

SUPPORTING INFORMATION

Redox-Responsive Multimetal Phosphides for Reverse Water–Gas Shift: Does High Entropy Improve Catalytic Activity?

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Table S1. Relative compositions of surface species determined by deconvolution of the corresponding XPS spectra.

Sample	State	Cr	Mn	Fe	Co	Ni	P	
		(%)	(%)	(%)	(%)	(%)	P–Me (%)	P–O (%)
FeP _x /SiO ₂	+2	-	-	80	-	-	22	78
	+3	-	-	20	-	-		
CoP _x /SiO ₂	Co–P	-	-	-	39	-	48	52
	+2	-	-	-	61	-		
NiP _x /SiO ₂	Ni–P	-	-	-	-	43	41	59
	+2	-	-	-	-	57		
FeCoNiP _x /SiO ₂	Me–P	-	-	0	44	32	31	69
	+2	-	-	59	56	68		
	+3	-	-	41	-	-		
CrMnFeCoNiP _x /SiO ₂	Me–P	-	-	0	39	42	57	43
	+2	-	100	66	61	58		
	+3	100	-	34	-	-		

Table S2. Selective studies of metal phosphide-based catalysts in RWGS.

Catalyst	T (°C)	P (MPa)	Feed	GHSV (L g _{cat} ⁻¹ h ⁻¹)	X _{CO2} (%)	S _{CO} (%)	E _a (kJ mol ⁻¹)	Ref
Ni ₂ P/CeO ₂	500	0.1	CO ₂ :H ₂ :N ₂ = 1:2:2	150.0	29	86	-	1
Ni ₁₂ P ₅ /Al ₂ O ₃	600	0.1	CO ₂ :H ₂ =	12.0	58	35	-	2
Ni ₁₂ P ₅ /CeO ₂ /Al ₂ O ₃			1:4		64	54	-	
Mo-P/SiO ₂	550	0.1	CO ₂ :H ₂ =	12.0	21	100	-	3
Mo-P/Al ₂ O ₃			1:4		26	83	-	
Mo-P/CeO ₂ /Al ₂ O ₃					25	88	-	
Ni ₁₂ P ₅ /SiO ₂	700	0.1	CO ₂ :H ₂ :N ₂	12.0	62	100	55.0	4
Ni ₂ P/SiO ₂			= 1:4:5		57	100	39.0	
NiP/SiO ₂					19	96	84.0	
NiP ₂ /SiO ₂					2	91	78.2	
Ni ₁₂ P ₅ /SBA-15	550	0.1	CO ₂ :H ₂ :N ₂	43.2	24	100	-	5
Ni ₁₂ P ₅ @SBA-15			= 1:4:1		31	100	-	
RuP (1:1)	400	0.1	CO ₂ :H ₂ :N ₂	30.0	2	100		6
RuP (5:1)			= 1:1:1		15	84		
RuP (10:1)					15	62		
FeCoNiP _x /SiO ₂	700	0.1	CO ₂ :H ₂ :N ₂	7.2	51	100	63.4	This
CrMnFeCoNiP _x /SiO ₂			=1:3:4		42	100	75.6	work

