Sustainable Energy & Fuels

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Journal:	*Sustainable Energy & Fuels*
Manuscript ID	SE-COM-04-2019-000206.R1
Article Type:	Communication
Date Submitted by the Author:	25-Apr-2019
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COMMUNICATION

Low Temperature Dry Reforming of Methane over Plasmonic Ni Photocatalysts Under Visible Light Irradiation

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Low temperature CO_2 conversion with CH_4 into syngas (dry reforming of methane, DRM) was achieved over plasmonic Ni/Al_2O_3 photocatalysts with high conversion of CO_2 (21%) and CH_4 (20%) using a fixed-bed flow reactor at 473 K. The formation rates of CO and H_2 were 1.87 and 1.20 mmol h^{-1}, respectively, and these values were over 47 times higher than that of the Ga_2O_3 photocatalyst previously reported by our group. To the best of our knowledge, this is the first report that the high formation rates of CO and H_2 were achieved at 473 K in the DRM reaction under visible light. Besides, the CO/H_2 ratio was successfully controlled by changing the CO_2/CH_4 ratio in the feed gas mixture.

Concentration of carbon dioxide (CO_2) in the atmosphere has been increasing year by year, and the CO_2 emissions are a serious problem because of its contribution to the climate change. To reduce the CO_2 emission amount, development of novel technologies for the chemical conversion of CO_2 are strongly-desired. Dry reforming of methane (DRM)[1, 2] is one of the promising technologies for the conversion of CO_2, where CO_2 reacts with abundantly available CH_4 gas to produce industrially important syngas (eq. 1).

$$\mathrm{CO_2 + CH_4 \rightarrow 2CO + 2H_2} \quad \Delta H_{298K} = 247\ \mathrm{kJ\ mol^{-1}} \qquad \text{eq. 1}$$

Typically, the DRM reaction has to be operated at high temperature of 1073–1273 K to obtain high equilibrium conversion (eq. 1) because the reaction is highly endothermic. Furthermore, carbon deposition is also serious problem in many DRM reactions[2] although extensive research has been conducted in this filed. To solve these problems, utilization of light energy is a potential method because the photocatalytic reaction occurs at low temperatures beyond the thermodynamic limit. Photocatalytic reaction between CO_2 and CH_4 was firstly reported over ZrO_2, and the authors confirmed that the evolved CO derives from only CO_2 molecules introduced.[3, 4] The same group reported that MgO worked as a photocatalyst for the reaction between CO_2 and CH_4 under UV-light irradiation although H_2 was not observed.[5] Our group firstly succeeded in the conversion of CO_2 and CH_4 into CO and H_2 using a Ga_2O_3 photocatalyst (photo-DRM) at mild temperatures around 473 K compared to the thermal DRM reaction condition.[6, 7] However, in that system, the photocatalytic activity is insufficient (CO: 1.1 µmol and H_2: 2.5 µmol after 3 h) even under UV light irradiation at 473 K.[7] Recently, photocatalytic approach has been investigated extensively for the DRM reaction.[8-15] In 2015, it was firstly proposed that a localized surface plasmon resonance (LSPR) by Au was effective for the activity enhancement of the DRM reaction at 773 K.[8] Other group reported a black-TiO_2 photocatalyst for the DRM reaction, and the activity was improved under visible light in the temperature range of 623–1050 K.[9] Recently, Ni based plasmonic photocatalysts were reported for photo-DRM at reaction temperatures over 673 K by several groups.[10, 11, 14] In spite of the extensive research, the reaction temperature is still high, and photo-DRM at a mild reaction temperature around 473 K has not been achieved yet. In the present study, we investigated various photocatalysts and reaction conditions to obtain the high yield of CO and H_2 in the photo-DRM reaction under light irradiation at a mild reaction temperature of 473 K.

The metal-loaded photocatalysts were prepared by an impregnation method. The catalytic activity tests were carried out using a fixed-bed flow reactor as described in our previous study,[16, 17] and the sample was irradiated by a 300 W Xe lamp with or without a long-pass filter (λ > 430 nm, Fig. S1). Before the catalytic activity test, the sample was reduced by H_2 (10%)/Ar gas at 623 K (typically). Ni K-edge XAFS measurements were performed at BL12C of the Photon Factory (PF, Tsukuba, Japan). The experimental detail was shown in ESI.

