SUPPORTING INFORMATION

Size and Promoter Effects on Stability of Carbon-Nanofiber-Supported Iron-Based Fischer–Tropsch Catalysts

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SI 1. Elemental loading

Table S1. Elemental loading of catalysts

	Fe	Na	S	Ni	K
Blank CNF	0.03	0.06	< 0.007	0.01	< 0.014
3Fe	1.92	0.03	< 0.005	0.08	< 0.002
4Fe	5.09	0.03	< 0.006	0.09	< 0.003
7Fe	9.24	0.02	< 0.004	0.11	< 0.002
9Fe	15.06	0.03	0.007	0.04	< 0.003
3FeP	2.02	0.10	0.02	0.07	< 0.004
4FeP	4.94	0.24	0.04	0.07	< 0.004
7FeP	9.34	0.41	0.07	0.06	< 0.002
9FeP	15.60	0.68	0.11	0.05	< 0.004

SI 2. TEM images of fresh and spent catalysts

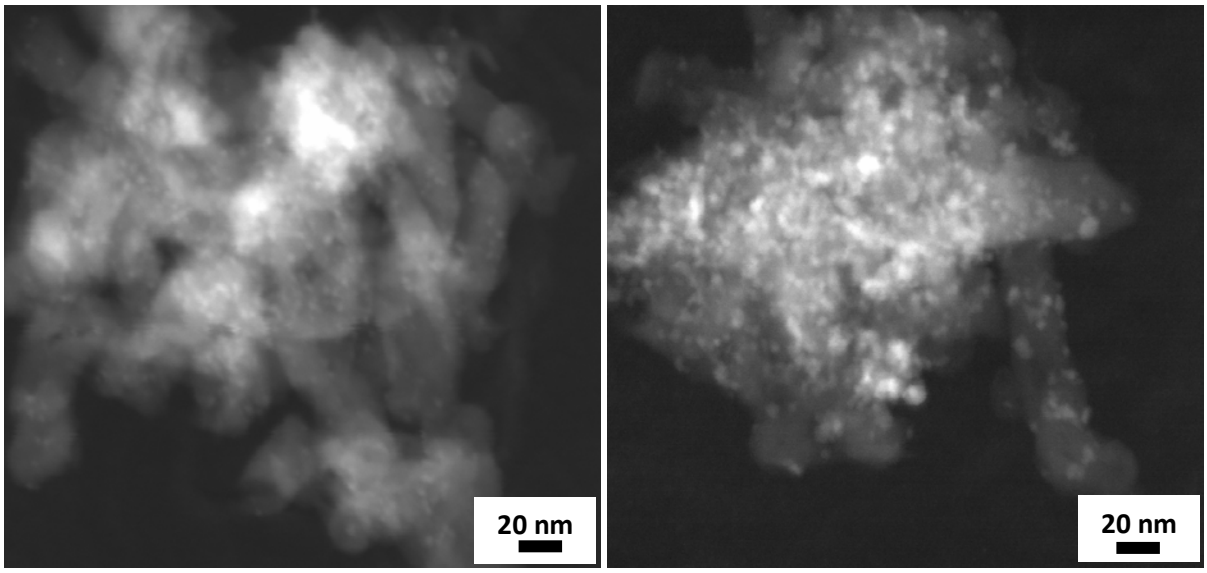

Figure S1. TEM images of 2PFeCNF (left) and 20PFeCNF (right).

