

Enhanced hydrogen production performance through the controllable redox exsolution within CoFeAlO_x spinel oxygen carrier materials

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Experimental setup

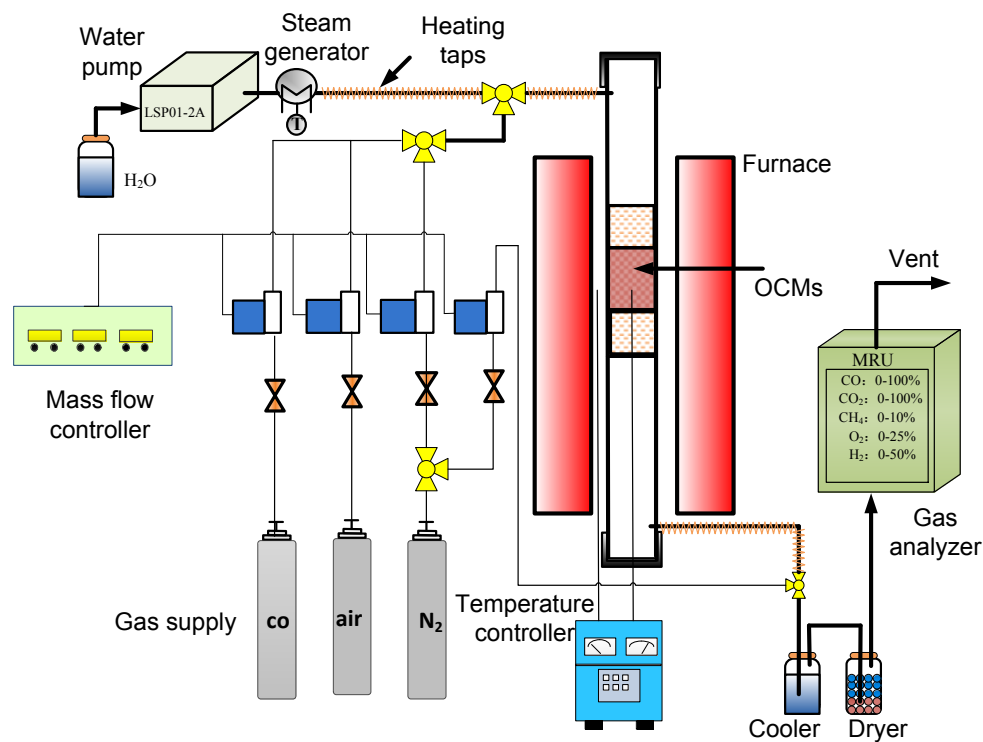


Fig. S1. Schematic diagram of the experimental apparatus.

The chemical looping redox experiments were performed in a stainless steel-made fixed-bed reactor with the inner diameter of 12 mm and the total length of 400 mm. The heat required for the redox reactions was provided by an electric furnace and the reaction temperature was controlled and monitored by two thermocouples, one (T_1) located between the tube and the furnace, and the other (T_2), inserted into the OCMs bed material. By adjusting T_1 , the desired T_2 could be reached, that is considered as the reaction temperature.

The gas flow rates were measured by the mass flow controllers (MFC, Beijing Sevenstar Co. Ltd). The distilled water was introduced by a liquid Longer Pump (LSP01-2A, $0.166\mu\text{l}\cdot\text{min}^{-1}$ - $10.831\text{ml}\cdot\text{min}^{-1}$) and evaporated by a steam generator operating at $250\text{ }^\circ\text{C}$. 500 mg of sample was packed between sand plugs. The samples were diluted by quartz with a ratio of 1: 5. The outlet gas was mixed with the diluting N_2 to accommodate the limited range of the MUR multi-component gas analyzer. The gas analyzer has a detection range of CO_2 (0-100%, 0.01% uncertain), CO (0-100%, 0.01% uncertain), O_2 (0-25%, 0.01% uncertain), and H_2 (0-50%, 0.1% uncertain). The concentration of N_2 was determined by extraction of CO , H_2 , CO_2 , O_2 from 100%.

Data evaluation

(1) Hydrogen yield

The volumetric flow rate of outlet hydrogen ($\text{l}\cdot\text{min}^{-1}$), V_{H_2} , was calculated based on a N_2 mass balance method:

$$V_{\text{H}_2} = \int_{t_1}^{t_2} V_{\text{out}} x_{\text{H}_2}(t) dt \quad (1)$$

With

$$V_{\text{out}} = V_{\text{N}_2,\text{in}} / x_{\text{N}_2,\text{out}}(t) = V_{\text{N}_2,\text{in}} / (1 - x_{\text{H}_2}(t)) \quad (2)$$

Where $x_{\text{N}_2}(t)$ and $x_{\text{H}_2}(t)$ are the detected concentration of N_2 and H_2 in the gas stream, t was the

reaction time, V_{in} and V_{out} are the total inlet and outlet volumetric gas flow rate, respectively.

