Supporting Information

Dry reforming of methane over alumina-supported rhodium catalysts at low temperatures under visible and near-infrared light

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Material and Preparation

Al_2O_3 (γ-phase, 170 m^2 g^{-1}, JRC-ALO-7, the Catalysis Society of Japan) was used as received without further purification. Precursors of the Ni and Rh metals were as follows; $Ni(NO_3)_2 \cdot 6H_2O$ (Wako, 99%), $Rh(NO_3)_3 \cdot nH_2O$ (Tanaka Kikinzoku Kogyo K. K.). The metal precursor was impregnated on the Al_2O_3 support using ion-exchanged water (100 ml) and the suspension was heated at 353 K to dryness under magnetically stirring. The powder was dried at 373 K overnight, and calcined at 673 K for 2 h to obtain Al_2O_3-supported Rh or Ni catalysts. They were referred to as $Rh(x)/Al_2O_3$ and $Ni(y)/Al_2O_3$, where x and y are the weight percentages of Rh and Ni, respectively.

Photocatalytic activity test

Activity test of the photo-assisted DRM reaction was carried out using a fixed-bed flow reactor as described in our previous study[1]. Before the activity test, the sample powder was pelletized and crashed into 300–710 μm. The catalyst granules of Ni/Al_2O_3 or Rh/Al_2O_3 (0.3 g) were filled into a quartz reactor (2 cm × 2 cm × 1 mm, Fig. S1). Before the activity test, the sample was oxidized by $100\%O_2$ gas (total flow rate: 5 ml min^{-1}) at 723 K for 30 min to remove organic impurities from the catalyst surface, and then reduced by $10\%H_2/Ar$ gas (total flow rate: 20 ml min^{-1}) at 723 K for 30 min. After the pretreatment, a reactant gas (typically $10\%CO_2/10\%CH_4/Ar$, total flow rate: 200 ml min^{-1}) was flowed into the reactor in the dark at the given temperatures (typically, 473 K). After 30 min, light irradiation was started using a 300 W Xe lamp (Excelitas Technologies, PE300BUV, light intensity: 190 mW cm^{-2} in the range of 254±10 nm). For the vis–NIR light irradiation, a long-pass filter (Y-43, Toshiba Co. Ltd., $\lambda > 430$ nm, Fig. S2) was used to remove the UV light. The outlet gas was analysed by online gas chromatography with a thermal conductivity detector (Shimadzu, GC-8A) using a Shincarbon ST column. The conversion, selectivity, and carbon balance in the DRM reaction were calculated from the following equations:

Conversion of CO_2 (%) = $(1 - [CO_2]_{out} / [CO_2]_{in}) \times 100$

Conversion of CH_4 (%) = $(1 - [CH_4]_{out} / [CH_4]_{in}) \times 100$

Carbon balance (%) = $([CO]_{out} + [CO_2]_{out} + [CH_4]_{out}) / ([CO_2]_{in} + [CH_4]_{in}) \times 100$

where $[X]_{in}$ and $[X]_{out}$ represent the molar concentrations of X (X = CO_2, CH_4 or CO) in the inlet and outlet gases, respectively.

For the activity test of the CO_2 hydrogenation, a reactant gas (10%CO_2/10%H_2/Ar, total flow rate: 200 ml min^{-1}) was flowed into the reactor. The other experimental procedures of the CO_2 hydrogenation reaction were the same as the activity test in the photo-assisted DRM reaction except for the reactant gas. The conversion, selectivity, and carbon balance in the CO_2 hydrogenation reaction were calculated from the following equations:

Conversion of CO_2 (%) = $(1 - [CO_2]_{out} / [CO_2]_{in}) \times 100$

Conversion of H_2 (%) = $(1 - [H_2]_{out} / [H_2]_{in}) \times 100$

Selectivity to CH_4 (%) = $[CH_4]_{out} / ([CO]_{out} + [CH_4]_{out}) \times 100$

Carbon balance (%) = $([CO]_{out} + [CO_2]_{out} + [CH_4]_{out}) / ([CO_2]_{in}) \times 100$

where $[Y]_{in}$ and $[Y]_{out}$ represent the molar concentrations of Y (Y = CO_2, H_2, CH_4 or CO) in the inlet and outlet gases, respectively.

