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COMMUNICATION

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

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Alumina supported metallic Rh catalyst (Rh/Al₂O₃) was found to be an effective catalyst in photo-assisted dry-reforming of methane around 473 K under visible and near-infrared light. Rh/Al₂O₃ showed higher catalytic activity than Ni/Al₂O₃ previously reported due to the higher turnover frequency and higher dispersion of Rh.

The concentration of atmospheric carbon dioxide (CO₂) has been increasing year by year, which can affect global climate, the environment, and the economy. Depletion of fossil resources is also a serious problem because they are indispensable for today's human life as both energy sources and carbon resources. In recent years, recycle of carbon dioxide has attracted much attention to reduce CO₂ emission and use it as a carbon resource, which will contribute to the solution of these problems.

Dry reforming of methane (DRM, eq. 1) is one of the promising catalytic technologies to reduce the carbon dioxide emission and produce synthesis gas (mixture gas of carbon monoxide and hydrogen) as a feedstock for C1 chemistry.



However, high temperature operation around 1073–1273 K is necessary to obtain high conversion because the reaction is highly-endothermic.¹ It is strongly desirable to develop the DRM reaction without adding heat energy from fossil fuels.

Utilization of solar energy is a promising way to compensate the energy for the DRM reaction. Many examples of semiconductor photocatalysts have been reported to promote DRM so far under ultraviolet (UV) light irradiation, such as ZrO₂, MgO³, Cu/CdS–TiO₂/SiO₂, Ga₂O₃, SrTiO₃,⁶ and Rh/SrTiO₃.⁷ However, UV light is necessary to excite these photocatalysts due to the large bandgap of these materials. For the effective use of solar light, it is strongly required to develop photocatalysts that function even under visible and near infrared (Vis–NIR) light.

In recent years, there are many reports in the utilization of Vis–NIR light for the enhancement of the catalytic activity of DRM using a photothermal conversion process over various materials, such as Pt/black-TiO₂,⁸ Rh–Au/SiO₂,⁹ Ni catalysts^{10,11,12,13,14,15}, Pt/CeO₂,¹⁶ Pt–Au/CeO₂,¹⁷ and Co/TaC¹⁸. In these reaction systems, the supported metal particles convert the light energy to heat, and the resulting increase of the local temperature enhances the DRM reaction. It is well known that metal particles exhibit significant absorption of Vis–NIR light^{12,19}, meaning a wide range of the selection of metal for the photo-assisted DRM reaction. Focused on the catalytic active sites, Rh is known to be an effective metal to catalyse the thermal DRM reaction at low temperatures^{20,21}, and it also works as a absorption site of Vis–NIR light.²² These properties inspired us to investigate the catalytic activity of the supported Rh catalysts in the photo-assisted DRM reaction at low temperatures. In the present study, we demonstrated the Rh/Al₂O₃ catalysts showed superior catalytic activity under Vis–NIR light at the low temperature of 473 K than the Ni/Al₂O₃ catalysts previously reported by our group¹⁵.

The Rh/Al₂O₃ and Ni/Al₂O₃ catalysts were prepared by an impregnation method using the corresponding nitrate salts as the metal precursors (ESI). The prepared catalysts are referred to as Rh(x)/Al₂O₃ and Ni(y)/Al₂O₃, where x and y are weight percentages of Rh and Ni, respectively. Photocatalytic reaction test was carried out using a fixed-bed flow reactor (Fig. S1) as described in our previous study.²³ Shortly, before the activity test, we carried out oxidation (100%O₂) and reduction (10%H₂/Ar) pretreatments at 723 K, and then the reactor was irradiated by Vis–NIR light using a 300W Xe lamp equipped with an optical long-pass filter (λ > 430 nm, Fig. S2).

