

Supplementary Information(SI)

**Mg-Doped Porous Ca-Fe Microsphere as Bifunctional
Oxygen Carriers for Chemical-Looping Hydrogen
Production**

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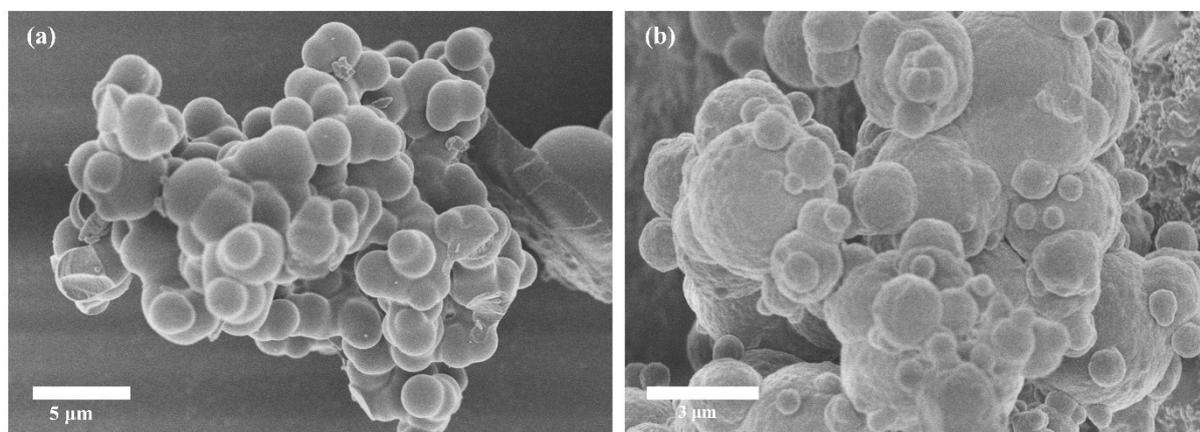


Fig. S1. SEM images of (a) the carbon template, and (b) the metal-containing precursor before calcination.

Table S1

Normalized hydrogen production performance of oxygen carriers.

Sample	Total H ₂ Yield (mmol·g ⁻¹)	OSC (mmol·g ⁻¹)	H ₂ Yield per unit OSC (mmol H ₂ ·mmol ⁻¹ OSC)
Mg0	10.23	9.550	1.07
Mg4	11.78	9.909	1.19
Mg5	12.27	10.181	1.21
Mg6	11.24	9.735	1.15
Mg10	9.53	9.142	1.04

1. Optimization of Operating Conditions

To maximize the hydrogen production efficiency of the Mg5 oxygen carrier, the key operating parameters—reaction temperature, steam-to-carbon ratio (modulated by water feed), and weight hourly space velocity (modulated by syngas flow)—were systematically optimized.

1.1 Effect of Reaction Temperature

Temperature is a decisive factor governing both reaction kinetics and thermodynamic equilibrium. As shown in Fig. S2a, when the temperature increases from 600 °C to 850 °C results in a substantial rise in hydrogen yield from 2.621 mmol·g⁻¹ to 12.820 mmol·g⁻¹. This indicates that temperature elevation significantly enhances the kinetics of both the reduction reactions of the oxygen carrier and the WGS reaction. This trend aligns well with the H₂-TPR results (Fig. 10), where the main reduction peak of Fe species (632–655 °C) falls within the region of rapid performance enhancement, confirming that higher temperatures promote the deep reduction of Fe species to generate more active sites.

Crucially, although the hydrogen yield at 850 °C is marginally higher than at 800 °C, the temperature of 800 °C is identified as the optimal operating condition. This

decision is justified by two critical factors beyond energy economy. According to the thermodynamic equilibrium of CaO carbonation, the capture efficiency diminishes drastically as the temperature approaches the decomposition point of CaCO₃. Consequently, at 850 °C, the equilibrium partial pressure of CO₂ rises significantly, which inevitably weakens the driving force for the sorption-enhanced WGS reaction.⁶⁵ This theoretical constraint is directly corroborated by the experimental gas composition (Fig. S2b), where the CO₂ concentration at 850 °C exhibits a notable rebound compared to that at 800°C, indicating compromised CO₂ removal efficiency. Furthermore, structural stability constitutes another critical concern. Excessive temperatures (>800 °C) are known to accelerate the sintering of both CaO and Fe species, posing a high risk of pore collapse and rapid deactivation during long-term operation.⁶⁶ Therefore, 800 °C represents the critical trade-off point that maximizes hydrogen yield while preserving efficient in-situ CO₂ capture and long-term structural integrity.