The hydrogen yield, Y_{H_2} , was defined as the accumulated molar amount of hydrogen (mol.g^{-1}) produced in the water splitting period divided by the loaded oxygen carrier materials.

$$Y_{H_2} = V_{H_2} / 22.4m \quad (3)$$

Where m was the oxygen carrier bed materials, which was 0.5g in all the tests.

(2) Hydrogen production rate

Hydrogen production rate, $R_{H_2}(t)$, was a function of reaction time. It was calculated by:

$$R_{H_2}(t) = V_{out} x_{H_2}(t) / 22.4m \quad (4)$$

(3) Average hydrogen production rate

Average hydrogen production rate, \dot{R}_{H_2} , was used to evaluate the activity of the reduced materials in water splitting reaction. It was determined by:

$$\dot{R}_{H_2} = Y_{H_2} / t_{total} \quad (5)$$

Where t_{total} was the total reaction time required for water splitting reaction.

(4) Relative solid conversion

Relative solid conversion, $X(t)$, as a function of time was determined by:

$$X(t) = (m(t) - m_{red}) / (m_{ox} - m_{red}) \quad (6)$$

Where m_{red} , m_{ox} , and $m(t)$ are the weights of the oxygen carrier materials at the fully reduced state, the fully oxidized state, and the actual weight at the reaction time t , respectively.

Synthesis of the reference samples

Three reference materials (pure Fe_2O_3 , $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3/\text{ZrO}_2$) were prepared by sol-gel method as described in the main text. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ were used as the Fe, Al,

Zr sources. The mass loading of the active phase in CoFeAlO_x was 75.2 wt%. To ensure same active phase loadings in the two supported materials, the molar ratio of Fe:Al and Fe:Zr was controlled at 1.96 and 4.7 respectively. The resultant gel network was calcined at 900 °C to obtain the final OCMs.

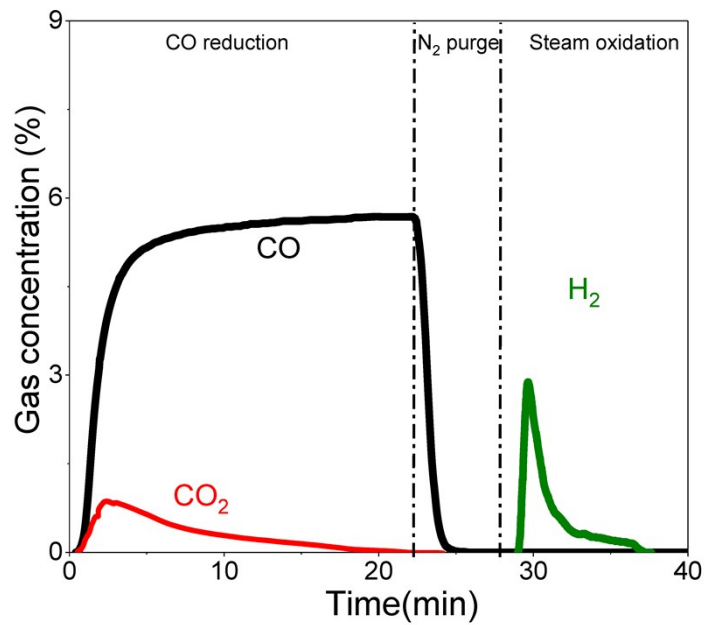


Fig. S2. Representative profiles of the CO reduction and steam oxidation redox cycle for CoFeAlO_x.

