Supplementary Information

Sequential hydrogen production system from formic acid and H_2/CO_2 separation under high-pressure conditions

Masayuki Iguchi,[1] Maya Chatterjee,[1] Naoya Onishi,[2] Yuichiro Himeda[2] and Hajime Kawanami*[1]

[1] Research Institute for Chemical Process Technology, Department of Material and Chemistry, National Institute of Advanced Industrial Science and Technology, Nigatake 4-2-1, Miyagino-ku, Sendai, Miyagi 983-8551, Japan

[2] Research Institute of Energy Frontier, Department of Energy and Environment, National Institute of Advanced Industrial Science and Technology, Higashi 1-1-1, Tsukuba, Ibaraki 305-8565, Japan

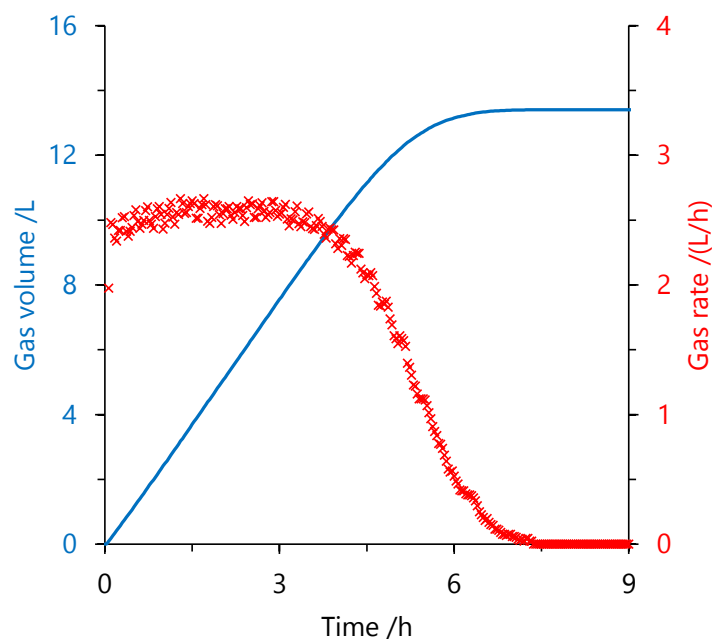* Corresponding author E-mail address: h-kawanami@aist.go.jp

