

Electronic Supporting Information

High-Yield Reduction of Carbon Dioxide into Formic Acid by Zero-Valent Metal/Metal Oxide Redox Cycles

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Materials and Methods

In this study, NaHCO₃ was used as the CO₂ source for experimental convenience with respect to safety and handling. The zero-valent metals and metal oxides were in powder form with a particle size of 200-mesh. All reagents were in analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd.

Most of the experiments were conducted using batch reactors that consisted of SUS 316 tubing (9.525 mm o.d., 1-mm wall thickness and 120-mm length) with two end fittings, giving an inner volume of 5.7 mL. Details of apparatus have been described (1-3). The typical reaction procedure used was as follows: (1) for hydrothermal reduction of CO₂, a desired amount of NaHCO₃, metal powders and 2 mL deionized water were loaded into the reactor that occupied about 35% of the total reaction volume; (2) for the metals oxides reduction, the desired amount of FeCl₂ · 4H₂O or FeCl₃ or Fe(OH)₃ (as source of Fe⁺² or Fe³⁺), glycerin (as a reductant), NaOH (as an alkaline catalyst) were loaded into the reactor. *SAFETY: reactor loadings were limited to less than 2.5 mL water to avoid dangerous pressures.* Pressures at the highest temperature of 573 K would be around 8.6 MPa according to the loading limit conditions. After loading, the reactor was sealed and then immersed into a salt bath, which had been preheated to the desired temperature. The typical heat-up time required to raise the temperature of the reactor from 20 to 573 K was about 30 s. After the preset reaction time, the reactor was removed from the salt bath and immediately immersed in a cold-water bath. The reaction time was defined as the time period during which the reactor was kept in the salt bath.

In experiments for reducing metal oxides using glycerin, in addition to the same stainless-steel reactor mentioned above, a glass flask reactor was used. The procedure using the stainless-steel reactors was the same as that mentioned above. The desired amount of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ or FeCl_3 or $\text{Fe}(\text{OH})_3$ (as a source of Fe^{2+} or Fe^{3+}), glycerin (as a reductant), NaOH (as an alkaline catalyst) were loaded into the reactor for reactions. Reaction temperatures were varied from 423 to 473 K. For the procedure using the glass flask reactor, the flask filled with 200 mL of glycerine was heated up to 373 K, then the desired amount of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and NaOH were added into the flask for an hour. To examine the effect of impurities in actual glycerin and crude glycerin on the reduction of the metal oxides, a glycerin mixture with the addition of methanol, methyl esters, and fatty acids was also used as a test material.

In the experiments for confirming the cycle, the reduced Fe^0 with glycerin and $\text{Fe}(\text{OH})_x$ obtained by the reaction of the oxidized Fe_3O_4 with first HCl and then NaOH were also used starting materials. The oxidized Fe_3O_4 was obtained by separating from the solid residue after the first step reaction with magnetic separation. The $\text{Fe}(\text{OH})_x$ was prepared by adding NaOH into the solution after dissolving the oxidized Fe_3O_4 in 30% NaCl solution, and then drying the obtained precipitation in an oven at 60°C . The reduced Fe^0 powder was obtained by the reaction of the obtained $\text{Fe}(\text{OH})_x$ and glycerin at 523 K for 5 min to 30 min with SUS316 reactor. In the experiments with glycerin mixtures, the liquid samples after the reaction were separated into water and hexane samples, which were then analyzed by GC/MS and HPLC, respectively.

Teflon-lined stainless steel reactors with an inner volume of 22.8 mL were used to examine possible catalytic effects of Ni existing in the stainless-steel reactor wall on the reaction for experiments of both hydrothermal conduction of CO_2 with metals and reducing metal oxides using glycerin. After loading the reactor with the desired starting material, the reactor was put in an oven, which had been preheated to the desired temperature of 523 K. During the reaction, the reactor was rotated to enhance mixing of the reactants. In the experiments using the teflon-lined reactors, the temperature was limited to 523 K due to the maximum durable temperature of the teflon material. After a given time, the reactor was taken out of the oven and cooled to room temperature with an electric fan.

Sample Analyses

After the reactors were cooled, the liquid, gaseous and solid samples were collected and treated by washing or diluting with water or ethanol when required for analysis. Liquid samples were analyzed by HPLC, GC/FID/MS, ICP and a TOC analyzer (Shimadzu TOC 5000A), respectively. HPLC analysis was performed on KC-811 columns (SHODEX) with a HPLC system (Agilent Technologies 1200), which was equipped with a tunable UV/Vis absorbance detector adjusted at 210 nm, and a differential refractometer detector. Mobile phase was 2 mmol/L HClO₄ solution at an isocratic flow rate of 1.0 mL/min. Quantitative estimation of formic acid concentration was based on the average value obtained from at least three samples by the HPLC analysis. For GC/MS analysis, a Hewlett-Packard model 7890A Gas Chromatograph system equipped with a model 5975C Mass Selective Detector was used. The initial temperature of oven in the gas chromatograph was kept at 313 K for 1 min and then programmed to increase at a rate of 7 °C/min to a final temperature of 503 K that was held at this value for 20 min. Samples were separated with a HP-INNOWAX polar capillary column (25 m long, 0.25 mm i.d., 0.5 μm film thickness) using helium as carrier gas. For GC/FID analyses, a Hewlett-Packard model 5890 Series II Gas Chromatograph was used with analytical conditions being the same as those used for the GC/MS method. Gas samples were analyzed with a GC system (HP-5890 Series II), equipped with a HP-1 packing column (30 m×0.25 mm i.d.) and a TCD detector. ICP analysis was performed on ICP-MS 7700 (Agilent). Solid samples were washed with deionized water several times and dried in air and then characterized by X-ray diffraction (XRD) (D/MAX2550, Rigaku, and Bruker D8 Advance) using Ni-filtered Cu K α radiation at an acceleration voltage of 40 KV and emission current of 100 mA for D/MAX2550 and 40 mA for Bruker D8 Advance, respectively. The step scan covered angles of 5-70 ° (2 θ), at a rate of 10 °/min for D/MAX2550, Rigaku and 1.2°/s for Bruker D8 Advance, respectively.