Characterization

UV–vis–NIR diffuse reflectance spectra (UV–vis–NIR DRS) were recorded on a V-570 instrument (JASCO, Japan) using the barium sulfate ($BaSO_4$) plate as a reference. Prior to the measurement, the sample was diluted 10 times with $BaSO_4$. X-ray diffraction (XRD) pattern was obtained using the powder sample on an X-ray diffractometer (LabX XRD-6000, Shimadzu, Japan) with Cu Kα radiation. The CO pulse adsorption experiment was used to determine the dispersion and average particle size of Rh and Ni particles deposited on the Al_2O_3 support. Thermogravimetry and differential thermal analysis (TG-DTA) were performed on a Rigaku Thermo plus TG 8120 apparatus at a heating rate of 10 K min^{-1} under a dry air flow condition (200 mL min^{-1}) using Pt pans.
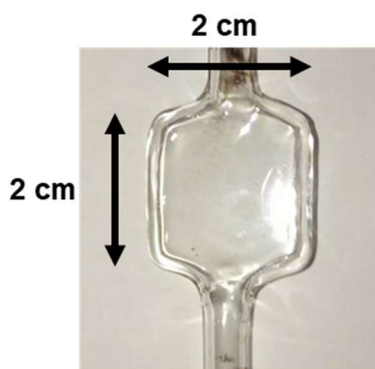
Fig. S1 The quartz reactor used for the catalytic activity test.
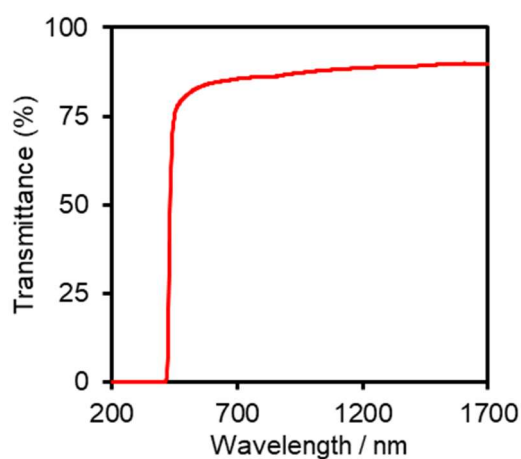
Fig. S2 Transmission property of a Y-43 long-pass filter used in the photo-assisted DRM reaction. The spectrum was obtained in a transmission mode by the UV–vis–NIR absorption spectrometer.

Estimation of metal particle sizes by the CO adsorption experiments

Table S1 Metal particle sizes estimated by the CO adsorption experiments.

Catalyst	Metal particle size (d) / nm				
	1 wt%[a]	5 wt%[a]	15 wt%[a]	25 wt%[a]	50 wt%[a]
Rh(x)/Al$_2$O$_3$	0.2	–[b]	1.0	1.6	–[b]
Ni(y)/Al$_2$O$_3$	–[b]	6.5	6.3	7.9	19
Rh(x)/Al$_2$O$_3$_C1073K	–[b]	–[b]	–[b]	6.7	–[b]

[a] Loading of metal (x or y). [b] Sample was not prepared.