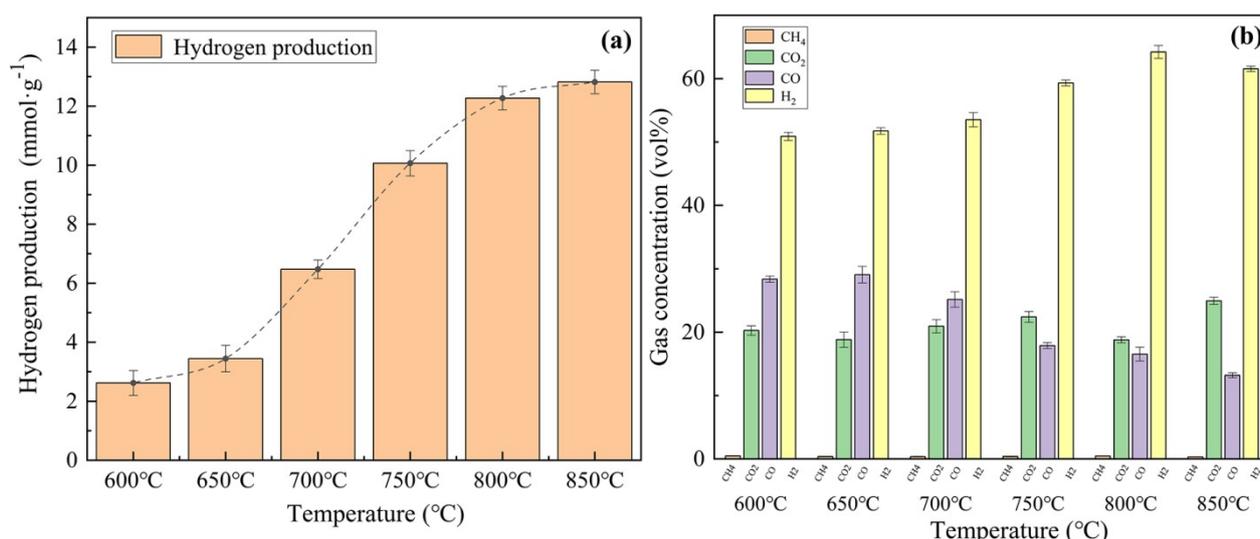


Fig. S2. Effect of reaction temperature on the performance of Mg5 (a) Net hydrogen yield; (b) Composition of outlet gases.

1.2 Effect of Steam-to-Carbon (S/C) Ratio

The balance between steam supply and reducing gas determines the reaction stoichiometry and the extent of the WGS reaction. Experiments were conducted by varying the steam feed rate ($0.2\text{--}1.4\text{ mL}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$) at a fixed syngas flow, which effectively modulates the S/C ratio.

As illustrated in Fig. S3a, the H_2 yield displays a distinct volcanic trend, reaching its maximum value of $13.403\text{ mmol}\cdot\text{g}^{-1}$ at a steam feed rate of $0.6\text{ mL}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$. At low steam feed rates ($<0.6\text{ mL}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$), the supply of oxidant (H_2O) is stoichiometrically insufficient to fully re-oxidize the reduced Fe species or to drive the WGS reaction to completion. This "oxygen starvation" limits the total hydrogen generation potential. Conversely, at excessive steam feed rates ($>0.6\text{ mL}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$), the hydrogen yield declines. This is likely due to the dilution of the syngas by excess steam, which decreases the reactant partial pressure and kinetically hinders the reduction step. Furthermore, high steam concentrations can induce sintering of the lime-based sorbent or shift the carbonation equilibrium.⁶⁷ Thus, $0.6\text{ mL}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$ is selected as the optimal condition.