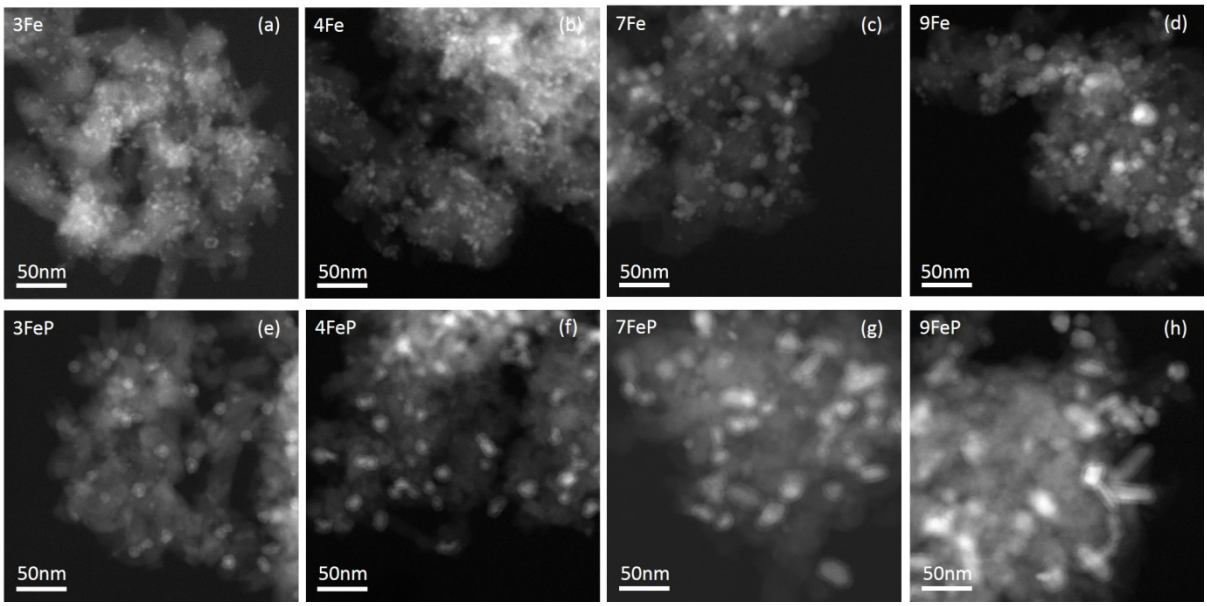

Figure S2. Particle size distribution of spent catalysts after carbon deposition studies (TOS = 4 h).

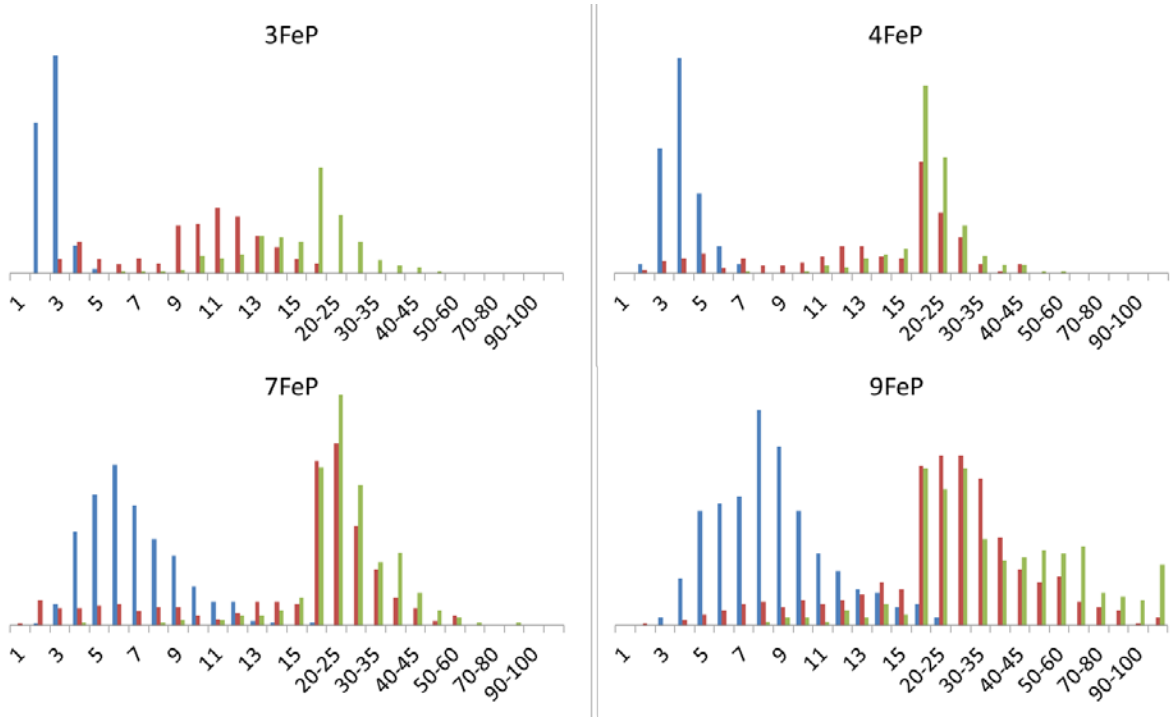

Figure S3. Particle size distribution of fresh and spent promoted catalysts (blue: fresh, red: after 4 h, and green: after 100 h)

