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Supporting Information

Iron as Recyclable Metal Fuel: Unraveling Oxidation Behavior and Cyclization Effects Through Thermogravimetric Analysis, Wide-Angle X-ray Scattering and Mössbauer Spectroscopy

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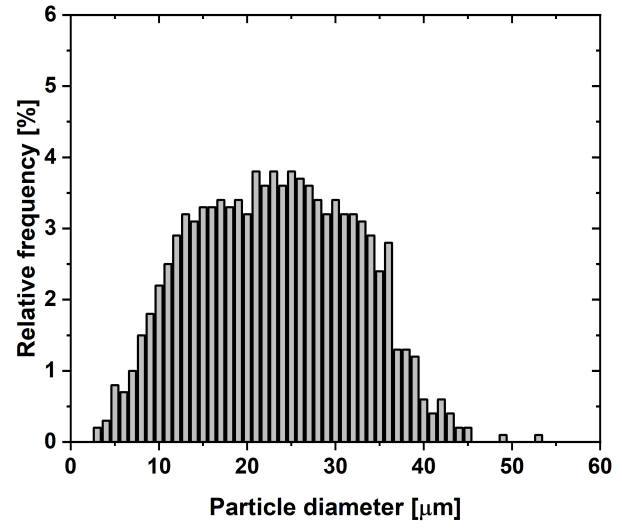
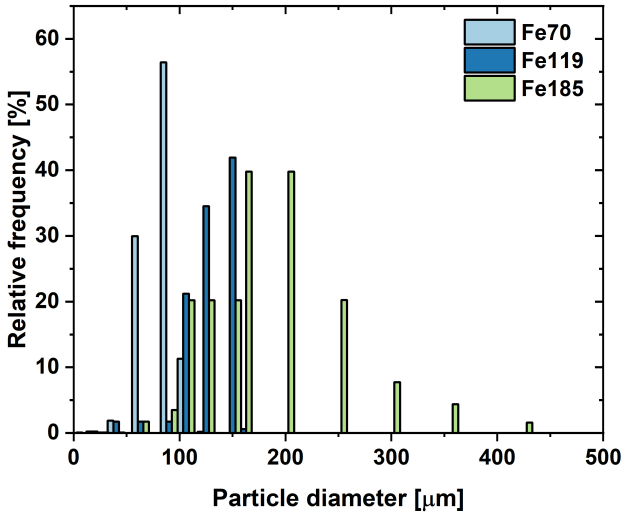
Supplemental Information

Particle size distribution



(a)



(b)

Figure S1. Particle size distribution of iron powder sample a) Fe23 and b) Fe70, Fe119 and Fe185. The particle size distribution of sample Fe23 is taken from Spielmann et al.[1] as the same powder batch is used.

Thermogravimetric experiments

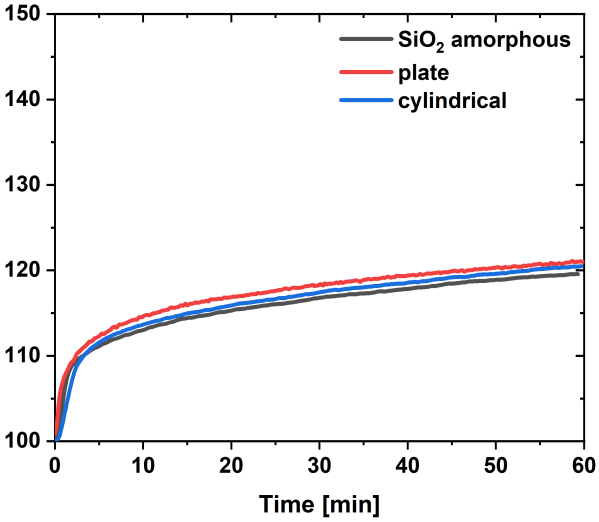


Figure S2. Isothermal oxidation of powder sample Fe23 at $600\,^{\circ}\mathrm{C}$. Comparison of samples diluted 1:4 with crystalline SiO_2 (blue) and 1:3 with amorphous SiO_2 (black) in cylindrical crucibles and with crystalline SiO_2 (red) in a plate-like crucible.