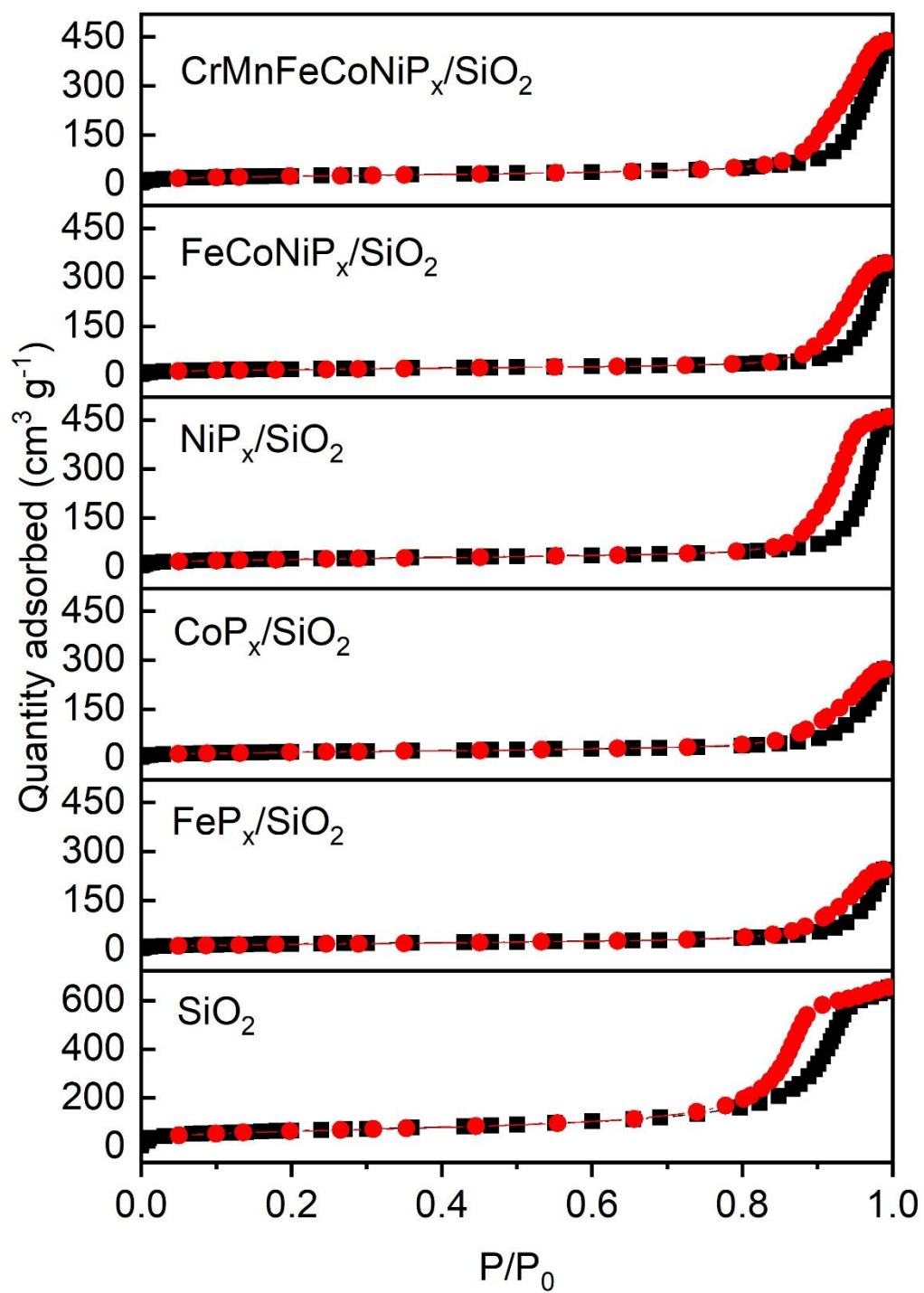


Figure S1. N₂ isotherms of tested catalysts. SiO₂ was also included as reference.

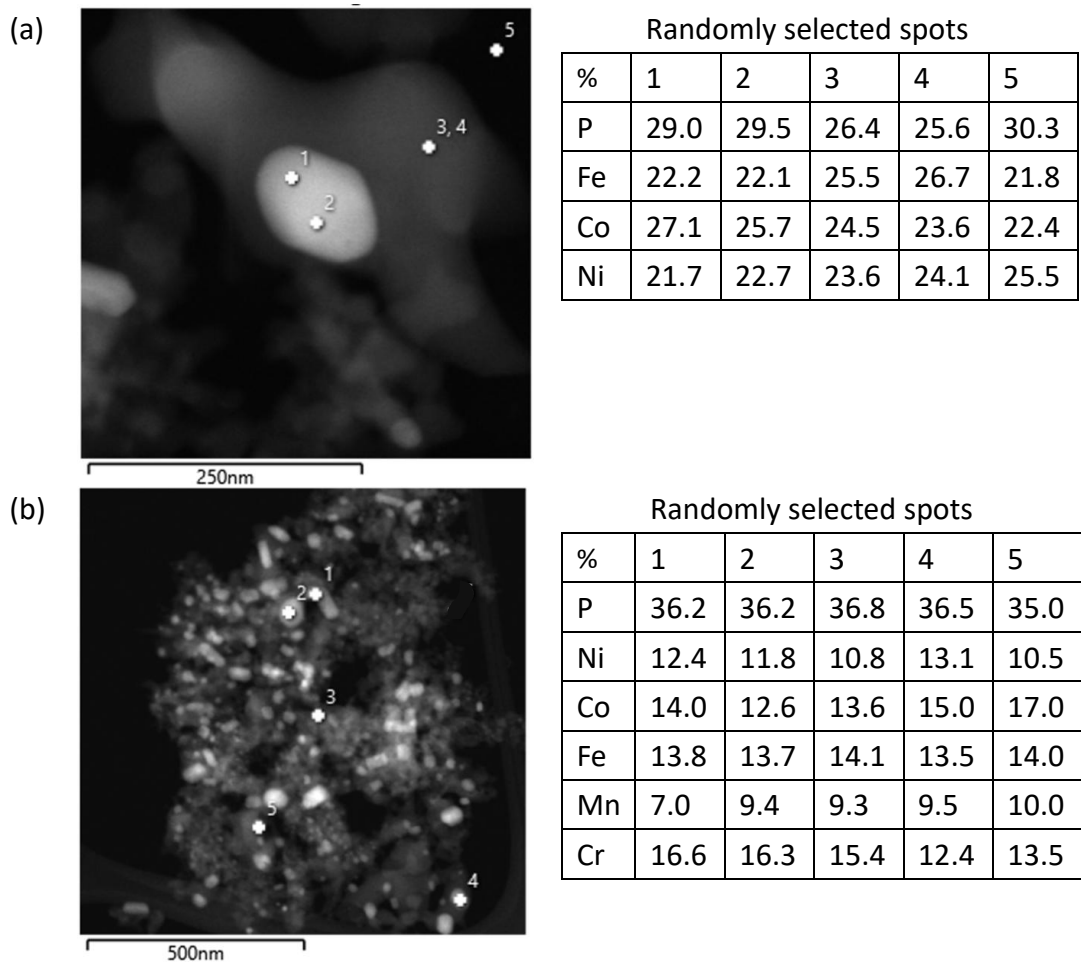


Figure S2. The elemental composition (atom%) of EDS mapping results by randomly selected 5 spots of (a) $\text{FeCoNiP}_x/\text{SiO}_2$ and (b) $\text{CrMnFeCoNiP}_x/\text{SiO}_2$.

