

Supplementary Information

CO₂ hydrogenation over unsupported Fe-Co nanoalloy catalysts

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Mass spectrometry

Table S1. Reference table for the assignments of mass spectrometer peaks.

Molecule	Major peak of molecule [m/z] (100% relative intensity)	Reference peak for molecule[m/z]	Relative intensity reference peak [%]	Minor contributions to peak. Relative intensity to the molecules major peak (greater than 5%)
CH ₄	16	15	89	MeOH (12%), EtOH (7%)
C ₂ H ₄	28	26	53	C ₂ H ₆ (23%), C ₃ H ₆ (10%), C ₃ H ₈ (9%), C ₄ H ₈ (8%), EtOH (10%)
C ₂ H ₆	28	30	26	MeOH (6%), EtOH (8%)
C ₃ H ₆	41	39	73	C ₃ H ₈ (18%), C ₄ H ₈ (34%), C ₄ H ₁₀ (17%), C ₅ H ₁₀ (14%), C ₅ H ₁₀ (27%), C ₅ H ₁₂ (19%),
C ₃ H ₈	29	29	100	C ₂ H ₆ (22%), C ₄ H ₈ (13%), C ₅ H ₁₀ (21%), C ₅ H ₁₂ (14%), MeOH (45%), EtOH (30%)
C ₄ H ₈	41	56	39	None
C ₄ H ₁₀	43	43	100	C ₃ H ₈ (18%), C ₅ H ₁₂ (100%)
C ₅ H ₁₀	42	70	39	None
C ₅ H ₁₂	43	57	20	None
CO ₂	44	44	100	C ₃ H ₈ (27%)
CO	28	28	100	C ₂ H ₄ (100%), C ₂ H ₆ (100%), C ₃ H ₈ (59%), C ₄ H ₈ (27%), CO ₂ (10%)
H ₂ O	18	18	100	None
MeOH	31	32	74	None
EtOH	31	45	51	None

Activation energy determination

Table S2. Activation temperature (T_a) of selected m/z mass spectrometer peaks, which are assigned to C₁-C₅ hydrocarbon products, the corresponding temperature of the maximum activity Tmax, the starting and ending temperature of the kinetically determined reaction range (T1 kin and T2 kin) and activation energy (E_a). %Tmax is an indicator that tells if the reaction is solely limited by the reaction kinetics; it gives the ratio of T2 kin compared to Tmax. R² is assigned to the Arrhenius plots (inverse T1 kin to T2 kin vs. the natural logarithm of the normalized MS signal) on which the activation energy is determined.

Sample 30Fe70Co.

m/z	ass. comp.	T_a [K]	Tmax [K]	T1 kin [K]	T2 kin [K]	Width kin [K]	% Tmax	Max signal	E_a [kJ/mol]	R ²
15	CH ₄	444	570	444	525	81	64%	9.47E-10	70	0.999
26	C ₂ H ₄	480	600	461	570	109	75%	7.39E-11	80	0.997
29	C ₃ H ₈	470	590	529	578	49	90%	1.66E-10	64	0.998
30	C ₂ H ₆	480	590	489	570	81	82%	5.26E-11	67	0.999
39	C ₃ H ₆	480	600	546	583	37	86%	7.32E-11	101	0.998
56	C ₄ H ₈	460	600	534	591	57	94%	1.98E-11	89	0.997
57	C ₅ H ₁₂	460	590	534	583	49	95%	7.28E-12	41	0.987
70	C ₅ H ₁₀	460	595	534	587	53	94%	6.14E-12	67	0.982

Sample 50Fe50Co.

m/z	ass. comp.	T_a [K]	Tmax [K]	T1 kin [K]	T2 kin [K]	Width kin [K]	% Tmax	Max signal	E_a [kJ/mol]	R ²
15	CH ₄	500	615	499	581	82	70%	3.41E-10	75	0.992
26	C ₂ H ₄	530	620	540	581	41	57%	5.04E-11	138	0.988
29	C ₃ H ₈	520	620	565	590	25	70%	1.14E-10	83	0.995
30	C ₂ H ₆	530	620	573	590	17	67%	2.54E-11	105	0.99
39	C ₃ H ₆	530	615	540	581	41	60%	5.24E-11	160	0.984
56	C ₄ H ₈	560	610	557	581	24	42%	1.49E-11	165	0.992
57	C ₅ H ₁₂	550	585	561	573	12	66%	6.20E-12	141	0.979
70	C ₅ H ₁₀	560	610	557	577	20	34%	5.28E-12	135	0.992