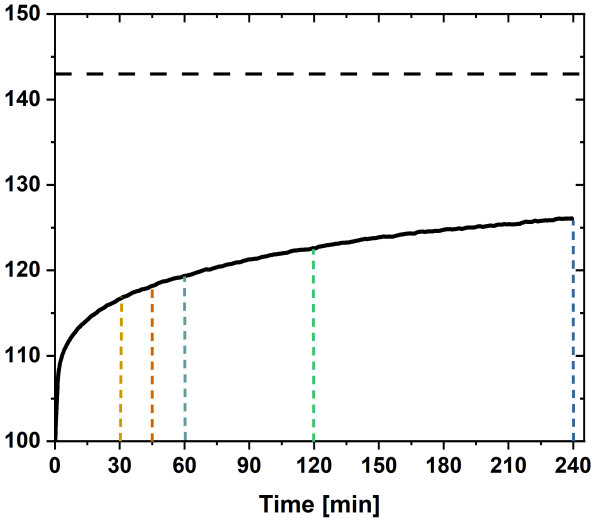


Figure S3. Isothermal oxidation of powder sample Fe23 at $600\,^{\circ}\mathrm{C}$. The dashed lines mark the points up to which the samples were oxidized and analyzed by WAXS.

Wide angle X-ray scattering

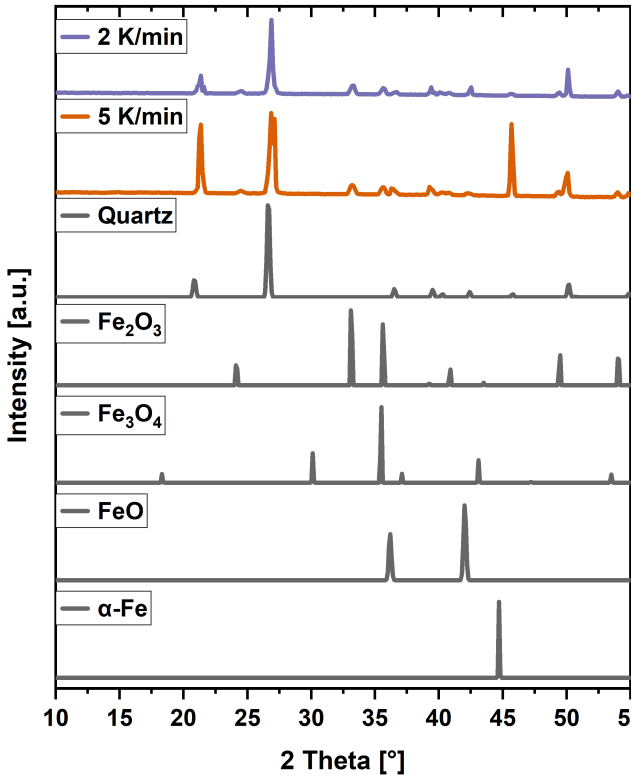
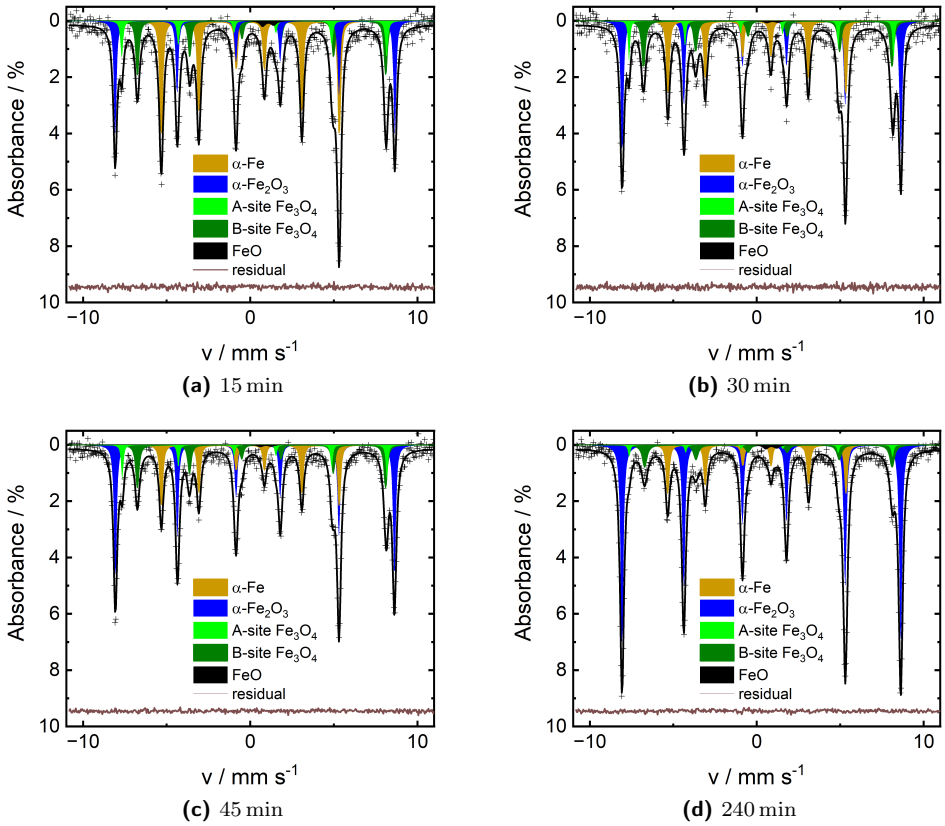


