

Supporting Information

Reduction of CO₂ with H₂S in simulated deep-sea hydrothermal vents system

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1 Experimental Procedures

1.1 Materials

$\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ was used as a source of HS^- and NaHCO_3 as CO_2 resource for experimental convenience in this study. NaHCO_3 ($\geq 99.5\%$) and $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ ($\geq 99.8\%$) were purchased from Sino-pharm Chemical Reagent Co., Ltd, Deuterium oxide (D_2O , 99.9% D) from Cambridge Isotope Laboratories (Inc. USA), formate (for mass spectrometry, 98%) from Sigma-Aldrich (Shanghai) Trading Co., Ltd, Gaseous N_2 ($> 99.99\%$) from Shanghai Pujiang Special Gas Co., Ltd, Gaseous H_2 ($> 99.999\%$) and CO_2 ($> 99.99\%$) from Shanghai Poly-Gas Technology Co. Ltd, respectively. All of the raw materials used in the experiment were analytical grade without further purification. The solvent used in the experiment is distilled water.

1.2 Experimental section

The experiments were conducted in a SUS316 lined reactor with an internal volume of 42 mL. The certain amount of NaHCO_3 (CO_2 source), $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (source of HS^-) and degassed water (according to a certain water filling) were added into the SUS316 lined reactor first, and then the reactor was purged with nitrogen for 5 min. After that the reactor was put into an induced heating furnace and heated to a desired temperature with an increasing rate of $15\text{ }^\circ\text{C}/\text{min}$. The induced heating furnace was swayed of 20 times/min during the reaction. The water filling was defined as the volumetric ratio of the water put into the reactor to the inner volume of the reactor in the experiments. The reaction time was defined as the time started when the temperature reached to the desired temperature. After a desired reaction time, the reactor was removed from the furnace and cooled by electric fan. The detail of this reactor has been described in Jin's previous papers.^{1, 2}

1.3 Product analysis

After filtered through a $0.22\text{-}\mu\text{m}$ -filter film, liquid samples were analyzed by HPLC (High-performance Liquid Chromatography, Agilent Technologies 1260 Infinity) and GC-MS (Gas Chromatography-Mass spectroscopy, Agilent Technologies 7890) analyzer. HPLC was equipped with a Shodex RSpak KC-811 packing column ($300\text{ mm}\times 8\text{ mm}$ i.d.) and a tunable UV detector (absorbance detector adjusted to 210 nm), and the flow rate of the eluent ($2\text{ mmol/L HClO}_4\text{ aq.}$) is $1.0\text{ mL}/\text{min}$. GC-MS was analyzed with Agilent Technologies 5975C inert MSD with Tripe-Axis Detector (with 7890A GC system). The solid samples were washed by deionized water and ethanol separately, and then dried in an oven at $80\text{ }^\circ\text{C}$ for 10 hours. The crystalline phases and morphology of the solid samples were characterized via X-ray powder diffraction (XRD, Shimadzu XRD-6100) and scanning electron microscope (SEM, S-4800). The XRD pattern was investigated with Cu $\text{K}\alpha$ radiation ($\lambda = 0.154056\text{ nm}$) and a scanning rate of $4\text{ }^\circ/\text{min}$ at an acceleration voltage of 40 Kv and emission current of 40 mA.

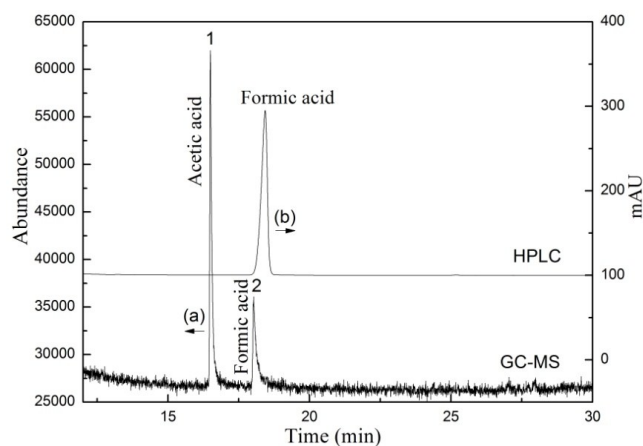


Figure S1. GC-MS and HPLC chromatogram of the liquid samples after reaction (T: $300\text{ }^\circ\text{C}$, t: 3 h, NaHCO_3 : 0.4 mol/L , $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$: 0.1 mol/L , Ni_3S_2 : 0.05 mol/L , Water filling: 35%).