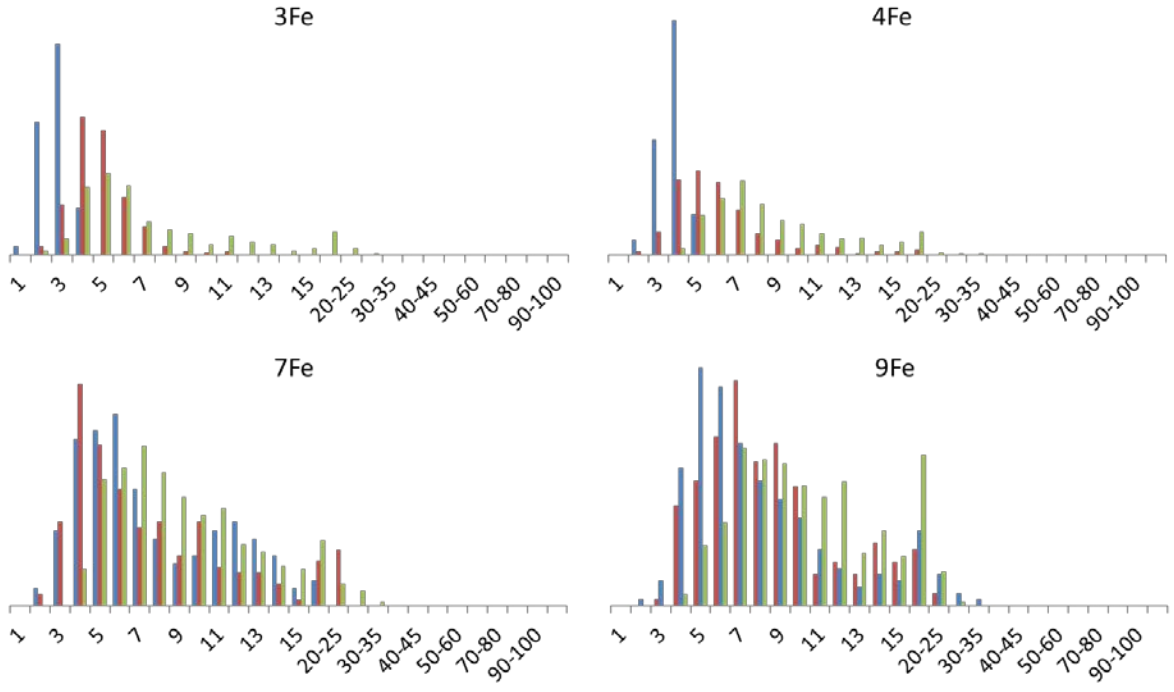

Figure S4. Particle size distribution of fresh and spent unpromoted catalysts (blue: fresh, red: after 4 h, and green: after 100 h).

SI 3. Catalytic performance

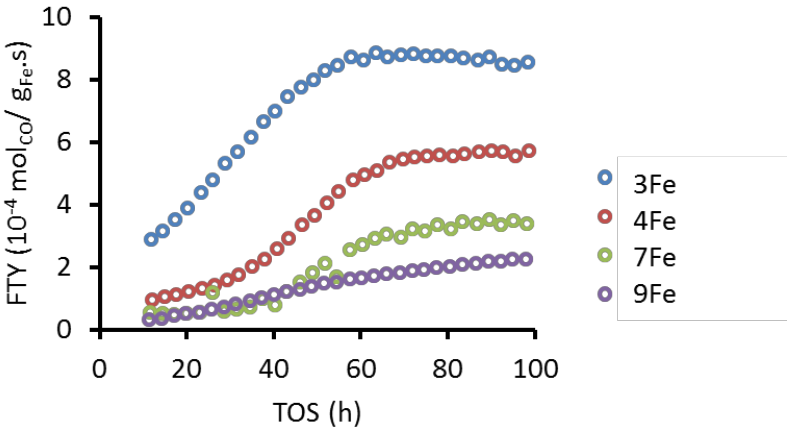

Figure S5. Iron time yield (FTY) of unpromoted catalysts (340 °C, 20 bar, H_2/CO/He = 45/45/10, and GHSV = 7 200 h^{-1}).

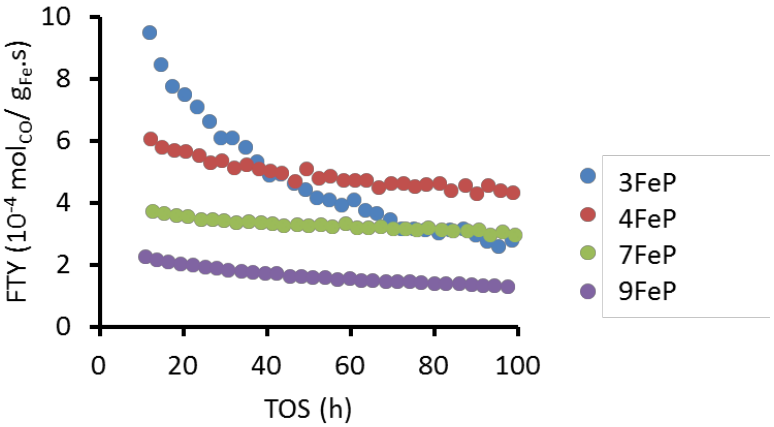

Figure S6. Iron time yield (FTY) of promoted catalysts (340 °C, 20 bar, H_2/CO/He = 45/45/10, and GHSV = 7 200 h^{-1}).

Table S2. Catalytic performance of CNF-supported Fe catalysts under FTO conditions (340 °C, 20 bar, H_2/CO/He = 45/45/10, GHSV = 7 200 h^{-1}, TOS = 12 h).

	CO conv. (%)	CO2 sel. (%)	FTY (10^{-4} $mol_{CO}/g_{Fe}.s$)	Product Selectivity (% C_{at}, CO_2 free)			
				CH_4	$C_2 - C_4$ olefins	$C_2 - C_4$ paraffins	C_{5+}
3Fe	9	23	2.9	59	10	28	2
4Fe	8	27	1.0	60	9	30	1
7Fe	9	32	0.6	53	13	28	6
9Fe	9	35	0.3	52	21	20	7
3FeP	31	46	9.5	20	40	28	12
4FeP	50	46	6.0	11	49	8	32
7FeP	61	47	3.7	8	54	6	33
9FeP	73	47	2.2	8	56	6	30

Table S3. Catalytic performance of CNF-supported Fe catalysts under FTO conditions (340 °C, 20 bar, H_2/CO/He = 45/45/10, GHSV = 7 200 h^{-1}, TOS = 100 h).