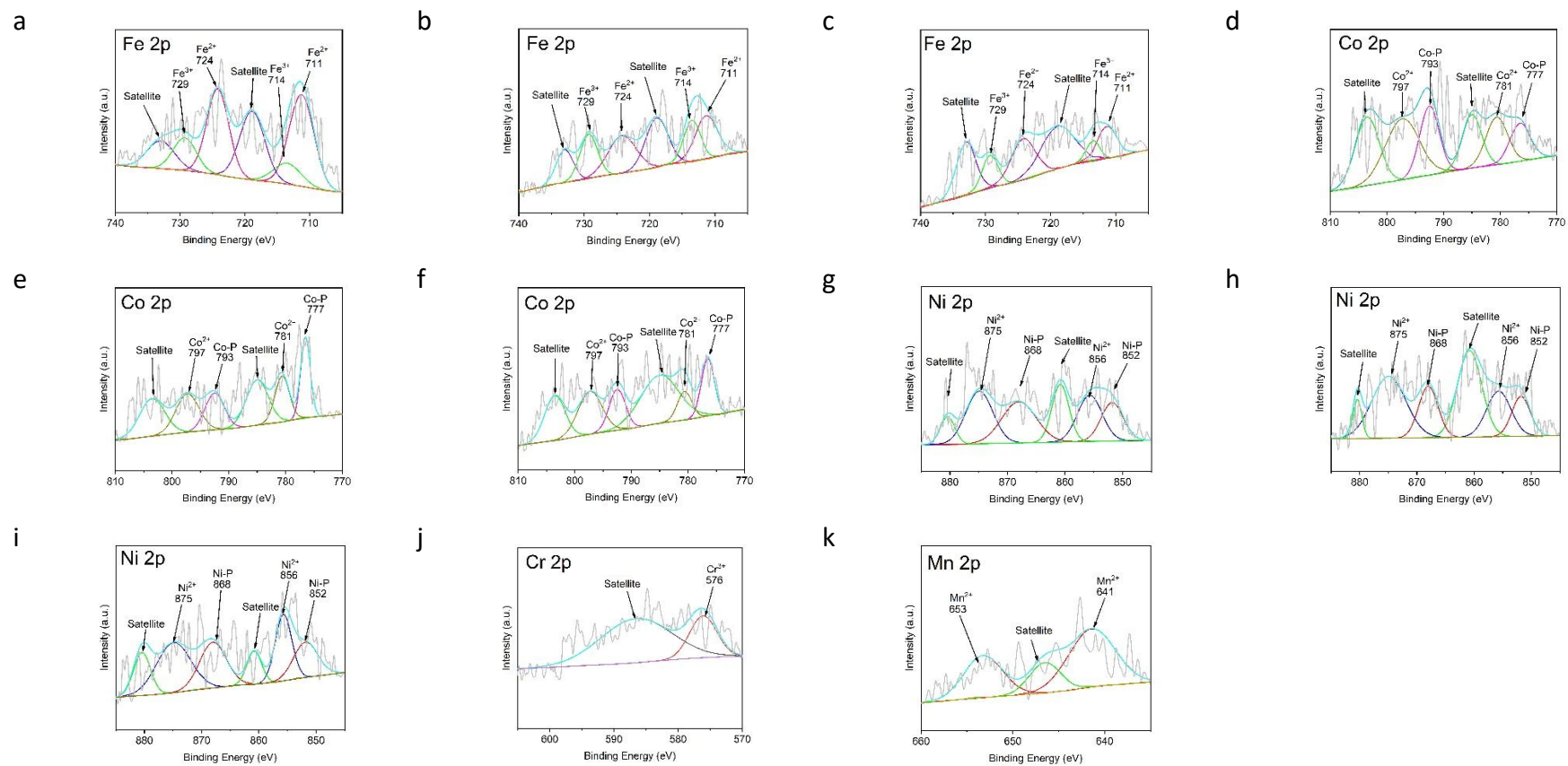


Figure S3. XPS spectra of Fe 2p for (a) $\text{FeP}_x/\text{SiO}_2$, (b) $\text{FeCoNiP}_x/\text{SiO}_2$, and (c) $\text{CrMnFeCoNiP}_x/\text{SiO}_2$; Co 2p for (d) $\text{CoP}_x/\text{SiO}_2$, (e) $\text{FeCoNiP}_x/\text{SiO}_2$, and (f) $\text{CrMnFeCoNiP}_x/\text{SiO}_2$; and Ni 2p for (g) $\text{NiP}_x/\text{SiO}_2$, (h) $\text{FeCoNiP}_x/\text{SiO}_2$, and (i) $\text{CrMnFeCoNiP}_x/\text{SiO}_2$; (j) Cr and (k) Mn 2p XPS spectra of $\text{CrMnFeCoNiP}_x/\text{SiO}_2$.