First, effect of the metal loading on a Ga_2O_3 photocatalyst was investigated under UV-visible light irradiation at 473 K (Fig. 1).

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

The pristine Ga_2O_3 (β-phase, specific surface area (S_a): 9.8 $m^2\ g^{-1}$) photocatalyst showed the activity in the photo-DRM reaction as previously reported,[6] although the fixed-bed flow reactor was used in this experiment for the first time. As a result of the screening test, the loading of Pt, Rh, and Ni drastically improved the photocatalytic activity, and the Ni/Ga_2O_3 photocatalyst showed the highest CO and H_2 formation rates. The formation rate of CO was higher than that of H_2 in many cases including the Ni/Ga_2O_3 photocatalyst, which will be discussed later.

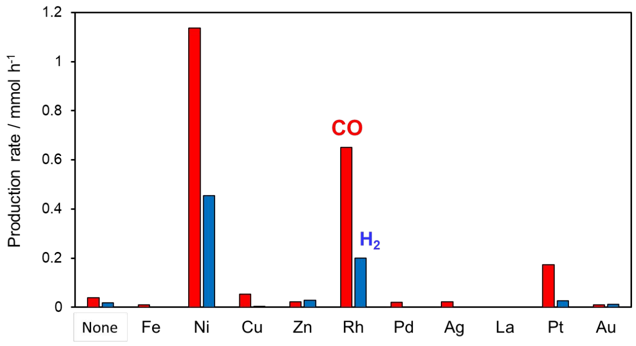

Figure 1. Production rates of CO and H_2 in the photo-DRM reaction over various M/Ga_2O_3 (M: metal) at 473 K. Metal loading was 1 wt% as a metal. Before the catalytic activity test, the sample was reduced at 623 K under H_2 (10%)/Ar gas. $CO_2/CH_4/Ar$ = 1/1/8. Total flow rate: 20 mL min^{-1}. A 300 W Xe lump was used without any optical filter.

Next, we carried out the activity test of Ni/Ga_2O_3, Ni/Al_2O_3 (γ-phase, S_a: 170 $m^2\ g^{-1}$) and Ni/TiO_2 (anatase, S_a: 300 $m^2\ g^{-1}$) with various Ni loadings. Under UV-visible light irradiation, CO and H_2 were effectively formed when the Ni loading is over 1 wt% in Ni/Ga_2O_3, 5 wt% in Ni/Al_2O_3 and 20 wt% in Ni/TiO_2 as shown in Fig. 2. The band gap of Al_2O_3 (7.6 eV, 160 nm)[18] is larger than the energy of the light used in this experiment (λ > 200 nm), which means that the band-gap excitation of the metal oxide is not necessary in the photo-DRM reaction over the supported Ni catalysts. Among the photocatalysts investigated, the highest formation rates of CO and H_2 were obtained in the 5 wt% Ni/Al_2O_3 catalyst.

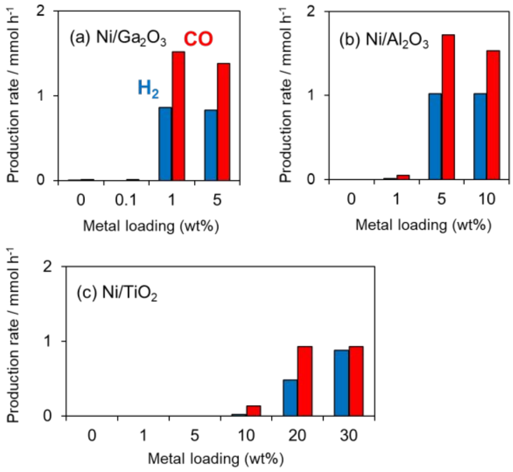

Figure 2. Effect of Ni loading on the activity in the photo-DRM reaction on Ni/Ga_2O_3, Ni/Al_2O_3, and Ni/TiO_2 under UV-visible light irradiation without any optical filter at 473 K. Before the catalytic activity test, the sample was reduced at 623 K under H_2 (10%)/Ar gas. $CO_2/CH_4/Ar$ = 1/1/8. Total flow rate: 20 mL min^{-1}.