Figure S4. WAXS spectra of the oxidation of iron with a mean particle diameter of $23\,\mu\mathrm{m}$ with a heating rate of $5\,\mathrm{K\,min^{-1}}$ and $2\,\mathrm{K\,min^{-1}}$ up to $1000\,^{\circ}\mathrm{C}$ according to Fig. 1.

Mössbauer fits

Table S1. Spectral area $A_{i,\%}$, amount of iron atoms $n_{i,\%}$ and the resulting molar and mass fractions of each species.

		$A_{i,\%}$							
Temp.	Time	Fe		Fe_2O_3		Fe_3O_4		FeO	
[°C]	[min]		error		error		error		error
600	15	38.5	1.7	31.0	1.7	28.9	3.4	1.6	0.7
600	30	27.1	2.0	42.6	2.3	29.6	4.2	0.7	0.9
600	45	24.2	1.3	46.9	1.6	28.2	2.9	0.7	0.9
600	240	18.0	1.1	65.8	1.5	15.0	2.1	1.3	0.5
		$n_{i,\%}$							
600	15	40.8	3.0	31.2	2.0	26.3	3.5	1.7	0.3
600	30	28.9	3.3	43.2	2.8	27.1	3.5	0.8	0.3
600	45	25.8	3.1	47.6	2.3	25.8	2.6	0.8	0.2
600	240	19.0	4.6	66.1	2.0	13.6	2.2	1.4	0.1
		mol%							
600	15	61.0	4.5	23.3	1.5	13.1	1.7	2.6	0.5
600	30	47.9	5.5	35.8	2.3	15.0	1.9	1.3	0.5
600	45	43.8	5.3	40.4	1.9	14.6	1.5	1.3	0.3
600	240	32.8	7.9	57.1	1.7	7.8	1.3	2.4	0.2
		wt.-%							
600	15	32.9	2.5	36.0	2.3	29.3	3.9	1.7	0.3
600	30	22.4	2.6	47.9	3.1	29.0	3.7	0.7	0.3
600	45	19.8	2.4	52.2	2.5	27.3	2.8	0.7	0.2
600	240	14.2	3.4	70.5	2.1	14.0	2.3	1.3	0.1



(a) 15 min **(b)** 30 min **(c)** 45 min **(d)** 240 min

Figure S5. Mössbauer fits of iron powder samples oxidized at 600 °C for 15 min to 240 min.

Table S2. Spectral area $A_{i,\%}$, amount of iron atoms $n_{i,\%}$ and the resulting molar and mass fractions of each species.

