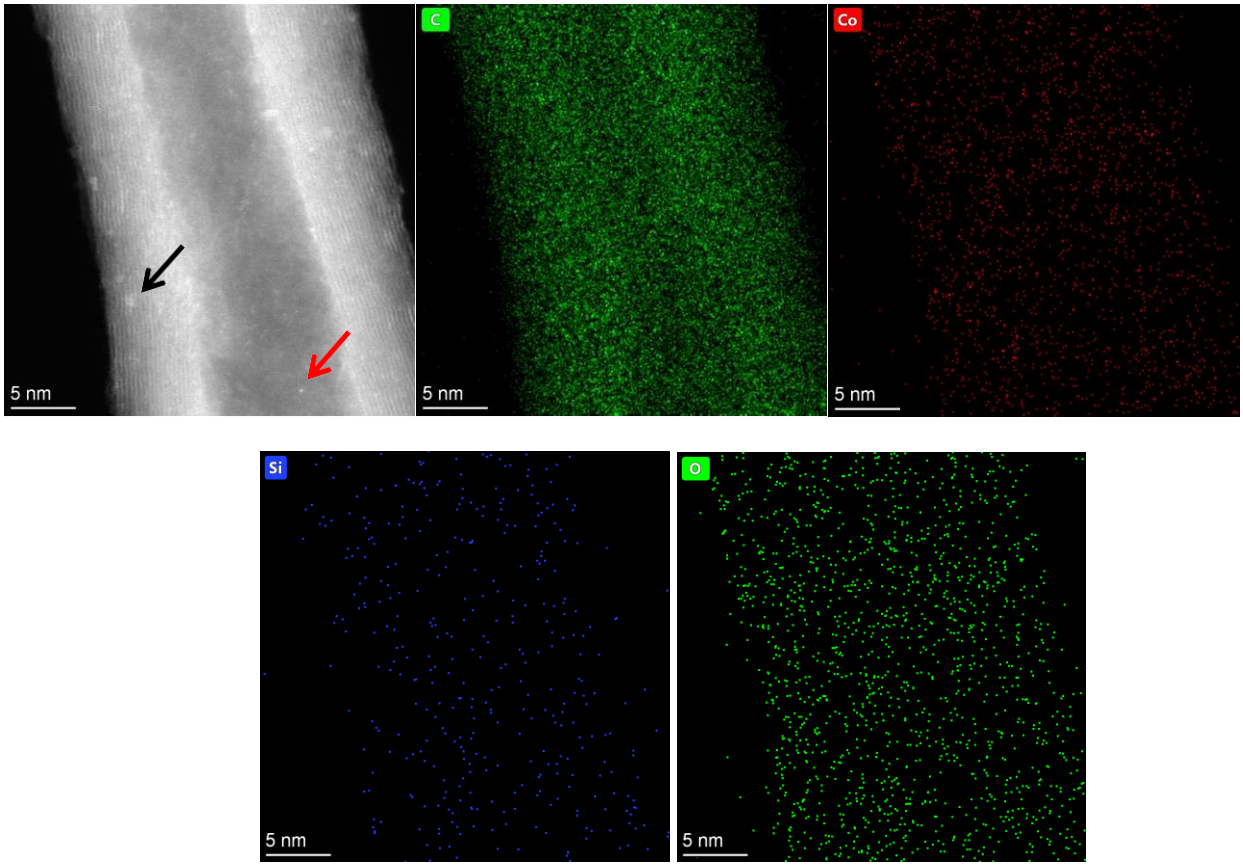
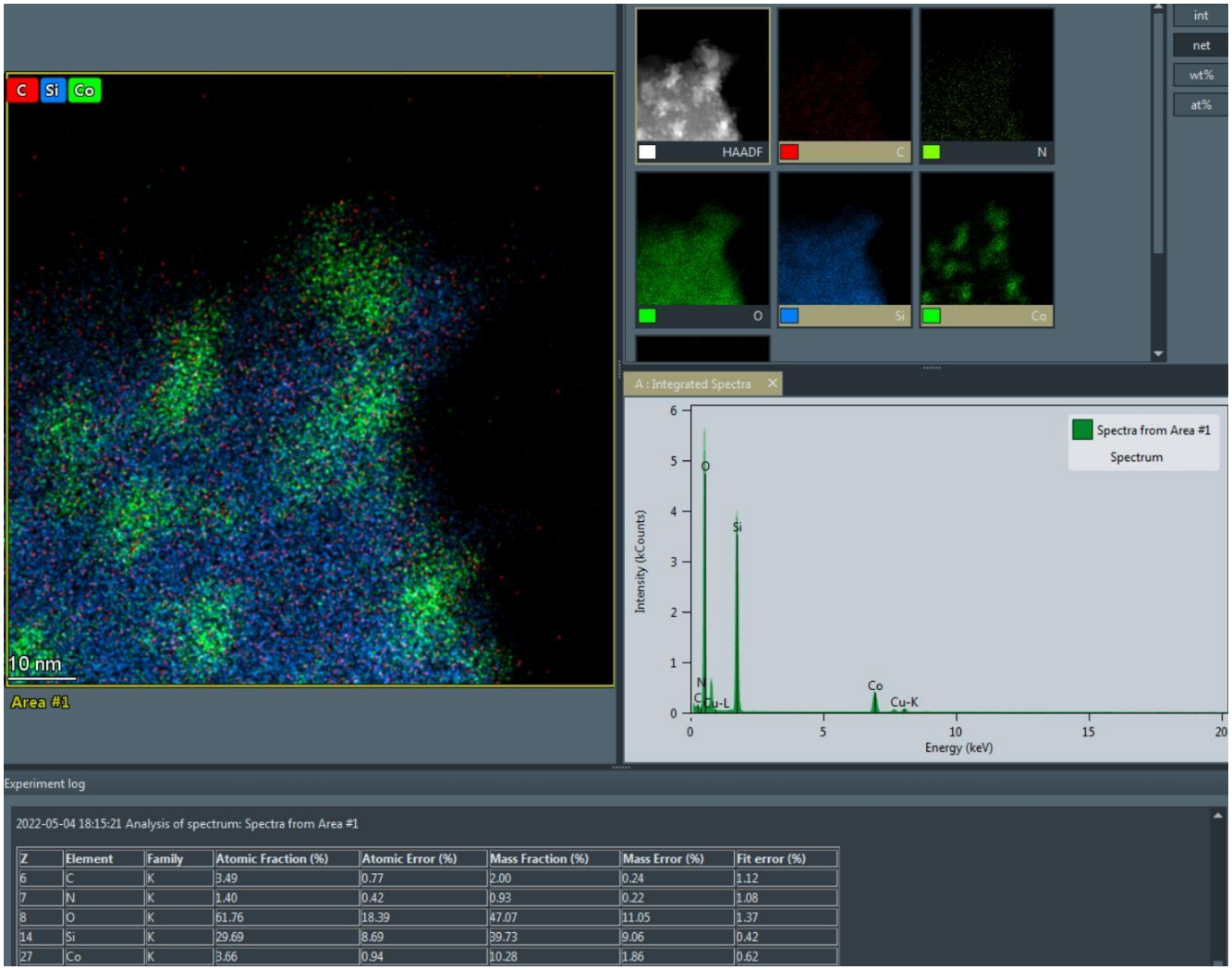