To clarify the role of Ni, the effective wavelength of light for the photo-DRM reaction was investigated in the 5 wt% Ni/Al_2O_3 photocatalyst after the H_2 pretreatment at 623 K (Table 1, entries 1 and 2). As a result, the reaction proceeded efficiently even under visible light although the reaction rate decreased to some extent compared with the result under UV-visible light irradiation. The conversions of CO_2 and CH_4 were 21% and 20%, respectively, under visible light. In the dark condition, the reaction did not proceed (entry 3), indicating the reaction is significantly accelerated by visible light at 473 K. The activity was further improved at 573 K under visible light (entries 2, and 4) although the CO and H_2 formation was confirmed in the dark at this temperature (entry 5). Besides pristine Al_2O_3 did not show the activity under visible light, indicating Ni is the active site in the photo-DRM reaction (entry 6).

Effect of the temperature of the H_2 reduction pretreatment was investigated (entries 2, 7–10). When the reduction temperature is below 473 K, no product was observed even under visible light. UV-vis spectroscopy elucidated the broad absorption band around 400–800 nm increased with the reduction temperatures

Table 1. Results of the activity test under various reaction conditions [a]

Entry	Cat. [b]	T_{Red} [c]	Light [d]	T [e]	r [f] / mmol h^{-1}		Conv. [g] (%)		C.B. [h] (%)
					CO	H_2	CO_2	CH_4	
1	Ni/Al_2O_3	623	UV+vis.	473	2.58	1.73	29.4	26.7	95
2	Ni/Al_2O_3	623	vis.	473	1.87	1.20	21.0	19.5	97
3	Ni/Al_2O_3	623	dark	473	n.d. [i]	n.d. [i]	0	0	100
4	Ni/Al_2O_3	623	vis.	573	3.22	2.21	40.3	33.7	91
5	Ni/Al_2O_3	623	dark	573	1.13	0.64	13.9	11.7	98
6	Al_2O_3	623	vis.	473	n.d. [i]	n.d. [i]	0	0	100
7	Ni/Al_2O_3	323	vis.	473	n.d. [i]	n.d. [i]	0	0	100
8	Ni/Al_2O_3	473	vis.	473	n.d. [i]	n.d. [i]	0	0	100
9	Ni/Al_2O_3	873	vis.	473	1.48	0.90	16.3	14.4	98
10	Ni/Al_2O_3	1073	vis.	473	1.50	1.08	18.0	17.2	96

[a] Reaction gas: $CO_2/CH_4/Ar$=1/1/8, total flow rate: 20 mL min^{-1}. [b] Metal loading: 5 wt% (if present). [c] Temperature of the H_2 pretreatment, [d] Light source: a 300 W Xe lamp, UV+vis.: λ > 200 nm, vis: λ > 430 nm (a long-pass filter was used, Fig. S1), dark: without irradiation. [e] Reaction temperature. [f] Formation rates of CO and H_2. [g] Conversion of X (%) = $([X]_{in} - [X]_{out})/[X]_{in} \times 100$ (X = CO_2 or CH_4). [h] Carbon balance (eq. 2). [i] Not detected.

higher than 623 K (Fig. 3a), possibly due to the formation of metallic Ni species. In addition, XAFS spectroscopy confirmed that the Ni species was partially reduced with the H_2 treatment above 623 K (Fig. 3b), although the XRD pattern did not change for the sample reduced at 623 K (Fig. S3). Thus, the spectroscopic results indicated that the small part of the Ni^{2+} species was reduced into metallic Ni species after the H_2 pretreatment at 623 K. The reduction temperature coincides with previous studies using temperature programed reduction (TPR) in Ni/Al_2O_3 samples.[19, 20] Combined with the results of the activity tests, it is noticed that the metallic Ni species is responsible for the formation of CO and H_2 under visible light irradiation. In literature,[10] it was proposed that the photo-DRM reaction with Ni catalysts can be accelerated by LSPR effect, where the LSPR effect was confirmed only at relatively high temperature (> 823 K). In our reaction system, the plasmonic excitation of Ni metal species would be essential for the photo-DRM reaction. Besides, the production rates of CO and H_2 increased with the light intensity (I) superlinearly (i.e., rate $\propto I^n$, $n > 1$, Fig. S2), suggesting that the role of the light is not only local heating via non-radiative plasmonic decay.[21] Moreover, surface temperature was measured using a remote proved thermometer, and the temperature was 577 K under visible light irradiation (temperature of the reactor: 473 K). In our reaction result at 573 K in the dark condition (Table 1, Entry 5), the formation rates of CO and H_2 were 1.13 and 0.64 mmol h^{-1}, and these values were less than those under visible light irradiation at 473 K (Table 1, Entry 2).

