Supporting Material

Hydrogenation of CO_2 on nanostructured Cu/FeO_x catalysts: The effect of morphology and Cu load on selectivity

Karolína Simkovičová[1,2], Muhammad I. Qadir[1], Naděžda Žilková[1], Joanna E. Olszówka[1], Pavel Sialini[3], Libor Kvítek[2*] and Štefan Vajda[1*]

[1] Department of Nanocatalysis, J. Heyrovský Institute of Physical Chemistry v.v.i., Czech Academy of Sciences, Dolejškova 2155/3, 182 23 Prague 8, Czech Republic.
[2] Department of Physical Chemistry, Faculty of Science, Palacký University Olomouc, 17. listopadu 12, 77900 Olomouc, Czech Republic.
[3] Laboratory of Surface Analysis, University of Chemistry and Technology, Technická 3, 16628 Prague, Czech Republic.
* Correspondence: stefan.vajda@jh-inst.cas.cz (SV) and libor.kvitek@upol.cz (LK)

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Temperature ramp

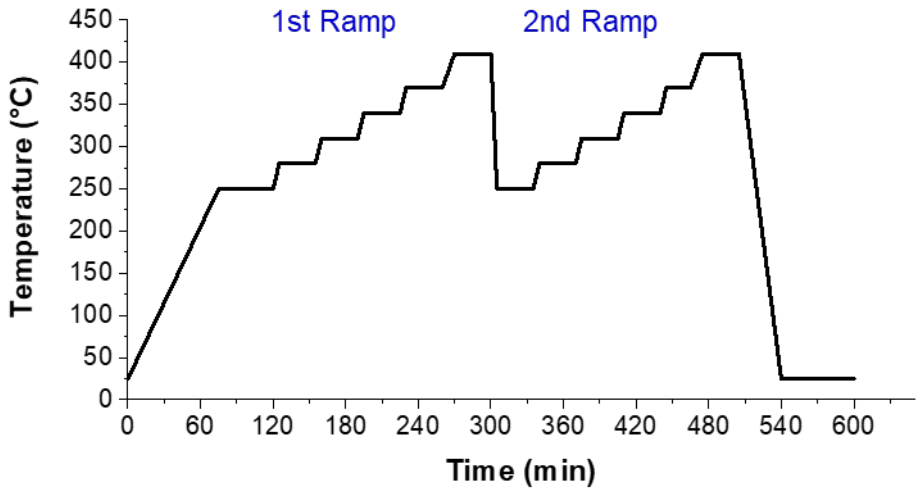

Figure S1. Double temperature ramp applied during catalytic testing. 200 mg of catalyst and CO_2/H_2/He (1:5:4, total flow 25 ml/min).

SEM/EDX of fresh catalysts

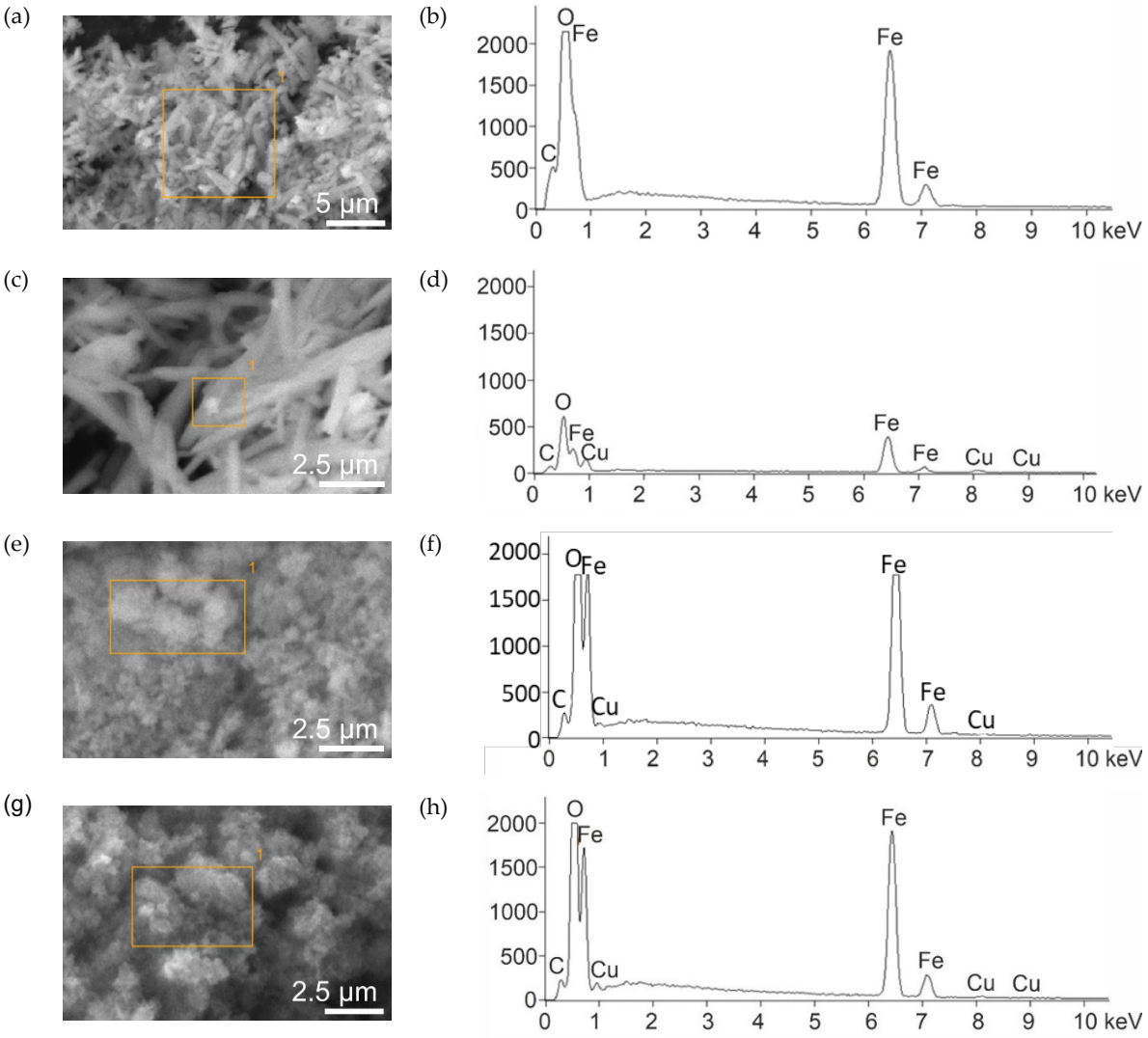

Figure S2. SEM images of fresh catalysts and EDX of the selected part of the image in highlighted rectangles with included particles, (a, b) FeO_x, (c, d) 1%-Cu/FeO_x, (e, f) 3%-Cu/FeO_x and (g, h) 5%-Cu/FeO_x.

STEM/HAADF images of fresh FeO_x

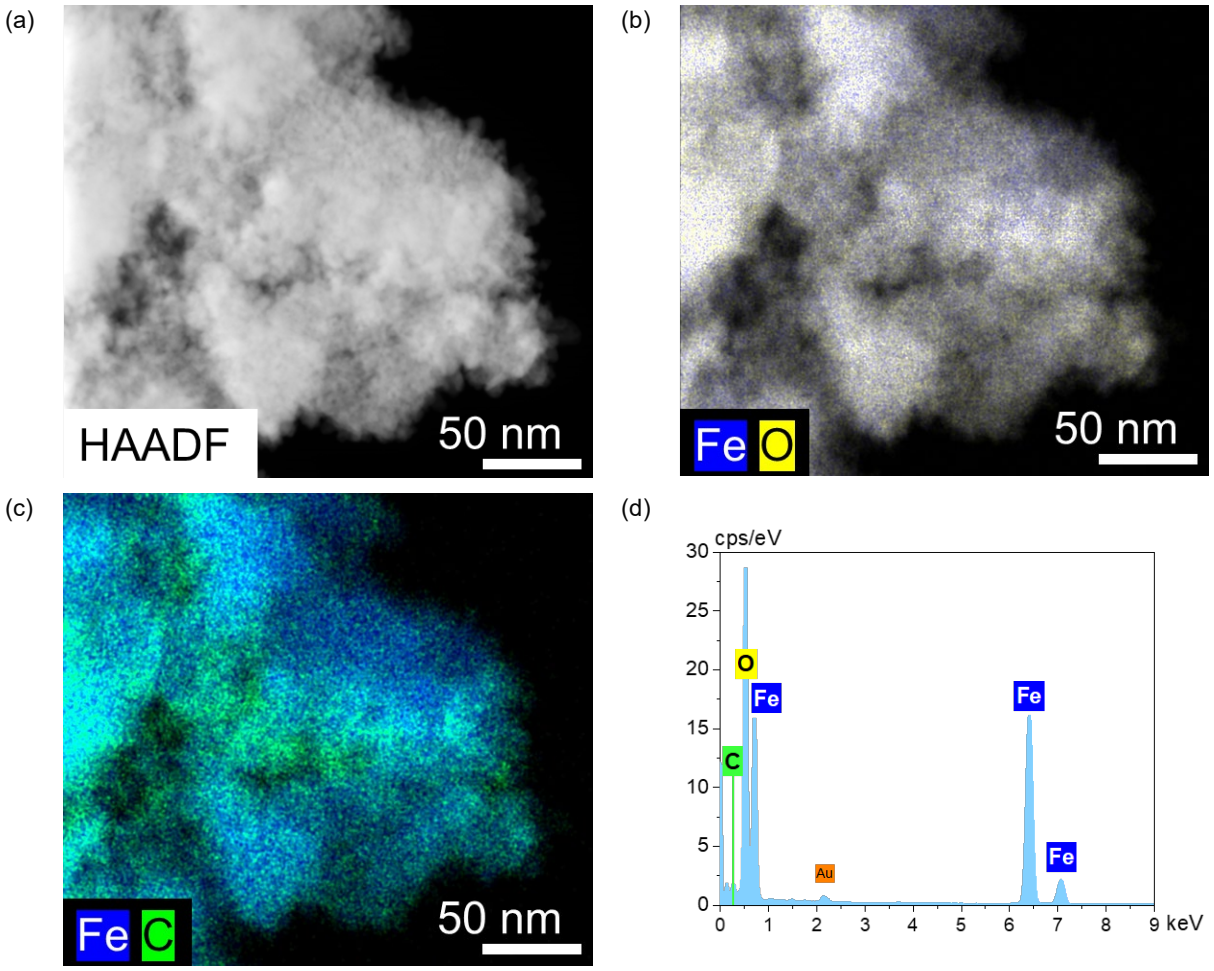

Figure S3. (a) STEM-HAADF of fresh FeO_x, and (b-d) EDX elemental mapping (red: Fe, yellow: O, green: C)

