

Supporting Information

Table S1 Mössbauer results of $\text{Co}_{0.7}\text{M}_{0.3}\text{Fe}_{2.0}$ catalysts ($\text{M} = \text{Cu}$ or Mn or Zn) after activation in CO at 270°C and 170 psig measured at 20 K

Sample	Param.	Co-Fe	$\chi\text{-Fe}_5\text{C}_2$			$\epsilon'\text{-Fe}_{2.2}\text{C}$	Fe_3O_4			Fe distribution (%)			
		S1	S2	S3	S4	S5	S7	S8	S9	Co-Fe	$\chi\text{-Fe}_5\text{C}_2$	$\epsilon'\text{-Fe}_{2.2}\text{C}$	Fe-Oxide
$\text{Co}_{0.7}\text{Cu}_{0.3}\text{Fe}_{2.0}$	H (kG)	353	250	211	122	178	499	480	-	24	53	15	8
	IS (mm/s)	0.01	0.27	0.25	0.12	0.23	0.49	0.2	-				
	QS (mm/s)	0.01	0.07	-0.14	-0.07	0.05	0.3	-0.06	-				
	Fe%	24	20	18	15	15	4	4	-				
$\text{Co}_{0.7}\text{Mn}_{0.3}\text{Fe}_{2.0}$	H (kG)	354	248	218	126	182	503	-	-	25	46	15	14
	IS (mm/s)	0.04	0.27	0.31	0.17	0.23	0.3	-	-				
	QS (mm/s)	0	0.1	-0.06	-0.06	0.06	-0.31	-	-				
	Fe%	25	18	14	14	15	14	-	-				
$\text{Co}_{0.7}\text{Zn}_{0.3}\text{Fe}_{2.0}$	H (kG)	349	255	216	126	184	515	477	-	24	22	8	46
	IS (mm/s)	0.03	0.24	0.32	0.24	0.23	0.35	0.5	-				
	QS (mm/s)	0.02	0.03	-0.13	-0.27	-0.02	-0.03	-0.35	-				
	Fe%	24	8	8	6	8	19	27	-				
$\text{Co}_{1.0}\text{Fe}_{2.0}$	H (kG)	344	249	211	120	182	-	-	-	30	56	14	0
	IS (mm/s)	0.02	0.27	0.27	0.15	0.24	-	-	-				
	QS (mm/s)	0.02	0.07	-0.1	-0.09	0.05	-	-	-				
	Fe%	30	22	16	18	14	-	-	-				

[#]Average uncertainties of Mössbauer parameters , ± 5 kG Hyperfine magnetic field, ± 0.03 mm/s Isomer shift, ± 0.05 mm/s Quadrupole splitting. The hyperfine field for $\alpha\text{-Fe}$ is 330 kG.

Table S2 Mössbauer results of $\text{Co}_{0.7}\text{M}_{0.3}\text{Fe}_{2.0}$ catalysts ($\text{M} = \text{Cu}$ or Mn or Zn) after the FT reaction measured at 20 K

Sample	Param.	Co-Fe	$\chi\text{-Fe}_5\text{C}_2$			$\epsilon'\text{-Fe}_{2.2}\text{C}$	Fe_3O_4			Fe distribution (%)			
		S1	S2	S3	S4	S5	S7	S8	S9	Co-Fe	$\chi\text{-Fe}_5\text{C}_2$	$\epsilon\text{-Fe}_{2.2}\text{C}$	Fe-Oxide
$\text{Co}_{0.7}\text{Cu}_{0.3}\text{Fe}_{2.0}$	H (kG)	-	245	220	117	203	513	391	-	0	23	7	70
	IS (mm/s)	-	0.29	0.25	0.12	0.25	0.34	0.22	-				
	QS (mm/s)	-	0.01	-0.08	0.04	-0.17	-0.09	0.05	-				
	Fe%	-	9	9	5	7	51	19	-				
$\text{Co}_{0.7}\text{Mn}_{0.3}\text{Fe}_{2.0}$	H (kG)	-	237	208	129	178	530	513	479	0	37	13	50
	IS (mm/s)	-	0.31	0.23	0.19	0.26	0.43	0.36	0.45				
	QS (mm/s)	-	0.02	-0.03	-0.07	0.06	-0.08	-0.09	-0.08				
	Fe%	-	15	15	7	13	5	15	24				
$\text{Co}_{0.7}\text{Zn}_{0.3}\text{Fe}_{2.0}$	H (kG)	-	236	211	124	184	513	466	-	0	25	4	71
	IS (mm/s)	-	0.28	0.26	0.31	0.36	0.36	0.41	-				
	QS (mm/s)	-	0.18	0.01	0.10	-0.02	-0.04	-0.08	-				
	Fe%	-	10	10	5	4	41	24	-				
$\text{Co}_{1.0}\text{Fe}_{2.0}$	H (kG)	-	243	214	124	197	531	513	487	0	42	8	50
	IS (mm/s)	-	0.27	0.27	0.18	0.14	0.51	0.3	0.34				
	QS (mm/s)	-	0	-0.14	-0.07	-0.1	-0.2	0	0				
	Fe%	-	16	16	10	8	14	18	13				