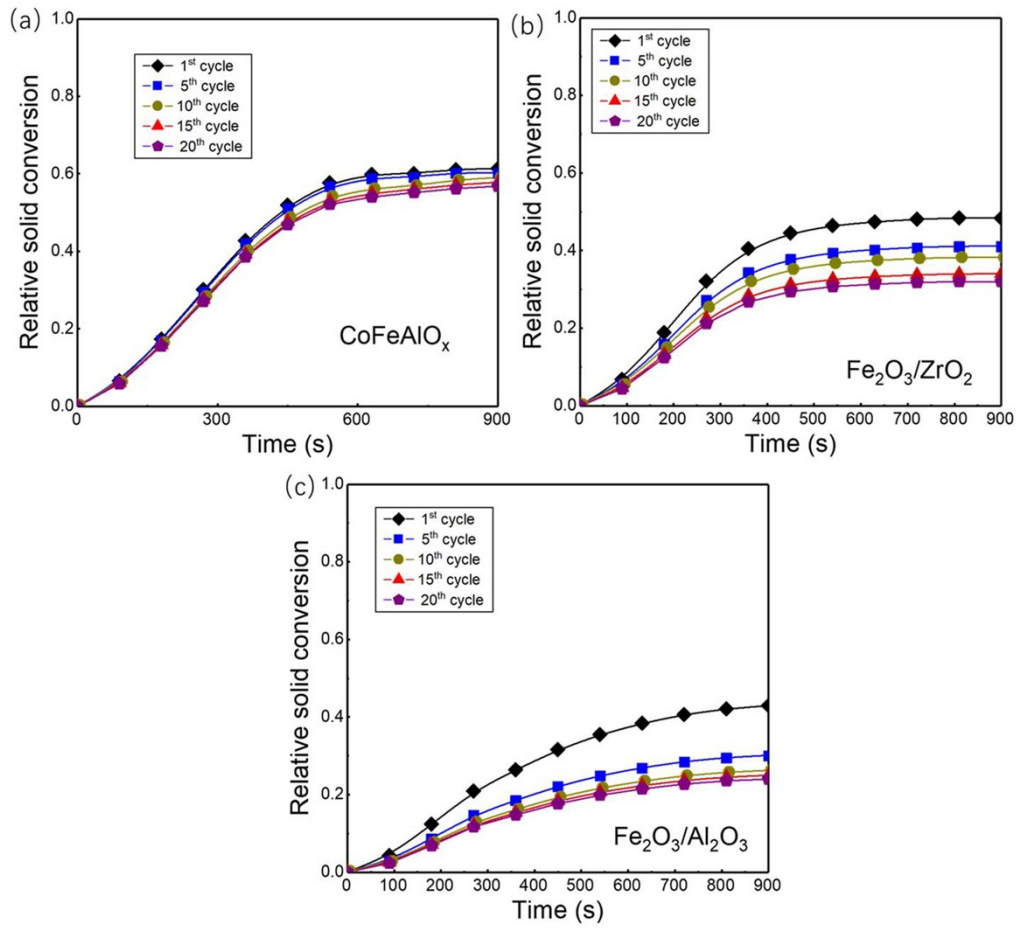


Fig. S3. The relative solid conversion in the reduction period versus reaction time of typical cycles under CO/CO₂ reduction.

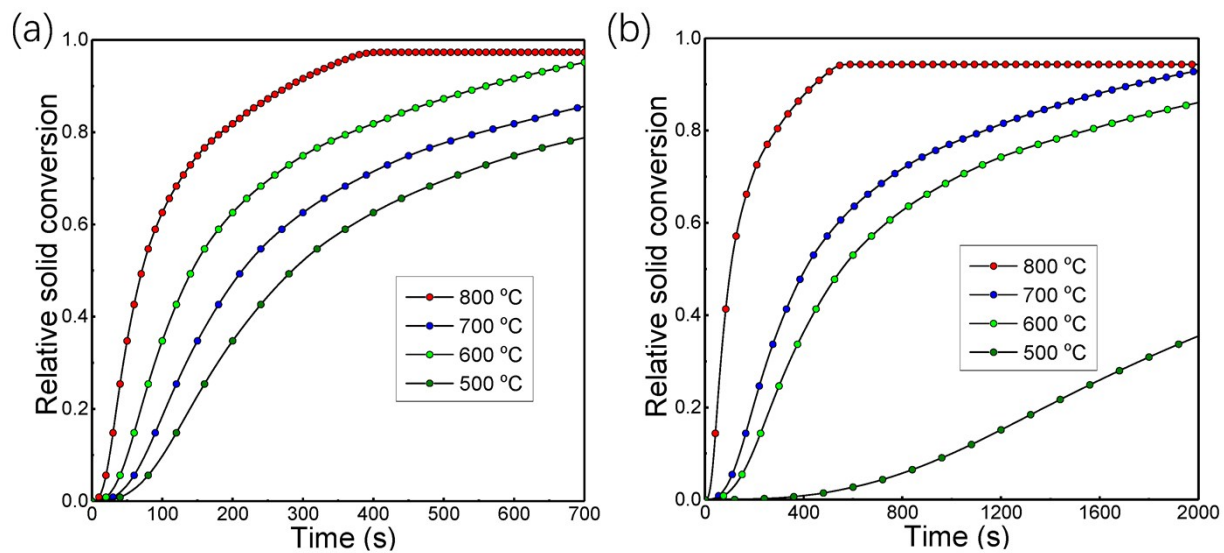


Fig. S4. The relative solid conversion versus reaction time in the oxidation period for (a) CoFeAlO_x, (b) Fe₂O₃ at different temperatures.

