Development of a novel catalytic reaction system consisting of dry reforming and carbon capture parts

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Abstract: The objective of this study was to develop the combined system of a continuous production of synthesis gas by a Ni/Al_2O_3 structured catalyst through dry reforming of methane (DRM part) and a carbon capture at the downstream of the catalyst (carbon capture part). The Ni/Al_2O_3 structured catalyst showed a stable performance for DRM reaction, and the solid carbon was captured at the downstream of the catalyst at the same time. The CO_2/CH_4 ratio and the capture temperature affected the amount of the deposited carbon. Especially, the largest amount of carbon was obtained at 650°C under $CO_2/CH_4=1.2$ condition, where the synthesis gas was stably produced by the catalyst.

Keywords: Dry reforming of methane, Carbon capture, Structured catalyst.

1. Introduction

The dry reforming of methane (DRM, *Eq.* (1)) is a useful reaction that converts greenhouse gases of CH_4 and CO_2, into a synthesis gas with a low H_2/CO ratio. We have already developed the Ni/Al_2O_3

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H^0_{298.15} = 247.6\ \mathrm{kJ \cdot mol^{-1}} \qquad (1)$$

structured catalyst for the DRM in the previous study[1]. The structured catalyst could efficiently transfer the external heat energy to the catalytic reaction field, which produced a synthesis gas stably for DRM reaction. In order to further improve the DRM system, we installed a stainless-steel tube at the downstream of the structured catalyst for capturing a solid carbon by CO disproportionation ($2CO \rightarrow C + CO_2$) and/or methane decomposition ($CH_4 \rightarrow C + 2H_2$). This novel DRM system was consisted with a continuous production of synthesis gas by the Ni/Al_2O_3 structured catalyst (DRM part) and a carbon capture at the downstream of the structured catalyst (carbon capture part). These reaction parts were divided into each reactor, where the reaction temperature could be controlled at each part.

In this study, we evaluated the novel system in terms of the production amount of a synthesis gas and the carbon capture. Additionally, the effect of the capturing temperature was investigated.

2. Experimental

A stainless-steel substrate was fabricated to be a shape of the star (outside diameter 20 mm, length 60 mm, surface area 158.4 cm^2). The Ni/Al_2O_3 structured catalyst was prepared on the star-shaped stainless substrate by a sol-gel method and electroless plating, as mentioned in the previous study[1,2]. A hollow stainless-steel tube (20 mmφ × 50 mm length) was used for capturing a solid carbon. Before installing into the reactor, the stainless-steel tube was activated with HCl *aq*. and washed with distilled water.

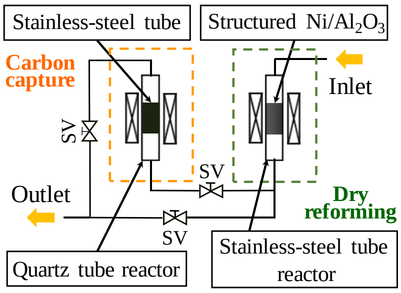

Fig. 1 A simple diagram of reaction apparatus.

A schematic diagram of the reaction system is shown in Fig.1. In order to control temperatures of DRM and carbon capture, the reactor was divided into each part. After hydrogen reduction treatment at 600°C for 2 h, the raw material gases were supplied to the reactor. Reaction conditions were as follows: the flow rate of methane was 3.0 $\mathrm{mmol \cdot min^{-1}}$; the feed ratio of CO_2/CH_4 was 1.2; the partial pressure of the raw material gas was 0.8 atm as balanced by N_2; the reforming temp. was 700°C; and capturing temp. was from 550 to 700°C. During initial one hour (0-1 h), the feed gases

$$\text{Carbon capture ratio [\%]} = \frac{\text{Captured carbon [mol]}}{F_{(CH_4 + CO_2)}\ \text{[mol/h]} \times 12\ \text{[h]}} \times 100 \quad (2)$$

was fed to only the DRM part to check the catalytic performance of the Ni/Al_2O_3 structured catalyst. After one hour passed (1-13 h), the reformed gas obtained through the DRM part was fed to the carbon capture part. The effluent gases were analyzed by GC-TCD. The carbon captured rate was calculated using Eq. (2).