First, we characterized the Rh/Al₂O₃ and Ni/Al₂O₃ samples (Fig. 1a) after the reduction pretreatment by 10%H₂/Ar at 723 K. XRD patterns showed the formation of Rh metal (2θ = 41.0, 47.8, and 69.9 degrees) and Ni metal (2θ = 44.4, 51.7, and 76.2 degrees) particles (Fig. 1b and 1c). The metal particle sizes (d) in the Rh/Al₂O₃ and Ni/Al₂O₃ samples were estimated by CO adsorption experiments (e.g., Rh(25)/Al₂O₃: d = 1.6 nm and Ni(25)/Al₂O₃: d = 7.9 nm, for detail see Table S1). The results were consistent with the values (D) obtained from the diffraction peaks by Scherrer equation (Rh(25)/Al₂O₃: D = 2.7

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nm and Ni(25)/Al₂O₃: $D = 8.0$ nm). To evaluate the light absorption property, we measured the UV–Vis–NIR absorption spectra of these samples after dilution with a barium sulphate powder (10 times). In the Rh/Al₂O₃ samples, the broad absorption appeared in a wide range up to 1700 nm (Fig. 1d), which corresponds to

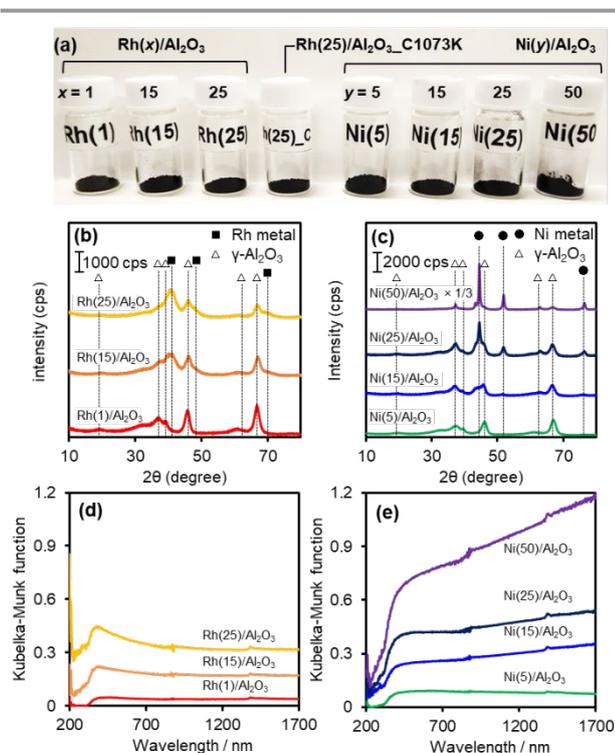


Fig. 1 Characterization results of the Rh(x)/Al₂O₃ and Ni(y)/Al₂O₃ samples after the reduction pretreatment at 723 K. (a) Photograph of the samples. XRD patterns of the Rh(x)/Al₂O₃ (b) and Ni(y)/Al₂O₃ (c) samples. UV–Vis–NIR diffuse reflectance absorption spectra of the Rh(x)/Al₂O₃ (d) and Ni(y)/Al₂O₃ (e) samples. For the UV–Vis–NIR absorption experiment, the samples were 10 times diluted with a barium sulphate powder.

the formation of Rh metal particles and the absorption increased with the loading. A similar trend was observed in the Ni/Al₂O₃ samples (Fig. 1e). These characterization results clearly

showed the formation of Rh and Ni metal particles that absorb the Vis–NIR light after the reduction pretreatment.

Next, we performed the catalytic activity tests of the Rh/Al₂O₃ and Ni/Al₂O₃ catalysts with various loadings at 473 K under Vis–NIR light (Fig. 2a). Most of the Rh/Al₂O₃ catalysts showed higher catalytic activities than the Ni/Al₂O₃ catalysts when compared with the same loading. Besides, the CO production rates increased with increasing the loading in the Rh/Al₂O₃ catalysts and became almost constant over 15wt%. In the Ni/Al₂O₃ catalysts, the CO production rates also increased up to 25wt%. The largest production rates of CO (6.0 mmol h⁻¹) and H₂ (2.4 mmol h⁻¹) were obtained with the Rh(25)/Al₂O₃ catalyst. On the other hand, a different tendency in the product distribution was observed; in Rh/Al₂O₃, the CO/H₂ ratio slightly increased with increasing the loading and drastically decreased in Ni/Al₂O₃ (Fig. 2b).