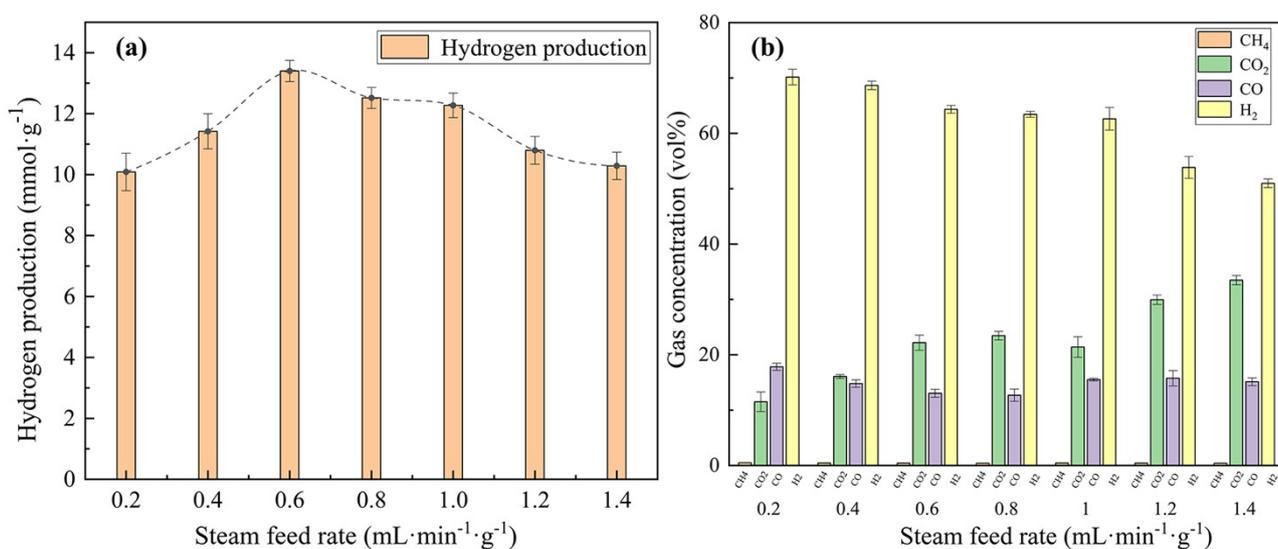


Fig. S3. Effect of steam feed rate (modulating the S/C ratio) on the performance of Mg5: (a) Net hydrogen yield; (b) Composition of outlet gases.

1.3 Effect of Weight Hourly Space Velocity (WHSV)

The influence of gas–solid contact time was investigated by varying the biomass–syngas flow rate (40–140 mL·min⁻¹·g⁻¹), which corresponds to changing the Weight Hourly Space Velocity (WHSV) of the reducing gas.

As shown in Fig. S4a, the hydrogen yield continuously increases with the gas-to-solid ratio rising from 40 to 140 mL·min⁻¹·g⁻¹ (from 10.343 mmol·g⁻¹ to 15.4659 mmol·g⁻¹), while the growth rate gradually slows down. At low flow rates, the supply of reducing gas is insufficient, resulting in a shortage of reactants for both Fe-based reduction and the WGS reaction and thus a low H₂ yield. With the increase of flow rate, sufficient reducing gas promotes the deep reduction of Fe species to generate abundant active sites and provides adequate reactants for the WGS reaction, which significantly enhances H₂ production. In this range, the CO concentration decreases owing to consumption in the WGS reaction, and the H₂ concentration exhibits a slight decline as a result of the dilution effect derived from the increased gas flow.

When the flow rate is excessively high, the H₂ yield still maintains an upward trend but with an obviously weakened increasing rate. The rapid gas flow shortens the residence time and contact time between the gas and solid phases, which reduces the conversion efficiency per unit of reactant gas. Additionally, the large amount of CO₂ generated during the reaction exceeds the instantaneous adsorption capacity of CaO, leading to a rise in the CO₂ concentration in the effluent gas. Considering the trade-off between maximizing H₂ yield and maintaining high feedstock utilization efficiency, a

flow rate of $100 \text{ mL} \cdot \text{min}^{-1} \cdot \text{g}^{-1}$ is determined as the optimal condition, with a hydrogen production of $15.09 \text{ mmol} \cdot \text{g}^{-1}$.