	CO conv. (%)	CO2 sel. (%)	FTY (10^{-4} $mol_{CO}/g_{Fe}.s$)	Product Selectivity (% C_{at}, CO_2 free)			
				CH_4	$C_2 - C_4$ olefins	$C_2 - C_4$ paraffins	C_{5+}
3Fe	27	35	8.4	44	18	29	9
4Fe	46	42	5.6	34	25	26	14
7Fe	57	40	3.5	38	31	21	10
9Fe	73	47	2.3	38	28	23	11
3FeP	10	39	2.9	28	49	16	7
4FeP	35	46	4.3	12	50	8	30
7FeP	48	47	3.0	9	55	5	30
9FeP	42	46	1.3	9	59	4	28

SI 4. In-situ Mossbauer spectroscopy

Table S4. The Mössbauer fitted parameters of 4Fe(P) samples, obtained at 300 K.

Sample/ Treatment	*IS ($mm \cdot s^{-1}$)*	*QS ($mm \cdot s^{-1}$)*	*Hyperfine field (T)*	*Γ ($mm \cdot s^{-1}$)*	*Phase*	*Spectral contribution (%)*
4Fe Fresh sample	0.33	0.72	-	0.64	Fe^{3+}	100
4Fe Ar/H_2=2 350 °C, 2 bar, 2 h	0.25 1.09	0.27 0.39	- -	0.38 0.75	Fe_xC Fe^{2+}	18 82
4Fe H_2/CO=1 340 °C, 20 bar, 20 h	0.21 1.08 1.23	0.13 0.30 1.41	- - -	0.45 0.55 0.43	Fe_xC Fe^{2+} Fe^{2+}	16 71 13
4FeP Fresh sample	0.34	0.71	-	0.70	Fe^{3+}	100
4FeP Ar/H_2=2 350 °C, 2 bar, 2 h	0.24 1.11	0.27 0.47	- -	0.41 0.77	Fe_xC Fe^{2+}	18 82
4FeP H_2/CO=1 340 °C, 20 bar, 20 h	0.27 0.26 0.18 0.21	- - - -	16.5 22.2 18.1 9.2	0.49 0.45 0.45 0.45	ϵ'-$Fe_{2.2}C$ χ-Fe_5C_2 (I) χ-Fe_5C_2 (II) χ-Fe_5C_2 (III)	47 21 16 16

Experimental uncertainties: Isomer shift: I.S. ± 0.02 mm s^{-1}; Quadrupole splitting: Q.S. ± 0.02 mm s^{-1}; Line width: Γ ± 0.03 mm s^{-1}; Hyperfine field: ± 0.1 T; Spectral contribution: ± 3%.

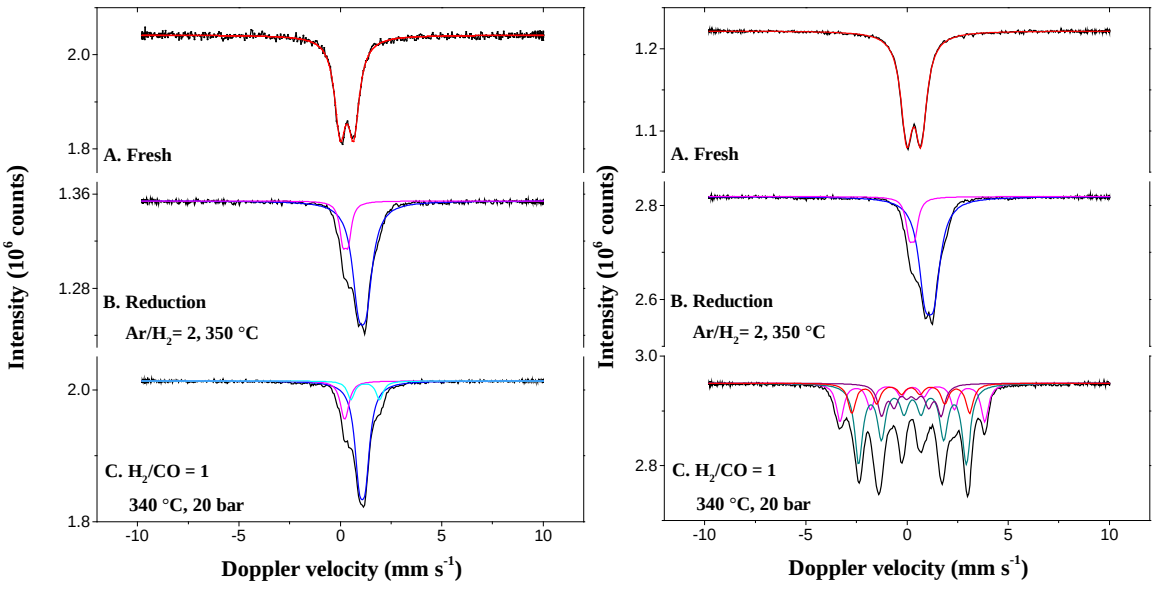

Figure S7. Mössbauer spectra obtained at 300 K with 4Fe (left) and 4FeP (right)

Table S5. The Mössbauer fitted parameters of 4Fe(P) samples, obtained at 4.2 K.