Particle size distribution (PSD) of iron powder was determined by an EyeTech instrument (Ankersmid, USA) with a 300 mm lens which enabled the measurement of particles in the range 0.1–

1000 μm . The samples were prepared by adding 0.07 g iron powder into 25 mL aqueous NaPO_3 with a concentration of 40 g/L for keeping a very low density suspension solution.

Effect of pH on the hydrogen production when using Zn and Al

As shown in Table 1 in the main text for both Zn and Al, the amount of hydrogen in the presence of CO_2 was much greater than that in absence of CO_2 . The hydrogen produced can probably be attributed to the effect of pH, because both Zn(OH)_2 and Al(OH)_3 are amphoteric oxides, which dissolve in alkaline solutions to form Zn(OH)_4^{2-} and Al(OH)_4^- that causes Zn or Al to have a fresh surface for reaction with water. This hypothesis was confirmed by further experiments with other initial pH values using NaOH in the absence of NaHCO_3 , which showed almost the same amount of hydrogen as that in the presence of CO_2 (Table 1, entries 11-13 for Zn and entries 15-16 for Al).

Mechanism of hydrogen production when using Fe

To investigate the mechanism of hydrogen production when using Fe, we analyzed the solid residues after reaction with Fe in the absence and in the presence of CO_2 with X-ray diffraction. In the absence of CO_2 , only Fe was detected, while almost no iron oxides were detected, which indicates that Fe^0 could not be oxidized at 573 K. On the other hand, Fe_3O_4 was detected in the presence of CO_2 (Figure S1 (A)), clearly indicating that the presence of CO_2 promoted the oxidation of Fe. A possible mechanism of hydrogen production from water when using Fe^0 in the presence of CO_2 can be explained as follows:



However, we did not detect FeCO_3 in the solid residues even at a very short reaction time of 5 min (Figure S1 (A)). Considering that only Mg(OH)_2 was detected in the experiments in which Mg was used as the reductant in the presence of CO_2 , we designed an experiment using a mixture of Fe and Mg metals and made measurements in the presence of CO_2 , to confirm the formation of FeCO_3 . If MgCO_3 and

Fe(OH)₂ formed in the experiments, it would be evidence for the formation of FeCO₃ in the experiment with Fe according to following reactions:



As expected, MgCO₃ and Fe(OH)₂ were formed in the experiments with the mixture of Fe and Mg (Fe:Mg mole ratio of 1:1) (Figure S1 (B)).

Proposed mechanism for conversion of glycerin into lactic acid

As illustrated in Figure S2, glycerin may be produced through glycerin alkoxide in alkaline conditions due to its weak acidity. Then, the hydride ion (H⁻) on the alkoxide group is removed, leading to the formation of an aldehyde group, because of the presence of the negative charge on glycerin alkoxide aids in the removal of the H⁻. At the same time, the H⁻ attacks the α -hydrogen (α -H) next to the aldehyde group, leading to the elimination of the α -H and β -OH⁻ since the α -H has high acidity. As a result, glycerin alkoxide is converted into 2-hydroxypropenal, with the formation of H₂ (Step 2). The formed H₂ reduces Fe²⁺ or Fe³⁺ into Fe. In step 2, the reaction should tend to shift toward the formation of 2-hydroxypropenal because 2-hydroxypropenal has a conjugated double bond. Then, the 2-hydroxypropenal formed is converted into pyruvaldehyde by keto-enol tautomerism, which subsequently undergoes a benzilic acid rearrangement reaction to lactic acid (Step 3). Notably, in step 2, the α -H abstraction by H⁻ could be considered as a hydride transfer reaction. Hydride transfer reactions can be observed in many organic reactions, such as, benzilic acid rearrangement and Cannizzaro reaction. In these reactions, it is generally considered that the carbon-hydrogen bond is not entirely broken, that is, H⁻ is not completely removed but present in a transition state. Thus, the hydride transfer reaction in step 2 could be explained as a transition state as shown in Figure S2 B.

Energy assessment for the production of formic acid from CO₂ under hydrothermal conditions

(1) Calculation of the heat of reaction of the first-step (hydrothermal reduction of CO₂ into formic acid with Fe⁰ as a reductant

According to the proposed reaction pathway, the overall reaction can be described by:



Output energy as the heat of reaction (6), which is equivalent to the enthalpy difference between the products and the reactants, can be written as:

$$q = H_{product} - H_{reactants} = \Delta H \quad (7)$$

where $H_{products}$ and $H_{reactants}$ are the enthalpy of reaction products and reactants, kJ/mol.

The enthalpy difference is related to the heat of formation (ΔH_f):

$$\Delta H = \Delta H_f = \sum_i \gamma_i \Delta H_f(i) \quad (8)$$

where $\Delta H_f(i)$ is the heat of formation of species i , kJ/mol; γ_i is the stoichiometric number of the corresponding species.

Furthermore, the dependence of ΔH_f on the temperature is given by:

$$\Delta H_f(T_2) = \Delta H_f(T_1) + \int_{T_1}^{T_2} \Delta C_p dT \quad (9)$$

where, $\Delta C_p = \sum_i \gamma_i C_{pm}(i)$, C_{pm} is the molar heat capacity of reaction at a constant pressure, J/K·mol; T_1 and T_2 are the initial and final temperatures, respectively, K.

Therefore, the heat of reaction for hydrothermal reduction of CO₂ into formic acid as shown in Eq. (9) can be calculated as follows.

At the temperature of 298 K, according to Eq.(8), the heat of reaction is given by:

$$\Delta H_f(298K) = \Delta H_f(298K) (Fe_3O_4) + 4 \Delta H_f(298K) (HCOOH) - 4 \Delta H_f(298K) (CO_2) - 4 \Delta H_f(298K) (H_2O) - 3 \Delta H_f(298K) (Fe)$$

By substituting the values of the formation heat of the reactants and products as listed in Table S1, the value of heat of reaction at 298 K can be obtained.

$$\begin{aligned}\Delta H_f(298K) &= -1117.1 + 4 \times (-409.2) - 4 \times (-393.514) - 4 \times (-285.835) - 3 \times 0 \\ &= -36.504 \text{ kJ/mol}\end{aligned}$$

