



Original research article

Development of a novel synthesis-gas production system combining with carbon capture

Wataru Kawasaki^a, Hidenori Kato^a, Ratchahat Sakhon^b, Ryo Watanabe^a, Choji Fukuhara^{a,*}^a Department of Applied Chemistry and Biochemical Engineering, Graduate School of Engineering, Shizuoka University, 3-5-1 Johoku, Naka-ku, Hamamatsu, Shizuoka 432-8561, Japan^b Amano Institute of Technology, 7955-98 Hosoe-cho Kiga, Kita-ku, Hamamatsu, Shizuoka 431-1305, Japan

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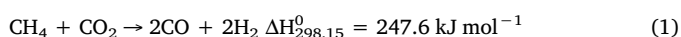
Dry reforming of methane
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ABSTRACT

The dry reforming of methane (DRM) is an important reaction process for producing useful synthesis gas from greenhouse gases such as CO₂ and CH₄. The objective of this study was to develop a combined system that continuously produced of synthesis gas (via dry reforming) and captured post-reformer carbon solids (via carbon capture). The relationship between the DRM reaction condition and the carbon deposition phenomena at the capture stage was investigated. The Ni/Al₂O₃ structured catalyst showed high DRM activity and stability under the conditions of CO₂/CH₄ ≥ 1.2 at 700 °C, whereas the most effective conditions for carbon capture occurred at 520–650 °C when the ratio of CO₂/CH₄ = 1.0. The carbon morphology (e.g., carbon nanotubes and nanofibers) also changed as a function of the capturing temperature. This constructed system would be a novel technology for the effective utilization of CO₂ and CH₄.

1. Introduction

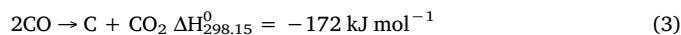
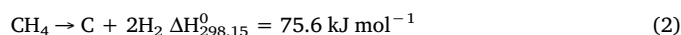
Greenhouse gases are considered a principal factor in the current rise in average global temperatures. Among these gases, CO₂ is a dominant contributor to the greenhouse effect. Recently, the dry reforming of methane (DRM, Eq. (1)) has been identified as an approach for reducing CO₂ emissions. The DRM



process converts the greenhouse gases, CH₄ and CO₂, into synthesis gas with a low hydrogen to carbon-monoxide (H₂/CO) ratio. This reaction has played a key role in the generation of the gaseous raw materials for many industrial syntheses, including the Fischer-Tropsch and alcohol synthesis process [1–3]. However, the DRM process, suffers the serious problem of a carbon deposition on the catalyst, which leads to catalyst deactivation.

The widely studied DRM catalysts recently reviewed by Muraza and Galaima [4], as well as Usman, et al. [5]. Most catalysts consist precious metals or nickel supported on alumina substrate [6–8]. In addition, promoters such as K, CaO, B, and ZrO₂ has been used to improve tolerance to carbon deposition [9–12]. In a previous study, Ni particles of a Ni-type catalyst prepared by an electroless plating were smaller size

and well-dispersed, compared with that of a Ni-type catalyst prepared by a conventional impregnation method [13]. We also found that the Ni-type structured catalyst prepared by the electroless plating combined with a sol-gel method showed higher activity and stable performance, stronger tolerance to carbon deposition than a commercial Ni/Al₂O₃ catalyst (METH134) in methane reforming [14,15]. Interestingly, during these DRM studies, we observed the accumulation of carbon on the inner wall of the stainless-steel tubes situated downstream from the reforming catalyst under some conditions. This phenomenon can be explained in thermodynamic terms using a carbon limit diagram, as shown in Fig. 1 [16]. In this diagram, the region of the carbon deposition in which carbon deposition occurs is calculated based on methane decomposition (Eq. (2)) and CO disproportionation (Eq. (3)) reactions. The diagram shows a typical example the carbon limit temperature as a function of O/C and H/C. For example, if both O/C and H/C values lie below the line for each temperature, the risk of carbon deposition is high. Using



the reported data [13], the gas composition after dry-reforming is in the halftone area of the screen as shown in the figure. Thus, carbon

* Corresponding author at: Applied Chemistry and Biochemical Engineering Course, Department of Engineering, Graduate School of Integrated Science and Technology, Shizuoka University, 3-5-1 Johoku Naka-ku Hamamatsu, 432-8561, Japan.