#Average uncertainties of Mössbauer parameters , ± 5 kG Hyperfine magnetic field, ± 0.03 mm/s Isomer shift, ± 0.05 mm/s Quadrupole splitting. The hyperfine field for $\alpha\text{-Fe}$ is 330 kG.

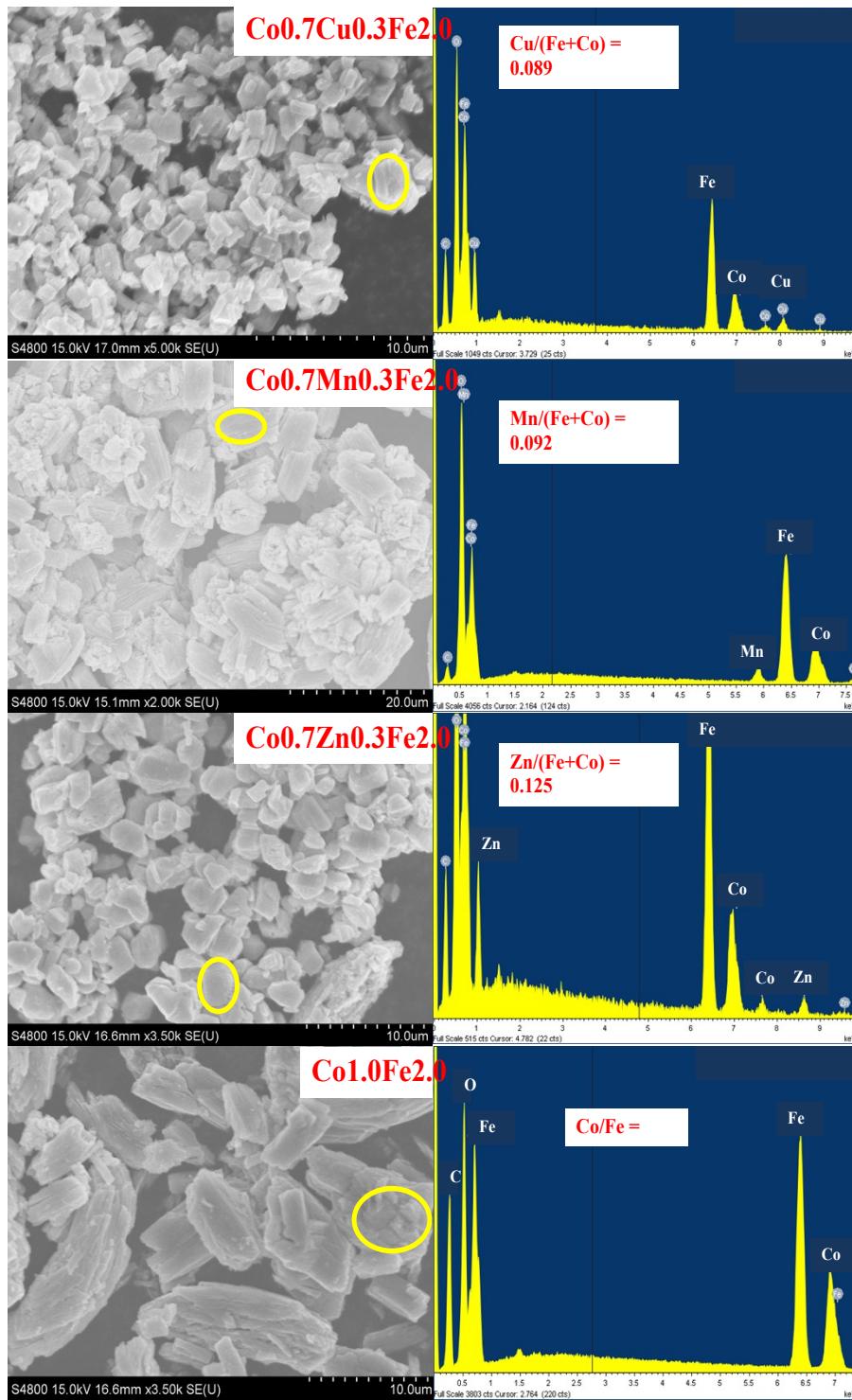


Figure S1 SEM images (left) of $\text{Co}_{0.7}\text{M}_{0.3}\text{Fe}_{2.0}$ samples ($\text{M} = \text{Cu}$ or Mn or Zn) after decomposition of the respective metal oxalates in N_2 at 400°C and the corresponding EDX graph (right) obtained from the circled region.

