

The role of surface oxidation and Fe-Ni synergy in Fe-Ni-S catalysts for CO₂ hydrogenation

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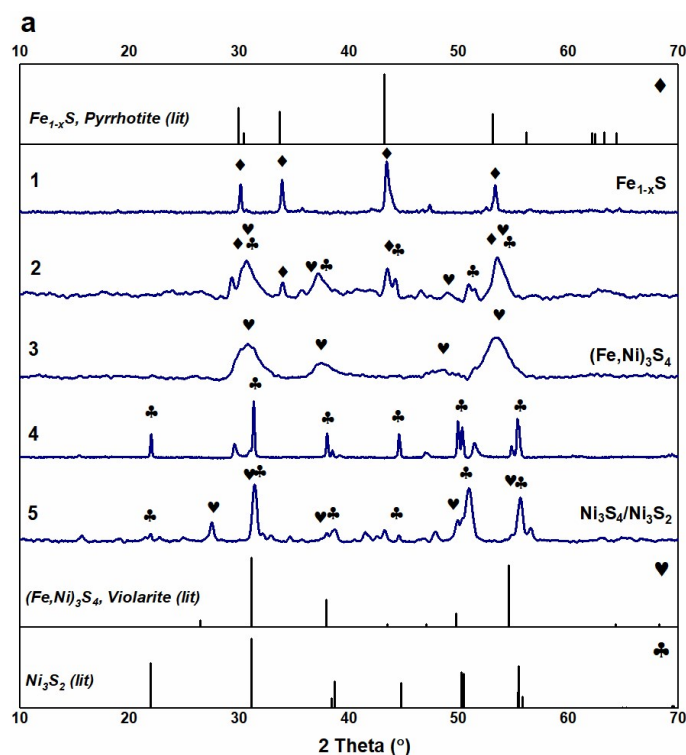
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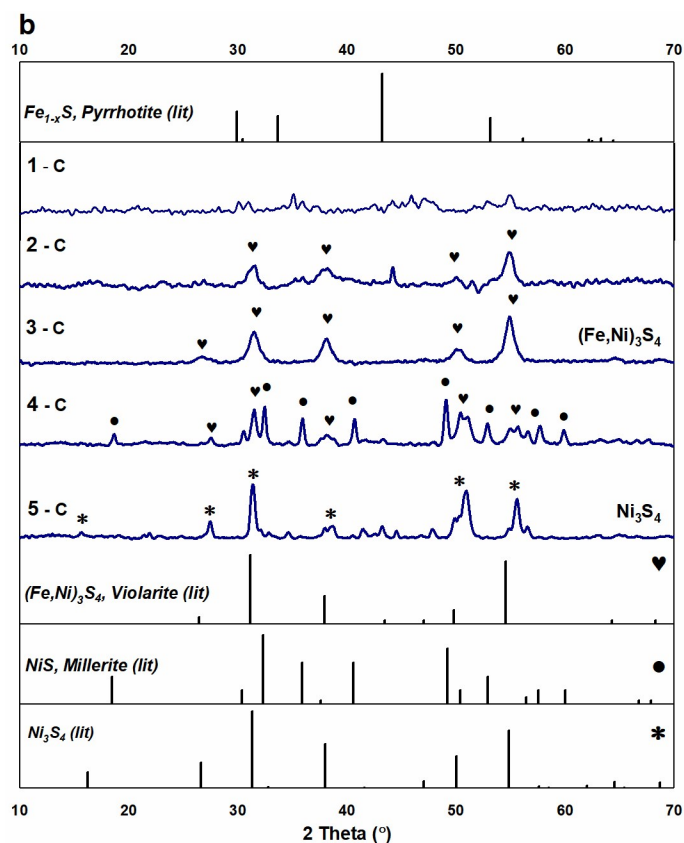


Figure S1: XRD spectra of iron nickel sulphide samples 1-6; fresh (a) and calcined at 200 °C (b). Sample numbers described in Table 1. Diffraction patterns correlate to $Fe_{1-x}S$ (diamond) (JCPDS 01-085-0987 PDF file), Ni_3S_2 (club) (JCPDS 01-076-1870 PDF file), $(Fe,Ni)_3S_4$ (heart) (JCPDS 00-002-0779 PDF file), NiS (dot) (JCPDS 00-003-0760 PDF file) and Ni_3S_4 (star) (JCPDS 01-076-1813 PDF file) reference patterns.

