

Conclusions/Summary

An advanced hydrogen production system integrated with CO₂ separation is introduced in this research, which is based on HyPr-RING and enhanced by dual chemical looping. The first chemical looping is for CO₂ separation using lithium ortho-silicate (Li₄SiO₄) as a solid CO₂ sorbent which can absorb CO₂ around 650°C with an exothermic reaction and regenerate around 850°C. This sorbent has high capacity of 30wt% and reduce the energy penalty due to temperature swing for CO₂ separation. Another chemical looping by red-ox reaction of a metal oxide is applied to oxygen carrier in the gasification reactor to cut off the electric power due to the air separation plant and the exothermic heat of oxidation is used for regeneration of the sorbent.

Copper oxide (CuO) is one of the suitable materials for oxygen carrier because reduction of CuO by carbon is exothermic reaction which benefits energy balance.

Hydrogen production from dry mixtures of CuO and graphite was confirmed even at around temperature of CO₂ absorption, but in any test conditions, a simple mixture of them mainly produced CO₂ by complete oxidation.

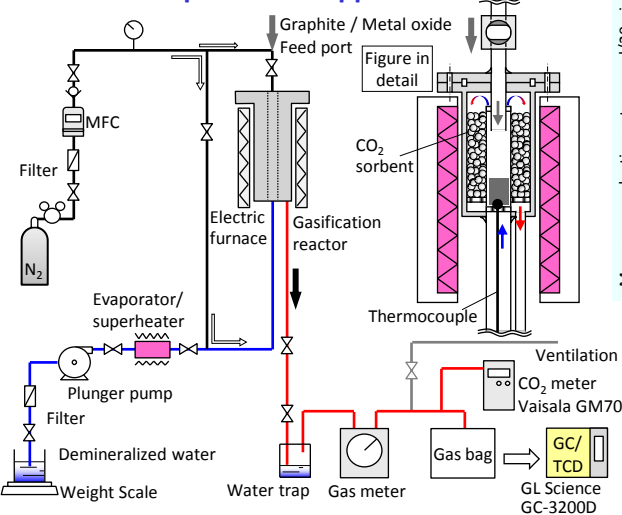
In the case of hematite (Fe₂O₃), hydrogen yield remarkably increased, but gas production rate decreased even at 700°C.

Thermodynamic data of reactions

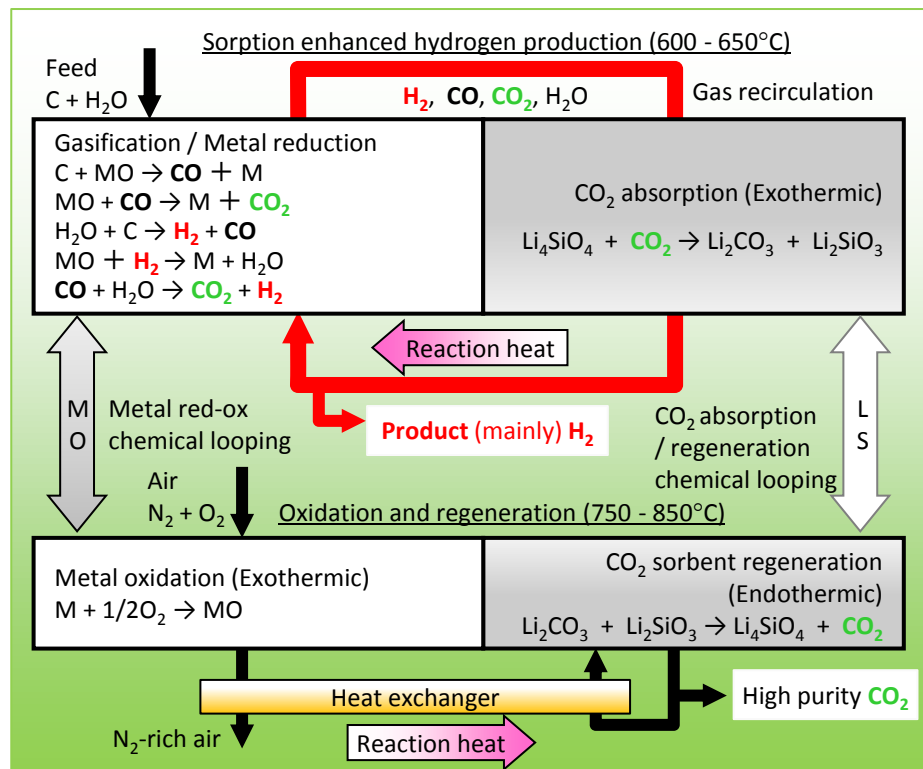
Eq.	Reactions	ΔH°_{923} kJ/mol	ΔG°_{923} kJ/mol
(1)	$\text{Li}_4\text{SiO}_4 + \text{CO}_2 \rightarrow \text{Li}_2\text{SiO}_3 + \text{Li}_2\text{CO}_3$	-63.8	-5.8
(2)	$\text{C} + \text{CuO} \rightarrow \text{Cu} + \text{CO}$	40.9	-119.3
(3)	$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$	-34.6	-5.9
(4)	$\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$	135.7	3.4
(5)	$\text{C} + 2\text{CuO} \rightarrow 2\text{Cu} + \text{CO}_2$	-88.6	-338.7
(6)	$\text{CO} + \text{CuO} \rightarrow \text{Cu} + \text{CO}_2$	-129.5	-128.6
(2)'	$\text{C} + \text{NiO} \rightarrow \text{Ni} + \text{CO}$	126.1	-40.4
(5)'	$\text{C} + 2\text{NiO} \rightarrow 2\text{Ni} + \text{CO}_2$	81.9	-90.1
(6)'	$\text{CO} + \text{NiO} \rightarrow \text{Ni} + \text{CO}_2$	-44.2	-49.7
(2)''	$\text{C} + 3\text{Fe}_2\text{O}_3 \rightarrow 2\text{Fe}_3\text{O}_4 + \text{CO}$	227.3	-214.2
(5)''	$\text{C} + 6\text{Fe}_2\text{O}_3 \rightarrow 4\text{Fe}_3\text{O}_4 + \text{CO}_2$	284.3	-437.8
(6)''	$\text{CO} + 3\text{Fe}_2\text{O}_3 \rightarrow 2\text{Fe}_3\text{O}_4 + \text{CO}_2$	57.0	-223.5