As listed in Table S1, the molar heat capacity of the reactants and products ($C_{p,m}$, J/K·mol) can be expressed as:

$$C_{p,m}(Fe_3O_4) = 167.03 + 78.09 \times 10^{-3} T - \frac{41.88 \times 10^5}{T^2}$$

$$C_{pm}^{\theta}(HCOOH) = 19.4 + 112.8 \times 10^{-3} T + 47.5 \times 10^{-6} T^2$$

$$C_{p,m}(Fe) = 19.25 + 21.0 \times 10^{-3} T$$

$$C_{p,m}(H_2O) = 53.5 + 117.15 \times 10^{-3} T$$

$$C_{p,m}(CO_2) = 44.14 + 9.04 \times 10^{-3} T - \frac{8.53 \times 10^5}{T^2}$$

$$\text{Thus, } \Delta C_p = C_{p,m}(Fe_3O_4) + 4 C_{p,m}(HCOOH) - 4 C_{p,m}(CO_2) - 4 C_{p,m}(H_2O) - 3 C_{p,m}(Fe)$$

$$= -203.68 - 38.47 \times 10^{-3} T + 190 \times 10^{-6} T^2 - \frac{33.55 \times 10^5}{T^2}$$

$$\int_{298}^{573} \Delta C_p dT = \int_{298}^{573} (-203.68 - 38.47 \times 10^{-3} T + 47.5 \times 10^{-6} T^2 - \frac{50.41 \times 10^5}{T^2}) dT$$

$$= -43949.5 \text{ J/mol}$$

Therefore, according to Eq. (9), the heat of reaction at the temperature of 573 K is obtained by:

$$\Delta H_f(573K) = \Delta H_f(298) + \int_{298}^{573} \Delta C_p dT$$

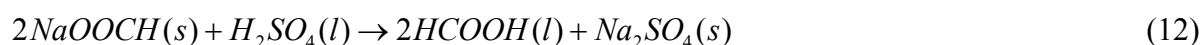
$$= -36.504 - 43.949 \text{ kJ/mol}$$

$$= -80.45 \text{ kJ/mol} = -1.749 \times 10^6 \text{ kJ/ton}$$

From the calculation, it can be seen that the hydrothermal reduction of CO₂ using Fe as reductant is exothermic. Notably, we did not consider the effect of pressure, because the values of heat capacities are weak functions of pressure.

(2) Comparison of the energy for producing formic acid between the hydrothermal reduction of CO₂ and the conventional method with fossil fuel as substrates

Applying the same thermodynamics method, we calculate the heat of reaction for the formic acid production at 298 K with a conventional method (Sodium Formiate Acidification Method).



$$\Delta H_f(298K)(HCOOH) = -537.99(kJ/mol)$$

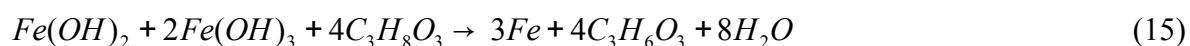
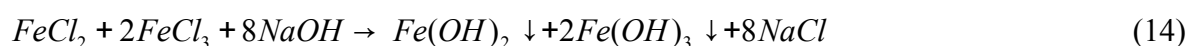
Thus, the energy required for producing one ton of formic acid could be obtained as follows:

$$\Delta H_m(298K) = \frac{1}{2} \times 537.99(kJ/mol) = 268.995(kJ/mol) = 5.845 \times 10^6 (kJ/ton)$$

Compared with the hydrothermal reduction of CO₂ into formic acid (-1.749 × 10⁶ kJ/ton) of this work, much more energy is required to produce one ton of formic acid from the current process with fossil fuel as substrates.

(3) Calculation of the heat of the second reaction (reduction of Fe₃O₄ with glycerin)

It is known well that the oxidation of metals in water and the hydrogenation of CO₂ are exothermic reactions. However, the heat of oxidation of the glycerin is not readily available and therefore, we calculated its value for reducing Fe₃O₄. According to the proposed mechanism, the overall reaction could be described by:



Total reactions can be obtained as,



Output energy as the heat of the reactions, which is equivalent to the enthalpy difference between the products and the reactants, can be written as:

$$q = H_{\text{product}} - H_{\text{reactants}} = \Delta H \quad (17)$$

where H_{products} and $H_{\text{reactants}}$ are the enthalpies of products and reactants, respectively, with units in kJ/mol.

The enthalpy difference is related to the heat of formation:

$$\Delta H = \Delta H_f = \sum_i \gamma_i \Delta H_f(i) \quad (18)$$

where $\Delta H_f(i)$ is the heat of formation of species i , and γ_i is the stoichiometric number of the corresponding species.

For the reduction of Fe_3O_4 at 298 K, according to Eq.(17) and Eq.(18), the heat of reaction is given by:

$$\Delta H_f(298\text{K}) = 4 \Delta H_f(298\text{K}) (\text{C}_3\text{H}_6\text{O}_3) + 4 \Delta H_f(298\text{K}) (\text{H}_2\text{O}) - \Delta H_f(298\text{K}) (\text{Fe}_3\text{O}_4) - 4\Delta H_f(298\text{K}) (\text{C}_3\text{H}_8\text{O}_3)$$

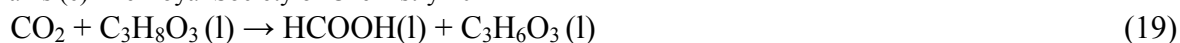
By substituting the values of the formation heat of the reactants and products as listed in Table S2, the value of the heat of reaction at 298 K can be obtained as:

$$\begin{aligned} \Delta H_f(298\text{K}) &= 4 \times (-675.017) \text{ kJ/mol} + 4 \times (-285.83) \text{ kJ/mol} - (-1117.1) \text{ kJ/mol} - 4 \times (-659.447) \text{ kJ/mol} \\ &= -88.5 \text{ kJ/mol} \end{aligned}$$

From the calculation, it can be seen that the reduction of Fe_3O_4 using glycerin as reductant is also exothermic. In addition, the molar heat capacities of glycerin and lactic acid at high temperature are lacking and therefore the heats of reaction at 573 K were not calculated.

(4) Calculation of the overall heat of reaction for reduction of CO_2 and oxidation of glycerin

According to the proposed mechanism, the reducing agent for CO_2 reduction is glycerin. By adding reaction (6) and (16), the overall reaction can be described by:



It is clear that the overall heat of reaction for the reaction at 298K can be obtained by adding reactions (6) and (16),

$$\begin{aligned} \Delta H_f (298\text{K}) &= -36.504 \text{ kJ/mol} + (-88.5 \text{ kJ/mol}) \\ &= -125.004 \text{ kJ/mol} \end{aligned}$$

From the calculation, it can be seen that the reduction of CO₂ using glycerin as reductant is exothermic.