Sample/ Treatment	*IS ($mm \cdot s^{-1}$)*	*QS ($mm \cdot s^{-1}$)*	*Hyperfine field (T)*	*Γ ($mm \cdot s^{-1}$)*	*Phase*	*Spectral contribution (%)*
4Fe	0.23	-	25.7	0.60	χ-Fe_5C_2 (I)	10
Ar/H_2=2	0.20	-	21.5	0.60	χ-Fe_5C_2 (II)	10
350 °C,	0.24	-	11.8	0.60	χ-Fe_5C_2 (III)	5
2 bar, 2 h	0.46	0.08	51.0	0.46	Fe^{3+}	4
	1.29	-1.84	38.8	1.19	Fe^{2+}	27
	1.25	-0.28	37.3	1.19	Fe^{2+}	40
	1.08	1.97	-	0.52	Fe^{2+}	4
4Fe	0.22	-	23.8	0.62	χ-Fe_5C_2 (I)	8
H_2/CO=1	0.20	-	19.0	0.62	χ-Fe_5C_2 (II)	7
340 °C,	0.24	-	11.3	0.62	χ-Fe_5C_2 (III)	5
20 bar, 20 h	0.57	-0.45	53.3	0.48	Fe^{3+}	4
	1.18	-1.01	39.5	1.27	Fe^{2+}	32
	1.21	-0.27	35.3	1.27	Fe^{2+}	40
	1.12	2.10	-	0.50	Fe^{2+}	4
4FeP	0.23	-	26.1	0.80	χ-Fe_5C_2 (I)	10
Ar/H_2=2	0.22	-	22.2	0.80	χ-Fe_5C_2 (II)	9
350 °C,	0.24	-	10.9	0.80	χ-Fe_5C_2 (III)	6
2 bar, 2 h	0.45	-0.06	52.0	0.49	Fe^{3+}	3
	1.17	-1.55	39.5	1.52	Fe^{2+}	31
	1.22	-0.26	37.3	1.52	Fe^{2+}	37
	1.15	1.99	-	0.60	Fe^{2+}	4
4FeP	0.26	-	18.6	0.48	ϵ'-$Fe_{2.2}C$	42
H_2/CO=1	0.27	-	26.1	0.47	χ-Fe_5C_2 (I)	26
340 °C,	0.15	-	20.9	0.47	χ-Fe_5C_2 (II)	17
20 bar, 20 h	0.20	-	10.5	0.47	χ-Fe_5C_2 (III)	15

Experimental uncertainties: Isomer shift: I.S. ± 0.02 mm s^{-1}; Quadrupole splitting: Q.S. ± 0.02 mm s^{-1}; Line width: Γ ± 0.03 mm s^{-1}; Hyperfine field: ± 0.1 T; Spectral contribution: ± 3%.

Table S6. The Mössbauer fitted parameters of 9Fe(P) samples, obtained at 300 K.

Sample/ Treatment	*IS ($mm \cdot s^{-1}$)*	*QS ($mm \cdot s^{-1}$)*	*Hyperfine field (T)*	*Γ ($mm \cdot s^{-1}$)*	*Phase*	*Spectral contribution (%)*
9Fe	0.34	0.78	-	0.65	Fe^{3+}	100
Fresh sample						
9Fe	0.16	0.22	-	0.45	Fe_xC	17
Ar/H_2=2	1.08	0.19	-	0.66	Fe^{2+}	66
350 °C,	1.15	1.32	-	0.51	Fe^{2+}	17
2 bar, 2 h						
9Fe	0.25	0.35	-	0.47	Fe_xC	17
H_2/CO=1	1.09	0.23	-	0.61	Fe^{2+}	68
340 °C,	1.11	1.58	-	0.55	Fe^{2+}	15
20 bar, 20 h						
9FeP	0.00	-	33.0	0.30	Fe^0	7
Fresh sample	0.34	0.69	-	0.66	Fe^{3+}	34
	0.38	0.05	45.6	1.52	Fe^{3+}	12
	0.38	-	-	1.73	Fe^{3+}	47
9FeP	0.00	-	33.3	0.28	Fe^0	50
Ar/H_2=2	0.28	0.29	-	0.41	Fe_xC	8
350 °C,	1.09	0.33	-	0.70	Fe^{2+}	42
2 bar, 2 h						
9FeP	0.25	-	17.1	0.39	ϵ'-$Fe_{2.2}C$	72
H_2/CO=1	0.22	-	22.4	0.35	χ-Fe_5C_2 (I)	7
340 °C,	0.18	-	18.6	0.35	χ-Fe_5C_2 (II)	13
20 bar, 20 h	0.20	-	9.1	0.35	χ-Fe_5C_2 (III)	8

Experimental uncertainties: Isomer shift: I.S. ± 0.02 mm s^{-1}; Quadrupole splitting: Q.S. ± 0.02 mm s^{-1}; Line width: Γ ± 0.03 mm s^{-1}; Hyperfine field: ± 0.1 T; Spectral contribution: ± 3%.