E-mail addresses: kawasaki.wataru.15@shizuoka.ac.jp (W. Kawasaki), watakawa18@gmail.com (H. Kato), sakhon_chula@hotmail.com (R. Sakhon), twatan@ipc.shizuoka.ac.jp (R. Watanabe), fukuhara.choji@shizuoka.ac.jp (C. Fukuhara).

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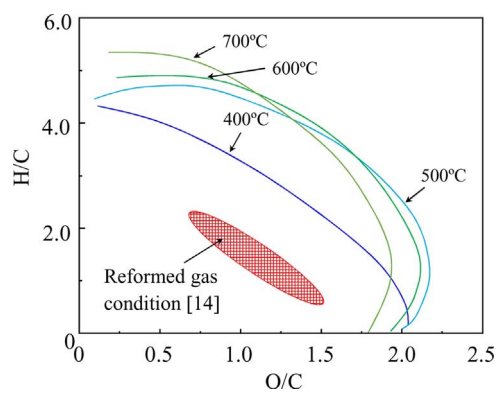


Fig. 1. Carbon limits diagram on nickel catalyst from principle of equilibrated gas.

deposition would occur at each temperature under any CO₂/CH₄ condition. This suggests that capturing the residual carbon as a solid would be possible through the DRM via the carbon deposition phenomenon. Thus, we envisioned a novel system that could not only continuously produce the synthesis gas (via dry reforming), but also capture solid carbon (via carbon capture). Furthermore, an exchangeable cartridge system for carbon capture could be incorporated to avoid the flow-path blockage due to carbon deposition.

In this study, to understand the post-reforming carbon deposition-process, we investigated the effects of the DRM reaction condition change on carbon capture, based on an estimation of the captured carbon rate and observation of the carbon morphology. Furthermore, the potential of the constructed combined dry-reforming/carbon-capture reaction system as a novel CO₂ utilization technology was evaluated.

2. Experimental

2.1. Catalyst preparation

A ferrite-type stainless-steel honeycomb-fin (18 mmφ × 50 mm length, 100 cpsi cell density, 250 cm² apparent surface area, 0.1 mm fin thickness) was used as the metallic honeycomb substrate. After activating with 6 M HCl aq. and washing, the substrate was uniformly coated with an aluminum-triisopropoxide sol [Al[OCH(CH₃)₂]₃: 12 g; HNO₃ aq.: 6 mL; HCHO: 4 mL; H₂O: 80 mL], and subsequently calcined at 800 °C (ramping time: 2.0 h, holding time: 1.0 h) to form a γ-alumina layer on its surface.

The substrate was alternately plated with Pd-Sn at 35 °C to deposit the Pd nuclei, which function as the catalyst in the anodic oxidation of the reducing agent. Thus, the fin substrate was alternately immersed 20 times in the activation liquid (PdCl₂: 1.4 × 10⁻³ mol L⁻¹; HCl aq.: 5.7 × 10⁻³ mol L⁻¹) and sensitization liquid (SnCl₂·2H₂O: 1.1 × 10⁻³ mol L⁻¹; HCl aq.: 5.7 × 10⁻³ mol L⁻¹). The Pd nuclei were reduced with 3 M hydrazine for 15 min. Finally, the substrate was immersed in a nickel plating bath (NiCl₂·6H₂O, 45 g/L; NaBH₄, 0.6 g/L; NaOH, 20 g/L; NH₂CH₂-CH₂NH₂, 60 mL/L) to deposit the nickel component onto its surface. The nickel plating bath included a sodium borohydride as a reducing agent. The plating time was 30 min and the plating temperature was 55 °C. After washing in a water bath, the prepared catalyst was dried in the open air at room temperature. An overview of the prepared honeycomb type catalyst is shown in Fig. 2. The loading of the nickel component is about 22 wt% and the catalyst weight on the substrate is 0.25 g. For carbon capture component, the inner wall surfaces of hollow stainless-steel tubes (Fe-20Cr-5Al, 20 mmφ × 50 mm length as shown in Fig. 2(b)) were activated with the 6 M HCl and then washed with distilled water.