(4) Calculation of the atom efficiency for the overall reaction

According to the proposed mechanism, the reducing agent for CO₂ reduction is glycerin. By adding reactions (6) and (16), the overall reaction can be described by:



The atom efficiency of the overall reaction can be obtained as:

$$\begin{aligned} \text{Atom efficiency \%} &= \frac{\sum \text{molecular mass for the products generated}}{\sum \text{molecular mass of participating reaction}} \times 100\% \\ &= \frac{44 + 90}{44 + 90} \times 100\% \\ &= 100\% \end{aligned}$$

The calculating results indicate that the reduction reaction of CO₂ by using glycerin as reductant was high atom efficiency.

References:

1. F. Jin, J. Cao, H. Enomoto, T. Moriya, *J. Supercritical Fluids* **19**, 251 (2001).
2. F. Jin, T. Moriya, H. Enomoto, *Environ. Sci. Technol.* **37**, 3220 (2003).
3. F. Jin, Z. Zhou, T. Moriya, H. Kishida, H. Higashijima, H. Enomoto, *Environ. Sci. Technol.* **39**, 1893 (2005).

4. Yin Y. et al., *Handbook of chemistry for academics*, Shandong Science & technology press, Jinan, (1985) (in Chinese).

Tables

Table S1 Heats of formation and the molar heat capacities of reactants and products at 298 K and normal pressure ^[4]

	$\Delta H_f^\theta(298K)$ (KJ mol ⁻¹)	$C_{pm}^\theta = a + bT + cT^2$ or $C_{pm}^\theta = a + bT + \frac{c'}{T^2}$ (JK ⁻¹ mol ⁻¹)			
		a	$b \times 10^3$	$c' \times 10^{-5}$	$c \times 10^6$
Fe (s)	0	19.25	21.0	-	-
H ₂ O (l)	-285.835	53.5	117.15	-	-
CO ₂ (g)	-393.514	44.14	9.04	-8.53	
Fe ₃ O ₄ (s)	-1117.1	167.03	78.09	-41.88	
Zn (s)	0	48.99	5.10	-	-9.12
ZnO (s)	-347.98	22.38	10.04	-	-
HCOOH (l)	-409.2	19.4	112.8	-	47.5

Table S2 Standard molar enthalpies of formation of related chemicals.

	$\Delta H_f(298K) / \text{kJ/mol}$
Glycerin*	- 659.447
Fe(OH) ₂	- 569
Fe(OH) ₃	- 823
Lactic acid*	- 675.017
Fe	0
H ₂ O	- 285.83

*Enthalpy values obtained from heat of combustion data.

Table S3 Distribution of particle size of the reduced Fe⁰ with glycerin and the purchased Fe⁰ with 200-mesh.

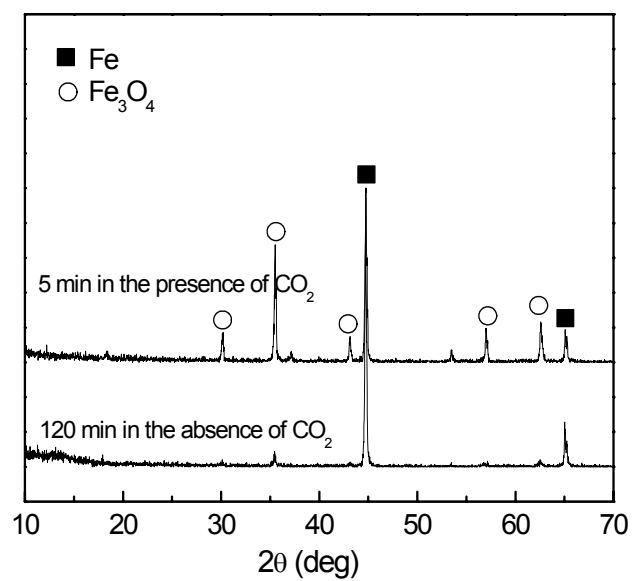
	Average diameter (μm)	D10 (μm)	D50 (μm)	D90 (μm)
Fe ⁰ powder 200-mesh	1.67	0.62	0.91	3.71
Reduced Fe ⁰	1.17	0.76	0.91	1.94

D10, D50 and D90 refer to 10%, 50% and 90% of the powder particles are smaller than this value, respectively.

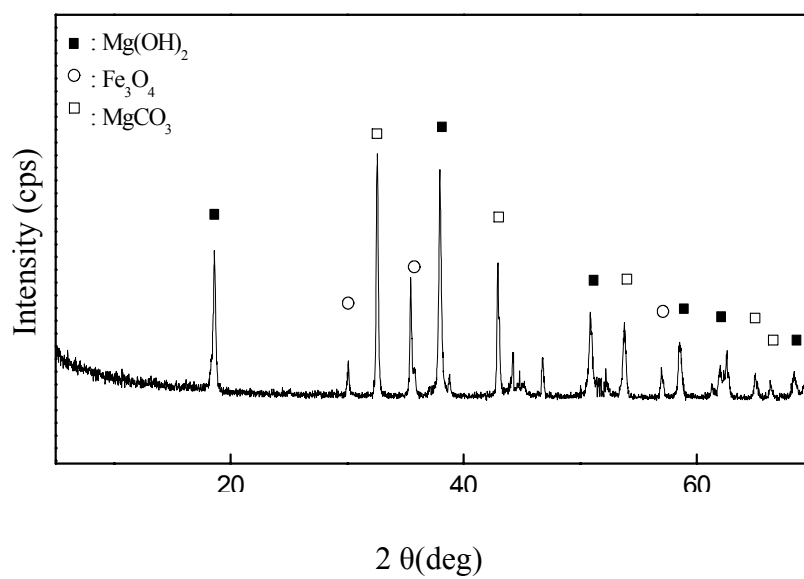
Table S4 Ratios of methanol, methyl stearate or methyl oleate and stearic acid or oleic in glycerin solutions used in evaluating the potential use of crude glycerin on conversions.