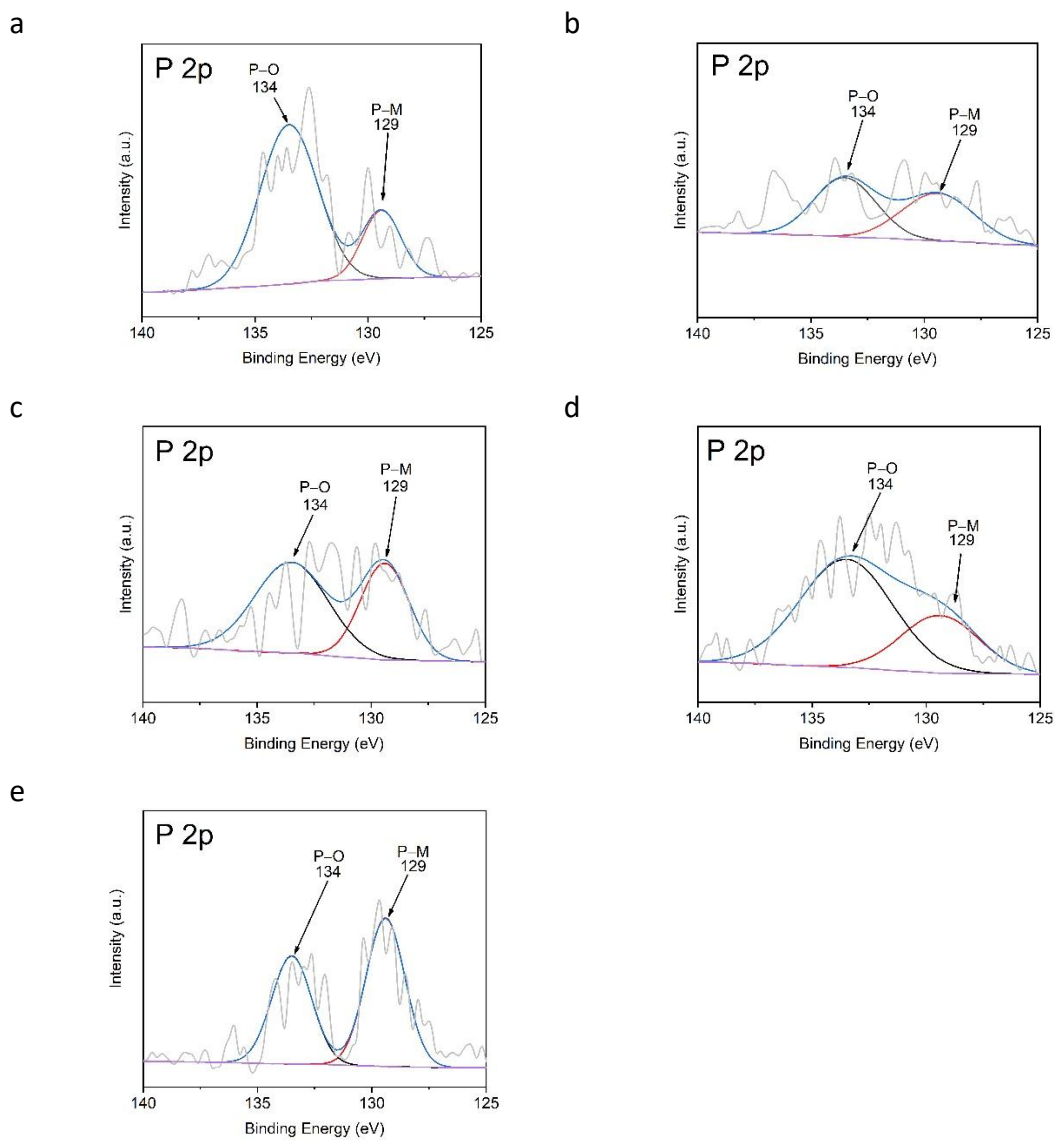


Figure S4. XPS spectra of P 2p for (a) $\text{FeP}_x/\text{SiO}_2$, (b) $\text{CoP}_x/\text{SiO}_2$ (c), $\text{NiP}_x/\text{SiO}_2$, (d) $\text{FeCoNiP}_x/\text{SiO}_2$, and (e) $\text{CrMnFeCoNiP}_x/\text{SiO}_2$.