2 Synthesis of metal sulphides

The metal sulphides catalysts (Ni_3S_2 , FeS_2 , CuS , MoS and CoS) used in the experiment were prepared by solvothermal and hydrothermal method. In a typical synthesis process, 0.2 mol/L $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.2 mol/L $(\text{H}_2\text{N})_2\text{CS}$ and 18 mL ethylene glycol were added to a 30ml Teflon-lined autoclave with the filling ratio of 60% at room temperature. After heating at 200 °C for 24 h, reaction vessel was cooled to room temperature is air. Black precipitates were collected by filtration, and washed by deionized water and anhydrous ethanol for several times, respectively. Finally, the as-prepared powders were dried at 60°C in air for 8h and then used as the CO_2 reduction catalyst. The preparation of FeS_2 , CuS , MoS_2 , MnS , CdS and CoS were performed by the partial substitution of an appropriate ratio of $(\text{H}_2\text{N})_2\text{CS}$ with $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ or $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, respectively. All chemicals were purchased from Sino-pharm Chemical Reagent Co., Ltd and used without further purification. XRD patterns of obtained Ni_3S_2 , FeS_2 , CuS , MoS_2 , MnS , CdS and CoS are shown in Fig. S2, S3, S4, S5, S6, S7 and S8, respectively.

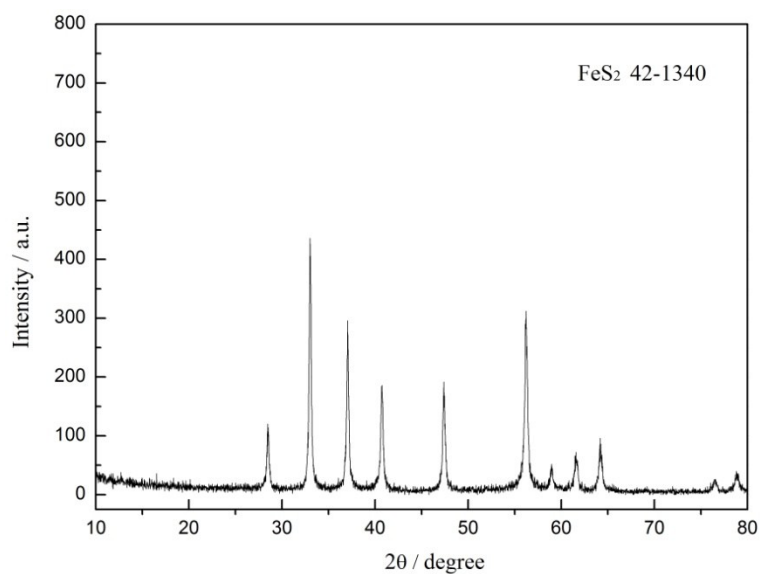


Figure S2. XRD pattern of obtained FeS_2 .

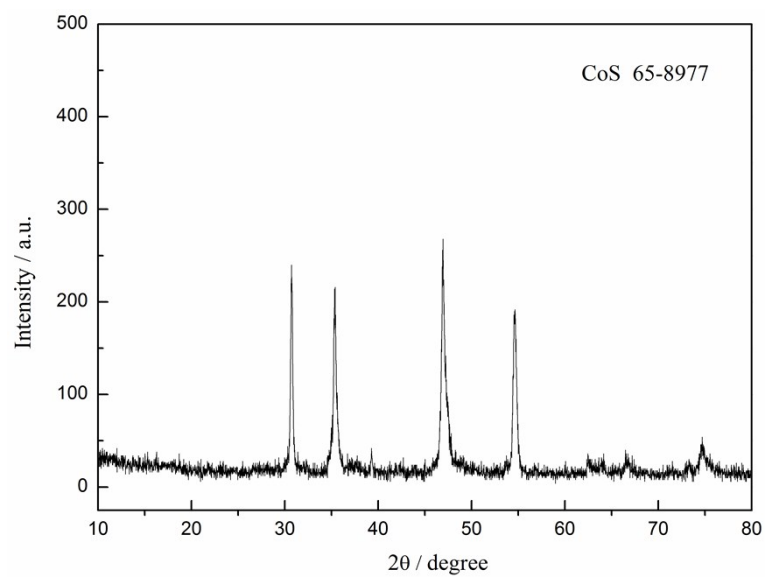


Figure S3. XRD pattern of obtained CoS.