Figure S1. Time course of FA decomposition in terms of volume and rate of gas release in the presence of catalyst **3**: gas volume (line), gas rate (cross). Reaction condition: 60 $^\circ$C, generated gas pressure: 40 MPa ($H_2:CO_2$ = 1:1), aqueous solution of FA (16 mol/L, 40 mL), catalyst (0.4 mmol/L). Time is defined as the time after reaching the pressure. The gas rate is averaged over 8 min.
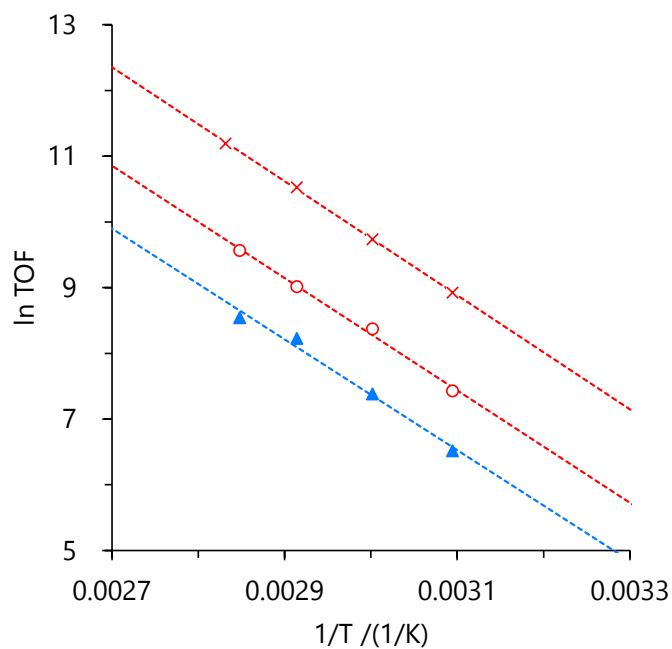
Figure S2. Arrhenius plot for FA dehydrogenation in the presence of catalyst **3**: (0.1 MPa, cross), (40 MPa, circle) and the catalyst **1** (10 MPa, triangle). Reaction conditions: 50-80 °C, FA aqueous solution (8-16 mol/L, 40 mL), catalyst (0.4 mmol/L). The TOF value of high pressures is averaged over several hours, and that of atmospheric pressure was taken from our previous work.[1]
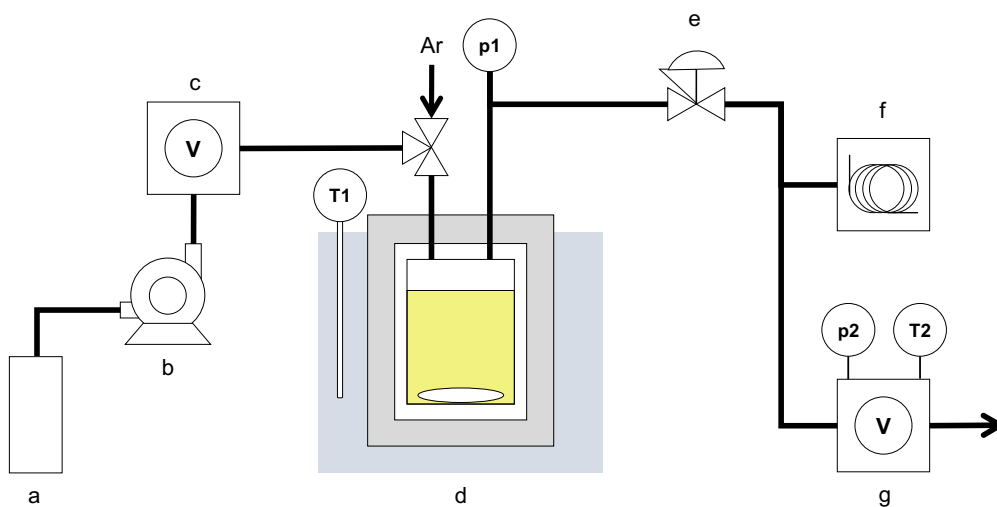
Figure S3. Schematic diagram of the system for high-pressure H_2 production from FA: liquid tank of neat FA (a), liquid pump (b), liquid flow meter (c), reactor (d), backpressure regulator (e), gas chromatography (f), gas flow meter (g). Pressure and temperature were recorded at T1–T2 and p1–p2, respectively.
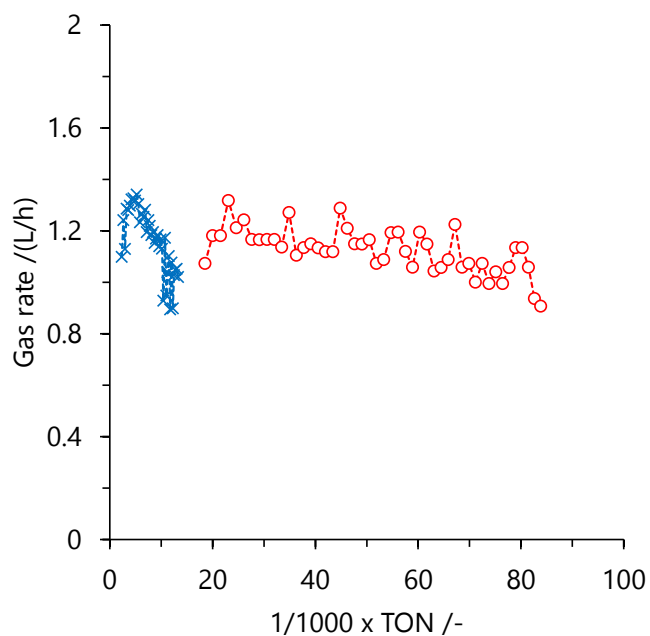