Table S1: Testing commercial materials for CO_2 hydrogenation

Catalyst	Formate (μmol)
$(Fe,Ni)_3S_4$ (calcined 200 °C)	5.08
$Fe_3O_4^*$	0.14
$FeSO_4^*$	0.05
$NiSO_4^*$	0.04

*Commercially sourced

Reaction conditions: catalyst: 20mg; 1M NaOH solution: 4 ml; pCO_2 : 10 bar (at 25 °C); pH_2 : 10 bar (at 25 °C); reaction temperature: 125 °C; reaction time: 3 days.

Table S2: Binding energy data, interpretations and atomic concentrations for the Fe2p, Ni2p and S2p spectra of fresh and calcined (Fe,Ni)₃S₄ samples. Peak reference correlating to spectra in Figure 4.

XPS spectra	Fresh			Calcined		
	B.E. (eV)	Chemical state	Atom Conc (%)	B.E. (eV)	Chemical state	Atom Conc (%)
<i>Fe2p</i>	707.1	Fe(II)-S	17.6	707.3	Fe(II)-S	5.0
	710.0	Fe(III)-O	46.6	710.3	Fe(III)-O	54.0
	711.8	Fe(III)-O	24.4	711.9	Fe(III)-O	30.3
	713.5	Fe(III)-O	11.5	713.4	Fe(III)-O	10.7
<i>Ni2p</i>	853.1	Ni(II)-S	25.7	853.3	Ni(II)-S	19.5
	854.9	Ni(II)-O	58.6	855.6	Ni(II)-O	53.9
	860.6	satellite	15.7	860.9	satellite	26.6
<i>S2p</i>	161.3	S ²⁻	46.6	161.3	S ²⁻	30.0
	162.5		23.3	162.5		15.0
	162.6	S ₂ ²⁻	2.1	162.4	S ₂ ²⁻	6.3
	163.7		1.1	163.6		3.2
	163.2	S _n ²⁻	7.3	163.3	S _n ²⁻	3.4
	164.4		3.6	164.5		1.7
	165.1	S ₈	2.1	164.7	S ₈	5.2
	166.2		1.1	165.8		2.6
	166.8	SO ₃ ²⁻	7.3	166.7	SO ₃ ²⁻	3.1
	167.9		3.5	167.8		1.5
	168.5	SO ₄ ²⁻	1.5	168.4	SO ₄ ²⁻	18.8
	169.7		0.7	169.6		9.4

Table S3: Binding energy data, interpretations and atomic concentrations for the Fe2p, Ni2p and S2p spectra of fresh (Fe,Ni)₃S₄ NiS and FeS samples.