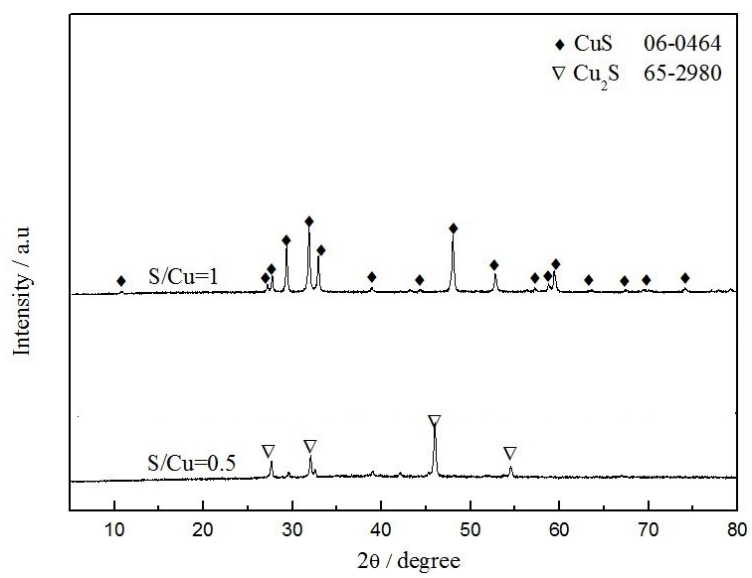


Figure S4. XRD pattern of obtained Cu₂S and CuS.

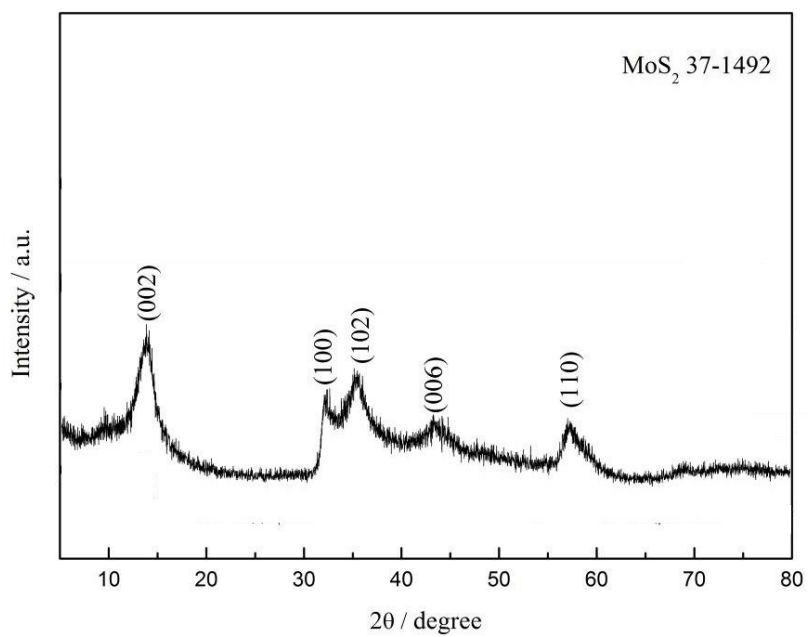


Figure S5. XRD pattern of obtained MoS₂.