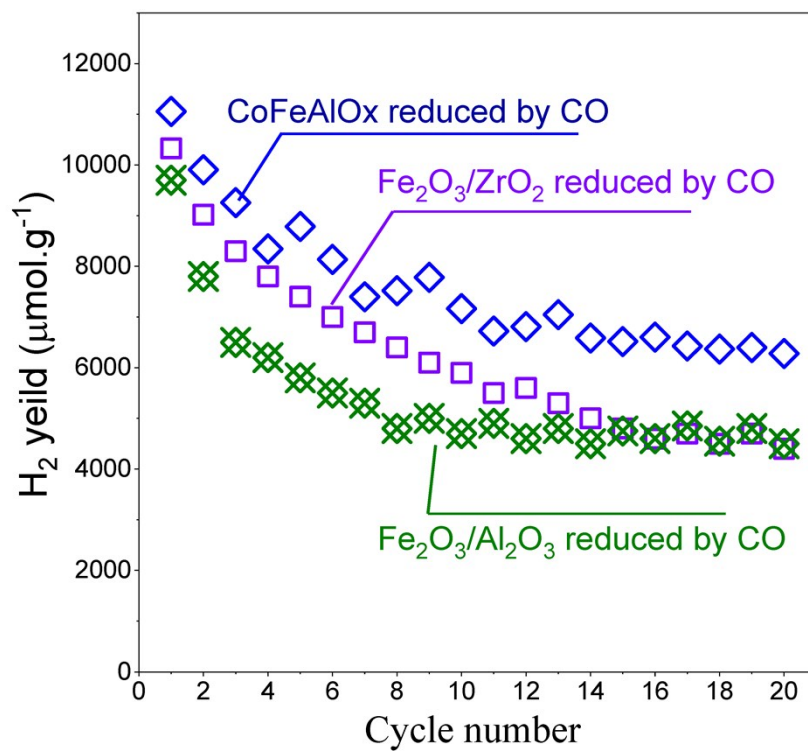


Fig. S5. Cyclic performance of the three supported materials.