Methanol (wt/wt, %)	Methyl stearate or methyl oleate (wt/wt, %)	Stearic acid or oleic acid (wt/wt, %)
0.8	5	0.1

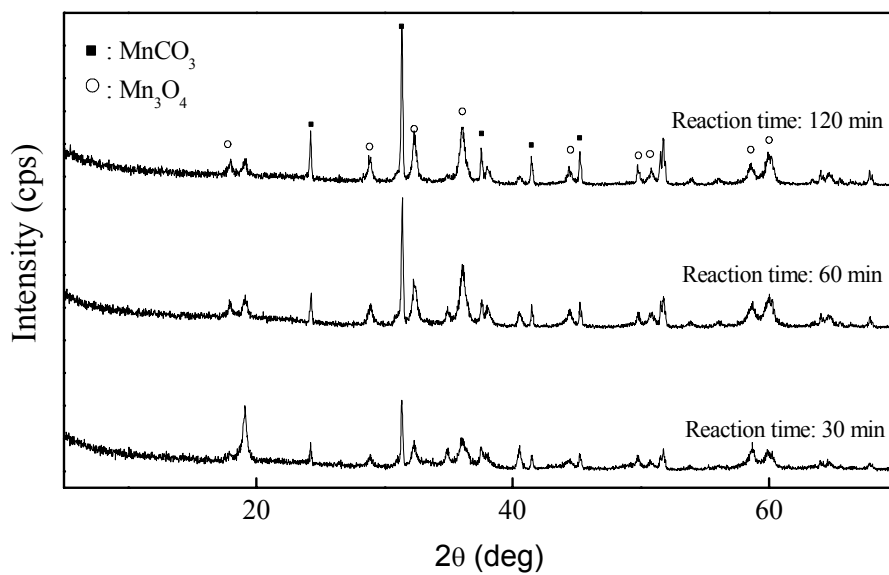
Figures



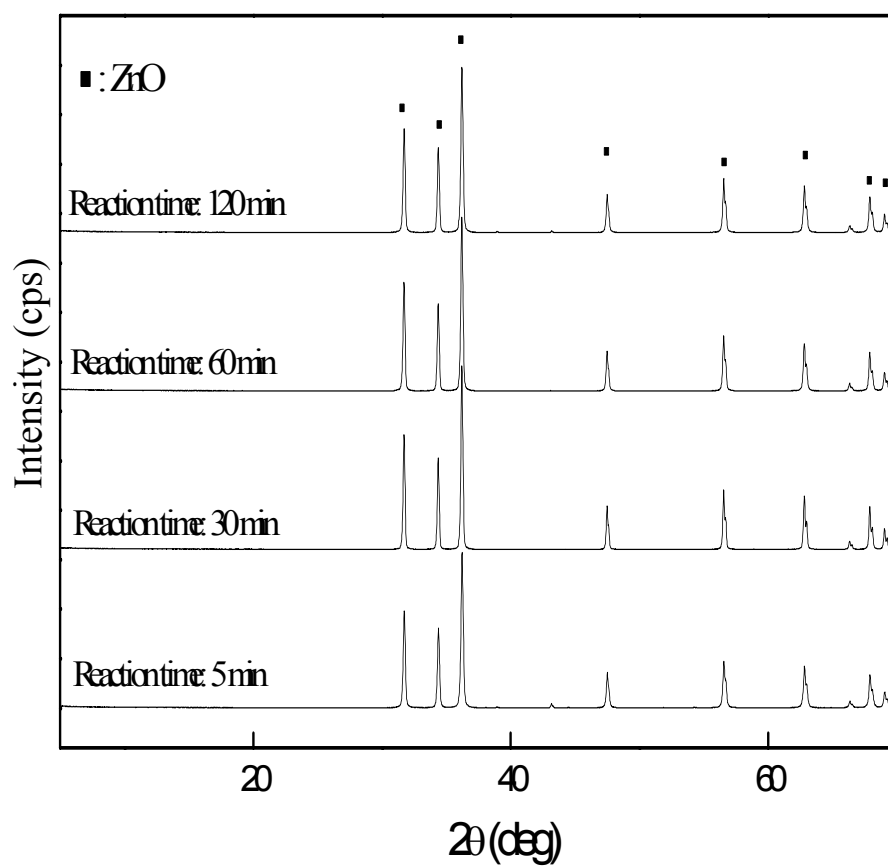
(A) For Fe



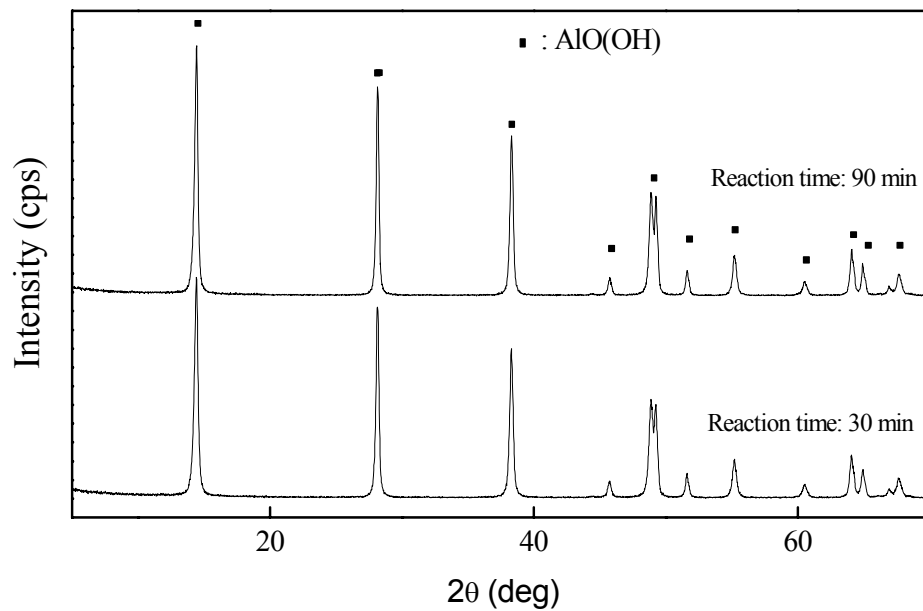
(B) For Mg



(C) For Mn

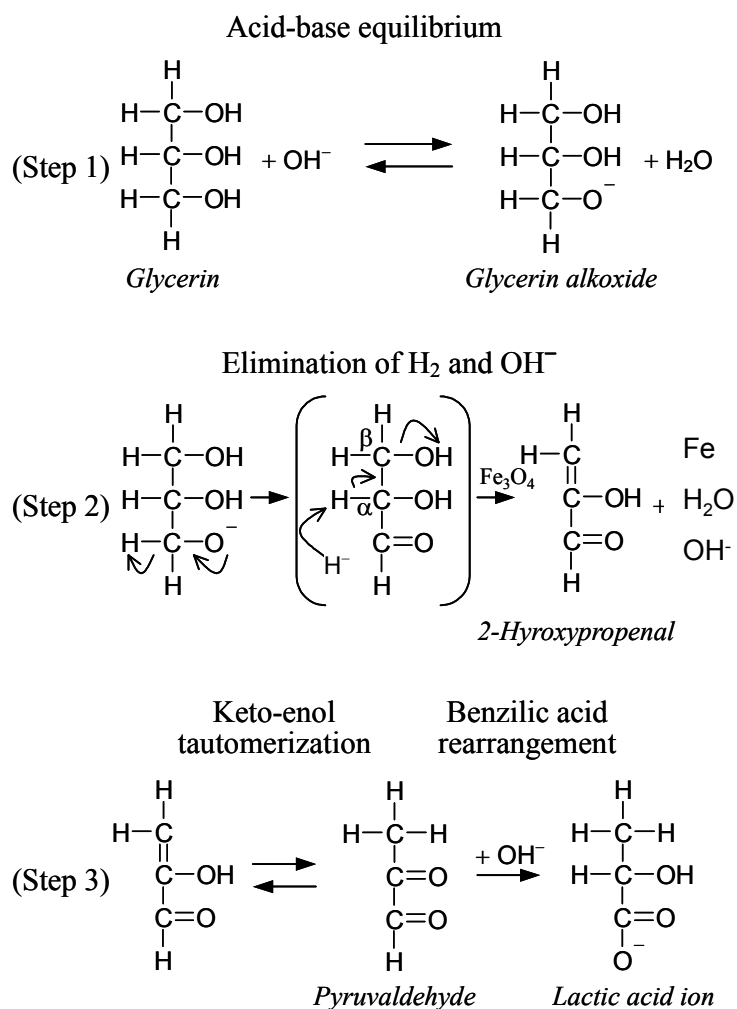


(D) For Zn

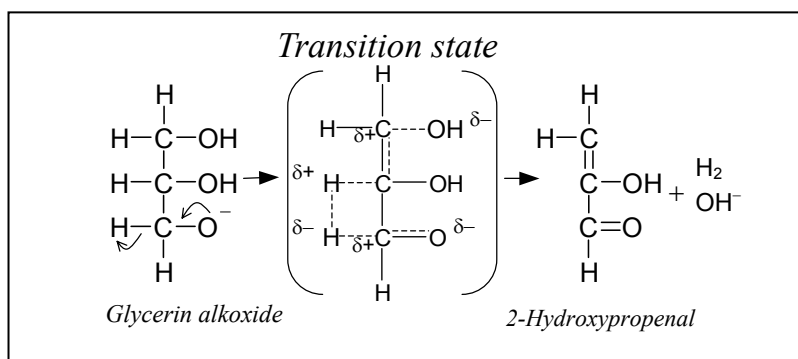


(E) For Al

Figure S1 X-Ray diffraction patterns of solid residues after hydrothermal reaction for metal reductants:



(A)



(B)

Figure S2 Possible mechanism for the conversion of glycerin into lactic acid.

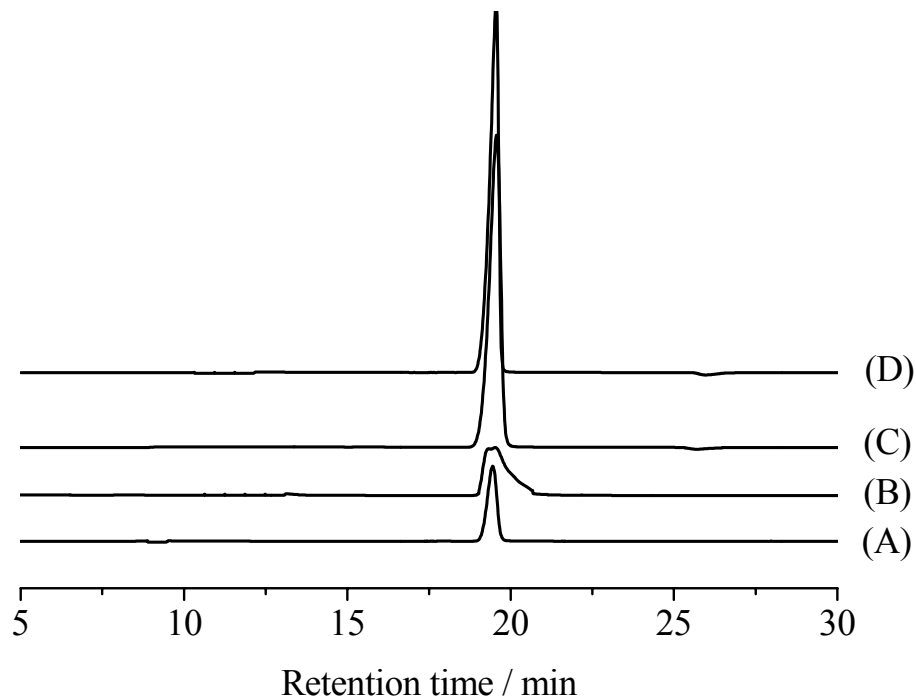


Figure S3 HPLC chromatograms of the liquid samples after the reaction. Conditions: 573 K, 120 min, $[\text{NaHCO}_3] = 1 \text{ mmol}$, (a) $[\text{Fe}] = 8 \text{ mmol}$, (b) $[\text{Mn}] = 8 \text{ mmol}$, (c) $[\text{Zn}] = 8 \text{ mmol}$, (d) $[\text{Al}] = 8 \text{ mmol}$.