STEM/HAADF images of fresh 1%-Cu/FeO_x

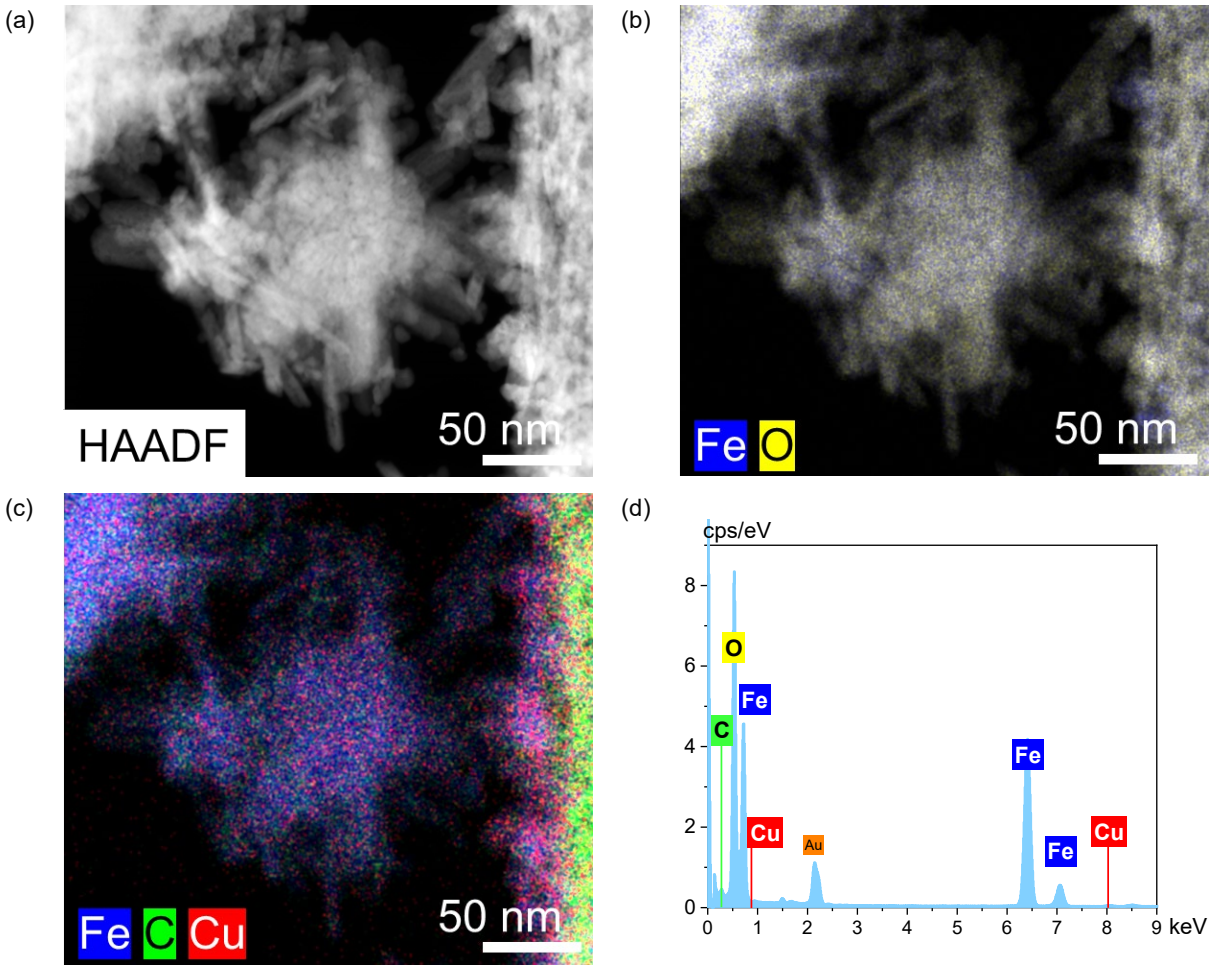

Figure S4. (a) STEM-HAADF of fresh 1%-Cu/FeO_x, and (b-d) EDX elemental mapping of Fe, O, C and Cu.

STEM/HAADF images of fresh 3%-Cu/FeO_x

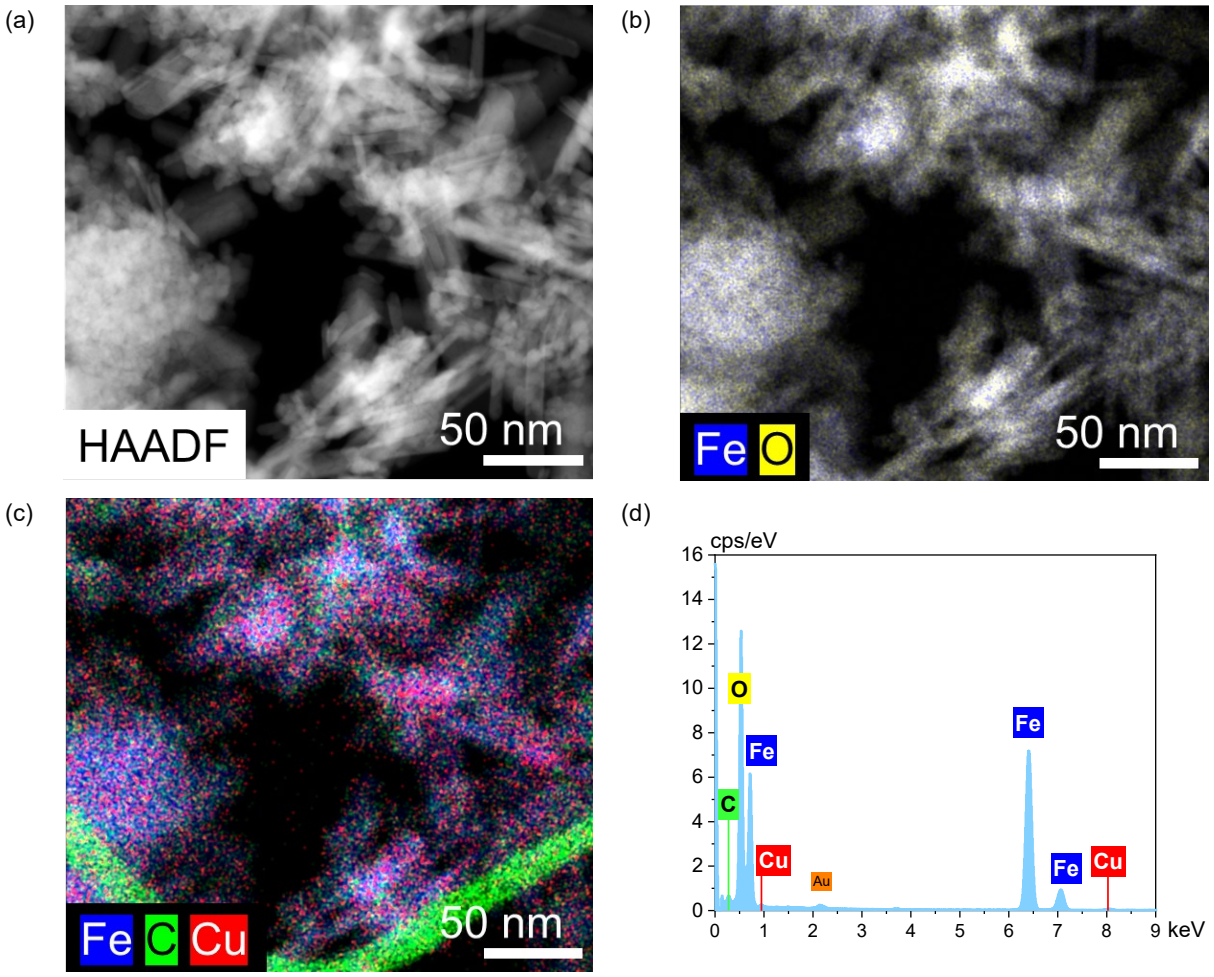

Figure S5. (a) STEM-HAADF of fresh 3%-Cu/FeO_x, and (b-d) EDX elemental mapping of Fe, O, C and Cu.

STEM/HAADF images of fresh 5%-Cu/FeO_x

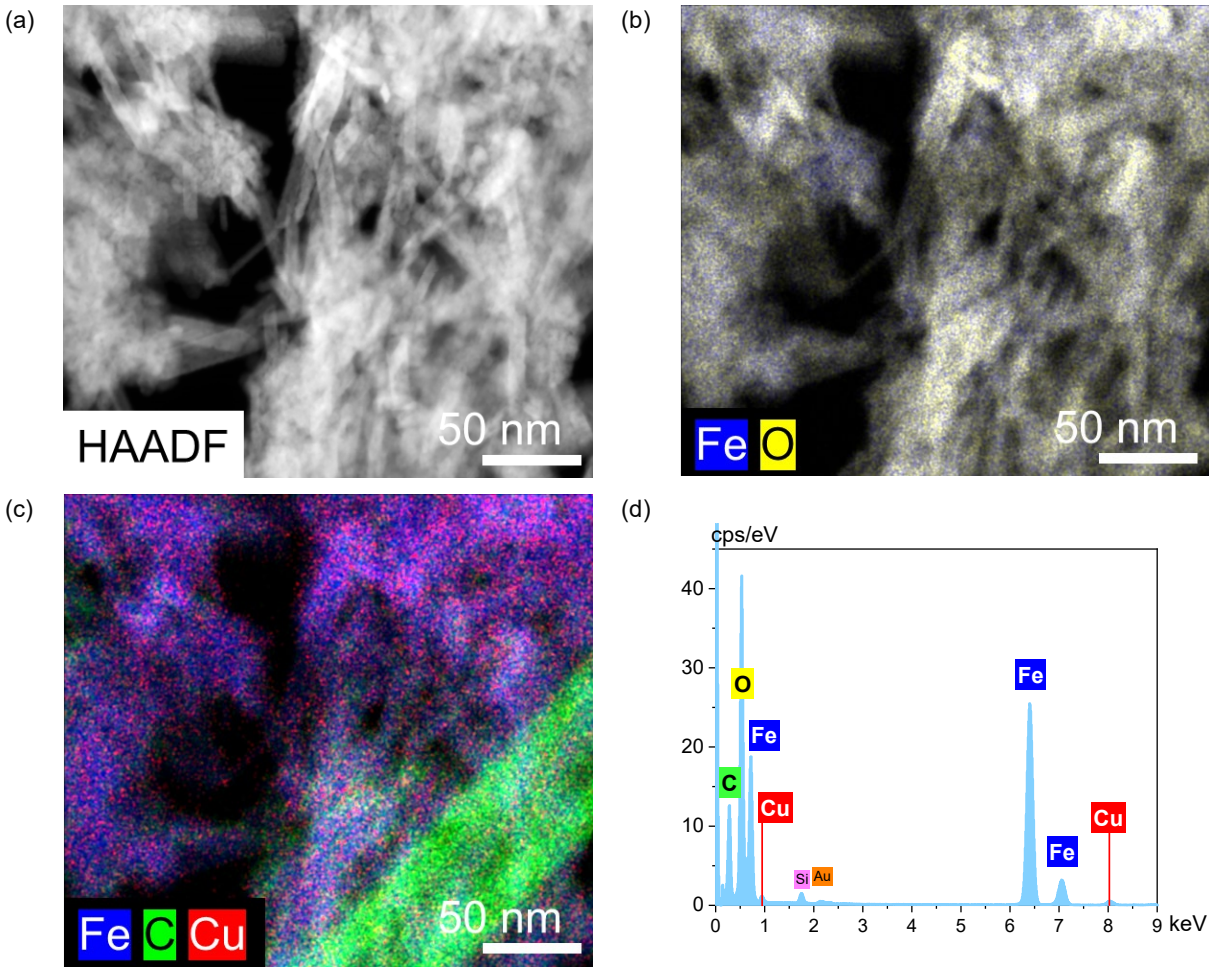

Figure S6 (a) STEM-HAADF of fresh 5%-Cu/FeO_x, and (b-d) EDX elemental mapping of Fe, O, C and Cu.