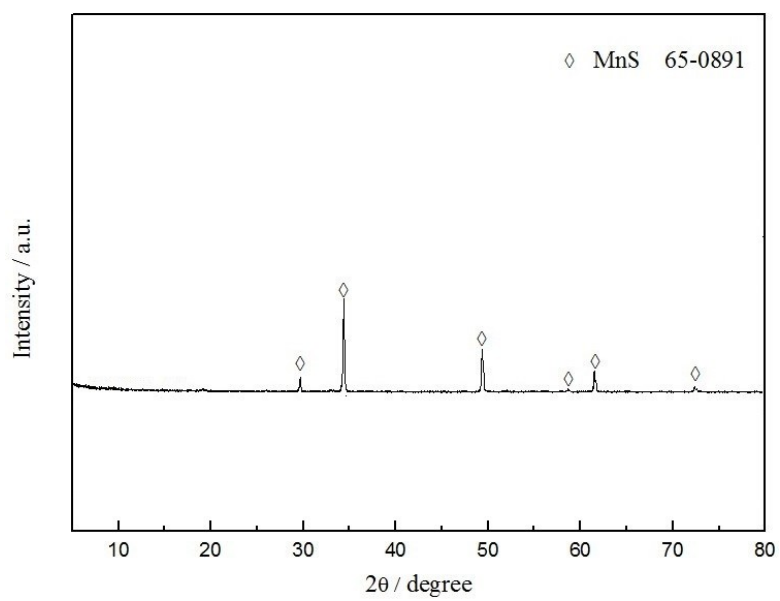


Figure S6. XRD pattern of the obtained MnS.

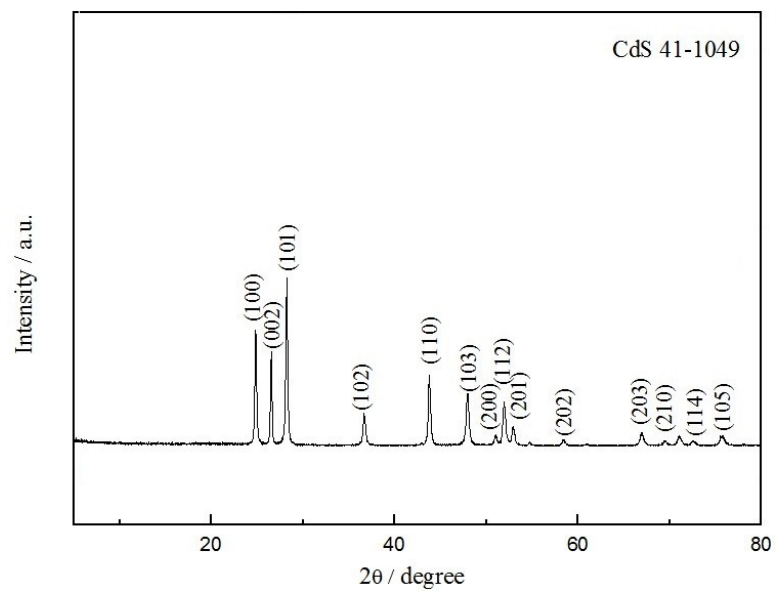


Figure S7. XRD pattern of obtained CdS.

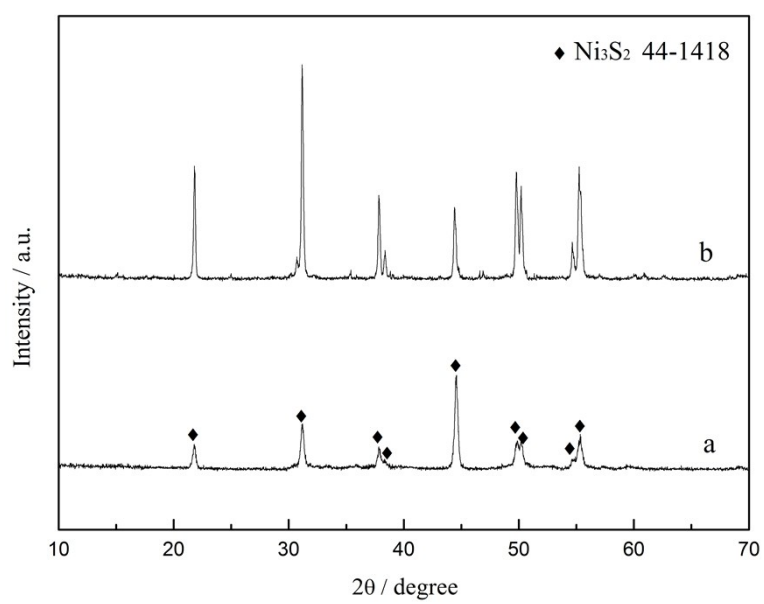


Figure S8. XRD patterns of Ni_3S_2 before (a) and after (b) hydrothermal reactions.