Figure S4. Stability test for generating high-pressure H_2 by the catalytic decomposition of FA under continuous addition of FA at high pressures: **3** (circle), **1** (cross). Reaction conditions: 60 $^{\circ}C$, generated gas pressure: 40 MPa (H_2:CO_2 = 1:1), initial FA aqueous solution (8 mol/L, 40 mL), FA addition (1.2mL/h, 50 h for **3** and 40 h for **1**), catalyst (16 μmol for **3** and 79 μmol for **1**). The gas rate is averaged over 8 min. The value of TON was calculated from the total volume of generated gas.
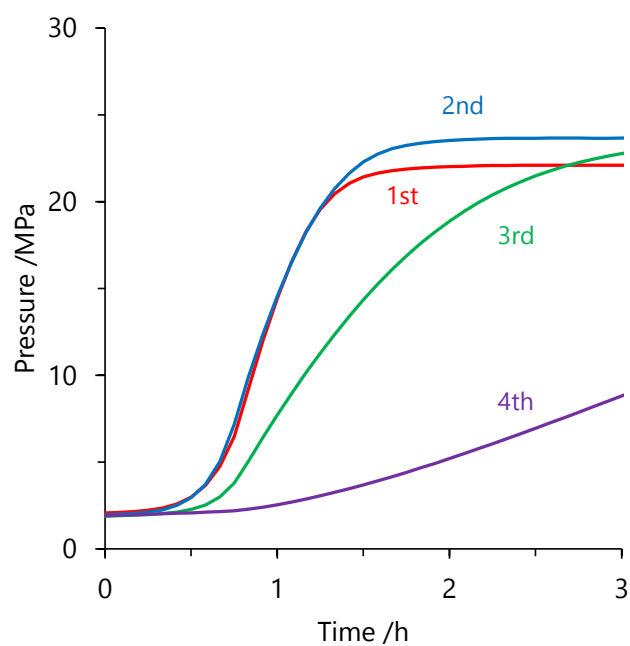
Figure S5. Reuse of the catalyst **3** for high-pressure gas generation by FA decomposition: 1st (red), 2nd (blue), 3rd (green), 4th (purple). Reaction conditions: 50 ºC, 2 MPa He, FA (1 mL), complex (8 µmol, 3 mL). FA (1 mL) was added to the solution after depressurization.
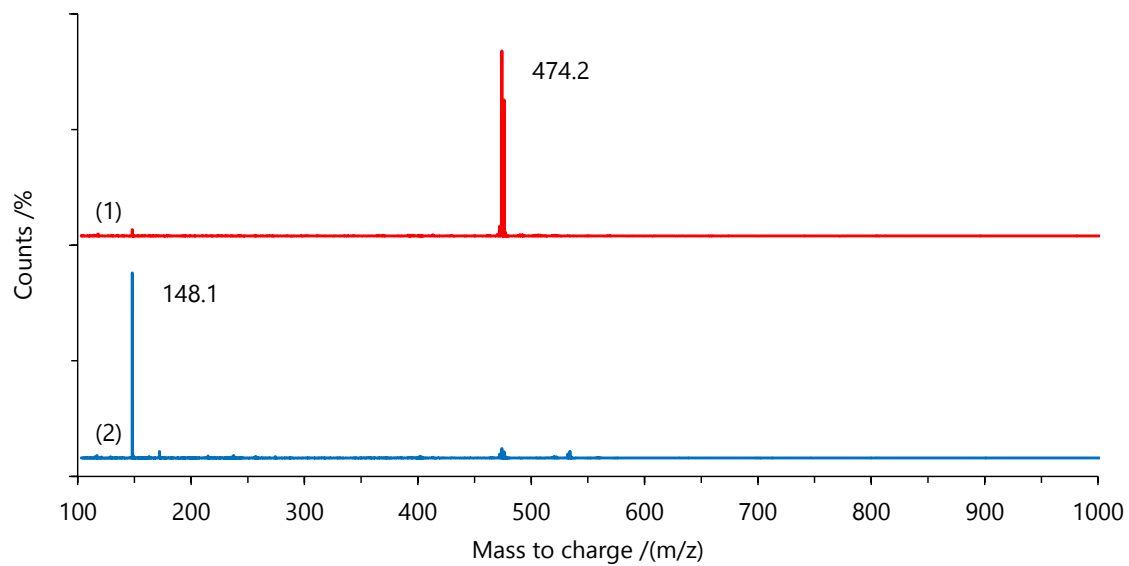
Figure S6. ESI-MS spectra of (1) the complex 3 and (2) the reaction solution after the continuous decomposition of FA using 3 at 40 MPa and 50 ºC. The peak at 148.1 m/z corresponds to 2-(2'-pyridyl)imidazoline).
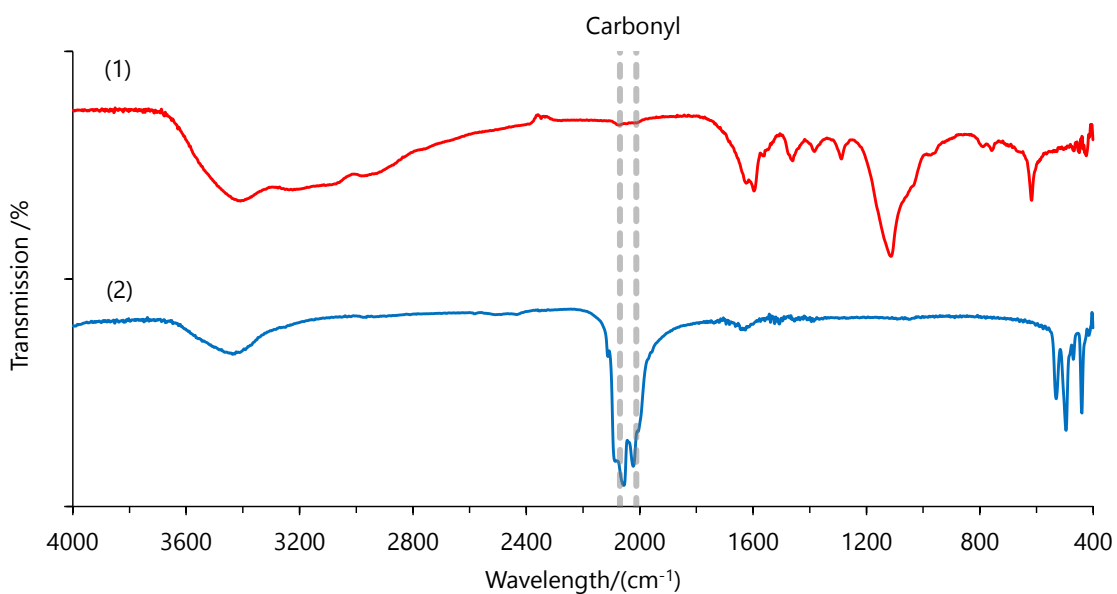
Figure S7. IR spectra of (a) the reaction residue after the continuous decomposition of FA using catalyst **3** at the high pressure and then evaporation in vacuum, and (b) authentic sample of tetrairidium dodecacarbonyl ($Ir_4(CO)_{12}$). The peaks between 2100 and 2000 cm^{-1} are assigned to the stretching vibrations of carbonyl groups.