		$A_{i,\%}$							
Temp.	Time	Fe		Fe_2O_3		Fe_3O_4		FeO	
[°C]	[min]		error		error		error		error
400	60	89.3	3.0	2.9	1.5	7.8	4.0	0.0	0.0
500	60	61.9	2.0	16.1	1.6	22.0	3.1	0.0	0.0
600	60	38.0	1.2	43.7	1.3	16.9	2.4	1.5	0.5
700	60	0.0	0.0	96.4	1.5	3.6	2.2	0.0	0.0
800	60	0.0	0.0	100.0	2.1	0.0	0.0	0.0	0.0
900	60	0.0	0.0	100.0	2.1	0.0	0.0	0.0	0.0
		$n_{i,\%}$							
400	60	90.4	3.5	2.8	1.4	6.8	7.7	0.0	0.0
500	60	64.4	2.8	15.9	1.6	19.6	4.9	0.0	0.0
600	60	39.8	3.1	43.5	1.7	15.2	3.4	1.6	0.2
700	60	0.0	0.0	96.8	1.9	3.2	1.9	0.0	0.0
800	60	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0
900	60	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0
		mol%							
400	60	96.1	3.7	1.5	0.8	2.4	2.7	0.0	0.0
500	60	81.6	3.6	10.1	1.0	8.3	2.1	0.0	0.0
600	60	58.4	4.5	31.9	1.3	7.4	1.7	2.3	0.3
700	60	0.0	0.0	97.8	2.0	2.2	1.3	0.0	0.0
800	60	0.0	0.0	100.0	2.0	0.0	0.0	0.0	0.0
900	60	0.0	0.0	100.0	2.0	0.0	0.0	0.0	0.0
		wt.-%							
400	60	87.1	3.4	3.9	2.0	9.0	10.3	0.0	0.0
500	60	56.4	2.5	19.9	2.0	23.7	5.9	0.0	0.0
600	60	31.8	2.4	49.8	2.0	16.8	3.7	1.6	0.2
700	60	0.0	0.0	96.9	1.9	3.1	1.9	0.0	0.0
800	60	0.0	0.0	100.0	2.0	0.0	0.0	0.0	0.0
900	60	0.0	0.0	100.0	2.0	0.0	0.0	0.0	0.0

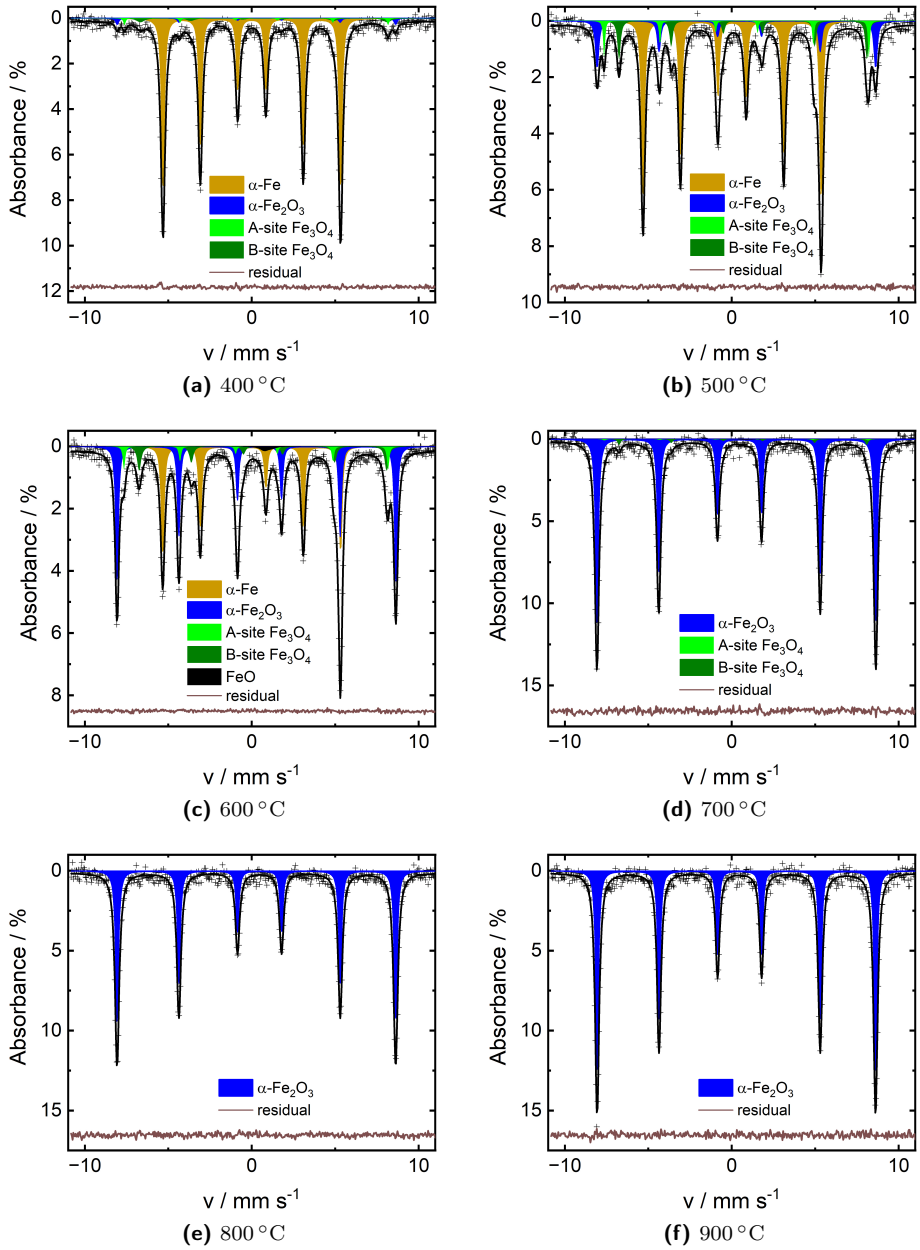
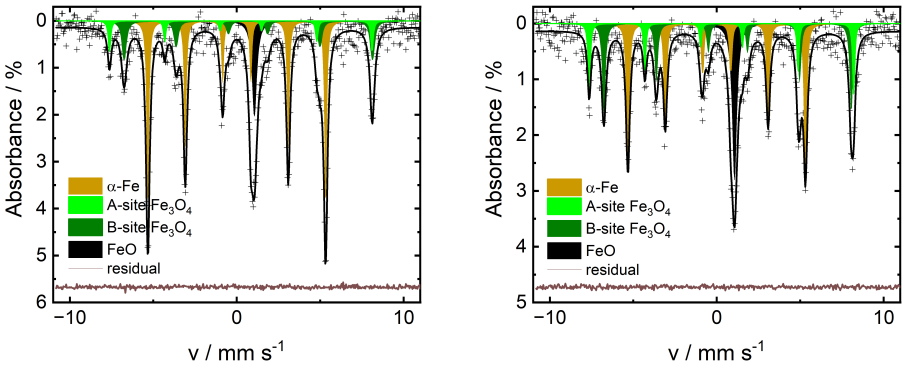