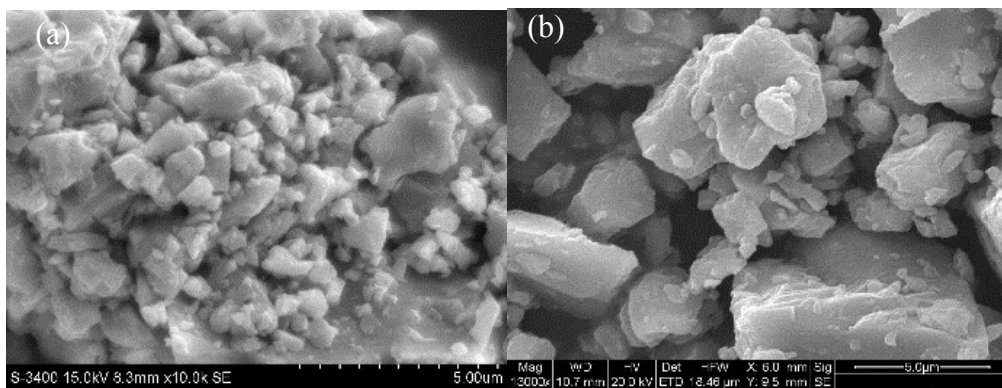


Figure S9. SEM pictures of Ni_3S_2 synthesized by solvothermal(a) and hydrothermal(b) reactions.

3 Investigation on reduction of gaseous CO₂ into formate

After the investigation on the reduction of CO₂ with NaHCO₃ as a CO₂ source, further research with gaseous CO₂ were conducted so as to know whether the formation of the formate can also be achieved with the gaseous CO₂. Formate obtained with different amounts of gaseous CO₂ is shown in Table S1. The formate yield was few (65 mg/L) when 0.5 MPa CO₂ was injected into the autoclave for reduction (Table S2, Entry 1), however with increasing gaseous CO₂ into 1.0 and 2.0 MPa (Table S2, Entry 2 and Entry 3), the formate yields of 327 and 675 mg/L were produced, respectively, suggesting that the formation of formate depended on the amount of CO₂, and the more the gaseous CO₂ used, the more the formate formed. As discussed previously, the formate may be formed via HCO₃⁻ rather than CO₂,^{3, 4} and a mildly alkaline pH was favorable to formate formation. When pumping plenitudinous CO₂ into alkaline solution, the reaction occurs as shown in Eq.1, while a deficient injection of CO₂, Eq.2 can be obtained. The low yield of formate achieved by a small gaseous CO₂ injected (Table S2, Entry 1) is likely that CO₃²⁻ is the main existing ions which results in a small yield of formate. With increasing the initial amount, plenitudinous gaseous CO₂ should be solved easily in alkaline solution to form more HCO₃⁻ in water, and the more HCO₃⁻ in turn leads to more formate formation (Table S2, Entry 2 and Entry 3). In order to further enhance the solubility of CO₂ in the alkaline solution, the solution with 2.0 MPa CO₂ injected (Table S2, Entry 4) was heated at 80°C for 3 h, and after the hydrothermal reaction, the yield of formate was found to reach up to 1079 mg/L. Although the yield is still not as high as the one obtained with NaHCO₃, from discussed above, we can draw the conclusion that gaseous CO₂ can be directly reduced into the formate with the Na₂S•9H₂O addition.



Table S1. Reduction of CO₂ with H₂S in different reactors

Entry	Reactor	T/°C	Time/h	catalyst	Formate (mg/L)
1	Teflon	250	24	None	0
2	Teflon	250	24	Ni ₃ S ₂	281
3 ^[a]	Teflon	250	24	Ni ₃ S ₂	0
4	quartz	300	2	None	0
5	quartz	300	2	Ni ₃ S ₂	2093
6 ^[b]	SUS316	300	3	None	24
7 ^[c]	SUS316	300	3	Ni ₃ S ₂	5986

Na₂S•9H₂O: 0.025 mol/L; NaHCO₃: 1 mol/L; Water filling:55%; [a] No NaHCO₃ ; [b][c] No Na₂S•9H₂O H₂: 1MPa; NaHCO₃: 0.4 mol/L; Water filling: 35%

Table S2. Yields of formate with gaseous CO₂ (T: 300 °C, t: 3 h, Water filling: 55%).

Entry	CO ₂ (MPa)	Na ₂ S·9H ₂ O (mol/L)	H ₂ O mL	Ni ₃ S ₂ (mol/L)	Fomic acid Yield (mg/L)
1	0.5	0.2	23.1	0.1	65 ^a
2	1.0	0.2	23.1	0.1	327 ^a
3	2.0	0.2	23.1	0.1	675 ^a
4	2.0	0.2	23.1	0.1	1079 ^b

[a] at room temperature.[b] The solution with gaseous CO₂ was maintained for 3 h at 80°C before the hydrothermal reaction.