a)

b)
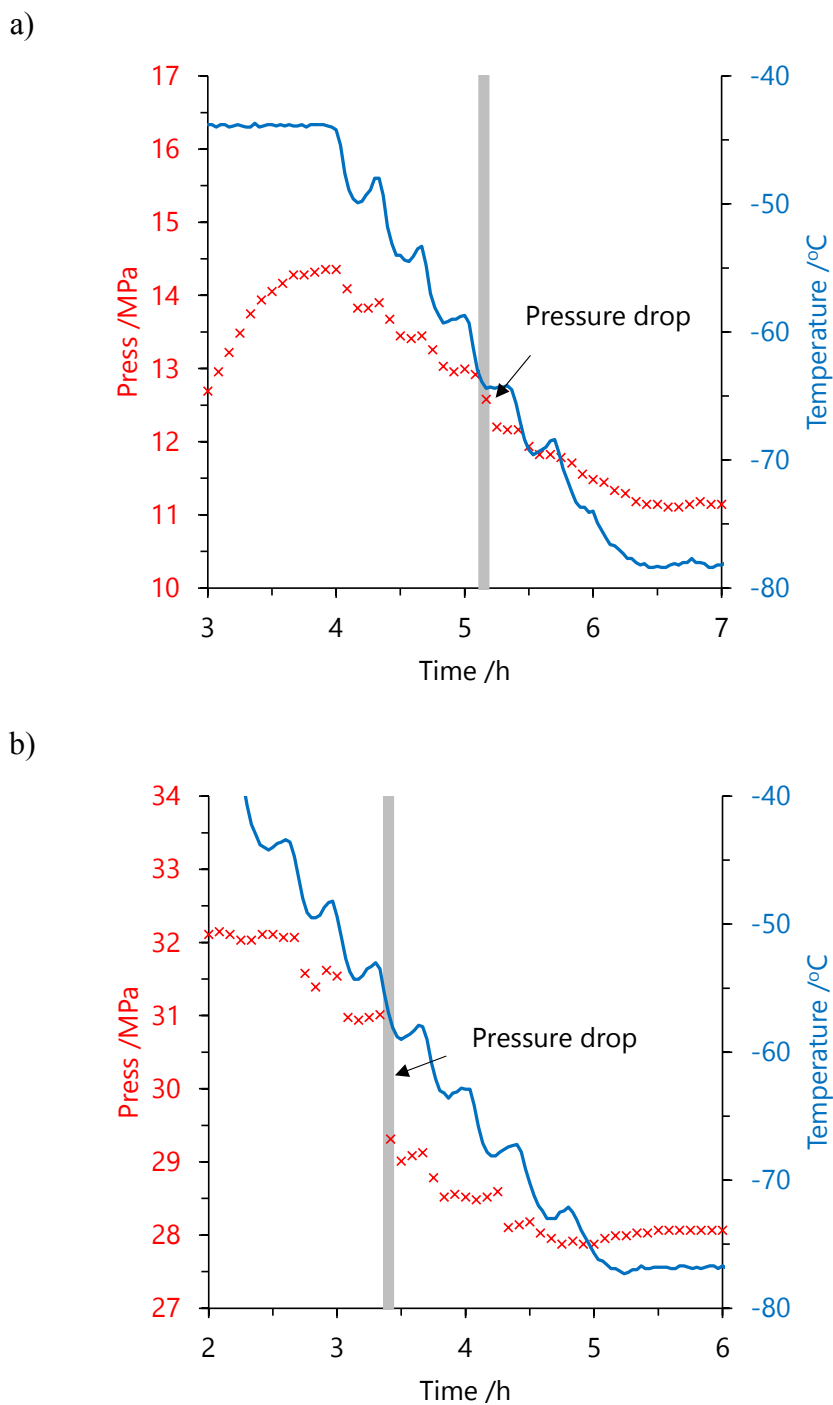
Figure S8. Time course of the separator pressure and temperature of gas release from FA decomposition: pressure (cross), temperature (line). Reaction condition: 60 ºC, FA aqueous solution (8 mol/L, 40 mL), catalyst **3** (0.2 mmol/L). Bars show the pressure drop during the separator was cooled.