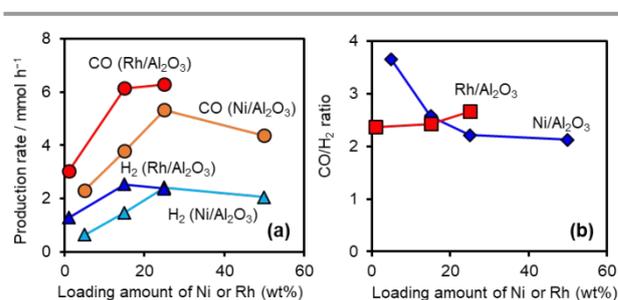


Fig. 2 Effect of the loadings of Rh or Ni on the production rates of CO and H₂ (a) and CO/H₂ ratio (b) in DRM under Vis–NIR light at 473 K. Feed gas: 10%CO₂/10%CH₄/Ar. Total flow rate: 200 ml min⁻¹. Light source: a 300 W Xe lamp ($\lambda > 430$ nm). Reaction temperature: 473 K.

The effect of the Vis–NIR light was investigated using the Rh(25)/Al₂O₃ and Ni(25)/Al₂O₃ catalysts (Table 1). In these activity tests, the carbon balance was almost 100%. In the dark at 473 K, the Rh(25)/Al₂O₃ catalyst produced a small amounts of CO and H₂, and the production rates of CO and H₂ were drastically enhanced by Vis–NIR light by 7.0 and 8.3 times, respectively (Table 1, Entries 1 and 2). This enhancement by light was also confirmed on the Ni/Al₂O₃ catalysts (Entries 3 and 4), which is consistent with the previous reports.^{11,15} The reaction did not proceed over the bare Al₂O₃ support (Table 1, Entry 7), indicating the Rh and Ni metal particles are necessary

Table 1 Results of the activity tests in DRM with and without Vis–NIR light irradiation.^a

Entry	Catalyst	Light ^b	Production rate / mmol h ⁻¹		T_{surf}^c / K	CO/H ₂	Carbon balance ^d (%)
			CO	H ₂			
1	Rh(25wt%)/Al ₂ O ₃	Vis–NIR	6.0	2.4	510	2.5	100
2	Rh(25wt%)/Al ₂ O ₃	Dark	0.86	0.29	–	3.0	100
3	Ni(25wt%)/Al ₂ O ₃	Vis–NIR	5.3	2.3	529	2.3	101
4	Ni(25wt%)/Al ₂ O ₃	Dark	0.25	0.04	–	6.3	101
5	Rh(25wt%)/Al ₂ O ₃ _C1073K	Vis–NIR	4.6	2.9	532	1.6	100
6	Rh(25wt%)/Al ₂ O ₃ _C1073K	Dark	0.13	0.05	–	2.6	101
7	Al ₂ O ₃	Vis–NIR	n.d.	n.d.	468	–	100

^a Feed gas: 10%CO₂/10%CH₄/Ar. Total flow rate: 200 ml min⁻¹. Reaction temperature: 473 K. ^b Light source: a 300 W Xe lamp, Vis–NIR: $\lambda > 430$ nm. Dark: without irradiation. ^c Surface temperature measured by an infrared thermometer. ^d Carbon balance (%) = $([\text{CO}]_{\text{out}} + [\text{CO}_2]_{\text{out}} + [\text{CH}_4]_{\text{out}}) / ([\text{CO}_2]_{\text{in}} + [\text{CH}_4]_{\text{in}}) \times 100$.