XRD patterns of fresh catalysts

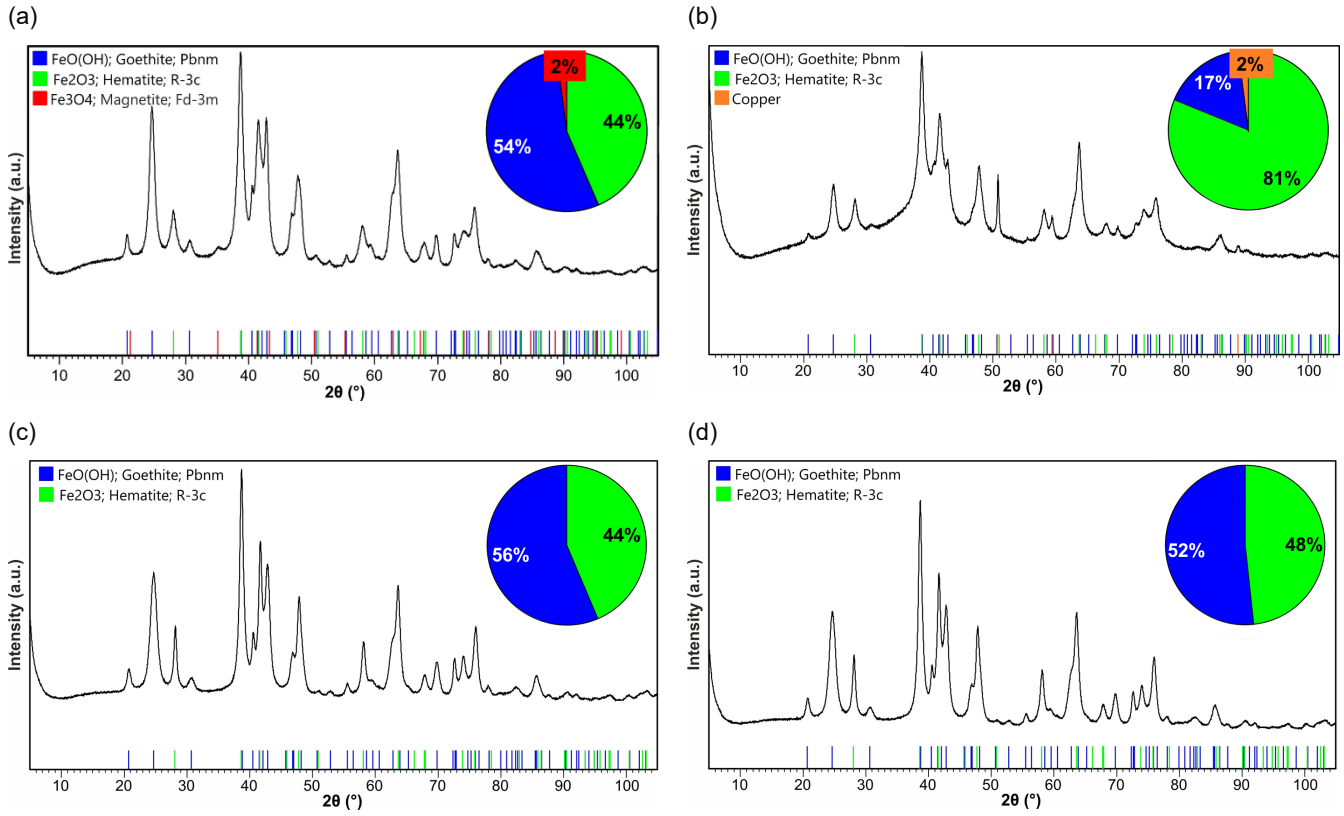

Figure S7. XRD patterns of fresh (a) FeO_x, (b) 1%-Cu/FeO_x, (c) 3%-Cu/FeO_x and (d) 5%-Cu/FeO_x.

Mean X-ray coherence length of fresh catalysts

Table S1. Mean X-ray coherence length of fresh catalysts obtained from XRD data using Rietveld refinement of analysis.

Catalyst	**α-Fe_2O_3 [nm]**	**α-FeO(OH) [nm]**	**Fe_3O_4 [nm]**
FeO_x	9	12	11
1%-Cu/FeO_x	12	11	0.0
3%-Cu/FeO_x	19	9	0.0
5%-Cu/FeO_x	19	10	0.0

XPS of fresh and spent catalysts

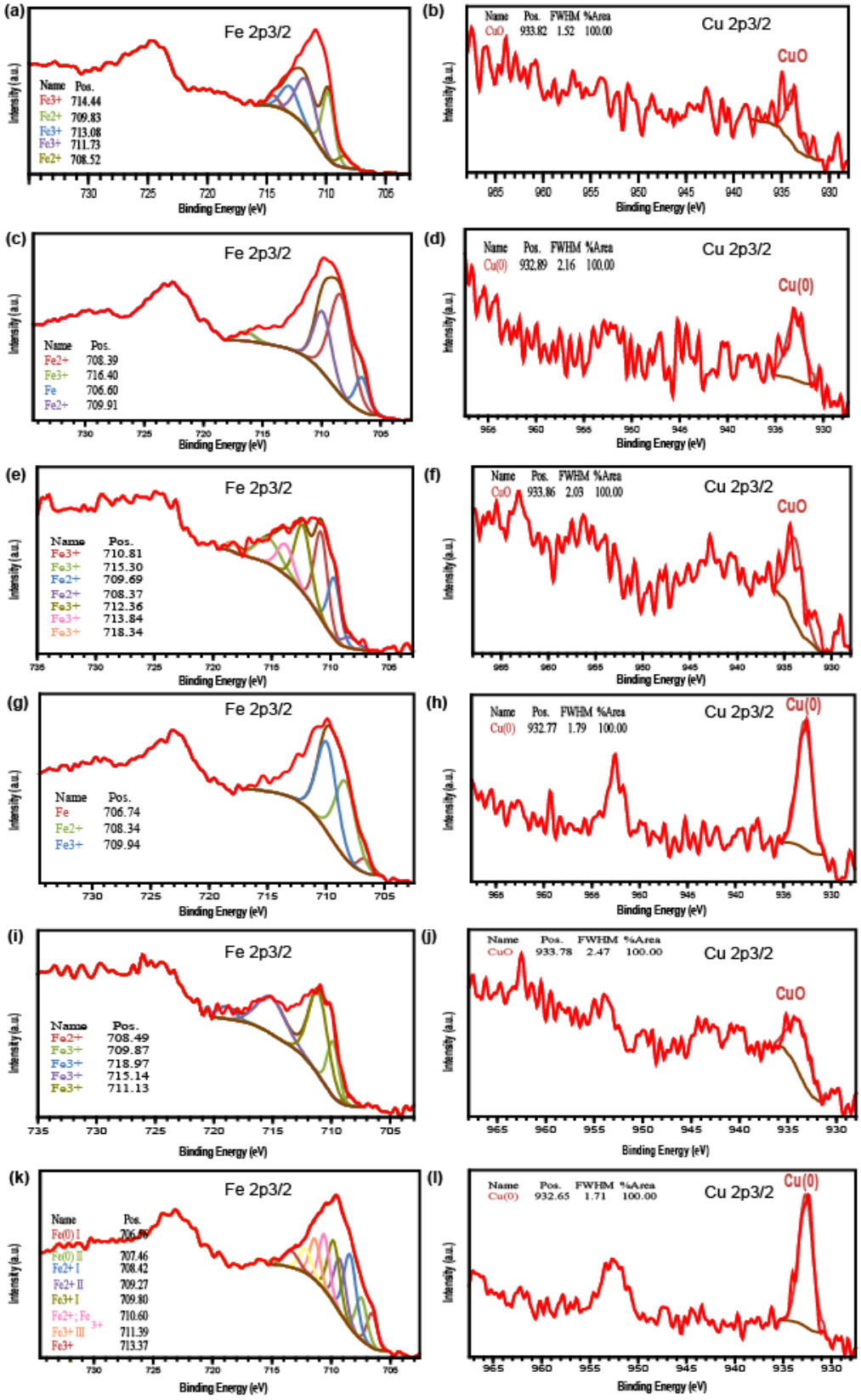

Figure S8. XPS analysis; quantification and deconvoluted spectra of copper and iron for catalysts (a, b) fresh 1%-Cu/FeO_x, (c, d) spent 1%-Cu/FeO_x, (e, f) fresh 3%-Cu/FeO_x, (g, h) spent 3%-Cu/FeO_x, (i. j) fresh 5%-Cu/FeO_x, and (k. l) spent 5%-Cu/FeO_x

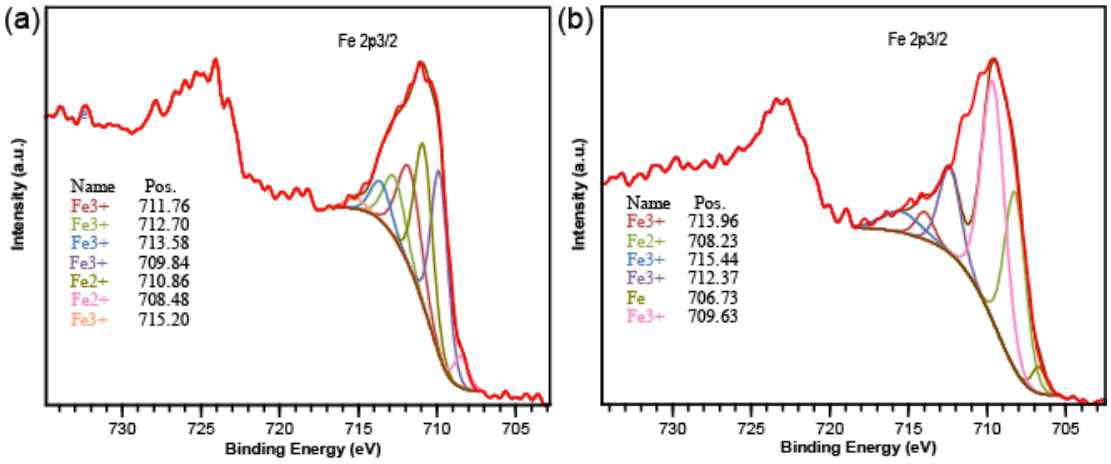

Figure S9. XPS analysis; quantification and deconvoluted spectra iron for catalysts (a) fresh FeO_x, and (b) spent FeO_x.

Table S2. Chemical composition of Fe and Cu in catalysts.