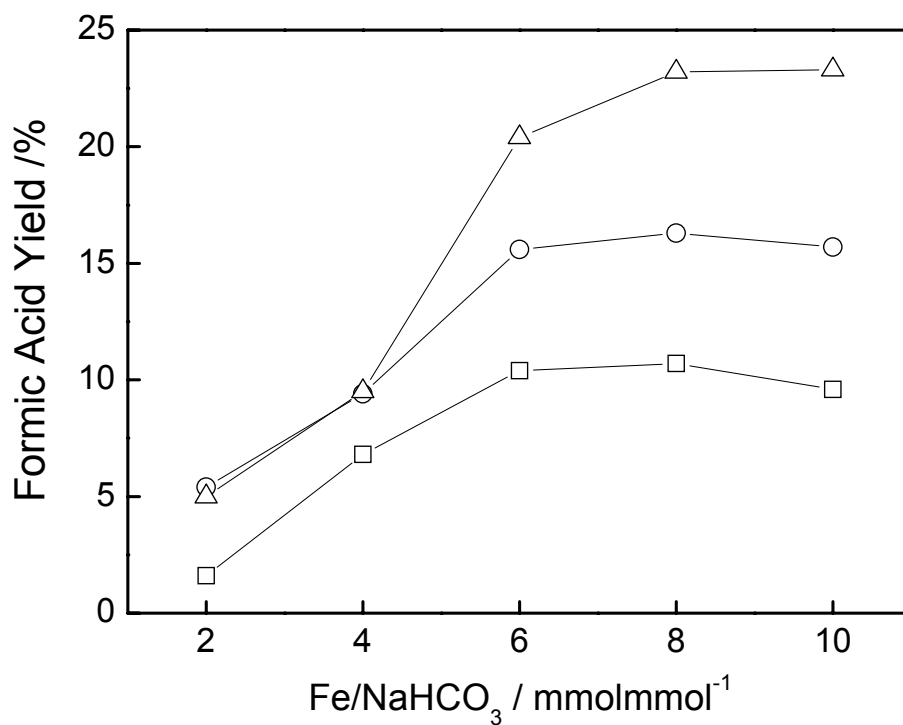
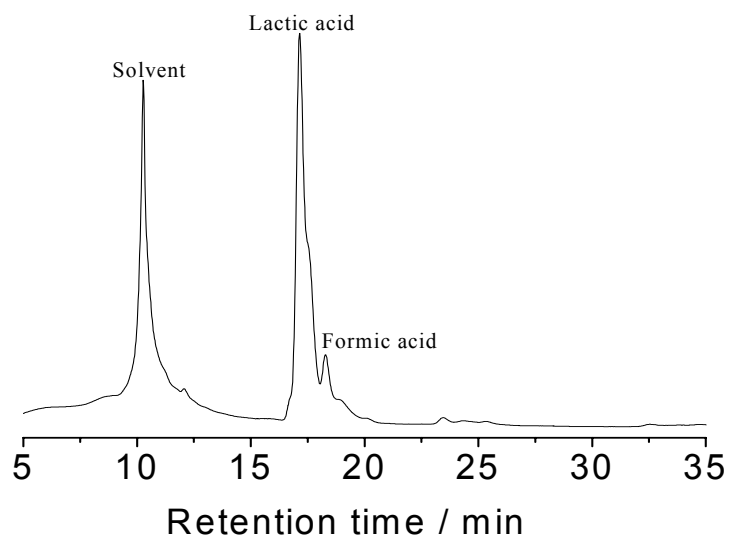
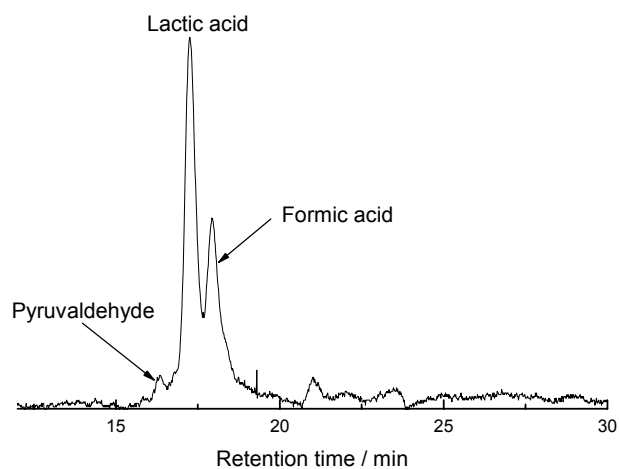


Figure S4 Effect of catalysts of Cu and Ni on the yields of formic acid with Fe reductant. Conditions: 623 K, 120 min, [NaHCO₃] = 1 mmol. Symbols: squares, only Fe, circles, Fe:Ni=1:1, triangle, Fe:Cu=1:1. Formic acid yield is defined as the percentage of formic acid of the initial NaHCO₃ converted on a carbon basis.



(A)



(B)

Figure S5 HPLC chromatograms of organic phase sample after the reaction of $\text{FeCl}_3 \cdot 4\text{H}_2\text{O}$ and glycerin at 523 K for 30 min according to (A) UV absorption at 210 nm (UV detector); (B) refractive index (RI detector).

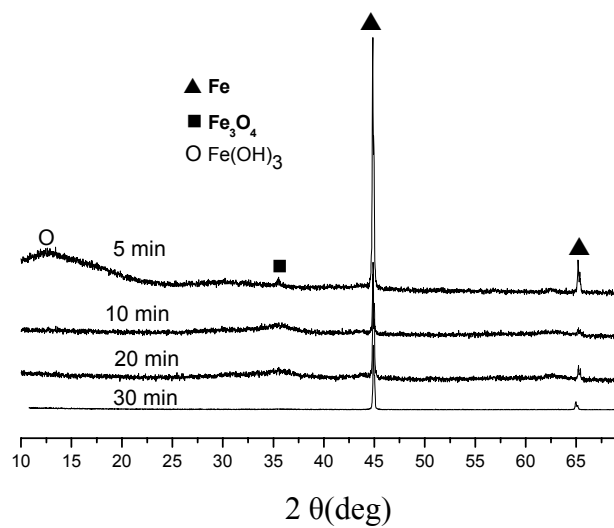


Figure S 6 X-Ray diffraction patterns of the reduced iron at different reaction times.