for the DRM reaction. **Fig. 3** shows the time-course of the photo-assisted DRM reaction over Rh(25)/Al₂O₃ at 473 K under Vis–NIR light, and the activity was maintained during 5 hours. The carbon balance was almost 100% through the reaction. These results suggest a significant coke formation does not occur during the reaction, and it was supported by thermogravimetry and differential thermal analysis (Fig. S3). Besides, the Rh(25)/Al₂O₃ catalyst showed a lower apparent activation energy than the Ni(25)/Al₂O₃ catalyst in both the cases with and without Vis–NIR light (**Fig. S4 and Table S2**). Although the origin of the lower apparent activation energy in the Rh catalysts is not clarified yet, it would contribute to the higher activity at low temperature.

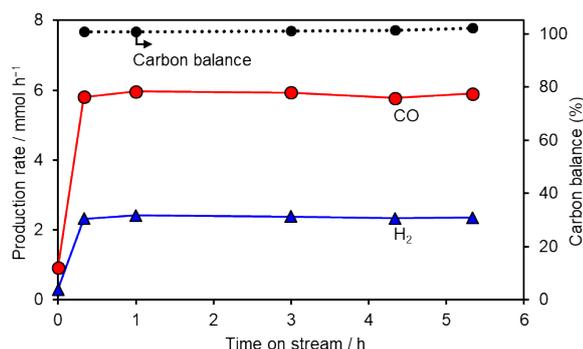
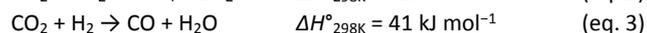
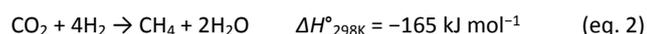


Fig. 3 Time course of the photo-assisted DRM reaction under Vis–NIR light at 473 K over Rh(25)/Al₂O₃. Feed gas: 10%CO₂/10%CH₄/Ar. Total flow rate: 200 ml min⁻¹. Light source: a 300 W Xe lamp ($\lambda > 430$ nm). Reaction temperature: 473 K.

In all the experiments under light irradiation (**Fig. 2 and 3, Table 1**), the production rate of CO was higher than that of H₂ although the CO/H₂ ratio is one according to **eq. 1**. As we reported previously¹⁵, the Sabatier reaction (**eq. 2**) and reverse water-gas-shift reaction (**eq. 3**) increased the CO/H₂ ratio over Ni/Al₂O₃ catalysts under Vis–NIR light.



To examine the contribution of these side reactions to the CO/H₂ ratio, we performed the reaction between CO₂ and H₂ (*i.e.*, CO₂ hydrogenation) with and without Vis–NIR light at 473 K. CO and CH₄ were produced over both catalysts under Vis–NIR light (**Table 2, Entries 1 and 3**) possibly according to **eq. 2 and**

3. Thus, in the DRM reaction under Vis–NIR light, the formed H₂ molecules would be consumed by the reactions with CO₂ (**eq. 2 and 3**), which would result in the higher CO/H₂ ratio than one.

Since the metal particles can convert the light energy to thermal energy in the photo-assisted DRM reaction, the actual temperature of the catalyst should be discussed. To obtain the information, we measured the surface temperature (T_{surf}) under the irradiation condition by an infrared thermometer (**ESI**). At the external temperature of 473 K (controlled by a thermocouple), T_{surf} of the Rh(25)/Al₂O₃, Ni(25)/Al₂O₃, and bare Al₂O₃ samples were 510 K, 529 K and 468 K, respectively (**Table 1**), indicating that photothermal conversion of metal particles increased the surface temperature and the Ni(25)/Al₂O₃ catalyst can be heated more easily than the Rh(25)/Al₂O₃ catalyst. As shown in **Fig. 1**, the absorption of Vis–NIR light in the Ni(25)/Al₂O₃ catalyst is almost the same level as that of the Rh(25)/Al₂O₃ catalyst, which means the absorption property does not cause the difference of the surface temperature between these materials. The reason for the higher T_{surf} of the Ni(25)/Al₂O₃ sample would be the larger size of Ni metal particles (**Table S1**), since a larger metal particle has a smaller specific contact area with the external environment (*i.e.*, gas phase and support) to decrease the heat dissipation via the interface. To confirm this, another Rh/Al₂O₃ sample was prepared by calcination at the higher temperature of 1073 K (referred to as Rh(25)/Al₂O₃_C1073K). This sample had larger size of Rh metal particles, $d = 6.7$ nm (**Fig. S5 and Table S1**), and exhibited higher T_{surf} (532 K at the external temperature of 473 K, **Table 1**) although the absorption efficiency was low (**Fig. S5b**). Thus, the higher T_{surf} of the Ni(25)/Al₂O₃ sample compared to the Rh(25)/Al₂O₃ sample should originate from the larger size of Ni metal particles.