3. Results and discussion

Figures 2(a)-(c) show CO_2 and CH_4 conversions at various capturing temperature, where the DRM reaction was performed at the fixed 700°C. During the initial one hour, these conversions were stable. After one hour passed, suppling the reformed gas to the carbon capture part, CO_2 conversion was decreased at early stage. Such decline of CO_2 conversion was depended on the temperature. Especially, the CO_2 conversion at 650°C dropped by 4.0%. These phenomena were derived from the carbon deposition phenomena via CO disproportionation ($2CO \rightarrow C + CO_2$). This reaction produced CO_2 with a generation of coke.

Table 1 shows the carbon captured rate at the capturing part and I_D/I_G ratio of the captured carbon (where I_D is intensity of the defect- and disorder-band, I_G is intensity of the graphite-band). The carbon captured rate was increased by increasing temperature from 550 to 650°C. However, further increasing temperature, the carbon captured rate was decreased. At higher temperature, the disproportionation, which is an exothermic reaction ($\Delta H^0_{298.15}$ = -172.0 kJ·mol^{-1}), is limited in the viewpoint of thermodynamics. Therefore, the optimum temperature (= 650°C) was considered to be observed. As for the I_D/I_G ratio of the captured carbon, the I_D/I_G ratio was decreased with an increase of the capturing temperature. The result meant that the crystallinity of the captured carbon was improved. Takenaka *et al.*[3] reported that fish-bone type fibers were formed at lower temperature (500°C), while multiwalled carbon nanotubes were formed at higher temperature (700°C). As for fish-bone type fibers, the edges of graphene layers are exposed at the surface of the wall. The presence of edges in the graphene layer would lead to a large D-band peak relative to that of the G band. Hence, the change of the carbon structure might affect the I_D/I_G ratio of the captured carbon. Based on these results, the proposed DRM system has a potential for the stable production of synthesis gas with the carbon capture at the downstream of the structured catalyst.

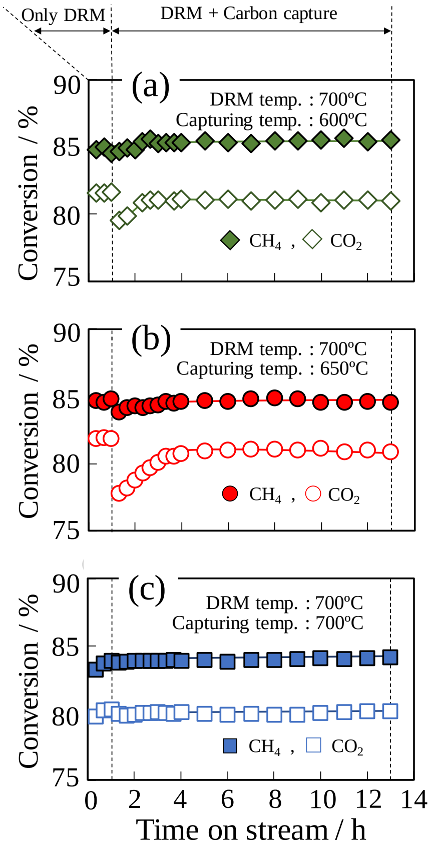

Fig. 2 CH_4 and CO_2 conversions at various capturing temperature.

Table 1 Carbon captured rate and I_D/I_G ratio of carbon in carbon capture part.

Temperature / °C	Carbon captured rate / %	I_D/I_G
550	0.04	-
600	0.32	1.84
650	1.39	1.10
700	0.89	0.72

4. Conclusions

We proposed the novel DRM system with a stable production of synthesis gas by Ni/Al_2O_3 structured catalyst and carbon capture at the downstream of the structured catalyst. The captured carbon was confirmed on stainless-steel in the capture part. The largest captured rate is obtained at 650°C among 550-700°C. The crystallinity of the captured carbon was improved with increased in the capturing temperature.

References

1. C. Fukuhara, R. Hyodo, K. Yamamoto, K. Masuda, R. Watanabe, *Appl. Catal. A: Gen.*, 468 (2013) 18-25.
2. W. Kawasaki, H. Kato, R. Sakhon, R. Watanabe, C. Fukuhara, *J. CO_2 Utilization*, 22 (2017) 91-96.
3. S. Takenaka, S. Kobayashii, H. Ogihara, K. Otsuka, *J. Catal.*, 217 (2003) 79-87.