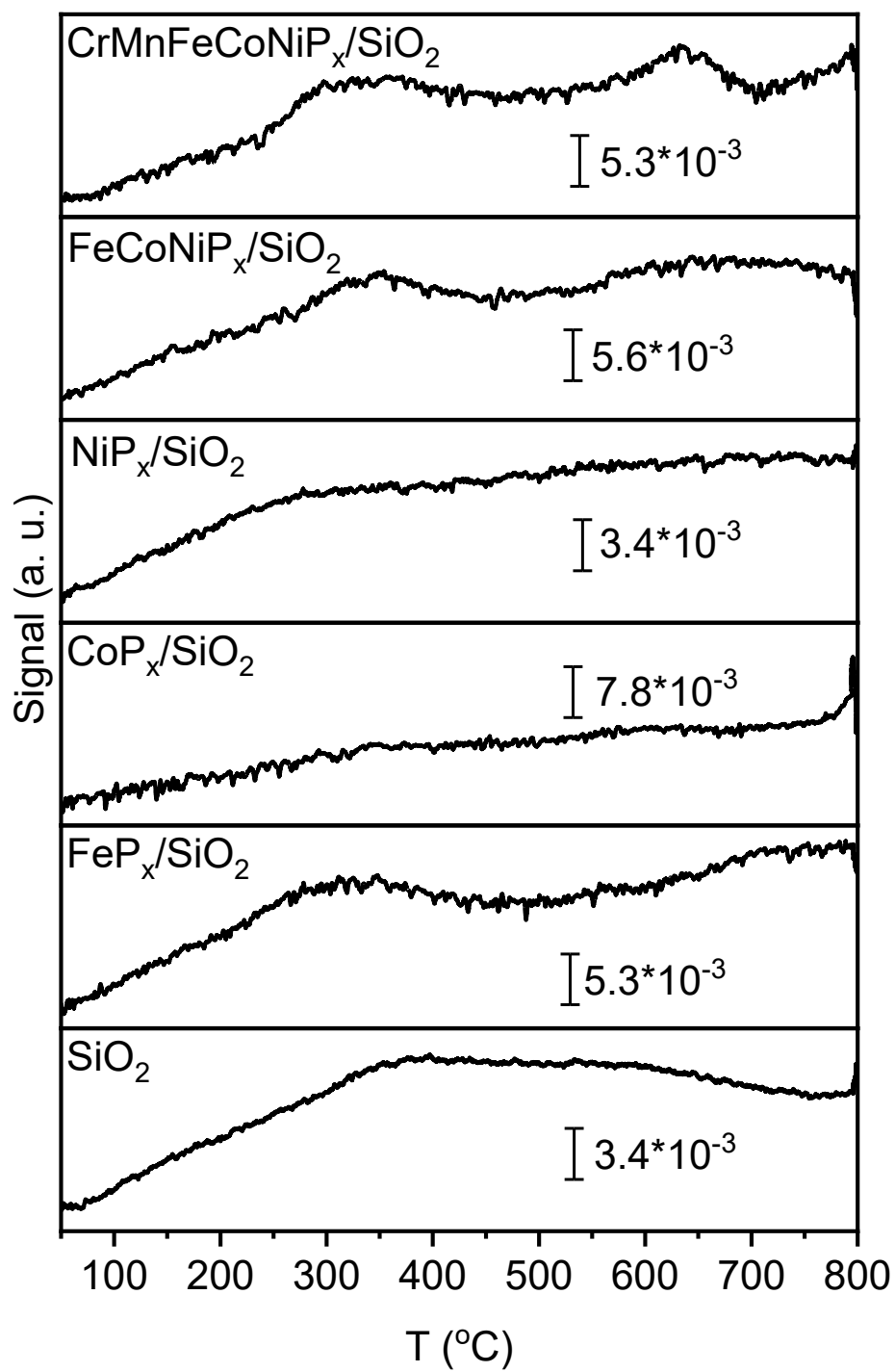
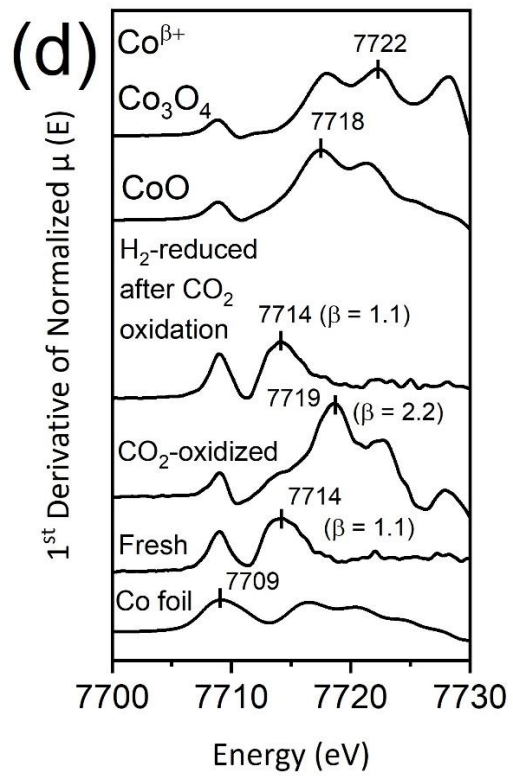
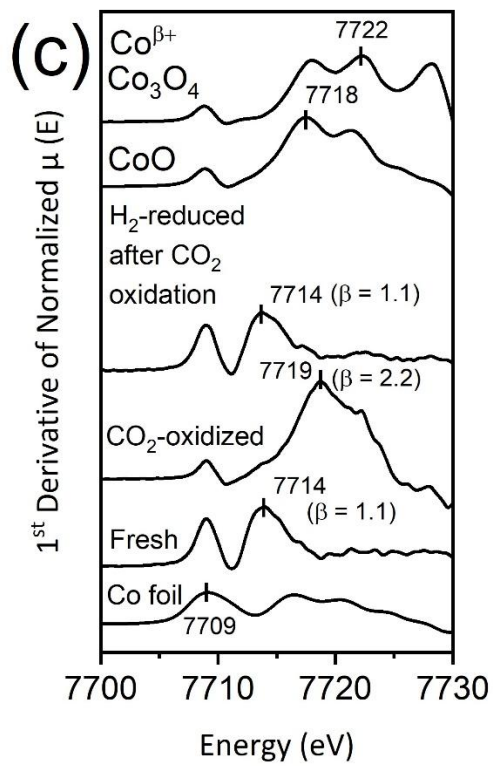