Reaction path	ΔH°_{923} kJ/mol			H ₂ production yield mol / C mol
	CuO	NiO	Fe ₂ O ₃	
Eqs. (2) → (3) → (1)	-57.5	27.8	129.0	1
Eqs. (4) → (6) → (1)				
Eqs. (4) → (3) → (1)		37.4		2

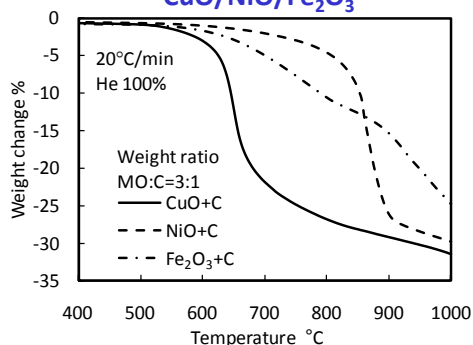
Experimental apparatus



Hydrogen production / CO₂ separation system



Graphite oxidation with CuO/NiO/Fe₂O₃



CO₂ absorption performance of lithium silicate

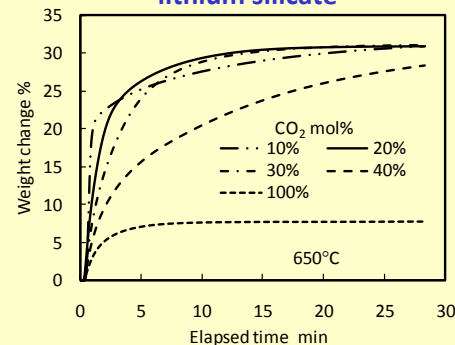
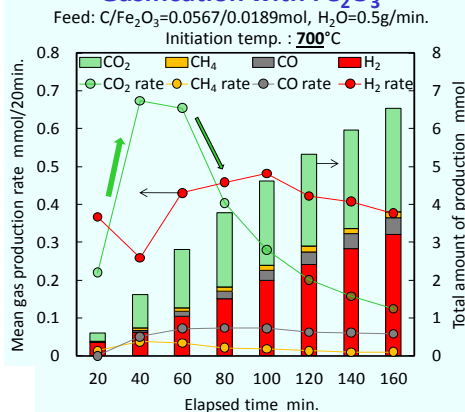
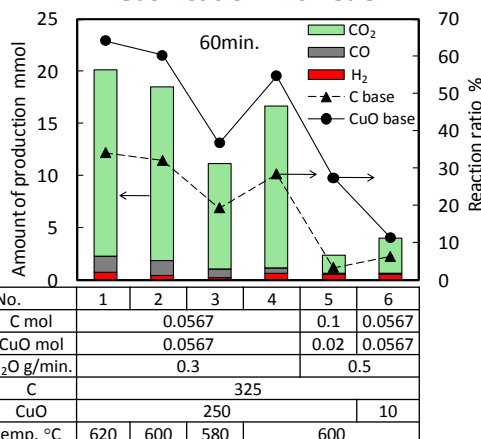


Photo: Li₄SiO₄ sorbent promoted by potassium carbonate additive (Prepared in our laboratory) *Patented by Toshiba

Gasification with Fe₂O₃



Gasification with CuO



*This work was supported by JSPS KAKENHI 20560785 of Grant-in-Aid for Scientific Research (C).