Catalyst	Fe(0)	Fe2+	Fe3+	Cu2+	Cu(0)
Fresh 1%Cu/FeO_x	-	+	+	+	-
Spent 1%Cu/FeO_x	+	+	+	-	+
Fresh 3%Cu/FeO_x	-	+	+	+	-
Spent 3%Cu/FeO_x	+	+	+	-	+
Fresh 5%Cu/FeO_x	-	+	+	+	-
Spent 5%Cu/FeO_x	+	+	+	-	+
Fresh FeO_x	-	+	+	-	-
Spent FeO_x	+	+	+	-	-

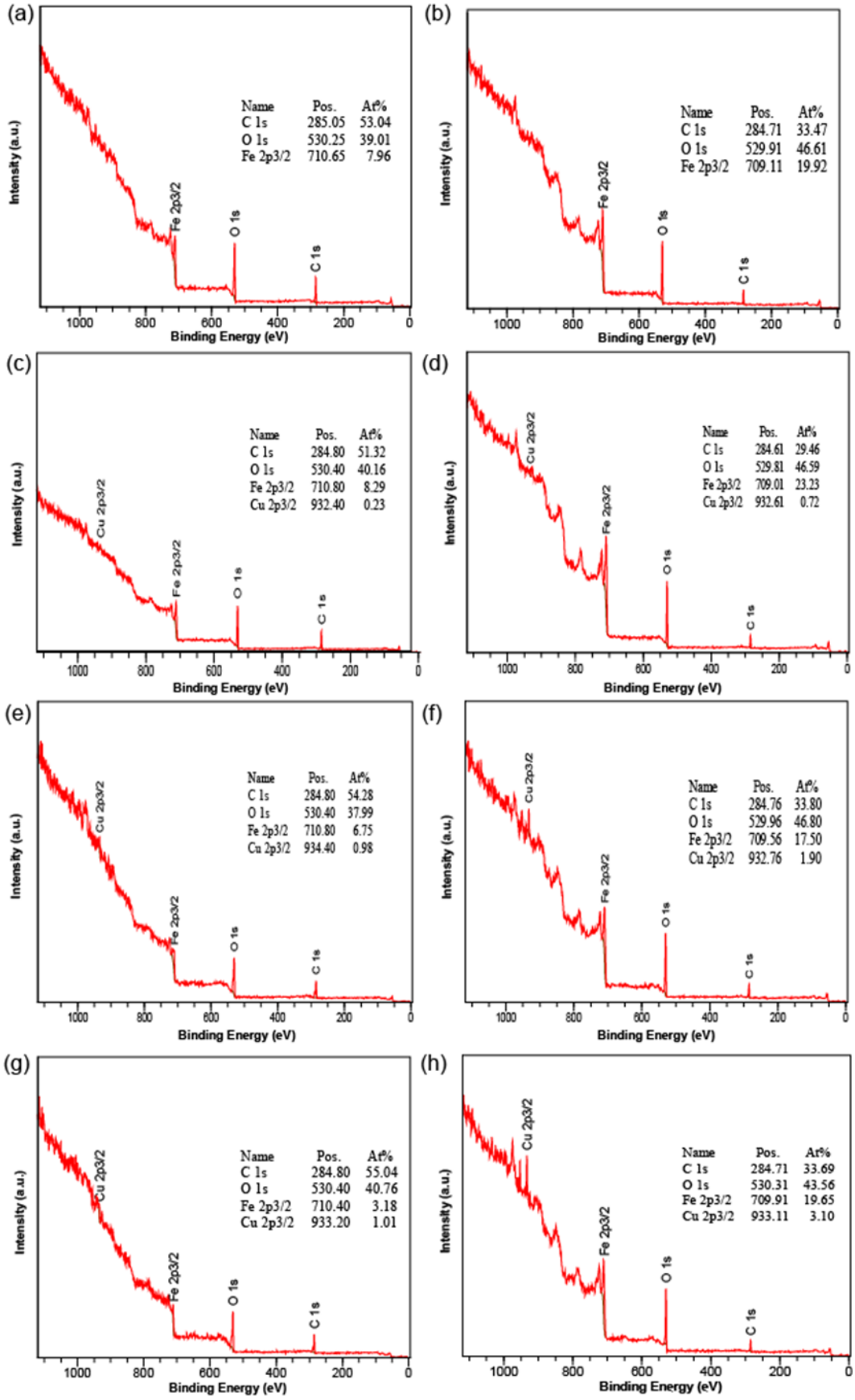

Figure S10. Wide scan XPS spectra of (a, b) fresh and spent FeO_x, (c, d) fresh and spent 1%-Cu/FeO_x, (e, f) fresh and spent 3%-Cu/FeO_x, (g, h) fresh and spent 5%-Cu/FeO_x, respectively.

Adsorption/desorption isotherms of fresh catalysts

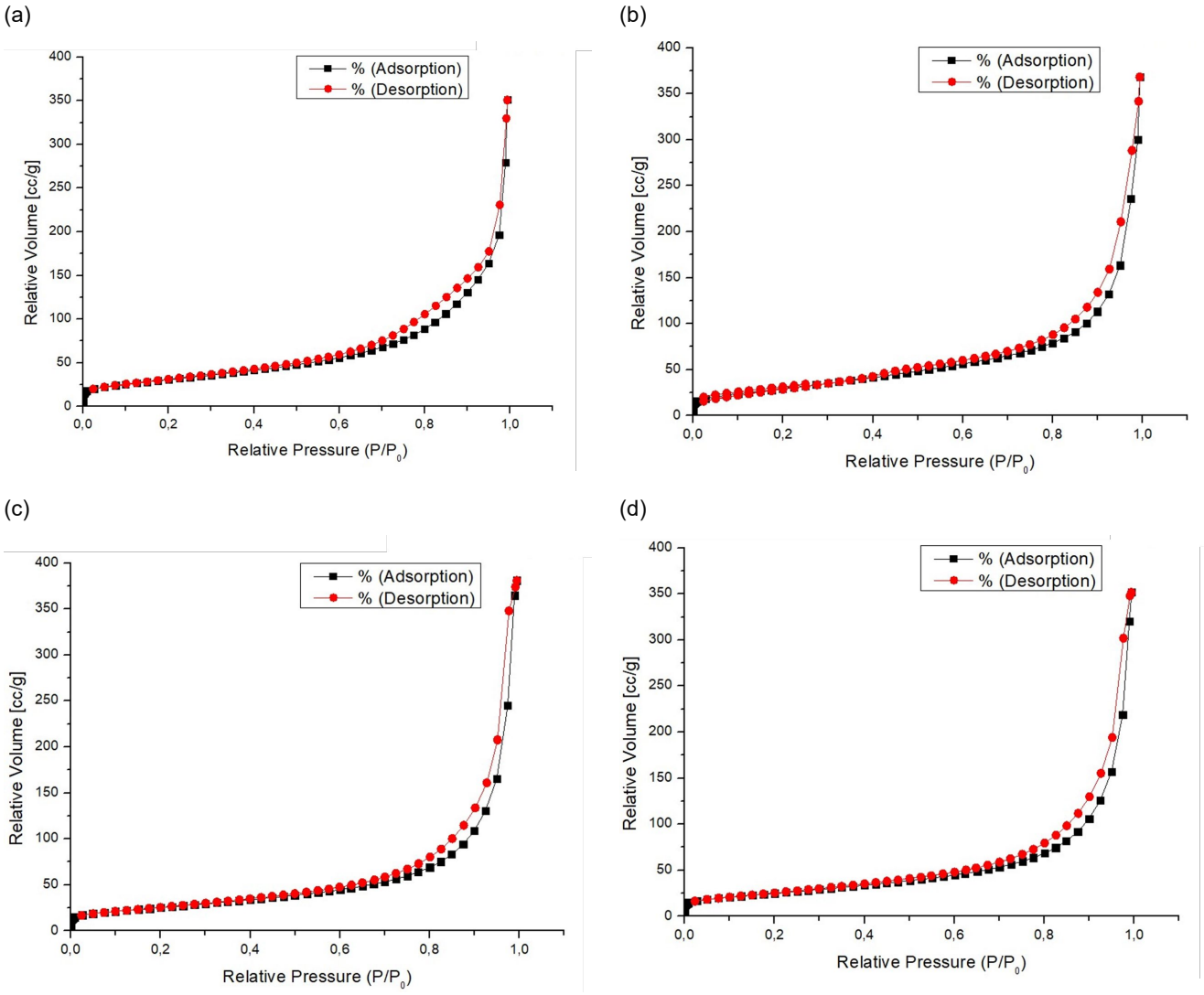

Figure S11. Adsorption and desorption isotherms of fresh (a) blank FeO_x, (b) 1%-Cu/FeO_x, (c) 3%-Cu/FeO_x and (d) 5%-Cu/FeO_x.

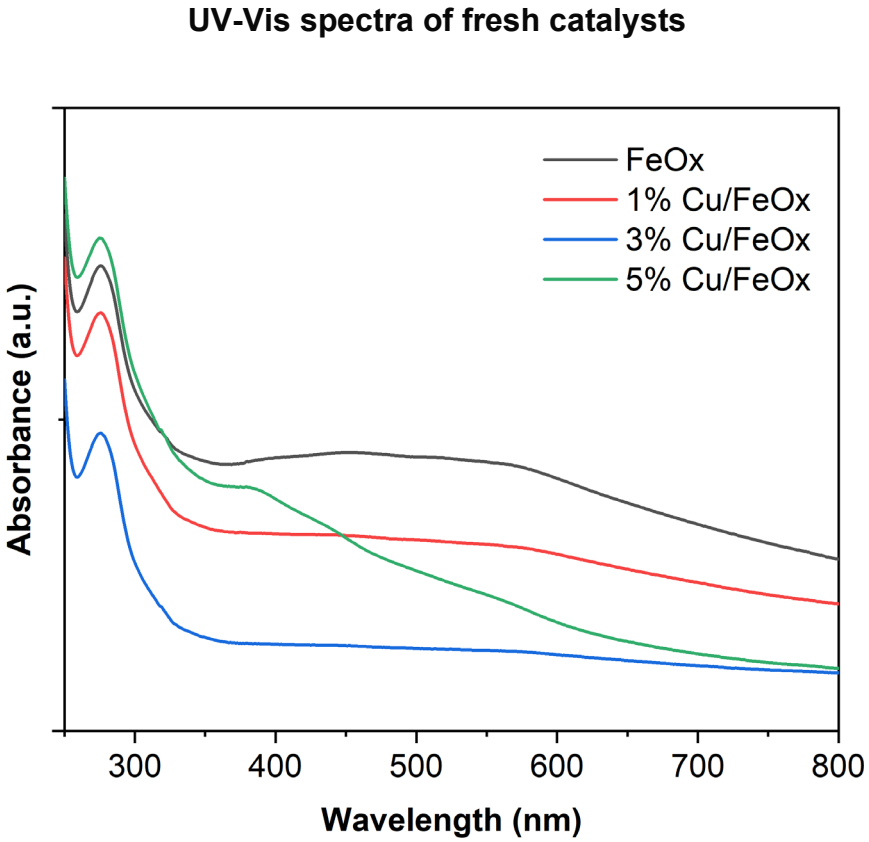

Figure S12. UV-Vis spectra of fresh catalysts. The spectra were recorded in glycerol.

Conversion and selectivities of FeO_x, 1%-Cu/FeO_x, 3%-Cu/FeO_x and 5%-Cu/FeO_x

Table S3: CO_2 conversion and product selectivities during 1st and 2nd temperature ramps. Reaction mixture was CO_2, H_2 and He in the ratio of 1:5:4 giving 11 % and 49 % of CO_2 and H_2 in He, respectively. Total flow 25 mL/min, pressure 1 bar. Products were analysed by gas chromatography.