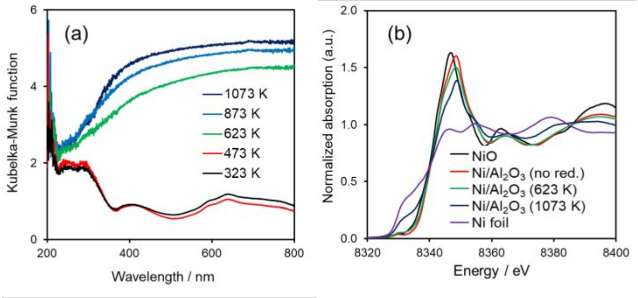

Figure 3. Effect of reduction temperature in the pretreatment on the UV-vis diffuse reflectance spectra (a) and XANES spectra (b) of the Ni/Al_2O_3 sample (Ni loading: 5 wt%).

In the typical DRM reaction using a thermal Ni catalyst, durability of the catalyst is a serious problem since coke formation drastically decreases the catalytic activity.[22, 23] To test the durability of the plasmonic Ni/Al_2O_3 photocatalyst, the activity test was carried out for 100 h (Fig. 4). Although the activity decreased to some extent, it became rather constant after 80 h, and the reaction continuously proceeded even after 100 h. Furthermore, the calculated TON was 280 based on the amount of Ni atoms in the catalysts after 100 h, indicating the reaction proceeds photocatalytically. To investigate the deactivation, we performed several characterizations of the Ni/Al_2O_3 photocatalyst after the reaction for 100 h. X-ray diffraction (XRD) revealed that carbon deposition and formation and/or aggregation of metalic Ni species occurred after the reaction (Fig. S4) although such a carbon species cannot be observed by TEM (Fig. S5). Besides, the content of carbon was estimated to be 3.8 wt% using thermogravimetry (TG) analysis (Fig. S6), and the value was relatively low compared with typical Ni/Al_2O_3 in thermal DRM reaction although it significantly depends on the reaction condition and catalyst properties. Besides, the carbon balance was calculated using eq. 2,

$$\text{Carbon balance (\%)} = \frac{[\mathrm{CO_2}]_{\mathrm{out}} + [\mathrm{CH_4}]_{\mathrm{out}} + [\mathrm{CO}]_{\mathrm{out}}}{[\mathrm{CO_2}]_{\mathrm{in}} + [\mathrm{CH_4}]_{\mathrm{in}}} \times 100 \quad \text{eq.2}$$

where $[X]_{in}$ and $[X]_{out}$ are partial pressures of X in inlet and outlet gas mixtures, respectively. The carbon balance is almost 100% during the reaction as shown in Fig. 4, which is consistent with the low carbon deposition amount.

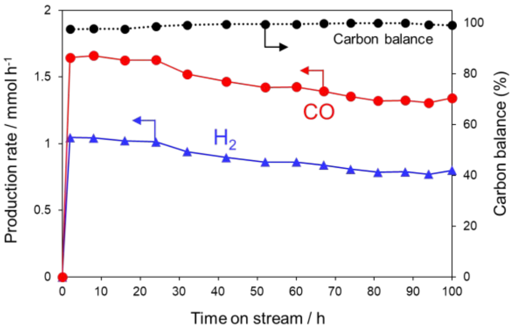

Figure 4. Long-time photo-DRM reaction under visible light on the Ni/Al_2O_3 catalyst. Ni loading: 5wt%. $CO_2/CH_4/Ar = 1/1/8$. Total flow rate: 20 mL min^{-1}.

Next, we investigated the effect of the partial pressures of CO_2 and CH_4 (P_{CO2} and P_{CH4}) on the formation rates. When P_{CO2} increased from 0.05 to 0.9 atm, the CO formation rate increased monotonically up to 2.7 times and the H_2 formation rate did not change significantly (Fig. 5a). Whereas, increment of P_{CH4} improved the formation rates of both CO and H_2 (Fig. 5b) up to 0.5 atm. In the condition of $P_{CO2} < P_{CH4}$, the photocatalytic activity markedly deceased with the reaction time (Fig. S8). This indicates that high P_{CO2}/P_{CH4} ratio in the feed gas is important for the stable photocatalytic DRM reaction.