XPS spectra	Fe _{1-x} S			(Fe,Ni) ₃ S ₄			Ni ₃ S ₄		
	B.E. (eV)	Chemical state	At. Conc. (%)	B.E. (eV)	Chemical state	At. Conc. (%)	B.E. (eV)	Chemical state	At. Conc. (%)
Fe2p	707.4	Fe(II)-S	26	707.1	Fe(II)-S	17.6	-	-	-
	710.2	Fe(III)-O	46	710.0	Fe(III)-O	46.6			
	711.7	Fe(III)-O	20	711.8	Fe(III)-O	24.4			
	713.3	Fe(III)-O	8	713.5	Fe(III)-O	11.5			
Ni2p	-	-	-	853.1	Ni(II)-S	25.7	852.9	Ni(II)-S	23.2
				854.9	Ni(II)-O	58.6	855.5	Ni(II)-O	47.2
				860.6	satellite	15.7	860.3	satellite	29.6
S2p	161.3	S ²⁻	34	161.3	S ²⁻	46.6	161.1	S ²⁻	15.2
	162.4		17	162.5		23.3	162.3		7.4
	162.3	S ₂ ²⁻	6	162.6	S ₂ ²⁻	2.1	161.9	S ₂ ²⁻	36.7
	163.4		3	163.7		1.1	163.0		18.0
	163.2	S _n ²⁻	7	163.2	S _n ²⁻	7.3	163.2	S _n ²⁻	6.8
	164.4		4	164.4		3.6	164.3		3.3
	164.2	S ₈	5	165.1	S ₈	2.1	164.9	S ₈	3.1
	165.4		2	166.2		1.1	166.0		1.5
	166.6	SO ₃ ²⁻	3	166.8	SO ₃ ²⁻	7.3	165.1	SO ₃ ²⁻	0.9
	167.7		2	167.9		3.5	166.3		0.5
	168.2	SO ₄ ²⁻	11	168.5	SO ₄ ²⁻	1.5	166.3	SO ₄ ²⁻	4.4
	169.3		6	169.7		0.7	167.5		2.2