Cat.	T [°C]	CO_2 conversion [%]		Selectivity [%]									
				CH_4		C_2-C_4		C_2-$C_4^=$		C_{5+}		CO	
	ramp	1.	2.	1.	2.	1.	2.	1.	2.	1.	2.	1.	2.
FeO_x	250	1.5	-	100	100	-	-	-	-	-	-	-	-
	280	2	0.7	100	100	-	-	-	-	-	-	-	-
	310	3.1	2.4	90.9	81.5	-	-	9.1	6.2	-	-	-	12.3
	340	7.9	6.9	26.2	71.2	18	-	36.4	14.4	19.5	-	-	14.5
	370	14.9	14	19.2	57.6	22.7	-	31.9	10.5	26.2	-	-	31.9
	410	30.3	28.2	29.7	80	25	-	31.6	20	13.7	-	-	-
1%-Cu/FeO_x	250	-	1.4	-	69.5	-	22.8	-	6.1	-	-	-	1.6
	280	-	3.4	100	69.1	-	17.9	-	10.1	-	1.25	-	1.6
	310	3.5	8.3	39.5	66.5	12	13.1	45	16.1	3.4	2.2	-	2.1
	340	14.7	13	50.1	65.4	13.6	8.5	27	21.8	6.6	2	2.7	2.4
	370	23.5	21.6	60.5	64.5	5.7	5.8	29	25.6	2.3	1.5	2.5	2.7
	410	34.7	34.4	73.3	75.2	3.4	4.3	19.9	17.4	0.5	0.4	3	2.7
3%-Cu/FeO_x	250	2.3	7.3	96	62.2	-	32.3	-	-	-	2.8	4	2.8
	280	6.2	10.9	83.5	58.5	5.2	34.2	8.3	2.2	-	2.4	3.3	2.6
	310	13	17.3	67.7	56.7	11.4	31.7	17.2	5.6	1.3	3.5	2.8	2.5
	340	19.1	22.9	60.9	59.6	15.1	24.2	18	10.9	3.5	2.8	2.5	2.6
	370	27.3	26.8	62.7	66.3	17.7	14.2	14.6	15.1	2.3	1.4	2.7	3.1
	410	36.5	36.8	82.6	82.2	6.5	6.2	6.9	8	0.4	-	3.6	3.6
5%-Cu/FeO_x	250	1.4	5.6	100	57	-	37.3	-	0.3	-	2.9	-	2.6
	280	5.6	11.8	78.4	55.3	8	36.4	7.1	1.8	-	3.9	6.5	2.5
	310	12	17	69.3	54.3	17.7	34.8	9	3.5	1.3	4	2.7	3.3
	340	20	23.7	66.9	57.6	20.4	29.7	6.8	6.4	1.9	3	4.1	3.3
	370	27.8	29.5	78.3	68.6	12.3	18.6	4.5	7.2	0.4	1.3	4.4	4.3
	410	35	35.6	92.3	86.6	2.4	4	0.2	2.7	-	1.3	5.1	5.4

TEM images of fresh of fresh and spent catalysts

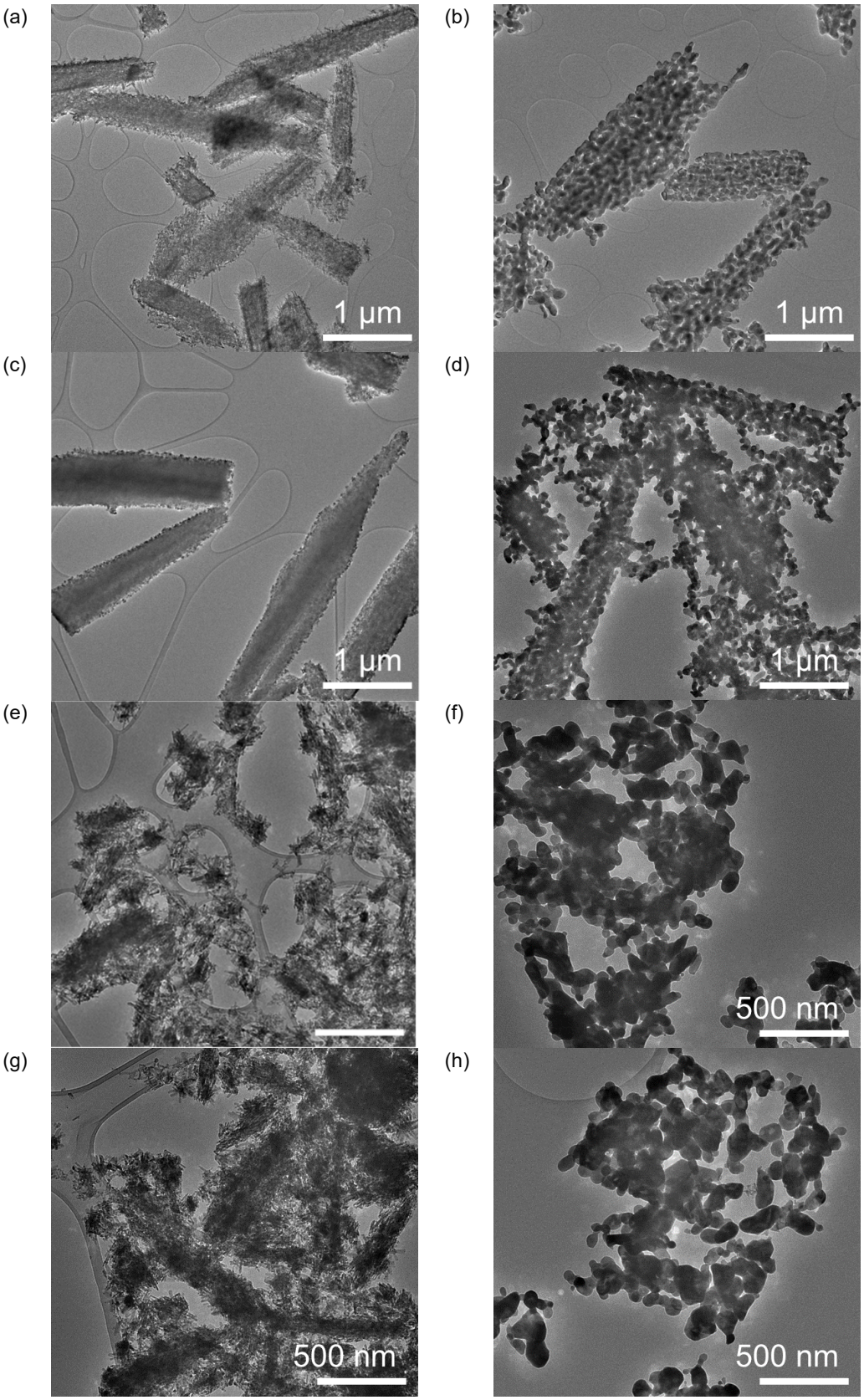

Figure S13: TEM images of (a) fresh FeO_x and (b) spent FeOx, (c) fresh 1%-Cu/FeO_x and (d) spent 1%-Cu/FeO_x,, (e) fresh 3%-Cu/FeO_x and (f) spent 3%-Cu/FeO_x,, (g) fresh 5%-Cu/FeO_x and (h) spent 5%-Cu/FeO_x catalyst.

SEM/EDX of spent catalysts

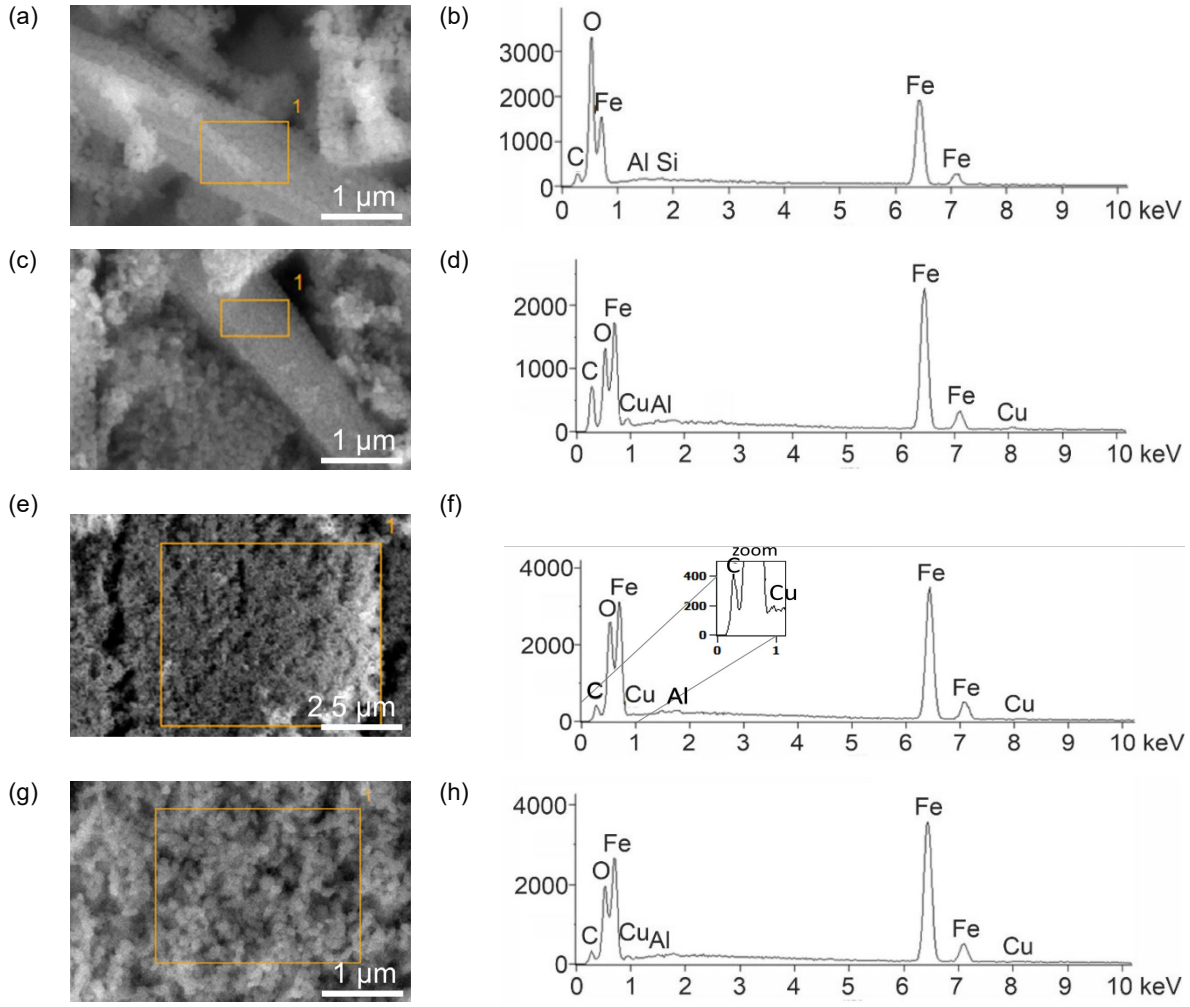

Figure S14. SEM images of the spent catalysts and EDX of the selected part of the image in highlighted rectangles with included particles, (a, b) spent FeO_x, (c, d) spent 1%-Cu/FeO_x, (e, f) spent 3%-Cu/FeO_x, (g, h) spent 5%-Cu/FeO_x.