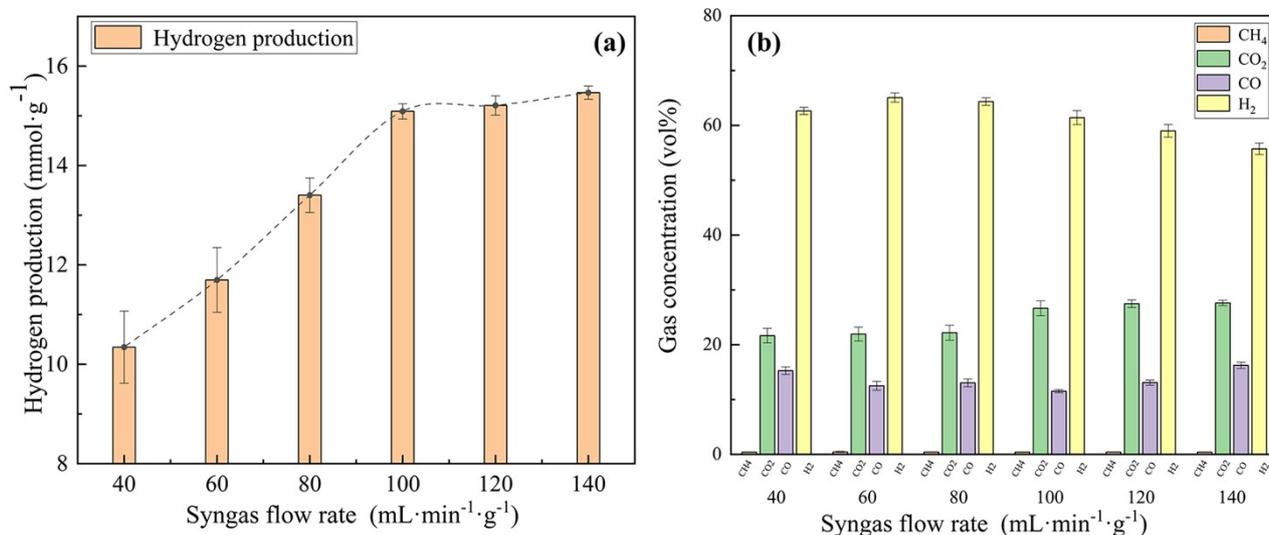


Fig. S4. Effect of syngas flow rate (modulating the WHSV) on the performance of Mg5: (a) Net hydrogen yield; (b) Composition of outlet gases.

Table S2

Comparison of representative oxygen carriers and their hydrogen production performance and cycling stability in CLH reported in the literature.

Oxygen carrier	Feedstock	Conditions	H ₂ yield (mmol/g)	Stability (Cycles)	Ref.
Mg5(CaO/Fe ₂ O ₃ -Ca:Fe=1:1, 1.66 wt% Mg incorporation, a one-pot hydrothermal-templating method)	Biomass syngas (CO 25 vol%, H ₂ 35 vol%, CO ₂ 30 vol%, balanced with N ₂)	800°C; water feed=0.3 mL/min (15 min); biomass-syngas flow rate=50 mL/min (20 min)	15.09	23	This work
Ca ₂ Co _{0.5} Fe _{1.5} O ₅ (Ca:Fe:Co=2:1.5:0.5, sol-gel method)	Pine sawdust (dried at 105°C for 24h, <300μm)	900°C; biomass/OC mass ratio=3g:6.5g; N ₂ flow rate=500 mL/min; steam injection rate=0.02 mL/min	10.92	5	58
FeAlNa ₅ (Na:Fe:Al=0.11:0.64:0.25, sol-gel method)	10 vol% CO in N ₂	800°C; reduction: 10 vol% CO/N ₂ (1.5 L/min, 15 min); steam oxidation: 23 vol% H ₂ O/N ₂ (1.94 L/min, 7 min); air oxidation: 5 vol% O ₂ /N ₂ (2 L/min, 5 min); N ₂ purge (1.5 L/min, 1 min) between steps	13.30	15	59
Ca ₂ Ni _{0.1} Al _{0.2} Fe _{1.7} O ₅ (Ca:Ni:Al:Fe=2:0.1:0.2:1)	5 vol% CH ₄ /95 vol% Ar	850°C; reduction stage: 5% CH ₄ /95% Ar (100 mL/min, 20 min)	4.40	15	60

7, sol-gel method)			min); N ₂ purge (100 mL/min, 20 min); steam oxidation stage: steam (0.1 g/min) + Ar (100 mL/min, 20 min)			
NF-Al _{0.3} (Ni:Fe:Al=1:2:0.3, 3.3 wt% Al incorporation, citrate sol-gel method)	CO		800°C; CO reduction: 5 sccm (20min); steam oxidation: 0.01mL/min liquid water vaporized + N ₂ carrier gas (20min); air oxidation: 5 sccm O ₂ (10min); N ₂ purge (10min) between steps; N ₂ carrier gas flow rate=40 sccm	8.20 mmol/g	25	61
CoFeO ₇ (Co-Fe binary spinel, citrate sol-gel method, calcined)	5 vol% CO + 95 vol% N ₂		650°C; reduction gas flow rate=1200 mL/min; steam flow rate=0.24 mL/min + N ₂ flow rate=1200 mL/min	11.17 mmol/g	10	62