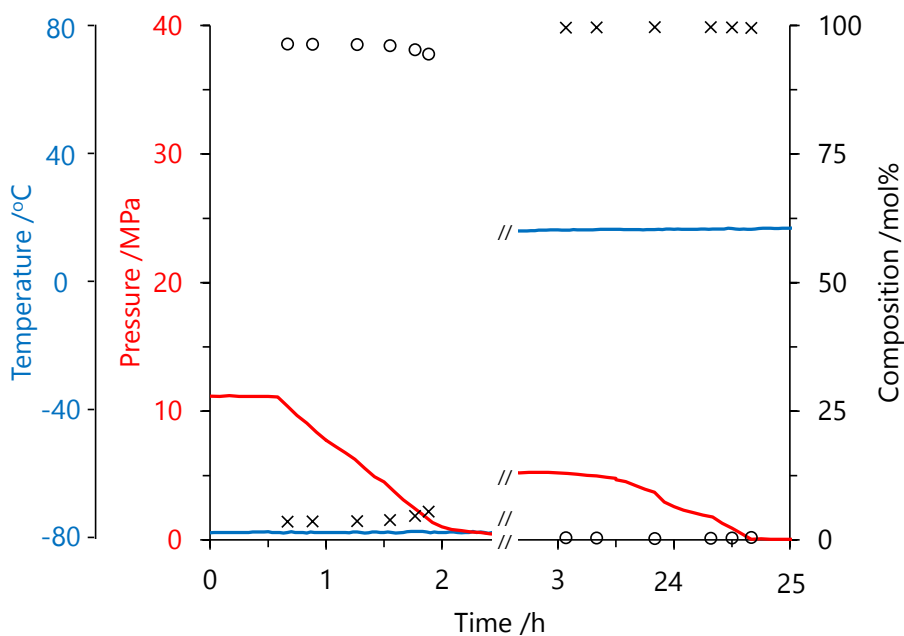**Figure S9.** Time course of the pressure, temperature and composition of gas release from FA decomposition at the separator: pressure (red line), temperature (blue line), H_2 composition (circle), CO_2 composition (cross). Reaction condition: 60 ºC, FA aqueous solution (8 mol/L, 40 mL), catalyst **3** (0.2 mmol/L).