STEM/HAADF images of spent FeO_x

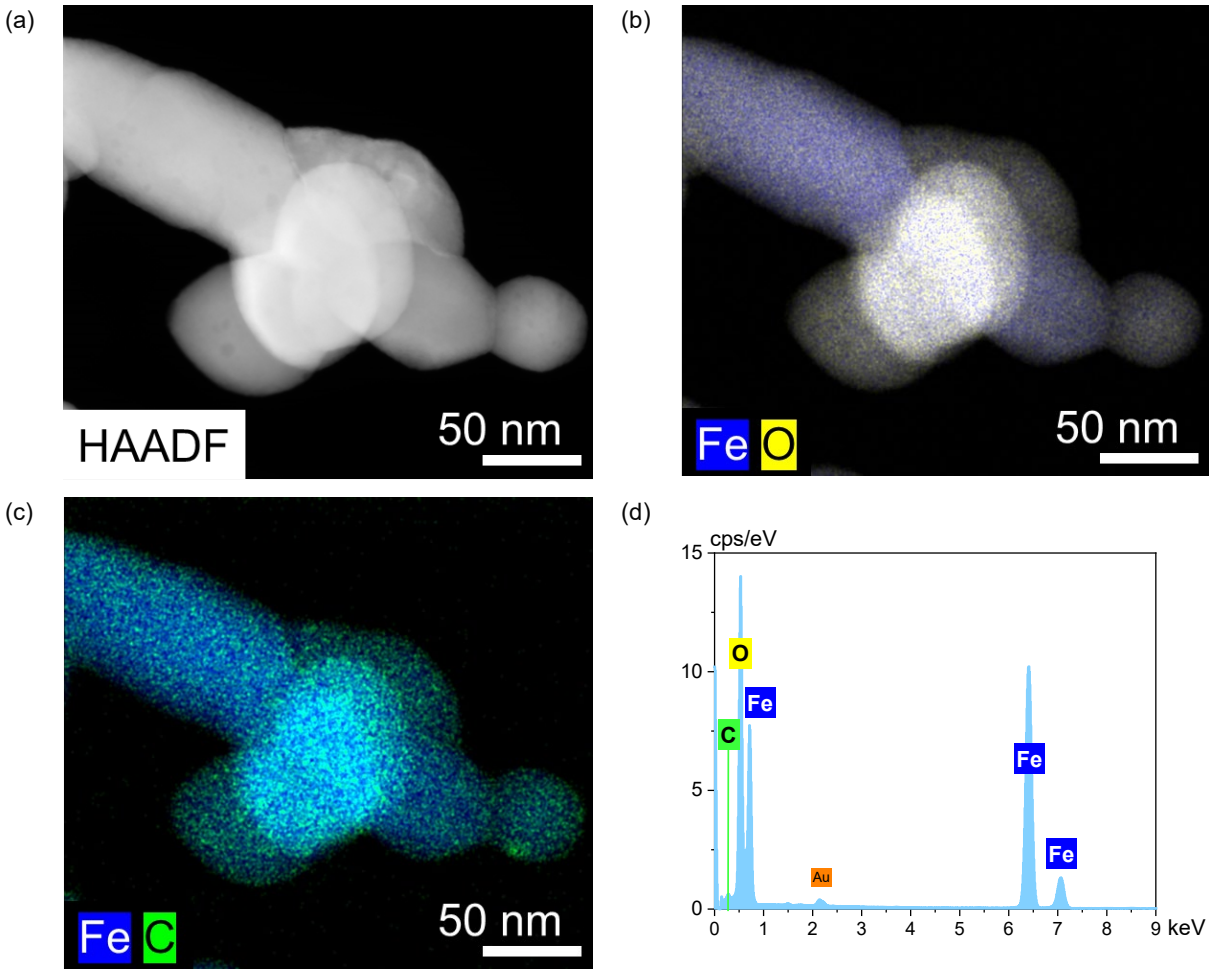

Figure S15. (a) STEM-HAADF of spent FeO_x, and (b-d) EDX elemental mapping of Fe, O, C and Cu.

STEM/HAADF images of spent 1%-Cu/FeO_x

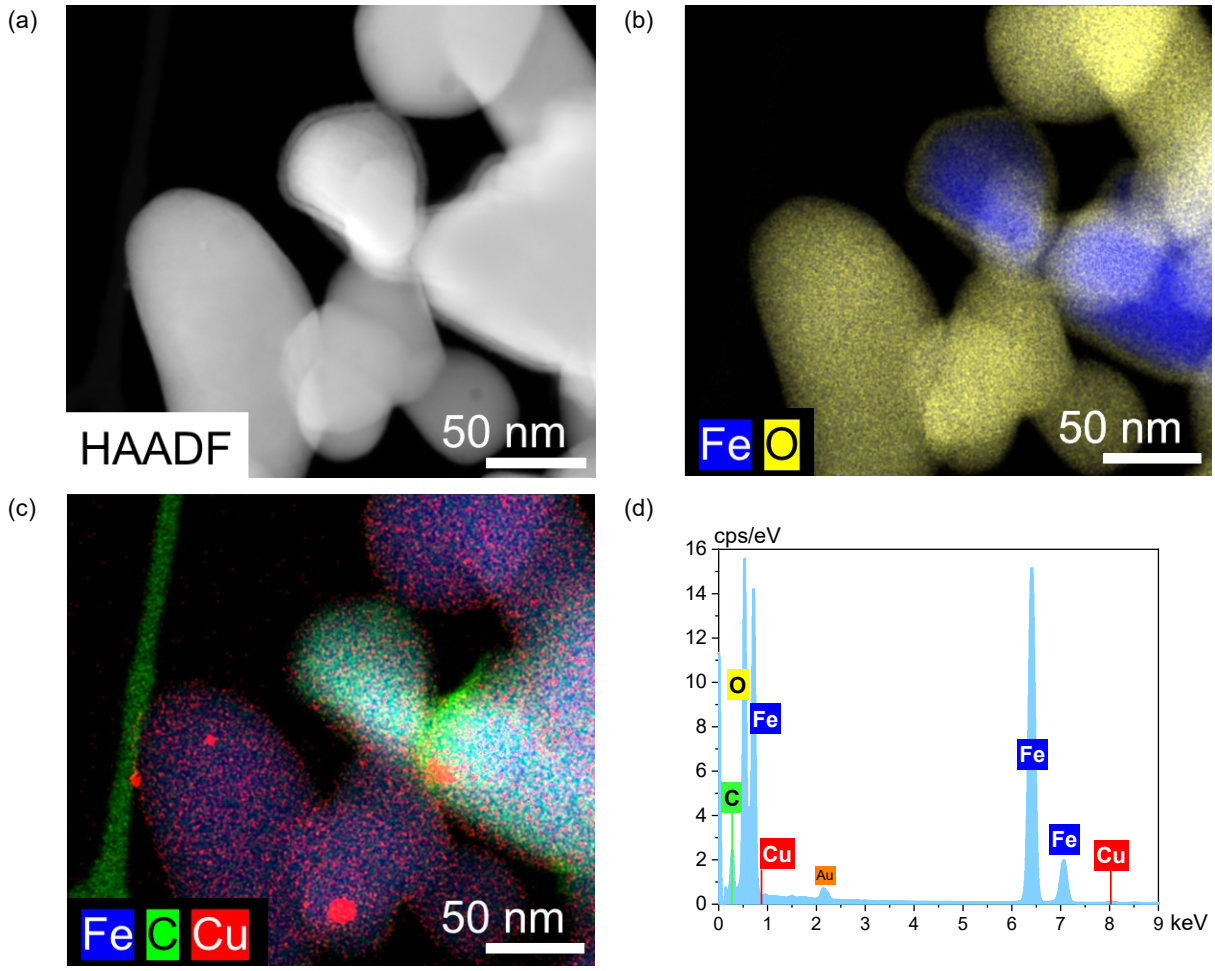

Figure S16. (a) STEM-HAADF of spent 1%-Cu/FeO_x, and (b-d) EDX elemental mapping of Fe, O, C and Cu.

STEM/HAADF images of spent 3%-Cu/FeO_x

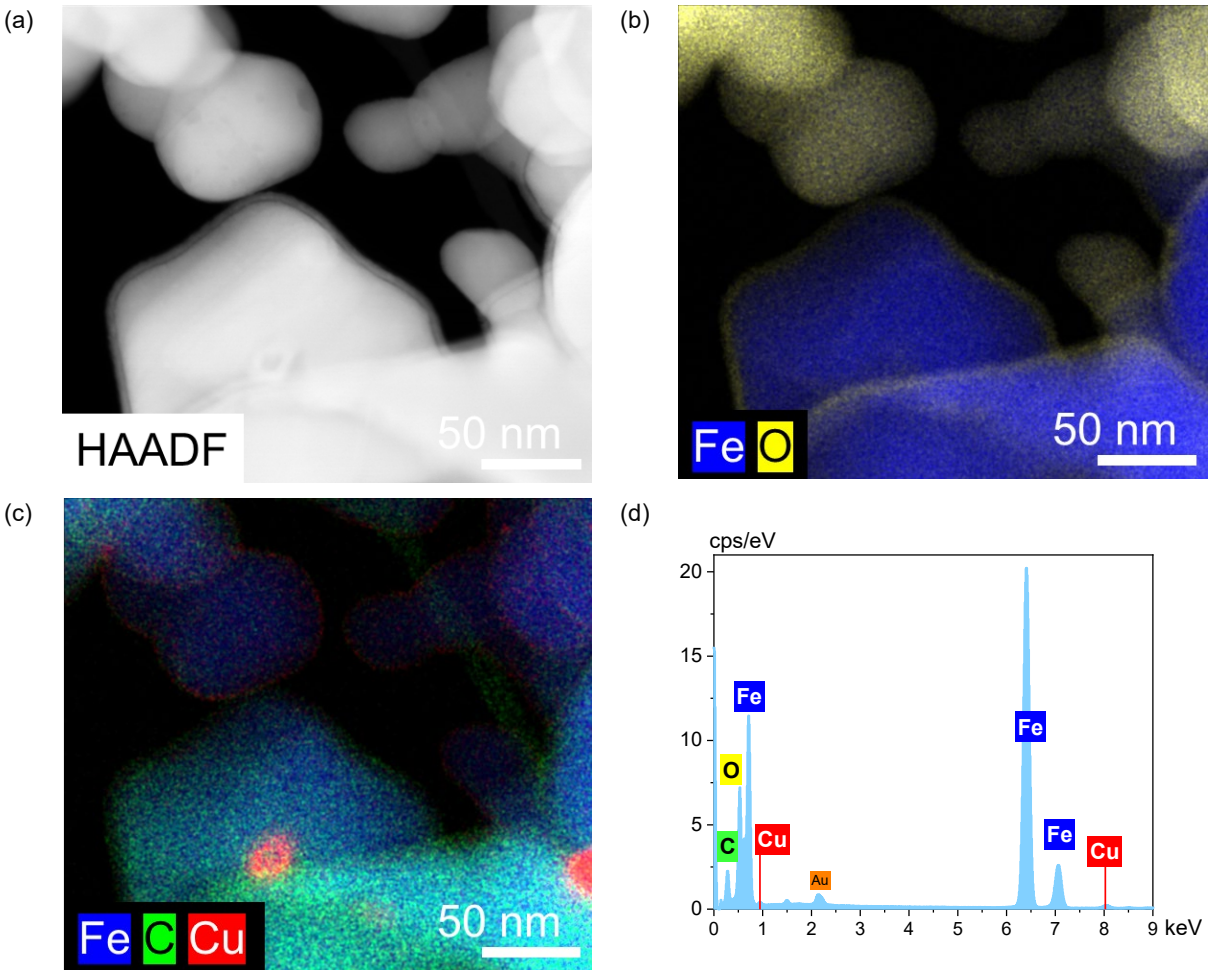

Figure S17. (a) STEM-HAADF of spent 3%-Cu/FeO_x, and (b-d) EDX elemental mapping of Fe, O, C and Cu.