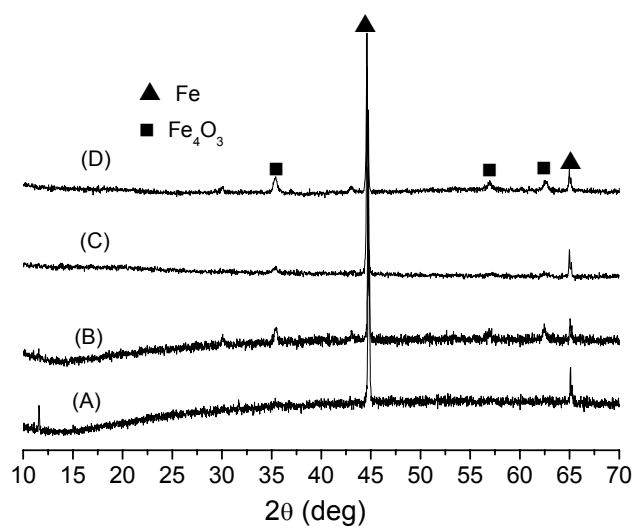
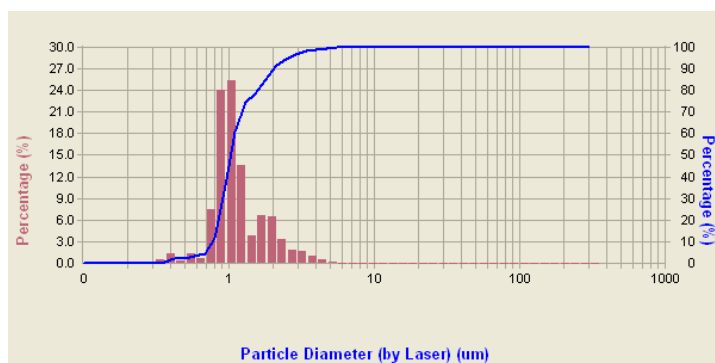
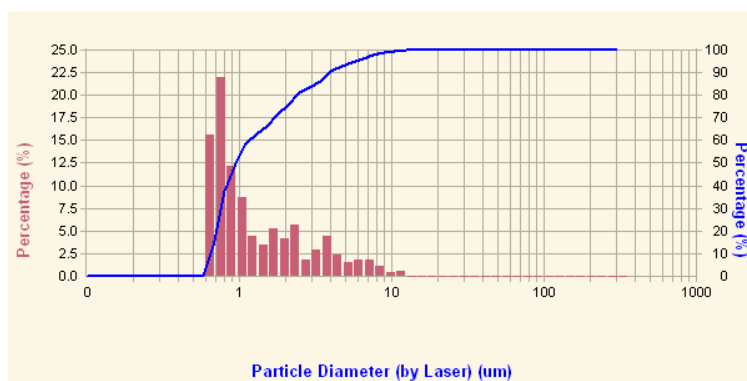


Figure S7 X-Ray diffraction patterns of the reduced iron after multiple reaction cycles: (A) first cycle, (B) second cycle, (C) third cycle, (D) fourth cycle.

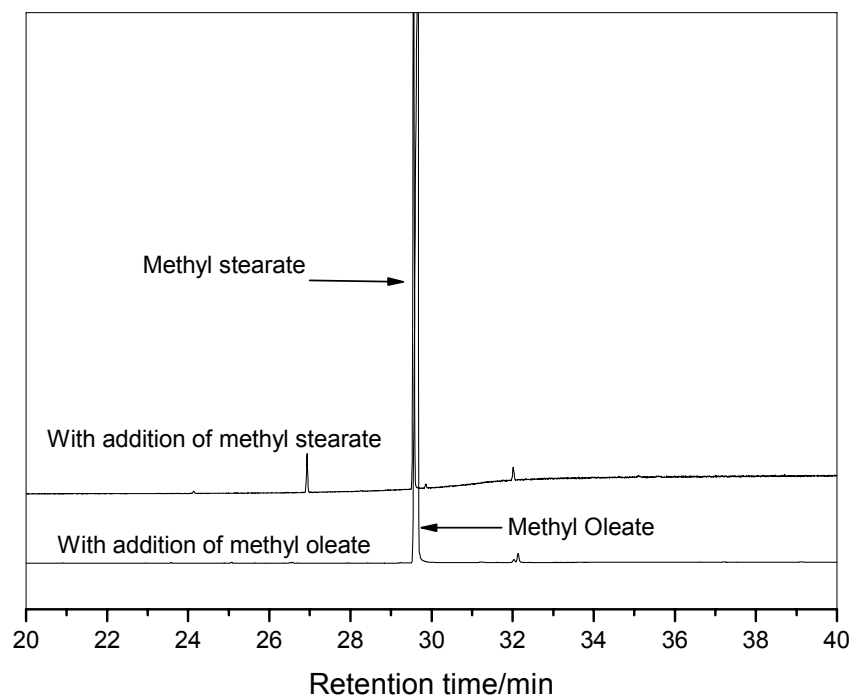


(A) Reduced Fe⁰

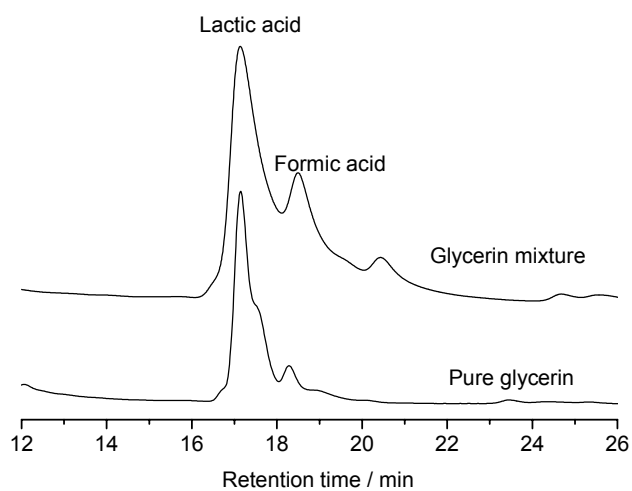


(B) Purchased Fe⁰ with 200-mesh.

Figure S8 Particle size distribution of (A) reduced Fe⁰ with glycerin and (B) commercial 200-mesh Fe⁰.



(A)



(B)

Figure S9 GC/MC (A) and HPLC (B) chromatograms of hexane (A) and water samples (B) after reaction of $\text{Fe}(\text{OH})_3$ and glycerin or glycerin mixture (250°C , 30 min).