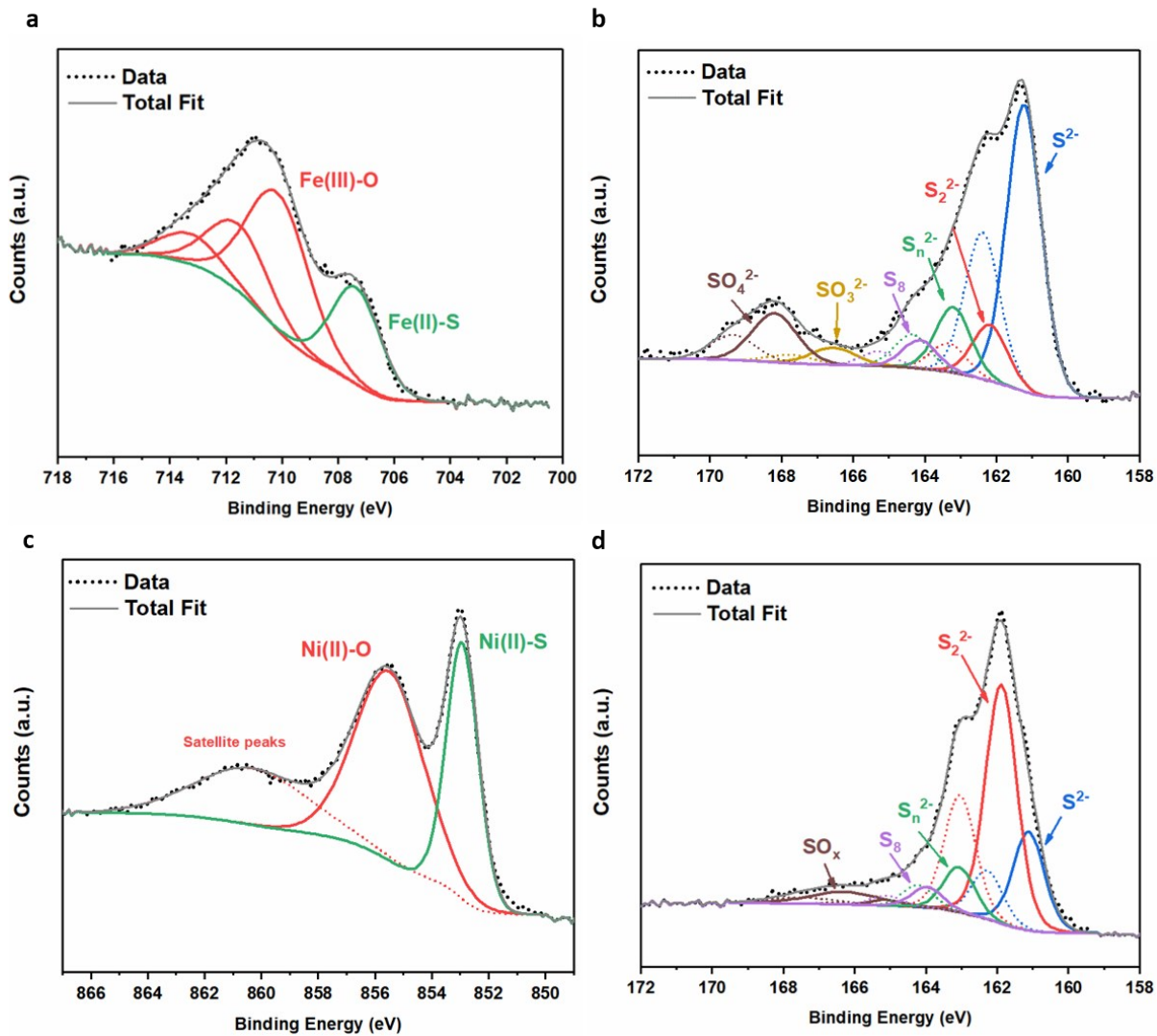


Figure S2: XPS spectra of $Fe_{1-x}S$ (sample 1) (a) Fe 2p (b) S 2p, Ni_3S_4 (sample 5, calcined 200 °C) (c) Ni 2p (d) S 2p. Binding Energies are listed in Table S3

Table S4: Binding energy data, interpretations and atomic concentrations for the Fe2p, Ni2p and S2p spectra of (Fe,Ni)₃S₄ calcined at 200 °C (Figure 4) and 300 °C (Figure S3)

XPS spectra	Calcined 200 °C			Calcined 300 °C		
	B.E. (eV)	Chemical state	Atom Conc (%)	B.E. (eV)	Chemical state	Atom Conc (%)
<i>Fe2p</i>	707.3	Fe(II)-S	6.0	708.1	Fe(III)-S	3.0
	710.4	Fe(III)-O	56.5	710.5	Fe(III)-O	52.6
	712.1	Fe(III)-O	28.7	711.9	Fe(III)-O	32.7
	713.8	Fe(III)-O	8.9	713.6	Fe(III)-O	11.8
<i>Ni2p</i>	853.3	Ni(II)-S	19.5	853.6	Ni(II)-S	3.0
	855.6	Ni(II)-O	53.9	856.3	Ni(II)-SO ₄	43.3
	860.9	satellite	26.6	858.6	Ni(II)-SO ₄	11.1
				861.7-866.4	satellite	57.4
<i>S2p</i>	161.3	S ²⁻	29.9	161.5	S ²⁻	9.3
	162.4		14.9	162.6		4.7
	162.5	S ₂ ²⁻	6.4	163.1	S ₂ ²⁻	10.1
	163.6		3.2	164.2		5.0
	163.3	S _n ²⁻	3.7	164.7	S _n ²⁻	0.7
	164.4		1.8	165.8		0.3
	165.0	S ₈	5.0	165.5	S ₈	1.4
	166.0		2.5	166.6		0.7
	166.7	SO ₃ ²⁻	2.8	167.2	SO ₃ ²⁻	3.5
	167.8		1.4	168.4		1.8
	168.4	SO ₄ ²⁻	18.9	168.7	SO ₄ ²⁻	41.7
	169.6		9.4	169.9		20.9