Figure S6. Mössbauer fits of iron powder samples oxidized for 60 min at temperatures from 400 °C to 900 °C.

Table S3. Spectral area $A_{i,\%}$, amount of iron atoms $n_{i,\%}$ and the resulting molar and mass fractions of each species.

Sample	$A_{i,\%}$							
	Fe		Fe_2O_3		Fe_3O_4		FeO	
		error		error		error		error
Fe23	55.0	2.2	0.0	3.0	30.0	4.3	15.0	1.0
Fe70	36.9	2.2	0.0	0.0	44.2	4.7	18.9	1.3
	$n_{i,\%}$							
Fe23	57.5	9.6	0.0	1.8	26.9	4.6	15.6	2.1
Fe70	39.3	8.4	0.0	0.0	40.5	3.4	20.1	0.4
	mol%							
Fe23	70.0	11.7	0.0	1.8	10.9	1.9	19.1	0.6
Fe70	53.9	11.5	0.0	0.0	18.5	1.6	27.6	0.6
	wt.-%							
Fe23	50.4	8.4	0.0	3.7	32.6	5.6	17.0	0.6
Fe70	32.7	7.0	0.0	0.0	46.5	3.9	20.8	0.5



(a) Fe23 **(b)** Fe70

Figure S7. Mössbauer fits of the iron powder samples of the cyclization experiments

Table S4. Summary of the Mössbauer fit parameter.