Carbon deposition during the reaction

We performed TG-DTA of the Rh(25)/Al$_2$O$_3$ catalyst after the reaction for 5 h under vis–NIR light (Fig. S3). The weight loss observed around 340 K should be derived from desorption of water. Besides, the weight loss derived from the coke was not observed clearly.
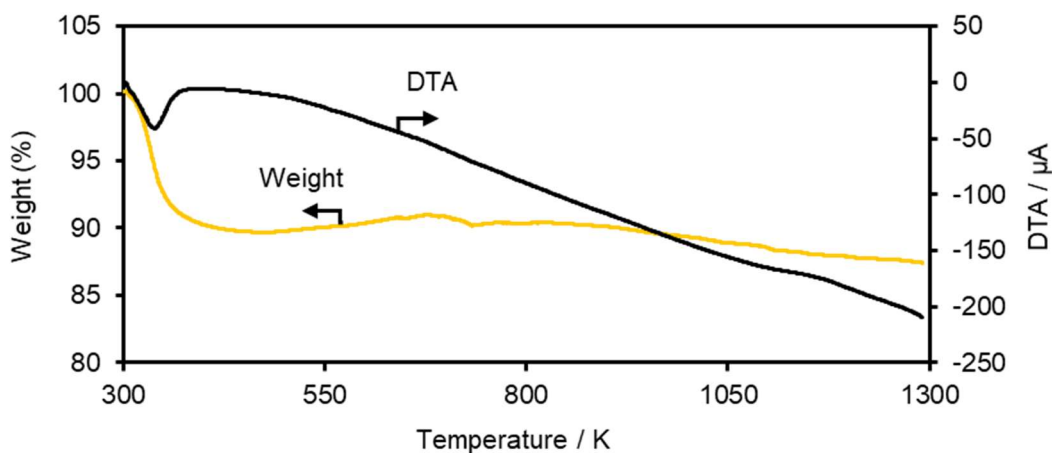

Fig. S3 TG-DTA profiles of the Rh(25)/Al$_2$O$_3$ catalysts after the reaction for 5 h.

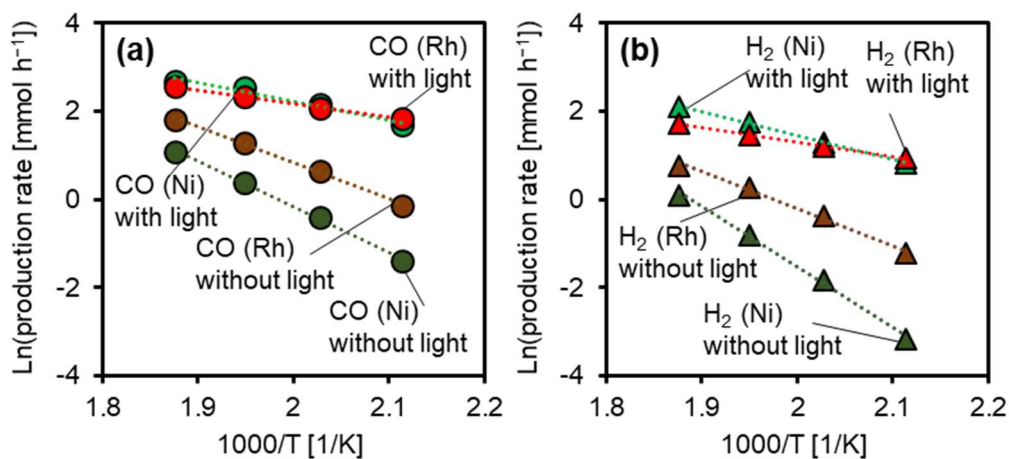**Apparent activation energy with and without light irradiation**

Fig. S4 Arrhenius plots for the production rates of CO (a) and H$_2$ (b) over the Rh(25)/Al$_2$O$_3$ and Ni(25)/Al$_2$O$_3$ samples with and without vis–NIR light. The range of external temperature used in the Arrhenius plots: 473–533 K.

Table S2 Apparent activation energies on the Rh(25)/Al$_2$O$_3$ and Ni(25)/Al$_2$O$_3$ catalysts with and without vis–NIR light.