Table S3. Reduction of CO₂ to formate with H₂S using different metal sulphides as catalysts

Entry	Cat	Formate (mg/L)	Entry	Cat	Formate (mg/L)
1	Ni ₃ S ₂	3477	7	MoS ₂	2916
2	CoS	2456	8	CdS	3455
3	CoS ₂	2337	9	Cu ₂ S	2535
4	FeS ₂ (Marcasite)	1651	10	CuS	616
5	FeS ₂ (Pyrite)	3026	11	ZnS	584
6	MnS	2659			

Catalyst: 0.1mol/L; Temp: 300 °C; time: 3 h; Na₂S•9 H₂O: 0.025 mol/L; Water filling: 55%; NaHCO₃: 1.4 mol/L; Catalysts were synthesized by hydrothermal or solvothermal methods.

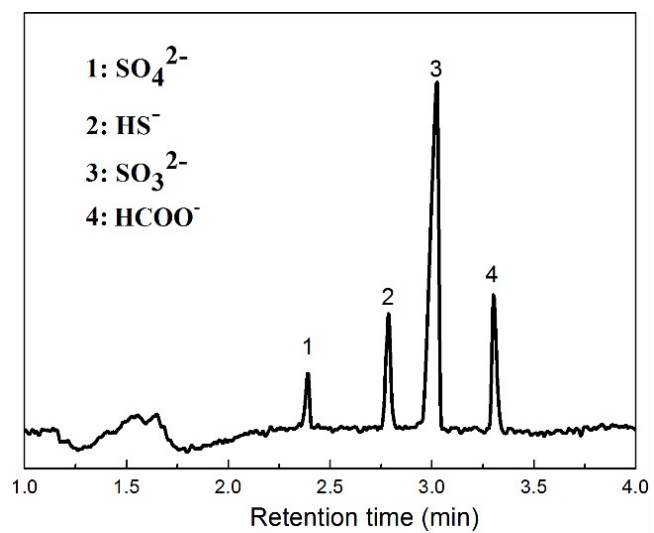


Figure S10. Typical capillary electropherograms of liquid samples after the reaction.

Table S4. Yield of SO_4^{2-} and SO_3^{2-} produced from H_2S

Ion ^[a]	Concentration ^[b] (mmol/L)	Ion	Concentration (mmol/L)
SO_4^{2-}	4.38	S^{2-}	0.74
SO_3^{2-}	19.26	HCOO^-	75.44

[a] Reaction Condition: Ni_2S_3 : 0.1mol/L; Temp: 300 °C; time: 3 h; $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$: 0.025 mol/L; Water filling: 55%; NaHCO_3 : 1.4 mol/L. [b] Sample were measured by a Thermo Scientific Dionex ICS-5000+/900 Ion Chromatography with Ionpac AS11-HC Analytical Column.

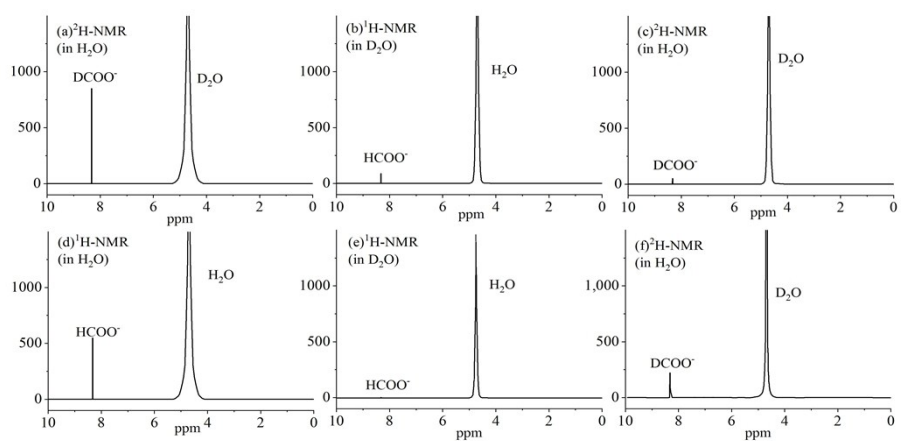


Figure. S11 ^1H - and ^2H -NMR spectra of the solutions after the hydrothermal reduction of CO_2 with HS- or H_2S in D_2O (or with DS^- in H_2O) (T: 300 °C, t: 3 h, NaHCO_3 : 1.4 mol/L, Ni_3S_2 : 0.1 mol/L, Water filling: 55%).