Table S1. Arrhenius plot for FA dehydrogenation.[a]

Entry	Catalyst	Catalyst conc. /(mmol/L)	FA conc. /(mol/L)	Pressure /MPa	E_a [b]	R^2 [b]
1	**3**	0.4	8-16	40	74.0	0.99
2[c]	**3**	0.05	2	0.1	72.1	>0.99
3[c]	**1**	0.4	8-16	10	70.5	0.99

[a] Reaction conditions: 50-80 °C, generated gas ($H_2:CO_2 = 1:1$), FA aqueous solution (20-40 mL). [b] Parameters E_a and R^2 represent the activation energy of catalyst and the coefficient of determination, respectively. [c] Data was taken from Onishi et $al.$[2] (Entry 2) and Iguchi et $al.$[1] (Entry 3).

Table S2. Continuous decomposition of FA under various conditions using the catalyst **3**.[a]

Entry	Pressure /MPa	Times of FA addition	FA addition rate /(mL/h)[b]	Gas release rate /(L/h)[c]	CO /ppm	TON /-[d]
1	20	1	0.6	0.63±0.10	n.d.[g]	17 200
		2	0.6	0.69±0.07	n.d.	26 300
		3	0.6	0.62±0.07	n.d.	35 500
		4	0.6	0.52±0.07	7±3	44 800
		5	0.6	0.38±0.06	10±3	53 900
2[e]	20	1	0.6	0.53±0.09	13±9	17 200
		2	0.6	0.34±0.07	111±19	25 200
		3	0.6	0.28±0.05	87±15	33 700
3[f]	20	1	0.6	0.67±0.06	66±25	18 300
		2	0.6	0.71±0.07	72±27	27 600
		3	0.6	0.65±0.10	46±23	36 900
		4	0.6	0.51±0.08	30±11	46 100
		5	0.6	0.29±0.04	27±3	53 100
4	20	1	1.2	1.38±0.11	n.d.	26 800
		2	1.2	1.34±0.09	n.d.	45 000
		3	1.2	1.09±0.10	<6	63 200
5	0.1	1	1.2	1.53±0.07	n.d.	18 400
		2	1.2	1.58±0.08	n.d.	38 100
		3	1.2	1.58±0.07	n.d.	58 000
		4	1.2	1.58±0.08	n.d.	77 900
		5	1.2	1.57±0.09	n.d.	97 900
		7	1.2	1.58±0.07	n.d.	137 800
		10	1.2	1.62±0.07	n.d.	198 500