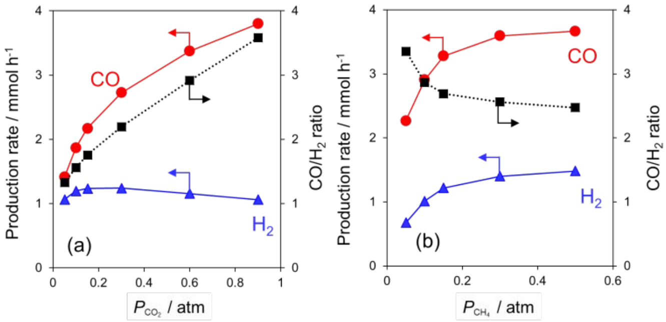

Figure 5. Effect of partial pressures of CO_2 (a) and CH_4 (b) on the formation rates and CO/H_2 ratio in the photo-DRM reaction at 473 K over the 5wt% Ni/Al_2O_3 photocatalysts. Total flow rate: 20 mL min^{-1}, P_{CH4}: 0.1 atm in (a), P_{CO2}: 0.5 atm in (b).

As shown in Fig. 5, the CO/H_2 ratio increased with increasing P_{CO2}, and decreased with increasing P_{CH4}. In addition, the CO formation rate is higher than that of H_2 formation rate in all the reaction conditions in Figs. 4 and 5 although the CO/H_2 ratio is unity in the reaction equation of DRM as shown in eq. 1. In a thermal DRM catalyst, the simultaneous occurrence of reverse water gas shift (RWGS) (eq. 3) reaction results in an increase of the CO/H_2 ratio over 1.[2] Thus, we investigated the possibility of hydrogenation of CO_2 over the Ni/Al_2O_3 photocatalyst under visible light irradiation in the reaction condition of $H_2/CO_2/Ar$ = 1/1/8 at a total flow rate of 20 ml min^{-1}. As a result, formation of CO (0.78 mmol h^{-1}) and CH_4 (0.62 mmol h^{-1}) was observed under visible light irradiation, indicating that RWGS (eq. 3) and Sabatier (eq. 4) reactions were promoted over the Ni/Al_2O_3 photocatalyst under visible light irradiation.

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \text{(RWGS reaction)} \qquad \text{eq. 3}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad \text{(Sabatier reaction)} \qquad \text{eq. 4}$$

In Table 1, CO_2 conversion was higher than that of CH_4 in many cases (Entries 1, 2, 4, 5, 9, and 10), which can be explained by the eqs. 3 and 4. Furthermore, we confirmed the formation of water in the photo-DRM reaction at 473 K under visible light using gas chromatography (Fig. S9). This result supports the simultaneous occurrence of RWGS and Sabatier reactions during the photo-DRM reaction, which results in the high CO/H_2 ratio in these reaction conditions. The selectivity change in the different partial pressure condition can be interpreted by the above reactions. The rate of RWGS reaction would increase with increasing CO_2 pressure, which results in the high CO/H_2 ratio as shown in Fig. 5a. Although further investigation is necessary to explain the change of the CO/H_2 ratio, the results of the partial pressure dependence clearly demonstrated that the CO/H_2 ratio was successfully controlled by just changing CO_2/CH_4 ratio in the feed gas in the present photo-DRM reaction system.

Conclusions

A plasmonic Ni photocatalyst supported on Al_2O_3 showed the high activity for the photo-DRM reaction under visible light at a mild temperature of 473 K. The metallic Ni species is essential for the high activity to produce CO and H_2, which supported the LSPR mechanism for the improvement of the catalytic activity. The CO/H_2 ratio in the product gas can be controlled by just changing CO_2/CH_4 ratio in the feed gas mixture.

Conflicts of interest

There are no conflicts to declare.

Acknowledgement

The present project is supported by CREST, JST (JPMJCR1541). This work was performed under the approval of the Photon Factory Program Advisory Committee (Proposal No. 2016G643 and 2018G625).

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Table of Content

CO_2 reforming with CH_4 proceeded at low temperature (473 K) to form syngas over plasmonic Ni catalysts under visible light