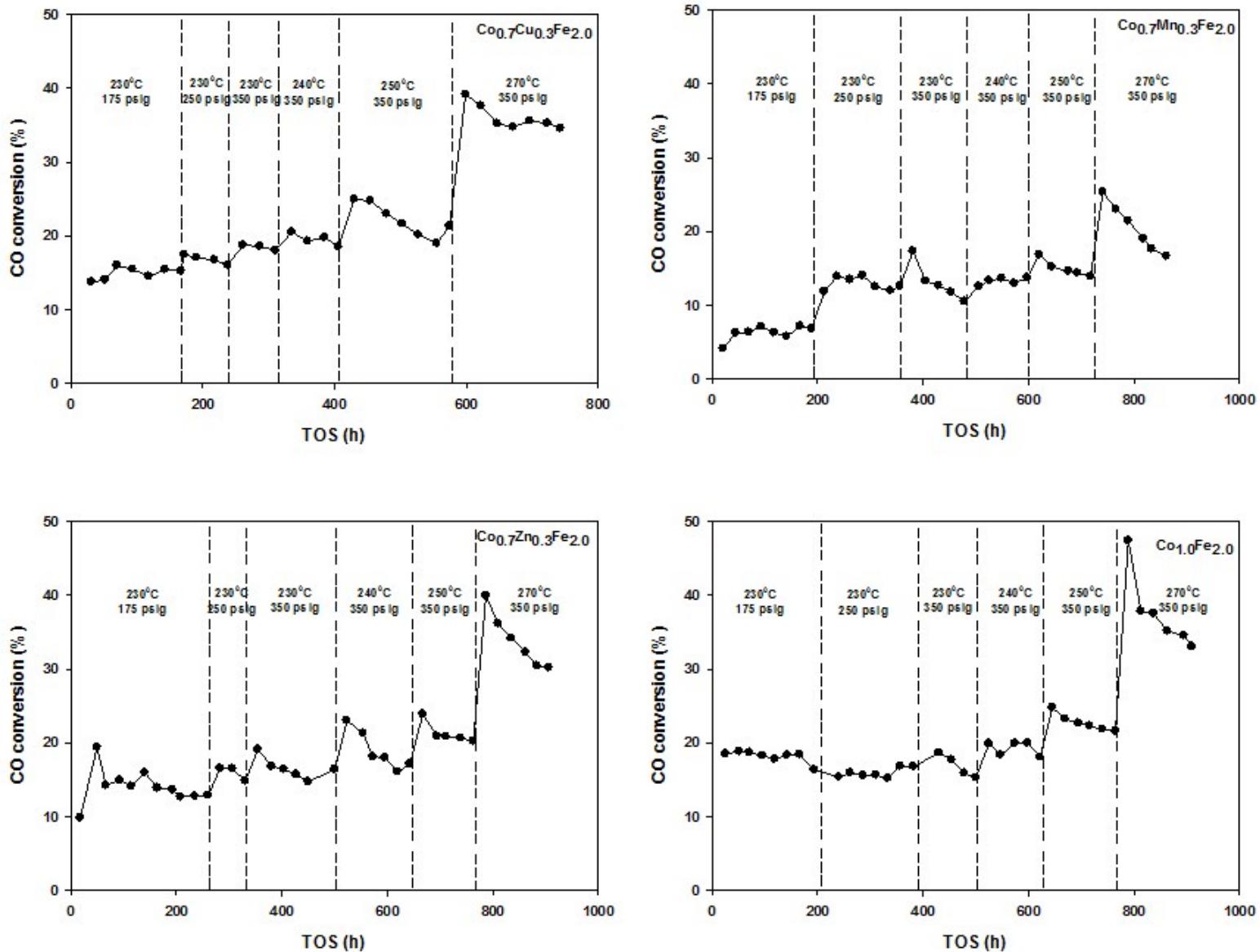


Figure S2 The effect of operating conditions on the conversion of CO for various cobalt ferrites after carburization.

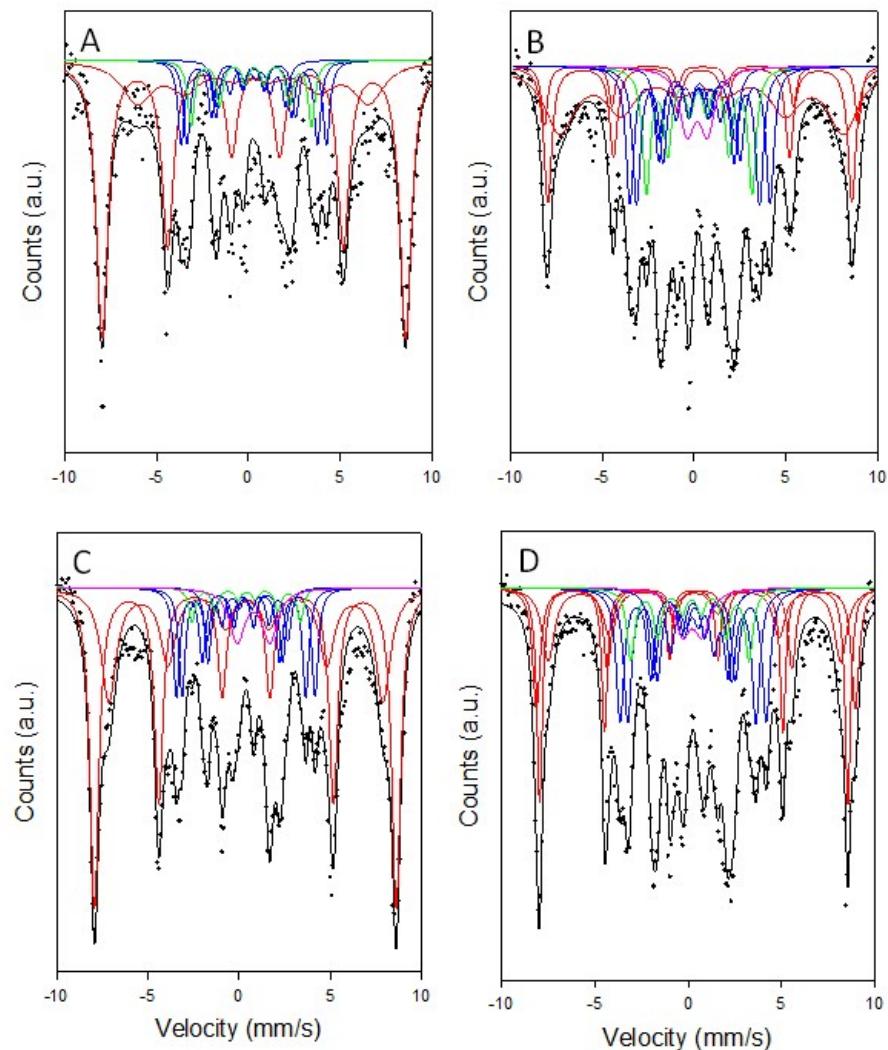


Figure S3 Mössbauer spectrum of $\text{Co}_{0.7}\text{M}_{0.3}\text{Fe}_{2.0}$ catalysts ($\text{M} = \text{Cu}$ or Mn or Zn) after FT synthesis performed at 20 K; (A) $\text{Co}_{0.7}\text{Cu}_{0.3}\text{Fe}_{2.0}$, (B) $\text{Co}_{0.7}\text{Mn}_{0.3}\text{Fe}_{2.0}$, (C) $\text{Co}_{0.7}\text{Zn}_{0.3}\text{Fe}_{2.0}$, (D) $\text{Co}_{1.0}\text{Fe}_{2.0}$. The fitted curves are shown in solid lines: black, total spectra; red, oxide; blue, $\chi\text{-Fe}_5\text{C}_2$; green, $\epsilon'\text{-Fe}_{2.2}\text{C}$, dark blue, FeCo bimetallic.