6	40	1	0.6	0.53±0.09	n.d.	23 000
		2	0.6	0.56±0.06	n.d.	30 500
		3	0.6	0.43±0.06	<6	37 800
		4	0.6	0.37±0.05	12±3	45 300
7	20	1	0.02	1.30±0.15	n.d.	25 800
		2	0.6	0.63±0.21	n.d.	34 200
		3	0.6	0.63±0.14	n.d.	43 500
		4	0.6	0.51±0.08	<6	52 400
		5	0.6	0.38±0.07	<6	61 400

[a] Reaction conditions: 50 ºC, initial FA aqueous solution (5 mol/L for 20 MPa and 8 mol/L for 40 MPa, 40 mL), catalyst (16 μmol). [b] FA was continuously added for 10 h and then stopped for several hours. [c] Average value over 8 h. [d] Calculated from the total volume of released gas after stopping the FA addition. [e] Sodium formate was added to the initial FA solution (FA/SF = 10/1 mol/mol). [f] Temperature was set to 70 ºC. [g] Below the detection limit (<2 vol ppm).

Table S3. Expansion of H_2/CO_2 gas mixture in the isentropic process [a]

Entry	Inlet		Outlet [b]	
	Pressure /MPa	Temperature /ºC	Pressure /MPa	Temperature /ºC
1	20	40	10	-6.1
2	20	60	10	3.6
3	20	90	10	29.2
4	40	90	10	-7.3
5	20	40	0.51	-80.0
6	20	90	0.44	-80.0
7	40	90	0.53	-80.0

[a] $H_2:CO_2$=1:1. [b] Values were calculated by the chemical engineering process simulator, COCO (AmsterCHEM, version 3.2) using the Peng-Robinson equation of state.

Process Simulation

 The energy required for cooling down the product gases (H_2:CO_2 = 1:1) from reaction temperature to separation temperature at high pressures was calculated by COCO (AmsterCHEM, version 3.2) using the Peng-Robinson equation of state. The process flow of gas cooling was shown in the Scheme S1. The process parameters of each stream are given in the Table S4. In the calculation of gas cooling process, the isentropic efficiency of expander was set to 1 and disregarded the pressure drop during cooling. Table S5 shows the energy production and consumption in the process of gas cooling. The gas expansion can reduce the energy for the gas cooling (14.5 kJ/mol) compared to the energy consumption by cooling down from 60 ºC to -78 ºC (22.2 kJ/mol).
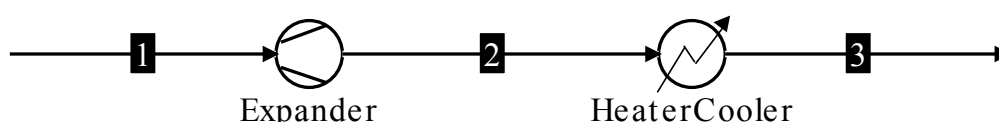
Scheme S1. Gas cooling flow diagram.

Table S4. Pressure and temperature conditions during the gas (H_2:CO_2 = 1:1) cooling.

Stream	1	2	3
p /MPa	20	10	10
T /ºC	60	3.59	-78

Table S5. Energy generation and heat duty in the process of gas cooling

Unit	Expander	Cooler	Total
Energy /(kJ/mol-H_2)	+2.93	-17.40	-14.47
Ratio based on LHV of H_2 /%[a]	1.2	7.2	6.0

[a] LHV: Lower heating value 241.8 kJ/mol-H_2.

References

1. M. Iguchi, H. Zhong, Y. Himeda and H. Kawanami, *Chem. - Eur. J.*, 2017, **23**, 17017-17021.

2. N. Onishi, M. Z. Ertem, S. Xu, A. Tsurusaki, Y. Manaka, J. T. Muckerman, E. Fujita and Y. Himeda, *Catal. Sci. Technol.*, 2016, **6**, 988-992.