Sample	Species	CS [mm s^{-1}]	error	FWHM [mm s^{-1}]	error	Int. [%]	error
600 °C	Fe	0.00	0.01	0.19	0.01	38.49	1.65
15 min	FeO	1.07	0.17	0.40	-	1.62	0.72
	Fe_3O_4 A-Site	0.26	0.02	0.17	0.06	9.93	1.82
	Fe_3O_4 B-Site	0.68	0.01	0.22	0.04	18.97	1.56
	Fe_2O_3	0.37	0.01	0.17	0.02	30.99	1.70
600 °C	Fe	0.00	0.01	0.18	0.03	27.10	1.96
30 min	FeO	0.93	-	0.40	-	0.71	0.92
	Fe_3O_4 A-Site	0.28	0.02	0.13	0.07	8.98	2.11
	Fe_3O_4 B-Site	0.65	0.02	0.25	0.05	20.58	2.13
	Fe_2O_3	0.37	0.01	0.18	0.02	42.64	2.31
600 °C	Fe	0.00	0.01	0.19	0.02	24.18	1.30
45 min	FeO	0.93	0.33	0.40	-	0.71	0.62
	Fe_3O_4 A-Site	0.27	0.01	0.15	0.05	9.54	1.50
	Fe_3O_4 B-Site	0.67	0.01	0.23	0.03	18.63	1.38
	Fe_2O_3	0.37	0.00	0.18	0.01	46.94	1.60
600 °C	Fe	0.01	0.01	0.20	0.02	17.95	1.09
240 min	FeO	0.86	0.15	0.40	-	1.29	0.51
	Fe_3O_4 A-Site	0.28	0.05	0.15	-	3.02	0.77
	Fe_3O_4 B-Site	0.67	0.03	0.32	0.06	11.96	1.35
	Fe_2O_3	0.37	0.00	0.19	0.01	65.78	1.51
Cycling	Fe	0.00	0.00	0.16	0.01	55.03	2.20
Fe23	FeO	1.06	0.01	0.35	0.04	14.99	1.00
	Fe_3O_4 A-Site	0.24	0.03	0.17	0.07	9.71	2.01
	Fe_3O_4 B-Site	0.68	0.02	0.29	0.06	20.27	2.33
Cycling	Fe	-0.01	0.01	0.17	0.02	36.88	2.17
Fe70	FeO	1.06	0.01	0.33	0.04	18.89	1.31
	Fe_3O_4 A-Site	0.28	0.02	0.15	0.05	15.67	2.26
	Fe_3O_4 B-Site	0.66	0.01	0.22	0.04	28.56	2.43
400 °C	Fe	0.00	0.00	0.20	0.01	89.27	3.00
60 min	Fe_3O_4 A-Site	0.27	-	0.27	0.24	3.40	2.02
	Fe_3O_4 B-Site	0.67	-	0.40	0.27	4.38	2.02
	Fe_2O_3	0.37	-	0.17	0.16	2.95	1.52
500 °C	Fe	0.02	0.00	0.20	0.01	61.93	1.95
60 min	Fe_3O_4 A-Site	0.29	0.02	0.16	0.06	8.30	1.67
	Fe_3O_4 B-Site	0.68	0.01	0.22	0.05	13.67	1.42
	Fe_2O_3	0.39	0.01	0.20	0.04	16.11	1.62
600 °C	Fe	0.00	0.00	0.20	0.01	38.50	1.19
60 min	FeO	0.93	-	0.40	-	1.06	0.50

Table S4. Summary of the Mössbauer fit parameter.

Sample	Species	CS [mm s^{-1}]	error	FWHM [mm s^{-1}]	error	Int. [%]	error
	Fe_3O_4 A-Site	0.27	0.02	0.15	0.06	5.82	1.24
	Fe_3O_4 B-Site	0.65	0.02	0.25	0.05	10.92	1.20
	Fe_2O_3	0.37	0.00	0.18	0.01	43.81	1.27
700 °C	Fe_3O_4 A-Site	0.27	-	0.20	-	0.68	1.17
60 min	Fe_3O_4 B-Site	0.67	-	0.20	-	2.88	1.01
	Fe_2O_3	0.37	0.00	0.20	0.01	96.44	1.51
800 °C	Fe_2O_3	0.37	0.00	0.20	0.01	100.00	0.00
60 min							
900 °C	Fe_2O_3	0.37	0.00	0.19	0.01	100.00	0.00
60 min							

Table S5. Summary of the Mössbauer fit parameter.