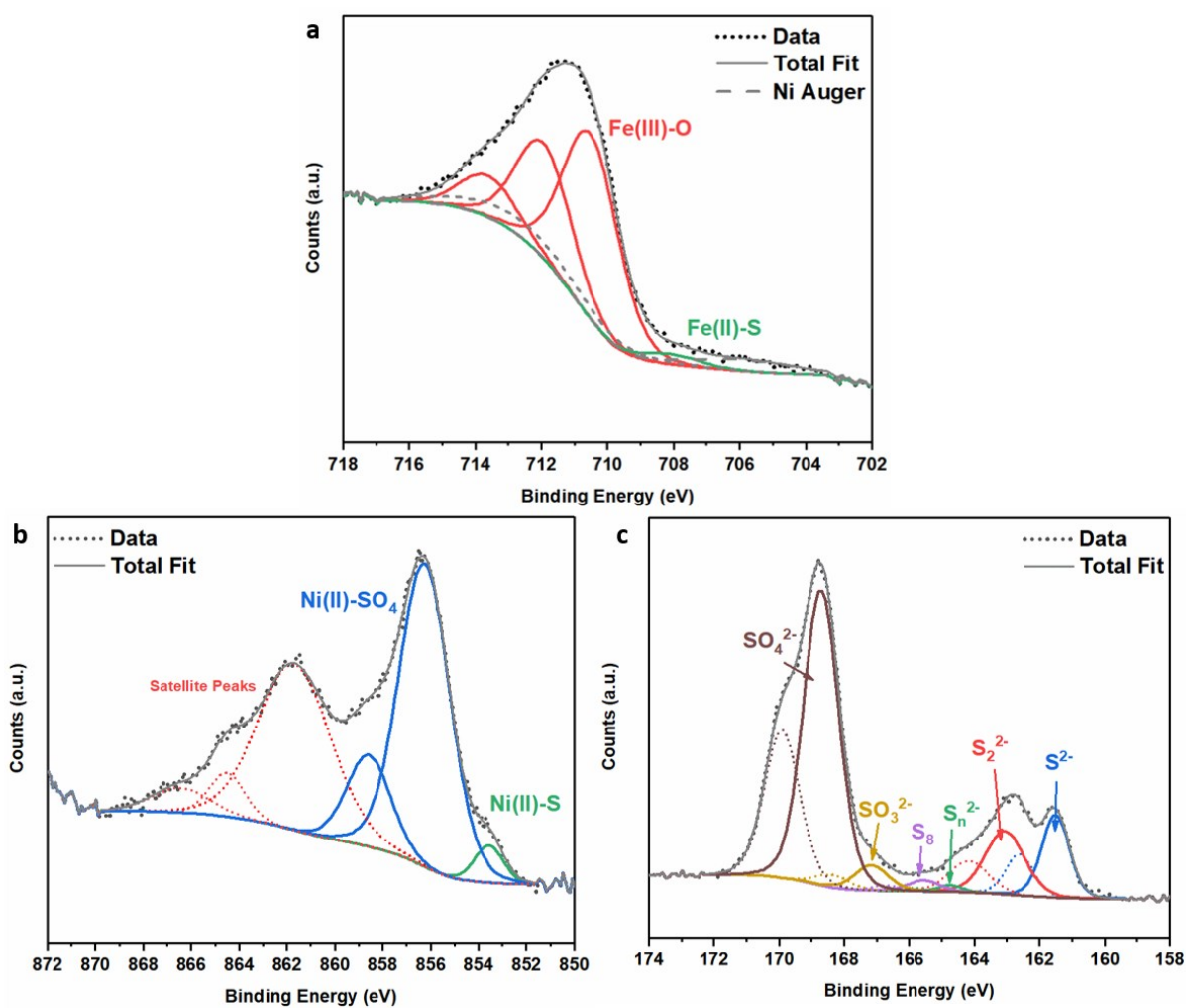


Figure S3: XPS spectra of $(\text{Fe,Ni})_3\text{S}_4$ calcined at 300 °C (a) Fe_{2p} (b) Ni_{2p} (c) S_{2p}. Binding Energies listed in Table S4.