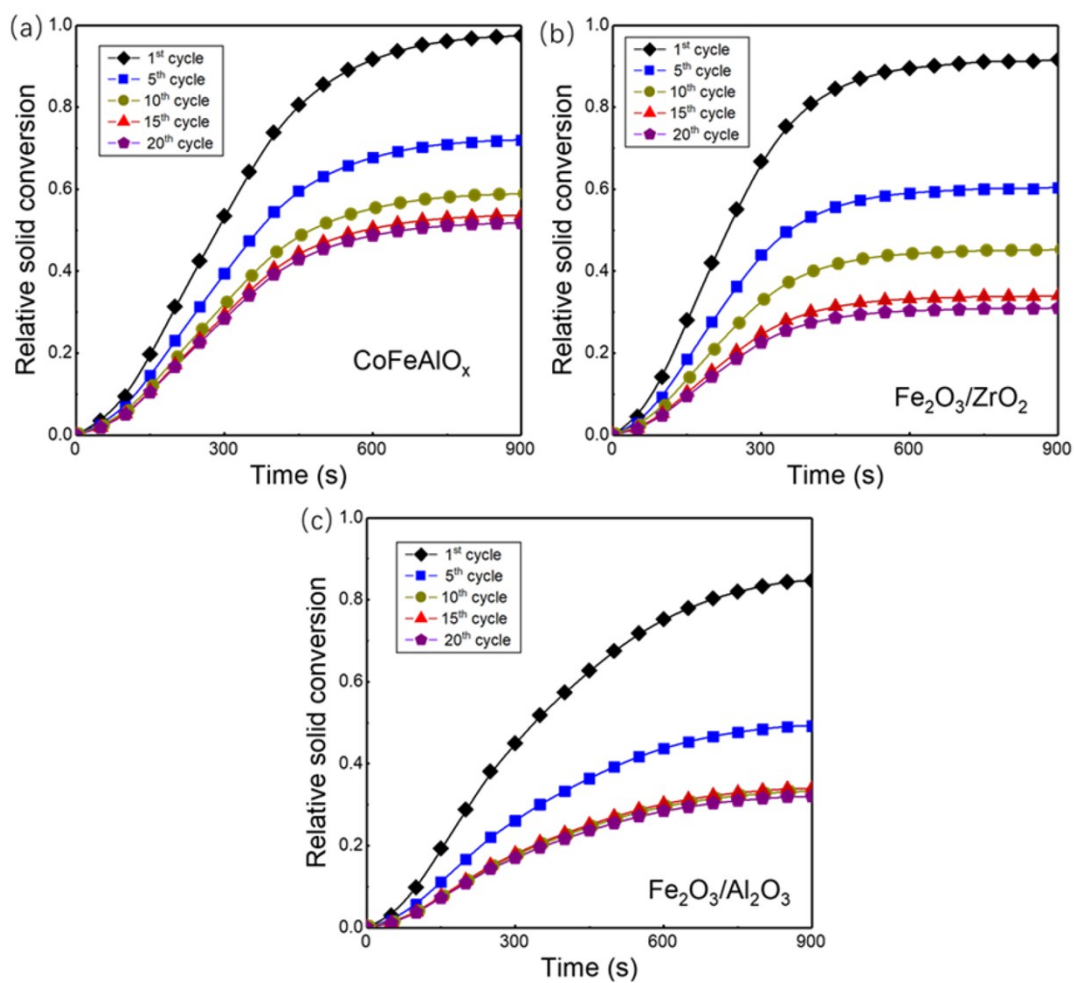


Fig. S6. The relative solid conversion in the reduction period versus reaction time under CO reduction.

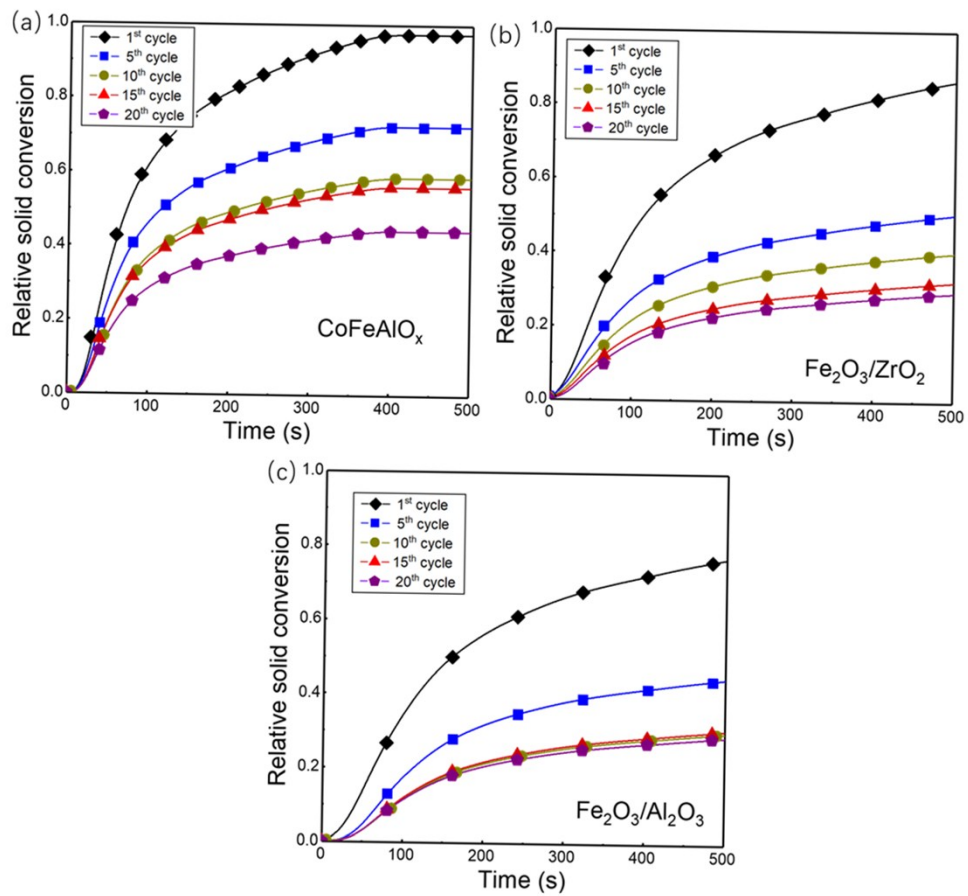


Fig. S7. The relative solid conversion in the oxidation period versus reaction time of typical cycles under CO reduction and steam oxidation.