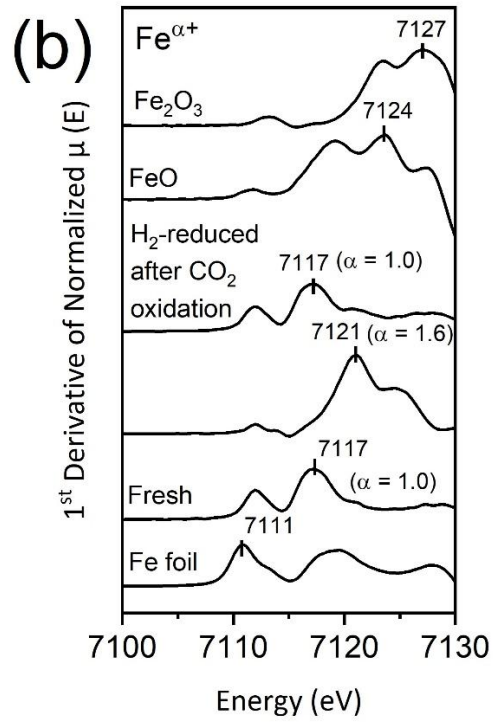
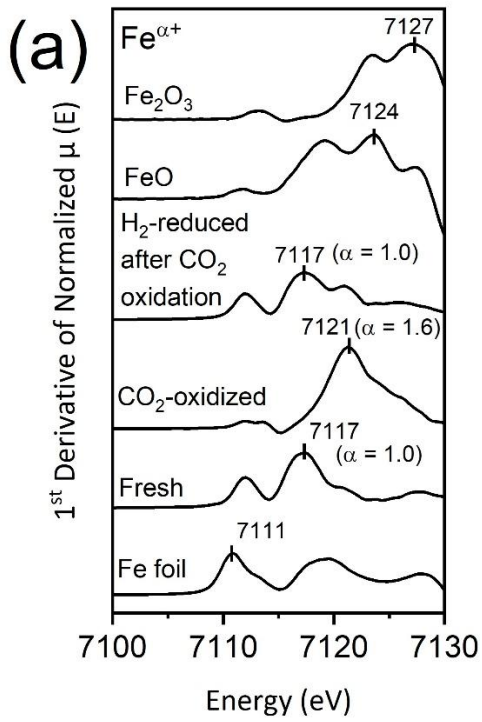