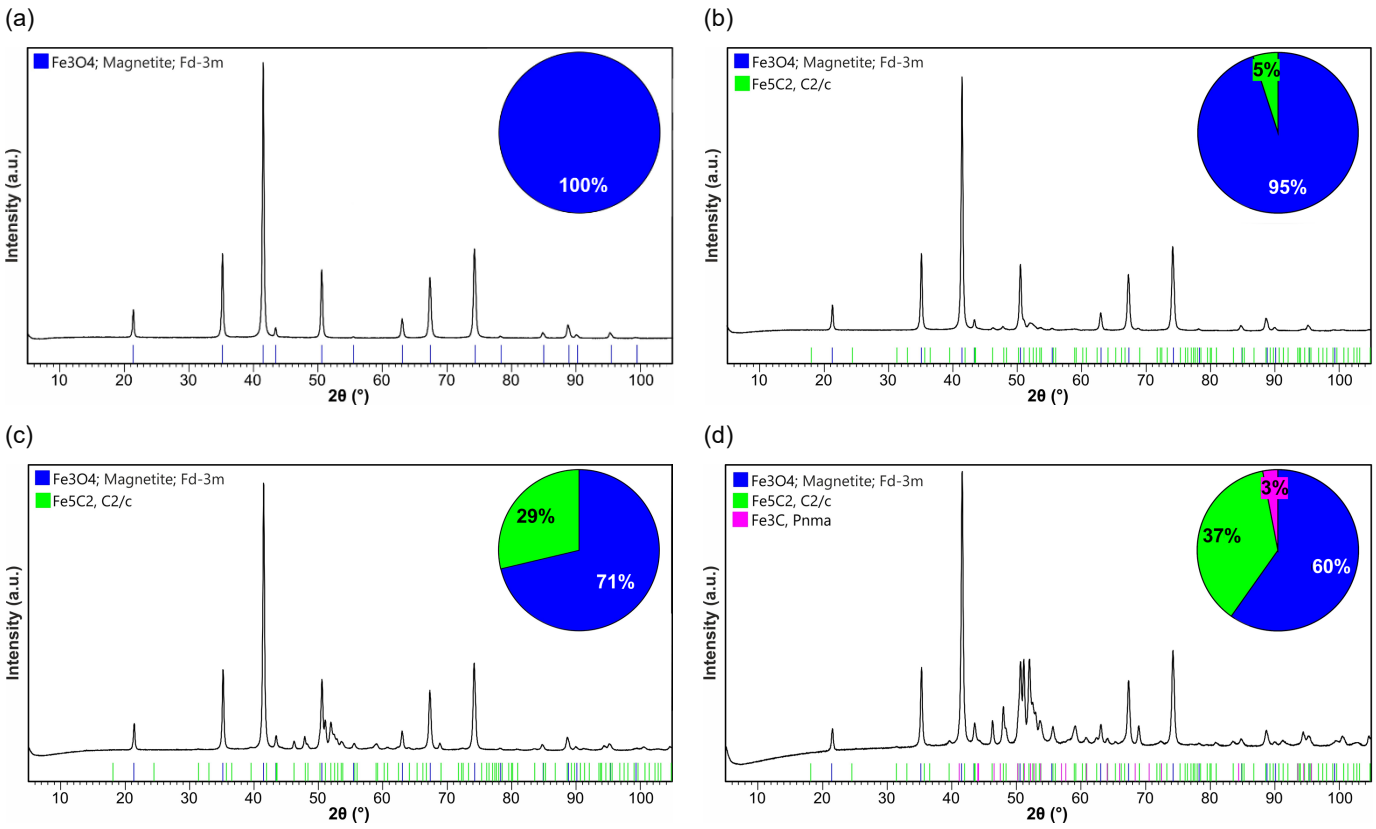

Figure S18. XRD patterns of spent (a) FeO_x, (b) 1%-Cu/FeO_x, (c) 3%-Cu/FeO_x and (d) 5%-Cu/FeO_x.

Mean X-ray coherence length of spent catalysts

Table S4. Mean X-ray coherence length of spent catalysts obtained from XRD data using Rietveld refinement of analysis.

Catalyst	**Fe_3O_4 [nm]**	**Fe_5C_2 [nm]**	**Fe_3C [nm]**
FeO_x	63.0	0.0	0.0
1%-Cu/FeO_x	63.0	29.0	0.0
3%-Cu/FeO_x	47.0	40.0	0.0
5%-Cu/FeO_x	36.0	35.0	23.0

Adsorption/desorption isotherms of spent catalysts

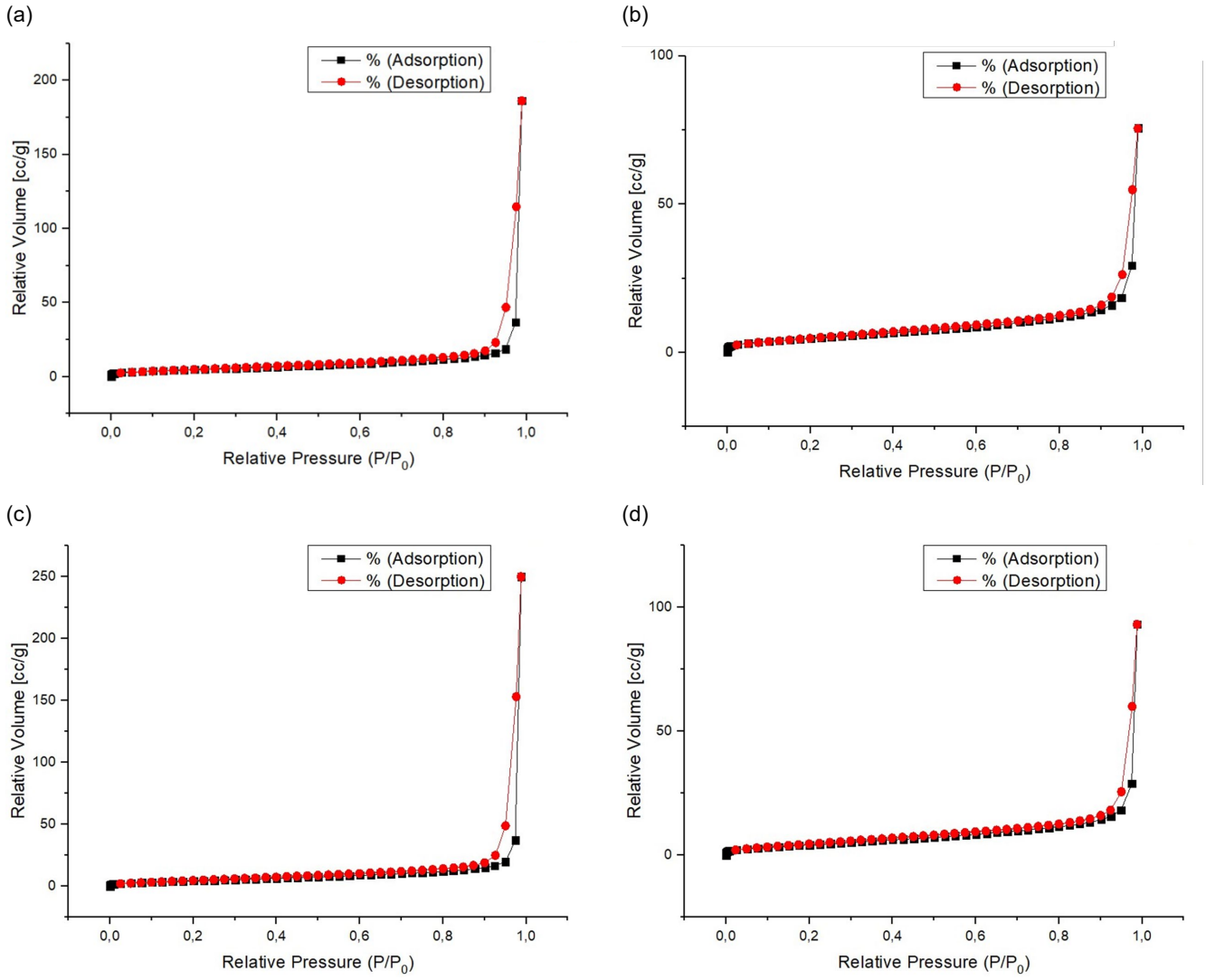

Figure S19. Adsorption and desorption isotherms of spent (a) FeO_x, (b) 1%-Cu/FeO_x, (c) 3%-Cu/FeO_x and (d) 5%-Cu/FeO_x.

Comparison of the performance of the catalysts as the function of temperature during the second ramp

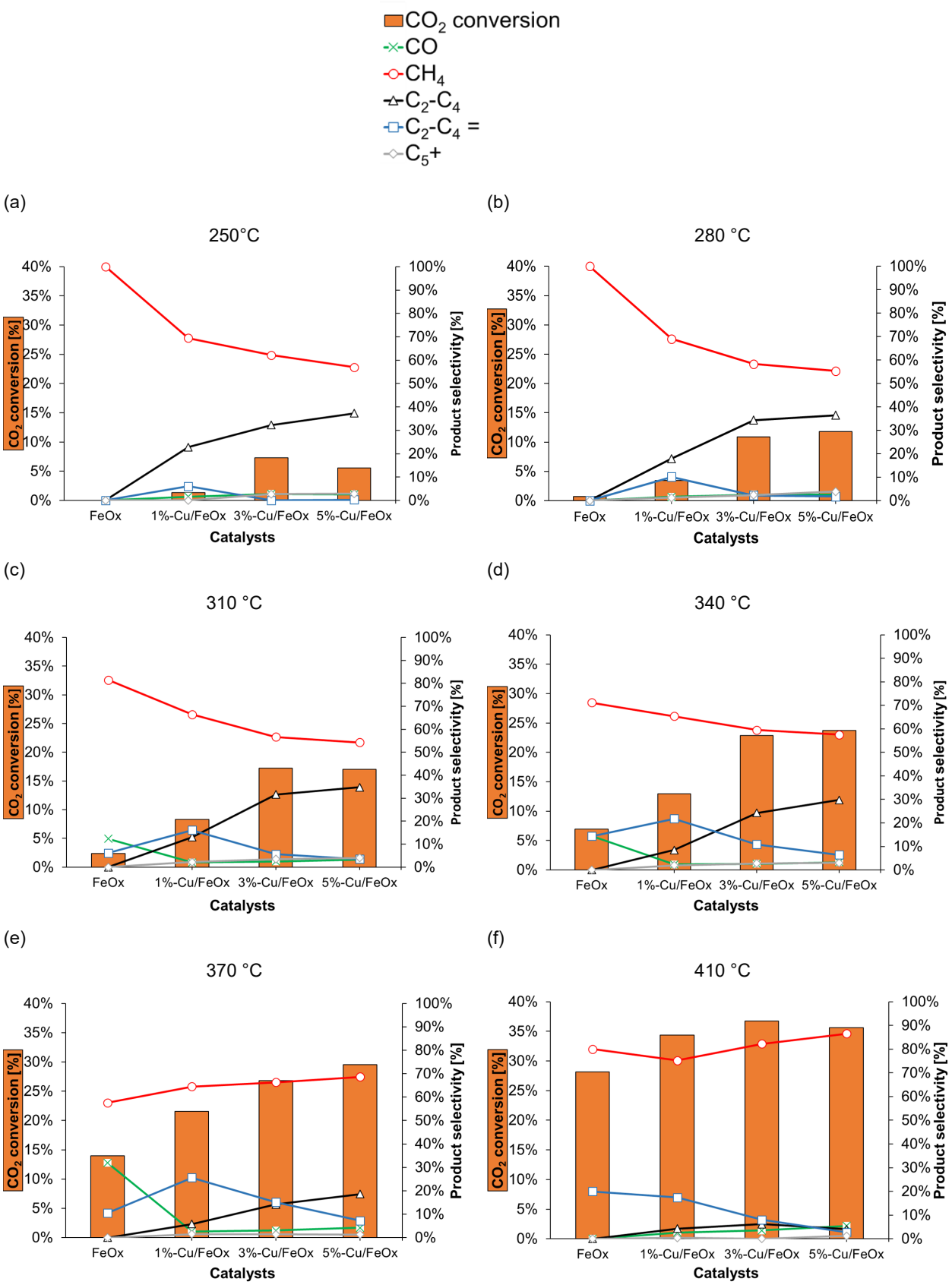

Figure S20. (a-f) CO_2 conversion and product selectivity of the studied catalysts as the function of temperature during the second temperature ramp.