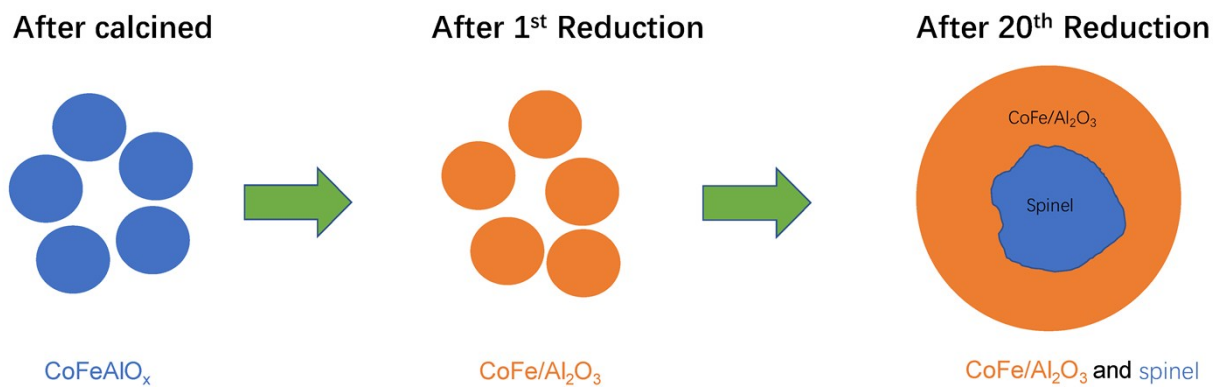


Fig. S8. The schematics of the particle growth along with the cycling.

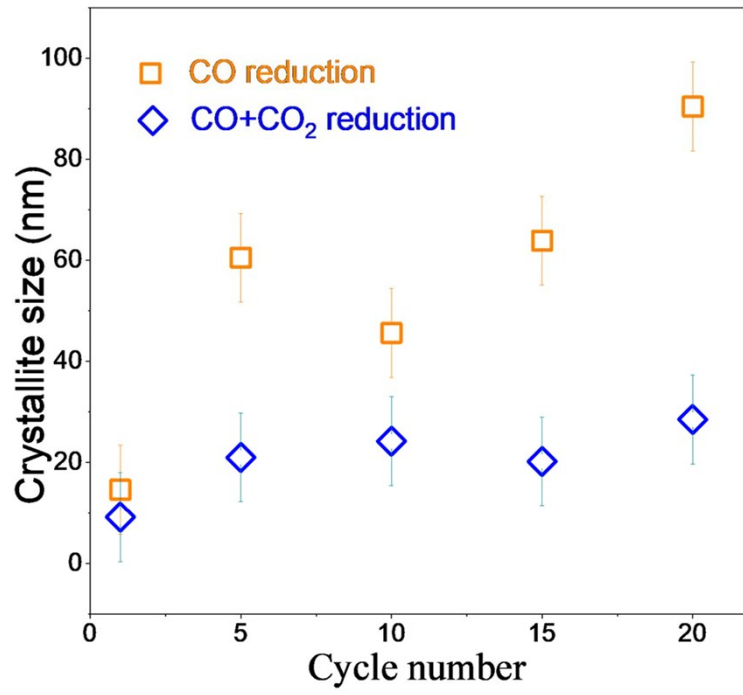


Fig. S9. Crystallite size of the exsolved CoFe alloy under the typical cycles.

Table. S1 Reaction equilibrium constant under different reaction temperature

Reaction	K ₇₈₀	K ₇₉₀	K ₈₀₀	K ₈₁₀	K ₈₂₀
$CoFe_2 + 4CO_2 \leftrightarrow CoFe_2O_4 + 4CO$	5.28	5.32	5.36	5.40	5.43
$CoFe_2 + 4H_2O \leftrightarrow CoFe_2O_4 + 4H_2$	8.91	7.75	6.75	5.90	5.17

CO₂ was used to substitute H₂O as the phase change experiments were carried out in a TGA instrument in which steam was not permitted. To demonstrate the feasibility of using CO₂ as a substitute in water-splitting reaction, the reaction equilibrium constant was calculated by HSC chemistry software. The results indicated CO₂ and H₂O have similar thermodynamic behavior at the operating chemical looping temperature (~800 °C).