Figure S5. CO₂-TPO profiles of tested catalysts. SiO₂ was also tested for comparison.



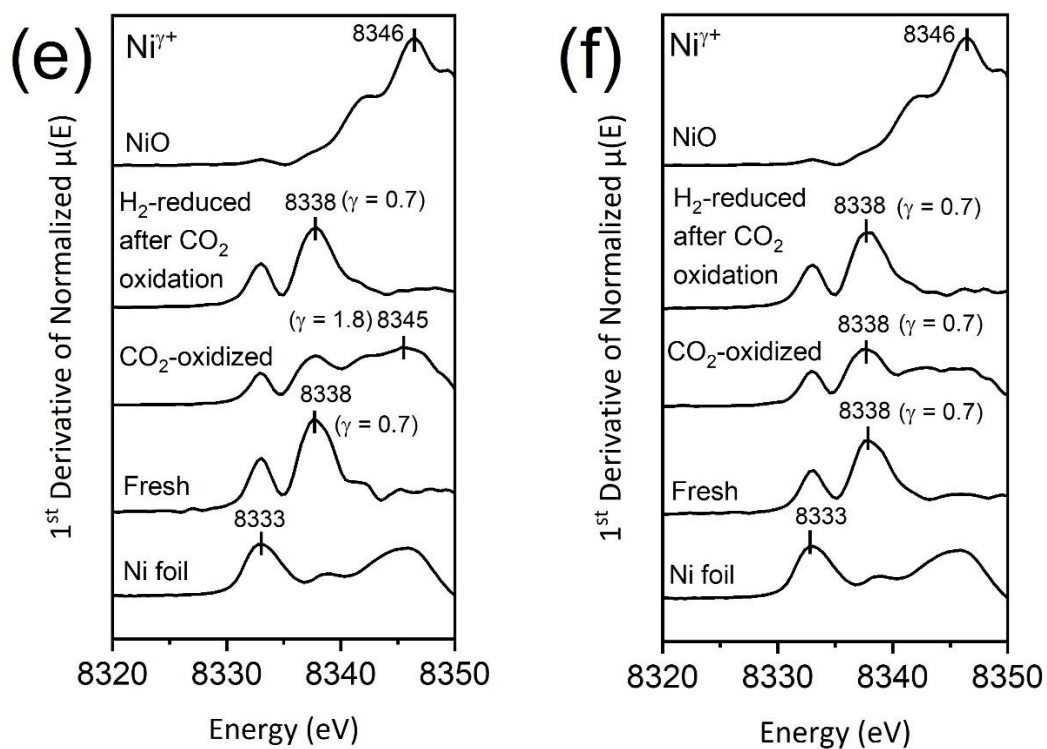


Figure S6. The 1st derivatives of (a, b) Fe (c, d) Co, and (e, f) Ni K-edge spectra of FeCoNiP_x/SiO₂ and CrMnFeCoNiP_x/SiO₂ in the forms of fresh, CO₂-oxidized, and H₂-reduced after CO₂ oxidation. Ni foil (Ni⁰) and NiO were included as references.

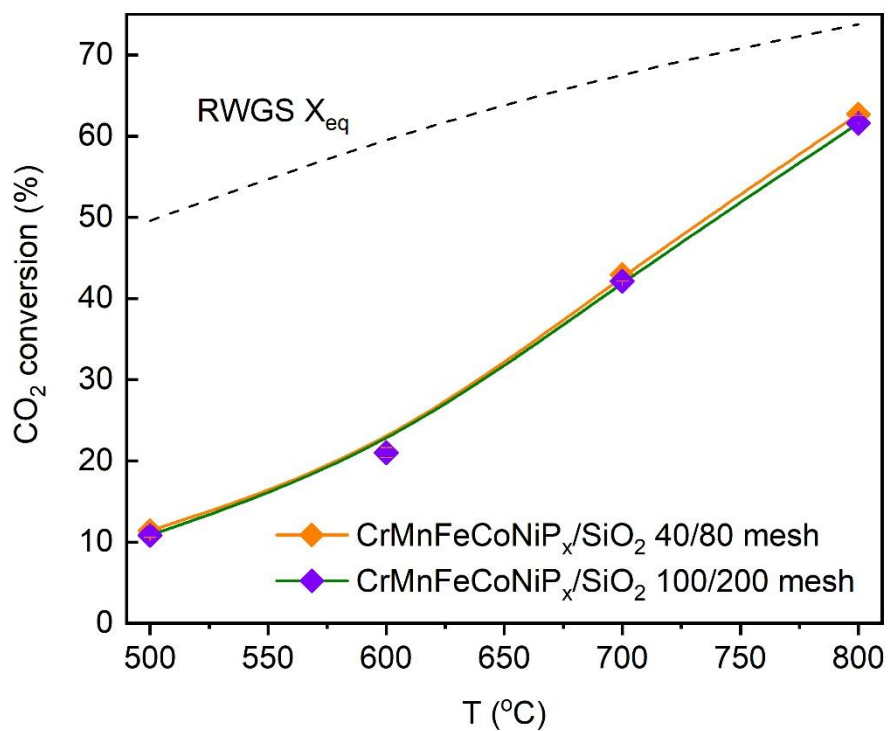


Figure S7. Conversions of CO₂ of CrMnFeCoNiP_x/SiO₂ by using 40-80 mesh and 100-200 mesh particle sizes (All catalysts had CO selectivity >99.9%). Reaction condition: P = 0.1 MPa, H₂/CO₂ = 3, and GHSV = 7200 mL g_{cat}⁻¹ h⁻¹.