Sample	Species	QS [mm s^{-1}]	error	H/T	error	A1/2	error
600 °C	Fe	0.00	0.01	33.00	0.04	1.30	0.07
15 min	FeO	0.66	-	-	-	0.56	-
	Fe_3O_4 A-Site	-0.05	0.04	49.11	0.15	1.50	-
	Fe_3O_4 B-Site	0.00	0.03	46.03	0.10	1.50	-
	Fe_2O_3	-0.18	0.01	51.85	0.04	1.50	-
600 °C	Fe	0.01	0.02	33.05	0.07	1.30	0.13
30 min	FeO	0.66	-	-	-	0.56	-
	Fe_3O_4 A-Site	-0.02	0.04	49.13	0.14	1.50	-
	Fe_3O_4 B-Site	0.01	0.03	46.15	0.12	1.50	-
	Fe_2O_3	-0.18	0.01	51.77	0.04	1.50	-
600 °C	Fe	0.00	0.01	32.98	0.05	1.30	0.09
45 min	FeO	0.66	-	-	-	0.56	-
	Fe_3O_4 A-Site	-0.03	0.03	49.08	0.11	1.50	-
	Fe_3O_4 B-Site	0.01	0.02	46.03	0.08	1.50	-
	Fe_2O_3	-0.19	0.01	51.74	0.03	1.50	-
600 °C	Fe	0.00	0.02	33.14	0.06	1.21	0.10
240 min	FeO	0.66	-	-	-	0.56	-
	Fe_3O_4 A-Site	-0.07	0.08	48.92	0.36	1.50	-
	Fe_3O_4 B-Site	0.05	0.04	45.97	0.21	1.50	-
	Fe_2O_3	-0.18	0.00	51.77	0.02	1.50	-
Cycling	Fe	0.00	-	33.03	0.03	1.40	0.06
Fe23	FeO	-	-	-	-	-	-
	Fe_3O_4 A-Site	0.00	-	48.76	0.22	1.50	-
	Fe_3O_4 B-Site	0.02	0.04	46.15	0.17	1.50	-
Cycling	Fe	0.00	-	32.98	0.05	1.31	0.13
Fe70	FeO	-	-	-	-	1.50	-
	Fe_3O_4 A-Site	0.00	-	49.13	0.11	1.50	-
	Fe_3O_4 B-Site	-0.02	0.03	45.97	0.09	1.50	-
400 °C	Fe	0.00	0.00	33.05	0.01	1.37	0.03
60 min	Fe_3O_4 A-Site	0.02	0.14	48.97	0.49	1.50	-
	Fe_3O_4 B-Site	0.09	0.17	45.92	0.60	1.50	-
	Fe_2O_3	-0.19	-	51.72	-	1.50	-
500 °C	Fe	0.00	0.01	33.11	0.02	1.33	0.04
60 min	Fe_3O_4 A-Site	-0.02	0.04	49.21	0.13	1.50	-
	Fe_3O_4 B-Site	0.01	0.03	46.05	0.10	1.50	-
	Fe_2O_3	-0.18	0.03	51.86	0.08	1.50	-
600 °C	Fe	-0.01	0.01	33.05	0.03	1.32	0.05
60 min	FeO	0.66	-	-	-	0.56	-
	Fe_3O_4 A-Site	-0.03	0.04	49.07	0.13	1.23	0.08

Table S5. Summary of the Mössbauer fit parameter.

Sample	Species	QS [mm s^{-1}]	error	H/T	error	A1/2	error
	Fe_3O_4 B-Site	0.00	0.03	45.96	0.11	1.50	-
	Fe_2O_3	-0.18	0.01	51.78	0.02	1.50	-
700 °C	Fe_3O_4 A-Site	0.00	-	49.00	-	1.50	-
60 min	Fe_3O_4 B-Site	0.00	-	46.00	-	1.50	-
	Fe_2O_3	-0.19	0.00	51.80	0.02	1.37	0.03
800 °C	Fe_2O_3	-0.19	0.00	51.75	0.02	1.36	0.03
60 min							
900 °C	Fe_2O_3	-0.20	0.00	51.72	0.01	1.38	0.03
60 min							

References

[1] J. Spielmann, D. Braig, A. Streck, T. Gustmann, C. Kuhn, F. Rainauer, A. Kurnosov, O. Leubner, V. Potapkin, C. Hasse, O. Deutschmann, B. J. Etzold, Scholtissek A., U. I. Kramm, *Phys. Chem. Chem. Phys.* **2024**.