Sample 76Fe24Co.

m/z	ass. comp.	T_a [K]	Tmax [K]	T1 kin [K]	T2 kin [K]	Width kin [K]	% Tmax	Max signal	E_a [kJ/mol]	R ²
15	CH ₄	560	645	566	599	33	46%	5.09E-10	137	0.998
26	C ₂ H ₄	560	640	557	591	34	39%	5.95E-11	241	0.991
29	C ₃ H ₈	560	630	574	603	29	61%	1.44E-10	109	0.996
30	C ₂ H ₆	560	635	566	603	37	57%	4.36E-11	161	0.996
39	C ₃ H ₆	560	630	557	578	21	26%	4.82E-11	277	0.996
56	C ₄ H ₈	560	620	557	578	21	30%	1.39E-11	228	0.992
57	C ₅ H ₁₂	560	600	557	578	21	45%	8.23E-12	198	0.99
70	C ₅ H ₁₀	560	605	562	574	12	31%	5.03E-12	226	0.988

Catalytic properties: product by product comparison

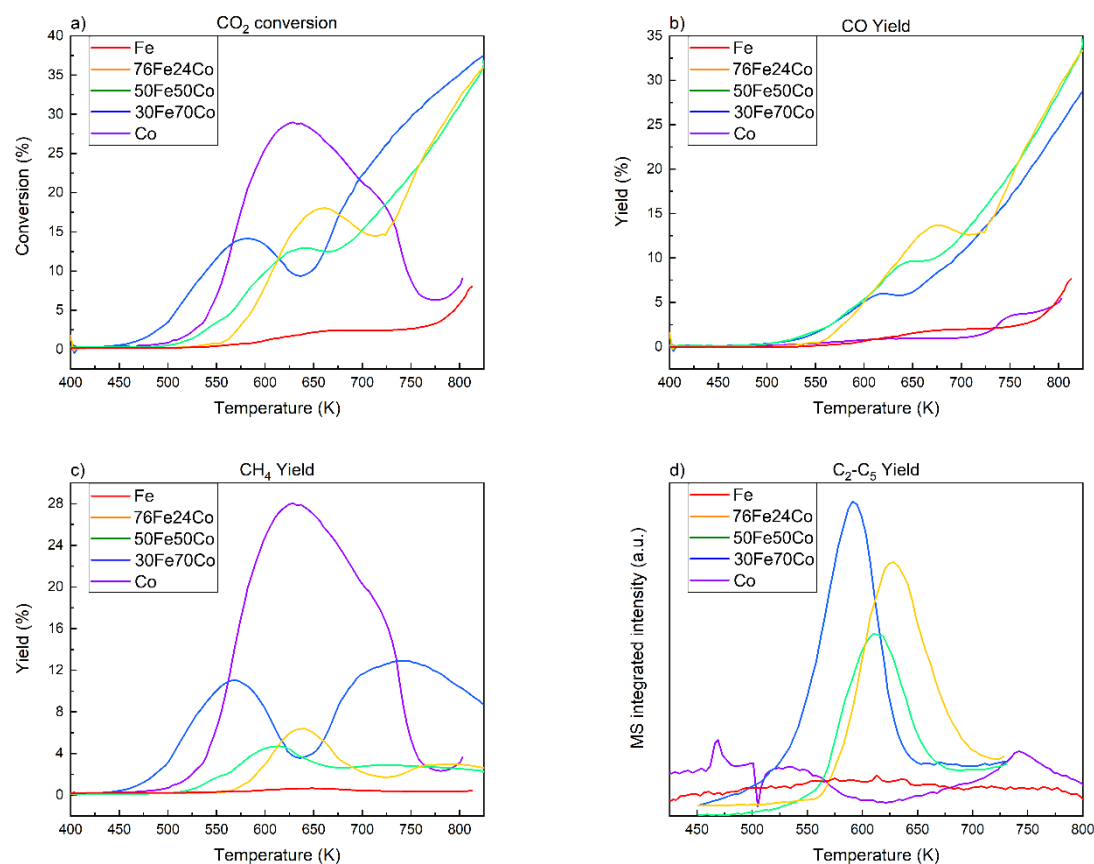


Figure S1. Catalytic properties of Fe, Co and Fe-Co NPs in a flow reactor with 4:1 H₂:CO₂ ratio, 1 bar and 10 ml_n min⁻¹, measured by mass spectroscopy. (a) CO₂ conversion (b) CO yield, (c) CH₄ yield (d) conversion curves of the summed up C2-C5 mass spectrometer normalized signals for m/z=26,29,30,39,56,57,70.