Catalyst	Light[a]	E_a^b / kJ mol^{-1}	
		CO	H$_2$
Rh(25)/Al$_2$O$_3$	Vis–NIR	25.5	27.3
Rh(25)/Al$_2$O$_3$	Dark	68.1	69.3
Ni(25)/Al$_2$O$_3$	Vis–NIR	35.5	45.0
Ni(25)/Al$_2$O$_3$	Dark	86.9	114

[a] Light source: a 300 W Xe lamp. Vis–NIR: $\lambda > 430$ nm. Dark: without irradiation. [b] The range of external temperature used in the calculation of the activation energy: 473–533 K

Surface temperature measurement

We measured the surface temperature of the reactor under vis–NIR irradiation by an infrared thermometer (testo 835-T1, Testo SE & Co. KGaA) at the external temperature of 473K. The surface temperatures of the Rh(25)/Al$_2$O$_3$, Ni(25)/Al$_2$O$_3$, and Rh(25)/Al$_2$O$_3$_C1073K samples were 510 K, 528 K, and 532 K, which were higher than that of the Al$_2$O$_3$ sample (468 K), indicating the increase of the temperature is due to the vis–NIR light absorption of the supported metal particles.

Table S3 Surface temperatures measured by the infrared thermometer under the reaction condition.

Catalyst	Surface temperature / K			
	473 K[a]	493 K[a]	513 K[a]	533 K[a]
Rh(25)/Al$_2$O$_3$	510	528	550	573
Ni(25)/Al$_2$O$_3$	529	551	568	587
Rh(25)/Al$_2$O$_3$_C1073K	532	553	568	597
Al$_2$O$_3$	468	488	508	531

[a] The external temperature controlled by an external heater and a thermocouple.

Characterizations of Rh(25)/Al$_2$O$_3$_C1073K
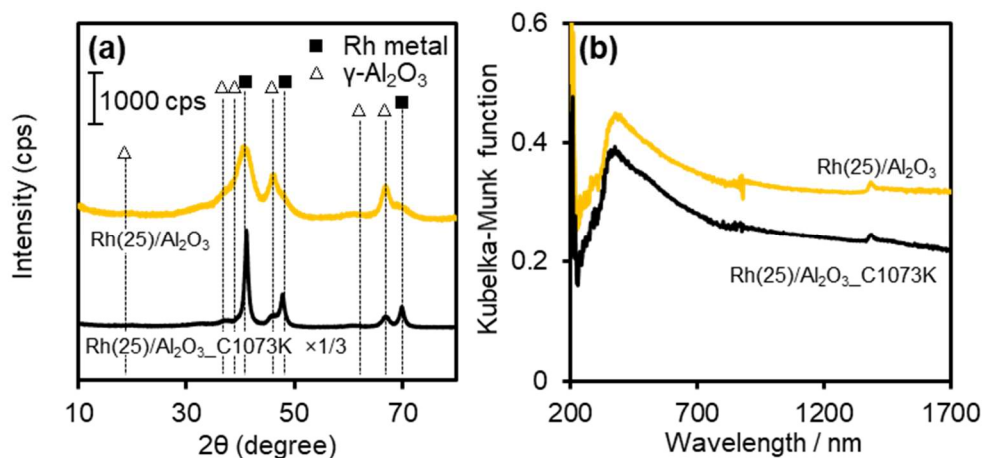
Fig. S5 XRD pattern (a) and UV–vis–NIR diffuse reflectance absorption spectra (b) of the Rh(25)/Al$_2$O$_3$ and Rh(25)/Al$_2$O$_3$_C1073K samples. Before the measurements, the samples were reduced at 723 K under 10%H$_2$/Ar. For the UV–vis–NIR absorption experiment, the samples were 10 times diluted with a barium sulphate powder.

Turnover frequency

Table S4 Turnover frequency (TOF) in the photo-assisted DRM reaction over the Ni(25)/Al$_2$O$_3$ and Rh(25)/Al$_2$O$_3$_C1073K samples calculated from the production rates of CO and H$_2$ at 473 K with and without vis–NIR light.

Catalyst	Light[a]	TOF[b] / min^{-1}	
		CO	H$_2$
Ni(25)/Al$_2$O$_3$	Vis–NIR	0.73	0.31
Ni(25)/Al$_2$O$_3$	Dark	0.41	0.15
Rh(25)/Al$_2$O$_3$_C1073K	Vis–NIR	0.86	0.51
Rh(25)/Al$_2$O$_3$_C1073K	Dark	0.40	0.21

[a] Light source: a 300 W Xe lamp. Vis–NIR: $\lambda > 430$ nm. Dark: without irradiation. [b] Turnover frequency at the external temperature of 473 K.