Besides, the turnover frequency (TOF) over the Rh(25)/Al₂O₃_C1073K catalyst was higher than that of the Ni(25)/Al₂O₃ catalyst by 1.2 times for CO and 1.6 times for H₂ (**Table S4**) in similar surface temperatures (**Table 1, Entries 3 and 5**). Although the Rh(25)/Al₂O₃ catalyst had smaller metal particles and thus lower T_{surf} than the Ni(25)/Al₂O₃ catalyst, the Rh(25)/Al₂O₃ catalyst showed higher catalytic activity than the Ni(25)/Al₂O₃ catalyst at the external temperature of 473 K. So that, it is strongly suggested that the higher reaction rate of the Rh(25)/Al₂O₃ catalyst is attributed to the higher dispersion and higher TOF of Rh metal particles on the Al₂O₃ support (**Table S1**).

Table 2 Results of the activity tests in CO₂ hydrogenation with and without Vis–NIR light irradiation.^a

Entry	Catalyst	Light ^b	Conversion ^c (%)		Production rate/mmol h ⁻¹		CH ₄ selectivity ^d (%)
			CO ₂	H ₂	CO	CH ₄	
1	Rh(25)/Al ₂ O ₃	Vis–NIR	23	91	0.35	13	97
2	Rh(25)/Al ₂ O ₃	Dark	14	56	n.d.	8.1	100
3	Ni(25)/Al ₂ O ₃	Vis–NIR	20	77	1.5	11	88
4	Ni(25)/Al ₂ O ₃	Dark	6.0	22	0.19	3.3	95

^a Feed gas: 10%CO₂/10%H₂/Ar. Total flow rate: 200 ml min⁻¹. Reaction temperature: 473 K. ^b Light source: a 300 W Xe lamp, Vis–NIR: $\lambda > 430$ nm. Dark: without irradiation. ^c Conversion of X (%) = $([X]_{\text{in}} - [X]_{\text{out}})/[X]_{\text{in}} \times 100$ (X = CO₂ or H₂). ^d CH₄ selectivity (%) = $[CH_4]_{\text{out}}/([CO]_{\text{out}} + [CH_4]_{\text{out}}) \times 100$.

In summary, we clearly demonstrated that the Rh/Al₂O₃ catalysts showed a superior catalytic activity in DRM under Vis–NIR light at the low temperature of 473 K than the Ni/Al₂O₃ catalysts previously reported.¹⁵ Vis–NIR light irradiation drastically enhanced the formation rates of CO and H₂ in the Rh(25)/Al₂O₃ catalyst by 7.0 and 8.3 times, respectively. Furthermore, we found the larger Rh particle size afforded the higher surface temperature although it was not effective for the DRM reaction possibly because the aggregation decreased the amount of the active sites. The trade-off relationship between the surface temperature of catalysts and the amount of the active sites is a key point to understand the catalytic activity in the photo-assisted DRM reaction. This fundamental insight will contribute to design and further development of the effective DRM system utilizing solar light.

Conflicts of interest

There are no conflicts to declare.

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Table of Contents