2.2. Reaction and characterization

DRM over the prepared catalyst was conducted at atmospheric pressure using a conventional flow reactor, with three hollow stainless-steel tubes for carbon capture situated after the reforming catalyst, as shown in Fig. 3. These tubes were denoted as Nos. 1, 2, and 3 positions in order from the end of the reforming stage. Before the reaction, the reforming catalyst was reduced under hydrogen atmosphere at 40 ml min⁻¹ and 600 °C. Then, the raw material gases were fed into the reactor for 24 h. The reaction conditions were as follows: the flow rate of methane, 3.0 × 10⁻³ mol/min; carbon dioxide to methane ratio (CO₂/CH₄) in the raw material, 0.5–2.0; partial pressure of the raw material, 0.8 atm (nitrogen balance); and reforming temperature, 600–800 °C. In the case of reforming at 700 °C, the temperature ranges on the carbon-capturing stainless-steel tubes were as follows: No. 1, 650–700 °C; No. 2, 520–650 °C; No. 3, 360–520 °C. The methane conversion over the structured catalyst was calculated using Eq. (4), and the captured carbon rate was calculated using Eq. (5). The effluent gas from the reactor was analyzed by gas chromatography using a thermal conductivity detection (TCD, GC-8A; Shimadzu Corp.).

$$\text{CH}_4 \text{ conversion} [\%] = \left(1 - \frac{\text{molar ratio of CH}_4 \text{ at outlet}}{\text{molar ratio of CH}_4 \text{ at inlet}} \right) \times 100 \quad (4)$$

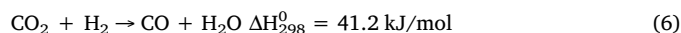
$$\text{Carbon capture rate} [\%] = \frac{\text{Captured carbon} [\text{mol}]}{F_{\text{CH}_4 + \text{CO}_2} [\text{mol/h}] \times 24 [\text{h}]} \times 100 \quad (5)$$

The captured carbon deposits were observed via field-emission scanning electron microscopy (FE-SEM, JSM-7001F; JEOL Ltd.), transmission electron microscopy (TEM, JEM-2100F; JEOL Ltd.), and scanning transmission electron microscopy-energy dispersive X-ray spectroscopy (STEM-EDX, JEM-2100F; JEOL Ltd.) analyses. The crystallinity and quality of the carbon were measured by Raman spectroscopy (inVia Raman microscope; Renishaw plc).

3. Results and discussion

3.1. Catalytic performance of the Ni/Al₂O₃ structured catalyst for DRM

Table 1 shows the catalytic performance of the Ni/Al₂O₃ structured catalyst for the DRM at 30 min passed at 600–800 °C and CO₂/CH₄ = 1.0. The catalyst weight on the substrate per flow rate (W/F) was 0.7 g h mol⁻¹. The equilibrium conversion and H₂/CO ratio were calculated in consideration of the DRM (Eq. (1)) and reverse water-gas shift reaction (Eq. (6)). Table 1 shows the methane conversion improves



and approaches equilibrium with increases in the reaction temperature. Indeed, at 800 °C, equilibrium conversion is achieved. In terms of product selectivity, H₂ selectivity decreases at lower temperature. In addition, the H₂/CO ratio is close to equilibrium at each reaction temperature. These results suggest that both the DRM and reverse water-gas shift reactions efficiently proceed on the Ni/Al₂O₃ structured catalyst.

Fig. 4 shows the durability performance tests for the Ni/Al₂O₃ structured catalyst with various CO₂/CH₄ ratios. Table 2 indicates the amount of carbon deposited on the Ni/Al₂O₃ structured catalyst after 24 h. The reaction temperature and CO₂/CH₄ ratio were set at 700 °C and 0.5–2.0, respectively. From Fig. 4, the initial conversion improves with an increasing CO₂/CH₄ ratio, as has also been observed with other catalysts [17]. At CO₂/CH₄ = 0.5 and 0.8, the reforming conversion is gradually deactivated with time. In addition, the H₂/CO ratio at CO₂/CH₄ ≤ 0.8 (especially CO₂/CH₄ = 0.5) is higher than that at CO₂/CH₄ ≥ 1.0. These trends are caused by methane decomposition (Eq. (2)) driven by the methane-rich conditions. In fact, the amount of the deposited carbon on the Ni/Al₂O₃ structured catalyst increases with

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