Effect of the reaction temperature
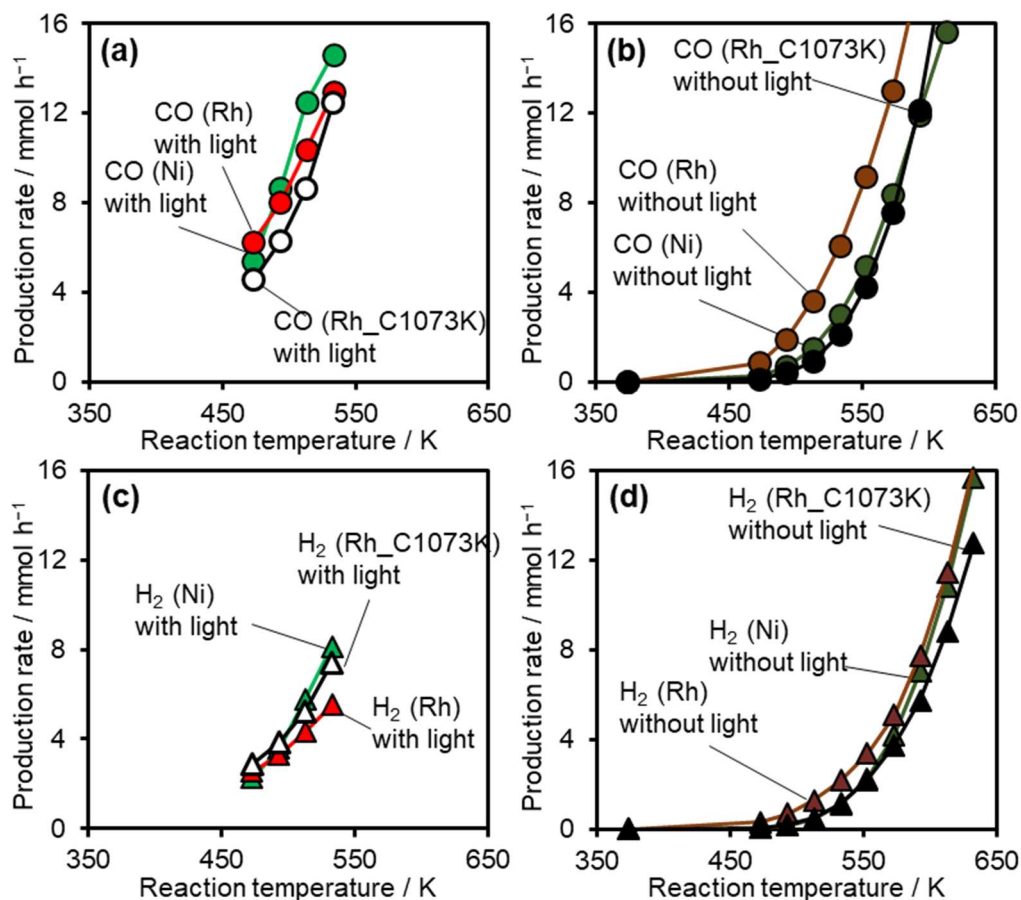
Fig. S6 Effect of the reaction temperature on the production rates of CO and H_2 over the Rh(25)/Al_2O_3, Ni(25)/Al_2O_3 and Rh(25)/Al_2O_3_C1073K samples with and without vis–NIR light. Feed gas: 10%CO_2/10%CH_4/Ar. Total flow rate: 200 ml min^{-1}. The temperatures employed here were the external temperature measured by the thermocouple.

References

1   D. Takami, Y. Ito, S. Kawaharasaki, A. Yamamoto, H. Yoshida, *Sustainable Energy Fuels*, 2019, **3**, 2968–2971.