Figure S6. HAADF and EDX-STEM C, Co, Si and O mapping images of a carbon nanotube grown out in the spent Co-N-C/SiO_2 catalyst (after 1 h of operation). Black arrow shows Co nanocluster. Red arrow shows a single atom of cobalt.



Z	Element	Family	Atomic Fraction (%)	Atomic Error (%)	Mass Fraction (%)	Mass Error (%)	Fit error (%)
6	C	K	3.49	0.77	2.00	0.24	1.12
7	N	K	1.40	0.42	0.93	0.22	1.08
8	O	K	61.76	18.39	47.07	11.05	1.37
14	Si	K	29.69	8.69	39.73	9.06	0.42
27	Co	K	3.66	0.94	10.28	1.86	0.62

Figure S7. HAADF and related EDX-STEM mixed elemental mapping images of Co-N-C/SiO_2-R1 catalyst, with atomic and mass fraction analysis.

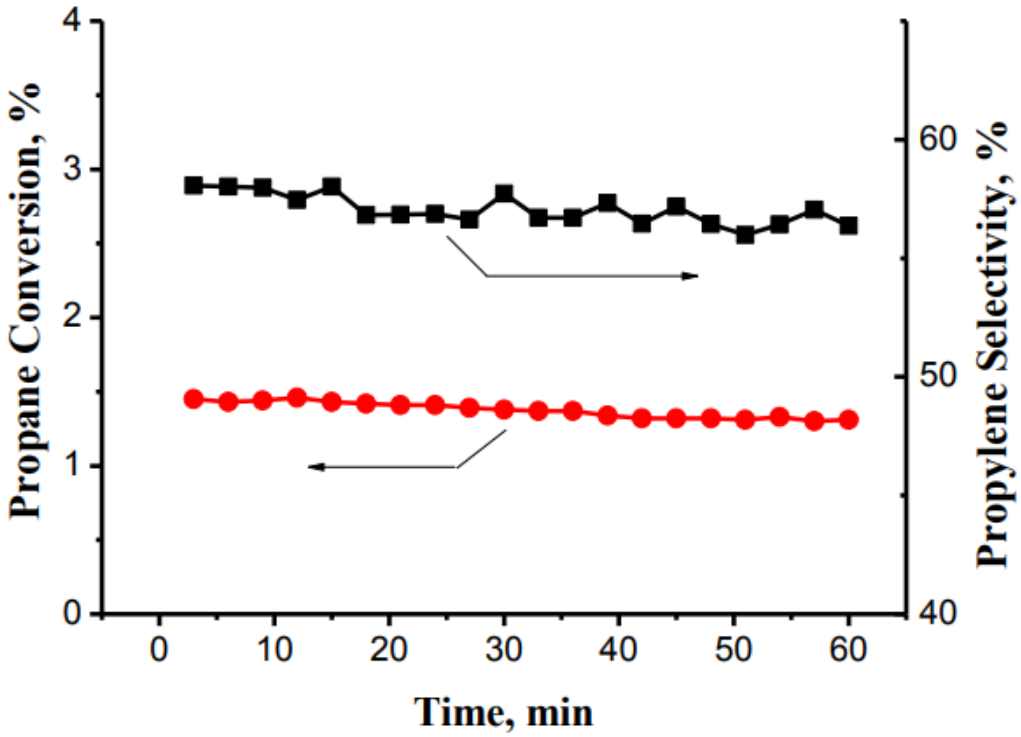


Figure S8. Propane conversion and selectivity to propylene as functions of time on stream over SiO_2 (1 mL, quartz particles of d = 0.45 to 1 mm) at T = 600 °C and P = 1 atm. Gas mixture: 10 vol% propane, N_2 balance; GHSV = 7500 mL h^{-1} g_{cat}^{-1}.