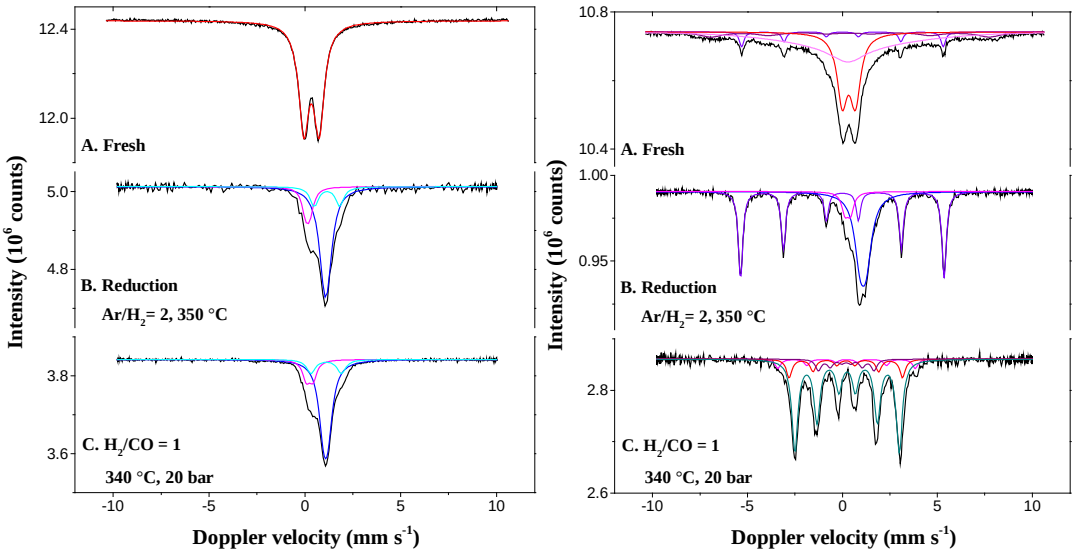

Figure S8. Mössbauer spectra obtained at 300 K with 9Fe (left) and 9FeP (right)

Table S7. The Mössbauer fitted parameters of 9Fe(P) samples, obtained at 4.2 K.

Sample/ Treatment	*IS ($mm \cdot s^{-1}$)*	*QS ($mm \cdot s^{-1}$)*	*Hyperfine field (T)*	*Γ ($mm \cdot s^{-1}$)*	*Phase*	*Spectral contribution (%)*
9Fe	0.24	-	25.9	0.80	χ-Fe_5C_2 (I)	11
Ar/H_2=2	0.20	-	22.2	0.80	χ-Fe_5C_2 (II)	12
350 °C,	0.22	-	11.9	0.80	χ-Fe_5C_2 (III)	5
2 bar, 2 h	0.37	-0.07	52.2	0.67	Fe^{3+}	5
	1.39	-1.38	39.5	1.17	Fe^{2+}	29
	1.12	-0.35	36.7	1.17	Fe^{2+}	31
	1.12	2.00	-	0.62	Fe^{2+}	7
9Fe	0.24	-	24.8	0.79	χ-Fe_5C_2 (I)	13
H_2/CO=1	0.20	-	20.2	0.79	χ-Fe_5C_2 (II)	9
340 °C,	0.22	-	12.8	0.79	χ-Fe_5C_2 (III)	5
20 bar, 20 h	0.50	-0.11	51.9	0.36	Fe^{3+}	3
	1.38	-1.37	39.9	1.16	Fe^{2+}	25
	1.17	-0.32	36.2	1.16	Fe^{2+}	37
	1.06	2.13	-	0.55	Fe^{2+}	8
9FeP	0.00	-	34.5	0.33	Fe^0	42
Ar/H_2=2	0.22	-	19.2*	0.37	Fe_xC	12
350 °C,	1.12	-0.57	39.4	1.26	Fe^{2+}	24
2 bar, 2 h	1.18	-0.90	35.0	1.26	Fe^{2+}	22
9FeP	0.25	-	18.7	0.42	ϵ'-$Fe_{2.2}C$	68
H_2/CO=1	0.25	-	25.6	0.40	χ-Fe_5C_2 (I)	11
340 °C,	0.18	-	20.4	0.40	χ-Fe_5C_2 (II)	14
20 bar, 20 h	0.20	-	10.1	0.40	χ-Fe_5C_2 (III)	7

Experimental uncertainties: Isomer shift: I.S. ± 0.02 mm s^{-1}; Quadrupole splitting: Q.S. ± 0.02 mm s^{-1}; Line width: Γ ± 0.03 mm s^{-1}; Hyperfine field: ± 0.1 T; Spectral contribution: ± 3%.*Average magnetic field.