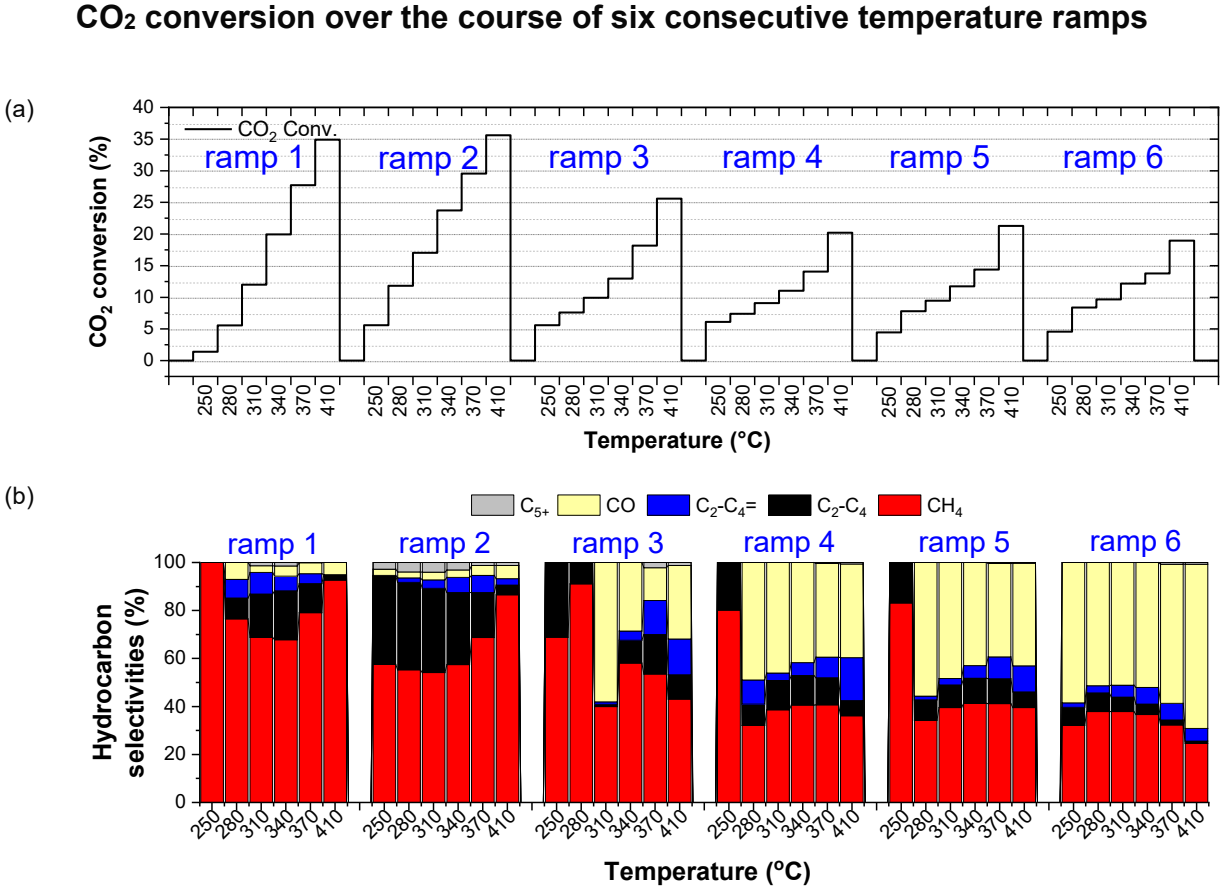

Figure S21. 5%-Cu/FeO_x. (a) CO_2 conversion throughout 6 consecutive temperature ramps. (b) Product selectivity throughout 6 consecutive temperature ramps. CO_2 200 mg of catalyst and CO2/H2/He (1:5:4, total flow 25 ml/min).

Literature comparison of CO_2 hydrogenation by different iron-based catalysts

Table S5. Literature review of Fe-based catalysts for CO_2 hydrogenation

Entry	Cat.	Temp. (°C)	Pretreatment	CO_2 Conv. (%)	Selectivity (%)					Ref.
					CH_4	CO	C_2-$C_4^=$	C_2-C_4	C_5+ and others	
1	**1%-Cu/FeOx**	**370**	**None**	**23.5**	**60.5**	**2.5**	**29**	**5.7**	**2.3**	*
2	**3%-Cu/FeO_x**	**370**	**None**	**27.3**	**62.7**	**2.7**	**14.6**	**17.7**	**2.3**	*
3	**5%-Cu/FeO_x**	**370**	**None**	**27.8**	**78.3**	**4.4**	**4.5**	**12.3**	**0.4**	*
4	Fe-Mn-K	300	H_2:CO=2:1, 320°C, 24h	38.2	10.4	5.6	25.2	2	61.9	[1]
5	Fe–Co/Al2O3-K	300	H_2, 400°C, 2h	36	16	13	-	71	-	[2]
6	Fe/Co-Y	300	H_2, 380°C, 8h	29.6	14	21	-	30	55	[3]
7	Na/FeOx	320	H_2, 350°C, 12h	36	8	10	64	18	-	[4]
8	Ru-FeOx/Al_2O_3	300	H_2, 300°C	18	55	-	-	45	-	[5]
9	Fe-Ru-K	300	H_2, 450°C, 5h	47	16.4	3.1	19.7	7.4	53	[6]
10	Fe-K/alumina	300	H_2, 450°C, 13h	31.3	11	7	-	36	46	[7]
11	Fe/CNT	350	H_2, 400°C, 2h	20	36	22	-	33	9	[8]
12	Cu/Fe_2O_3	300	H_2, 400°C, 2h	17	2-3	31	-	32	65	[9]
13	Na–Fe_3O_4/HMCM	320	H_2, 350°C, 8h	26	8	17	-	26	57	[10]
14	$ZnFe_2O4$	340	H_2, 400°C, 2h	28	44	22	-	34	-	[11]
15	Fe-Ru-Mn-K/Al_2O_3	300	10% H_2, 500°C, 2h	30	19	18	-	39	25	[12]
16	Co-Fe	270	CO, 250°C, 20h	23	31	53	-	12	-	[13]
17	Mn-Na-Fe	320	H_2, 350°C, 12h	38.6	11.8	11.8	30.2	4	42.1	[14]
18	Fe-Ce	300	33% H_2, 400°C, 16h; 33% CO, 400°C, 16h	25	38	19	-	38	4	[15]
19	Na-Fe_3O_4	320	H_2, 350°C, 12h	40.5	15.8	13.5	46.6	7.5	30.1	[16]
20	Mn/Fe3O4-EDA	320	None	20	40	41	1	36	23	[17]
21	K-FeC/ZrO_2	220	H_2, 400°C, 4h	40	13	32	25	-	30	[18]
22	Fe-Cu-K-Al	300	CO, 350°C, 4h	41	15.6	2.5	-	38	44	[19]
23	Fe-Cu-K	300	H_2, 400°C, 2h	29.7	7	17	22	-	54	[20]
24	Na-$CoFe_3O_4$	320	H_2, 400°C, 3h	34	15	-	39	6	40	[21]
25	Fe_2O_3	300	50% H_2, 500°C, 2h	23	14	n.a	-	-	65	[22]
26	K-Fe_2O_3	270	H_2:CO=1:1, 350°C, 1h	36	20	13	35	8	24	[23]
27	Mn-FeO	340	H_2, 400°C, 5h	30	40	7	-	52	n.a	[24]

* This work.

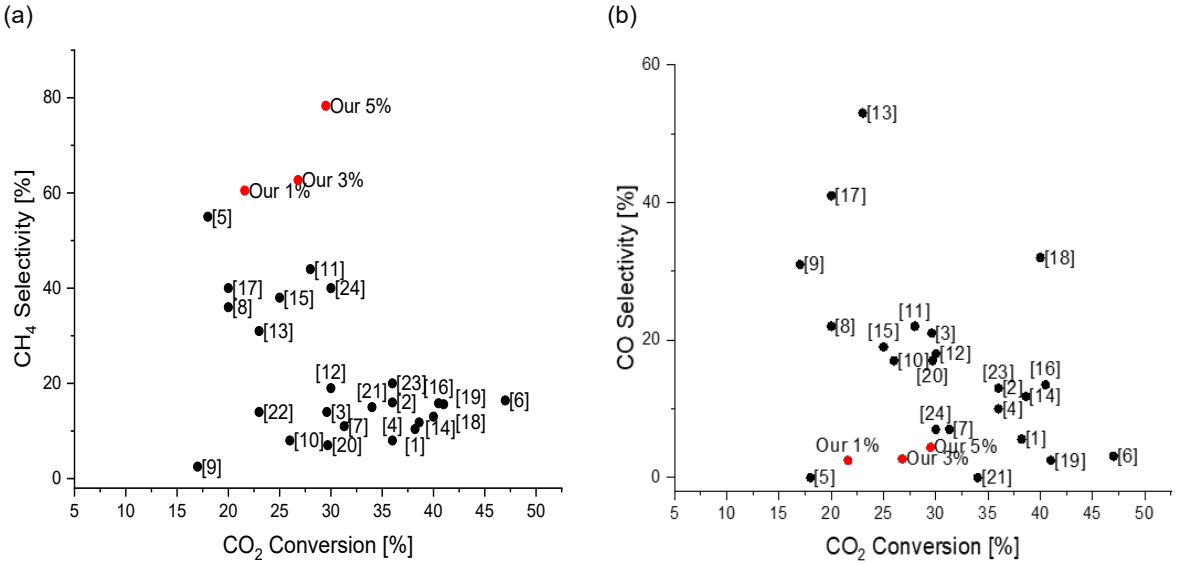

Figure S22. (a) CH_4 selectivity plotted against CO_2 conversion and (b) CO selectivity plotted against CO_2 conversion for catalysts from literature review (**Table S5**) including reference numbers. Our catalysts are red points.

References

1. Yao, B.; Xiao, T.; Makgae, O.A.; Jie, X.; Gonzalez-Cortes, S.; Guan, S.; Kirkland, A.I.; Dilworth, J.R.; Al-Megren, H.A.; Alshihri, S.M., et al. Transforming Carbon Dioxide into Jet Fuel Using an Organic Combustion-Synthesized Fe-Mn-K Catalyst. *Nat Commun* **2020,** *11* (1), 6395.
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