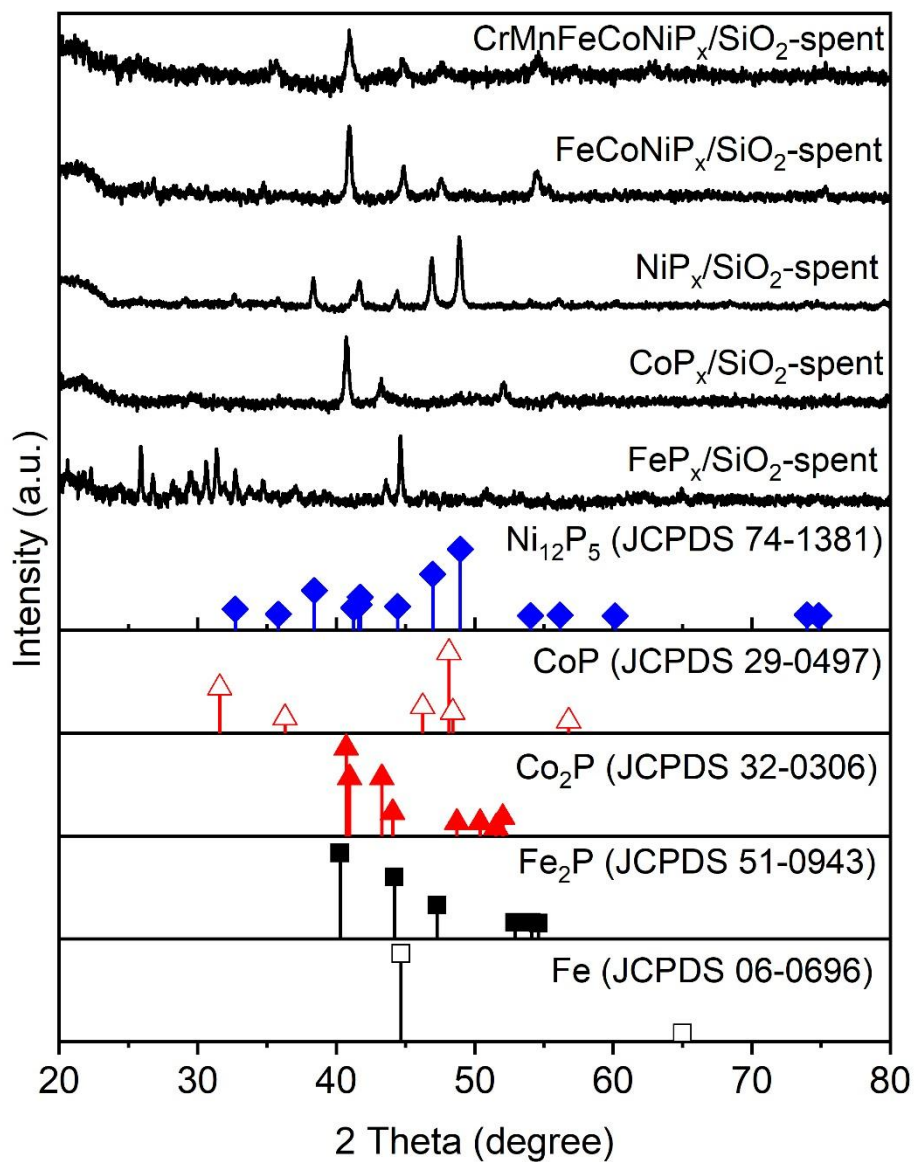


Figure S8. XRD patterns of the post-reaction silica-supported metal phosphide catalysts.

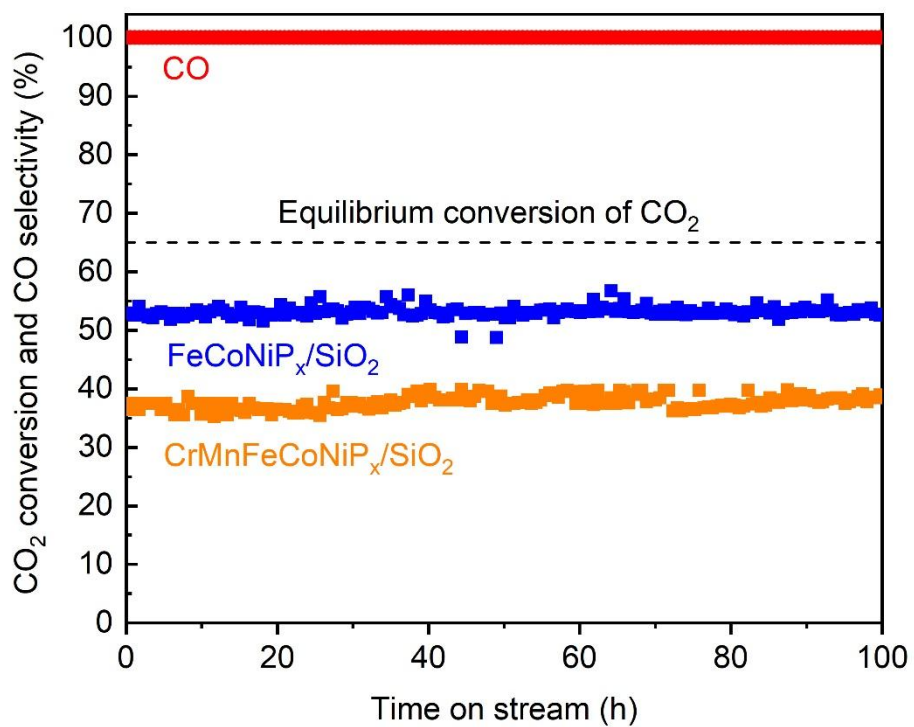


Figure S9. 100-h durability test for FeCoNiP_x/SiO₂ and CrMnFeCoNiP_x/SiO₂ at 700 °C. Reaction condition: P = 0.1 MPa, H₂/CO₂ = 3, and GHSV = 7200 mL g_{cat}⁻¹ h⁻¹.

References

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