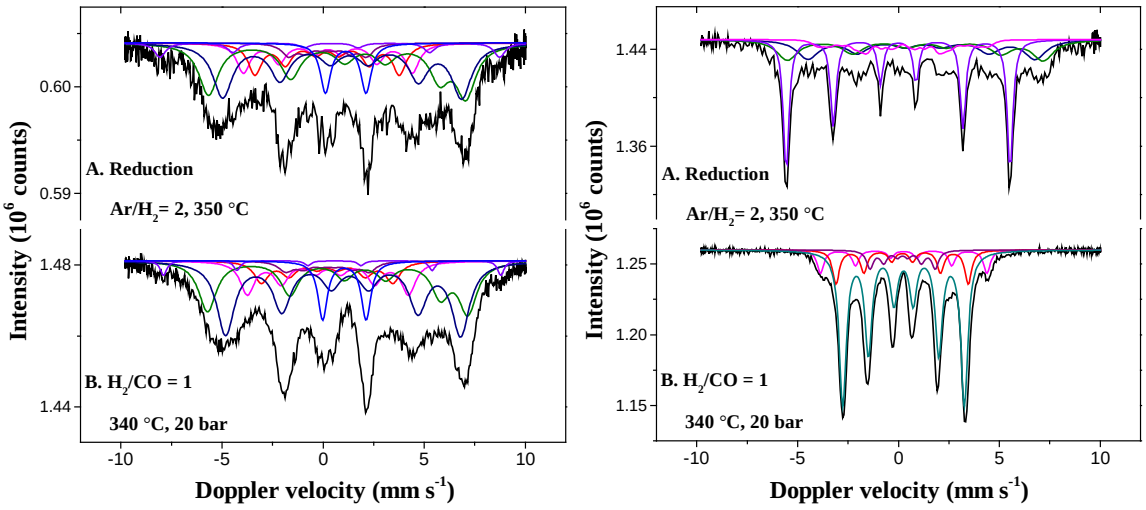

Figure S9. Mössbauer spectra obtained at 4.2 K with 9Fe (left) and 9FeP (right).

SI 5. Reduction profiles

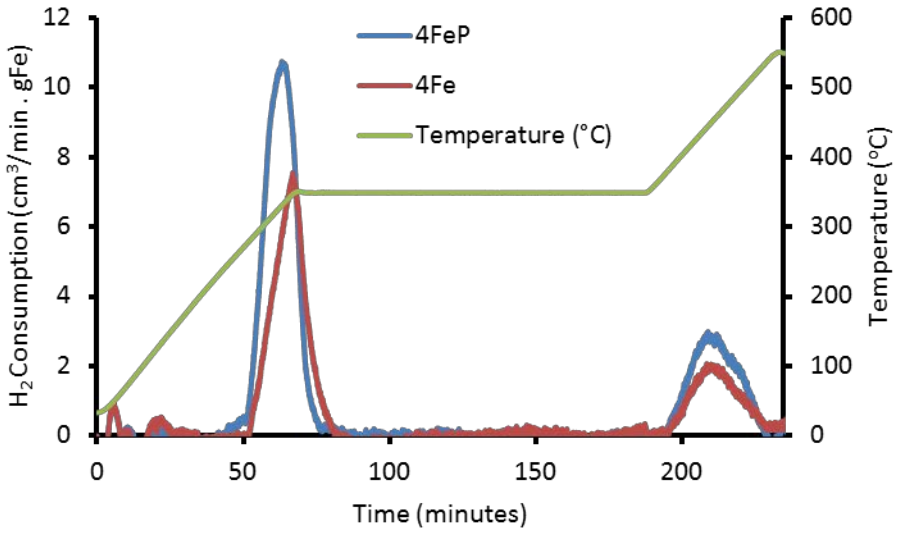

Figure S10. Temperature programmed reduction profiles of 4FeP and 4Fe.

Table S8. The Mössbauer fitted parameters of 7FeP sample, obtained at 300 K.

Sample/ Treatment	*IS ($mm \cdot s^{-1}$)*	*QS ($mm \cdot s^{-1}$)*	*Hyperfine field (T)*	*Γ ($mm \cdot s^{-1}$)*	*Phase*	*Spectral contribution (%)*
7FeP	0.02	-	32.7	0.35	Fe^0	8
Ar/H_2=2	0.23	0.31	-	0.51	Fe_xC	18
350 °C,	1.07	-	-	0.68	Fe^{2+}	65
2 bar, 2 h	1.07	1.47	-	0.51	Fe^{2+}	9
7FeP	0.01	-	32.8	0.40	Fe^0	24
Ar/H_2=2	0.23	0.31	-	0.63	Fe_xC	18
350 °C,	1.08	-	-	0.67	Fe^{2+}	51
2 bar, 24 h	1.06	1.50	-	0.55	Fe^{2+}	7

Experimental uncertainties: Isomer shift: I.S. ± 0.02 mm s^{-1}; Quadrupole splitting: Q.S. ± 0.02 mm s^{-1}; Line width: Γ ± 0.03 mm s^{-1}; Hyperfine field: ± 0.1 T; Spectral contribution: ± 3%.