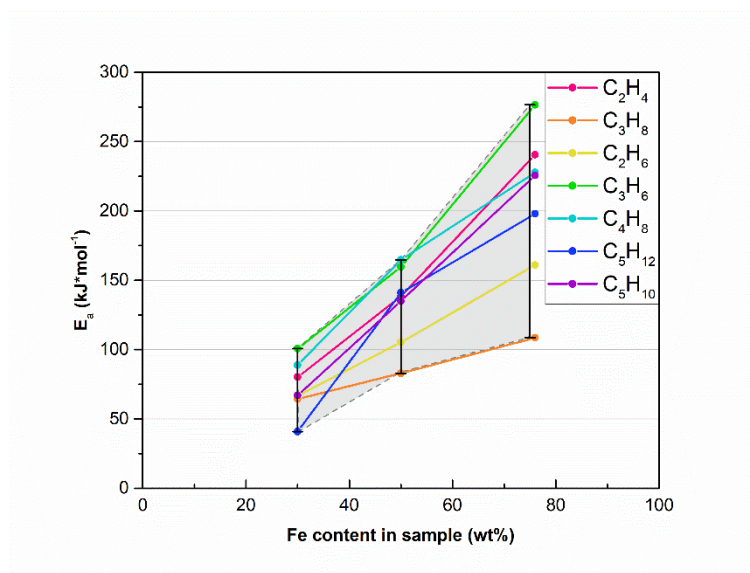


Figure S2. Activation energies of C₂-C₅ products formation as a function of the Fe content in the alloy precursor. The colours corresponding to the different products are listed in the legend, with the m/z ratio of the MS reference peak increasing from top to bottom.

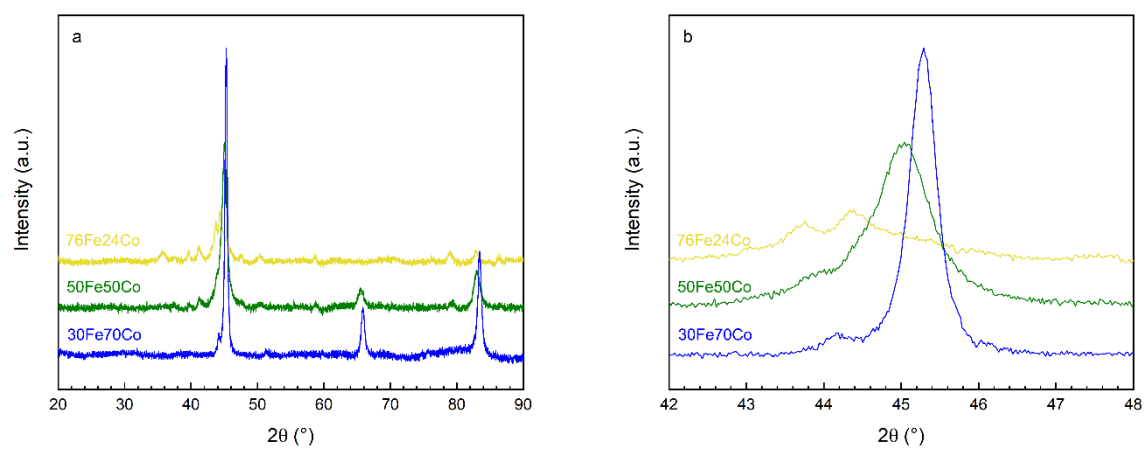


Figure S3. (a) XRD of the Fe-Co samples after the CO₂ hydrogenation experiments, background corrected; (b) a detail of the main FeCo *bcc* peak shifted to higher angular positions with increasing Co content.