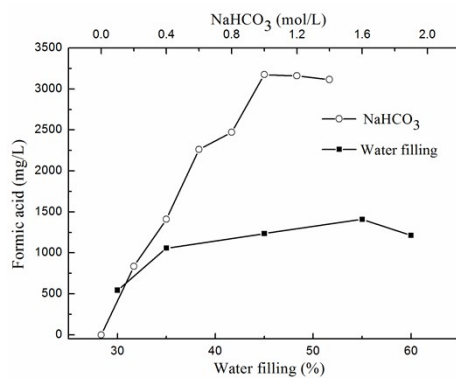


Figure S12. Effect of water filling and NaHCO₃ concentration on the formate production (T: 300 °C; t: 3 h; Na₂S•9 H₂O: 0.2 mol/L; Ni₃S₂: 0.05 mol/L; 0.4 mol/L NaHCO₃ for water filling; 55% water filling for NaHCO₃).

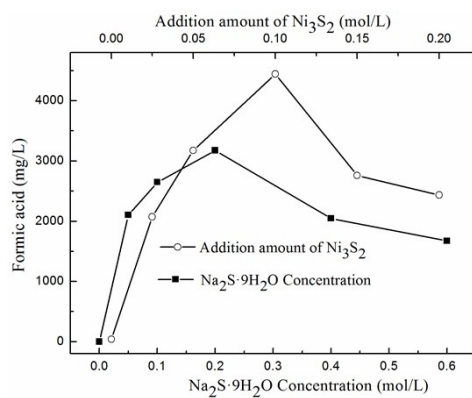


Figure S13. Effects of Na₂S·9H₂O concentration and addition amount of Ni₃S₂ on the formate production (T: 300 °C; t: 3 h; water filling: 55%; NaHCO₃: 1.0 mol/L; 0.05 mol/L Ni₃S₂ for Na₂S·9H₂O; 0.2 mol/L Na₂S·9H₂O for Ni₃S₂).

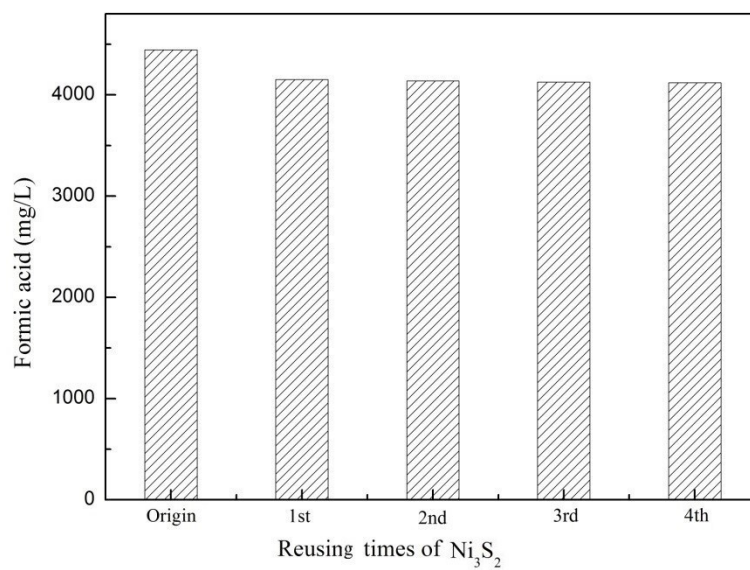


Figure S14. Effect of reused Ni_3S_2 on the formate yield (T: 300 °C; t: 3 h; NaHCO_3 : 1.0 mol/L; $\text{Na}_2\text{S} \cdot 9 \text{H}_2\text{O}$: 0.2 mol/L; Ni_3S_2 : 0.1 mol/L).