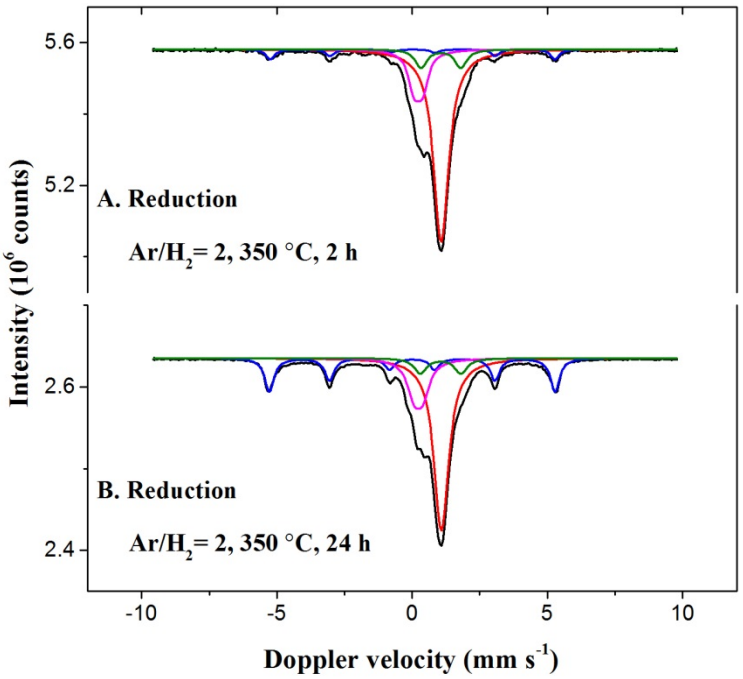

Figure S11. Mössbauer spectra obtained at 300 K with 7FeP sample.

SI 6. In-situ carbon deposition studies (TEOM)

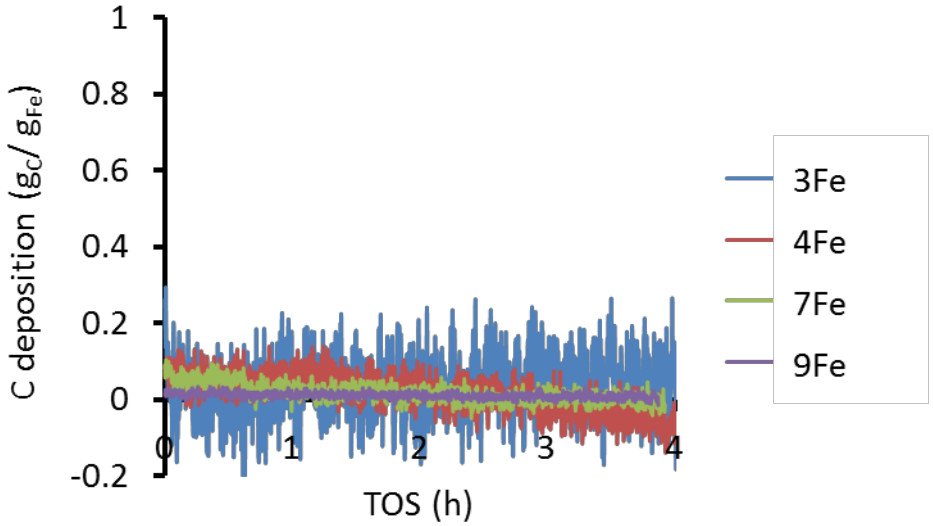

Figure S12. C deposition of unpromoted catalysts (340 °C, 20 bar, H2/CO = 1, and GHSV = 54 000 h^{-1}).

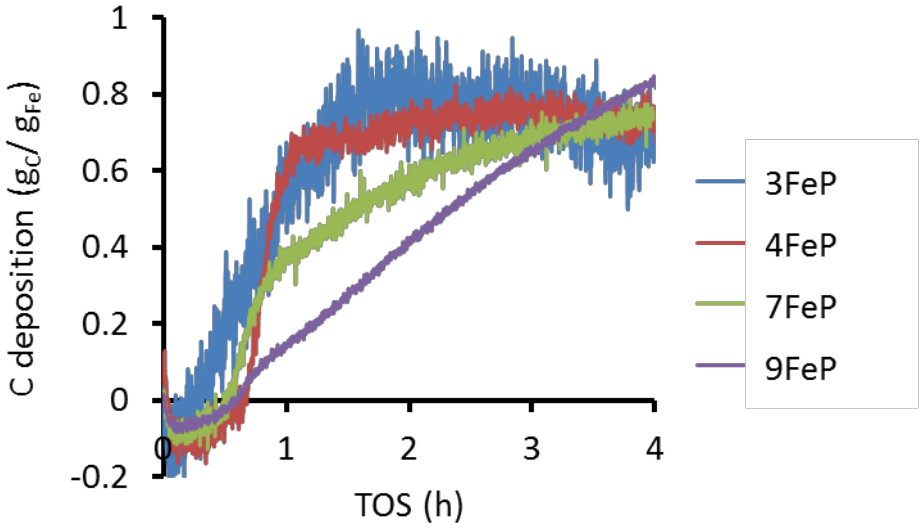

Figure S13. C deposition of promoted catalysts (340 °C, 20 bar, H2/CO = 1, and GHSV = 54 000 h^{-1}).