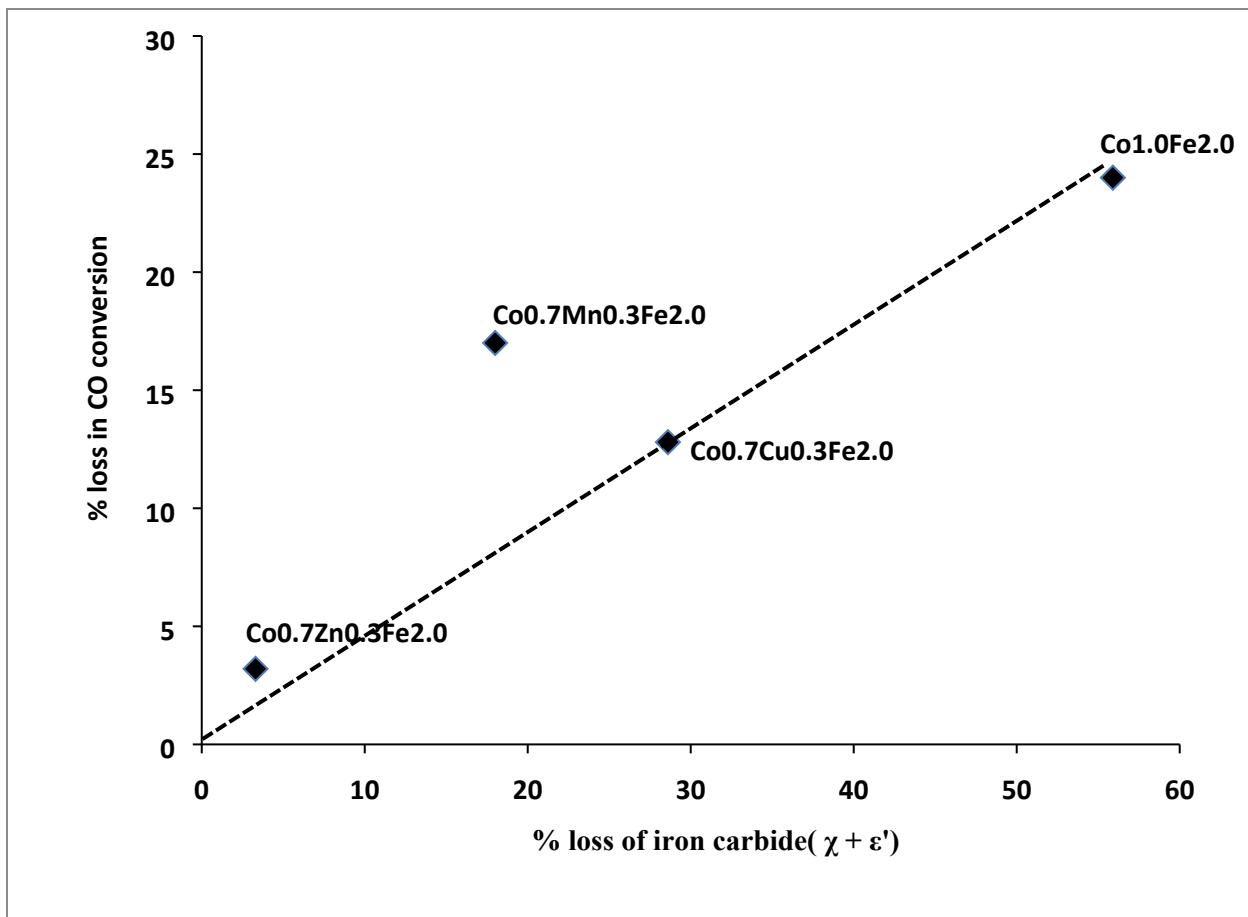


Figure S4 A comparison between the iron carbide content and the conversion of CO for various $\text{Co}_{0.7}\text{M}_{0.3}\text{Fe}_{2.0}$ catalysts (M = Cu or Mn or Zn).