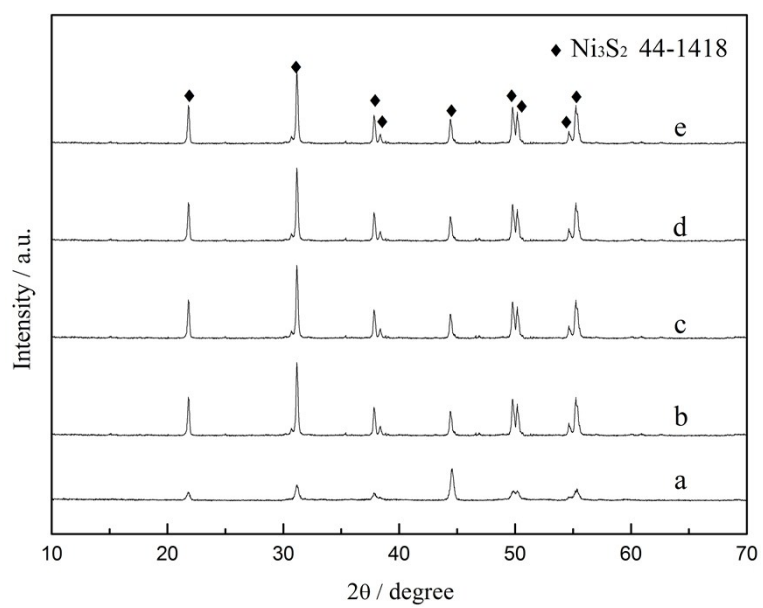


Figure S15. XRD patterns of (a) the original Ni_3S_2 , Ni_3S_2 recycled after (b) 1st, (c) 2nd, (d) 3rd and (e) 4th times.

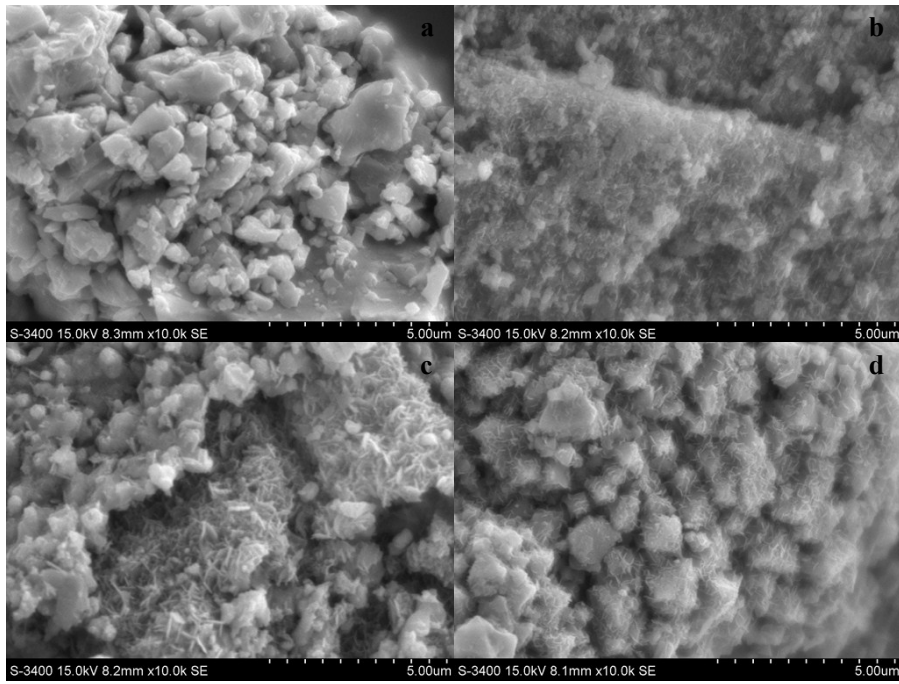


Figure S16. SEM images of (a) the original Ni_3S_2 , Ni_3S_2 recycled after (b) 1st, (c) 2nd, (d) 3rd times.

References

- 1 Kishida H., Jin F. M., Zhou Z. Y, Moriya T., Enomoto H. *Chemistry Letters*, 2005, **34**, 1560-1561.
- 2 Kishita A, Takahashi S.; Jin F, Yamasaki Y, Moriya T. Enomoto H. *J. Jpn. Petrol. Inst.*, 2005, **48**, 272-280.
- 3 Lyu, L. Y.; Zeng, X.; Yun, J.; Wei, F.; and Jin, F. M. *Environ .Sci. Technol.*, 2014, **48**, 6003-6009.
- 4 Jin, F. M.;; Zeng, X.; Liu, J. k.; Jin, Y. j.; Wang, L.Y.; Zhong, H.; Yao, G.D.; Huo, Z. B. *Sci. Rep.*, 2014, **4**, 4503.