Innovative CO_2 recycling system with powerful performance for converting GHG: Multi-stage structured catalyst system for methanation, dry reforming and carbon-capture

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Significance and Relevance

The multi-stage catalyst reaction system was established for post-treating the greenhouse gas (GHG), which consists of three reaction stages: a CO_2 methanation zone in the first stage, a CH_4 dry reforming (DRM) zone in the second stage, and a solid carbon capture zone in the third stage (a multi-stage system). All stages have a structured reaction system equipped with effective heat and mass transfers abilities (especially, a spiral-type catalyst system), indicating powerful and stable performances even under some mass processing conditions. The constructed system can efficiently convert GHG into some valuable materials such as methane, synthesis gas and solid carbon, contributing to carbon-neutral technology. From a thermodynamic evaluation using exergy, the usefulness of the constructed system was confirmed.

Introduction and Motivations

In order to achieve a carbon-neutral society, there is currently active research focused on developing catalysts and reaction systems that aid in reducing GHG (CO_2, CH_4). This research aims to introduce a novel approach to both reducing and effectively utilizing CO_2. Specifically, the primary goal of this study is to focus on the post-treatment of CO_2 emissions from some industrial processes and establish a comprehensive catalytic system for CO_2 utilization. The established catalytic system consists of three stages: a CO_2 methanation zone in the first stage[1], a CH_4 dry reforming (DRM) zone in the second stage, and a solid carbon capturing zone in the third stage [2,3]. The assessment of the system's characteristics showed that, even at a high flow rate of 2.0 L/min, the system consistently produced synthesis gas (H_2+CO) and efficiently recovered more than 56% of the CO_2 in the form of solid carbon. Furthermore, it was confirmed that the system operates more effectively when the hydrogen content is kept below (H_2/CO_2=2.0-3.0) the stoichiometric ratio of methanation. This modification significantly improves the performance of the DRM and the rate of carbon capturing. Moreover, a thermodynamic assessment of this system suggests that reducing the supplied amount of hydrogen has a beneficial effect on the system's exergy efficiency.

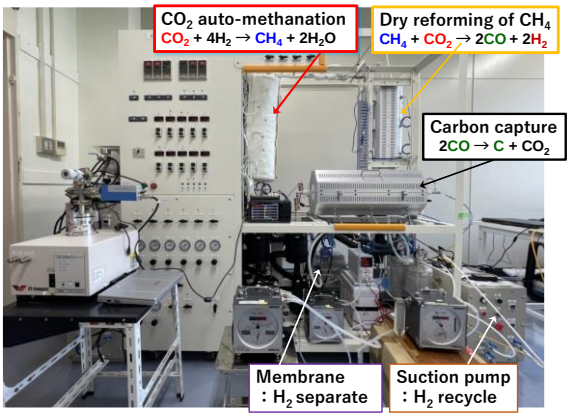

Figure 1 Multi-stage reaction system for converting GHG into useful materials

Reaction system and Structured catalyst

Figure 1 shows the multi-stage reaction system designed to simultaneously reduce CO_2 and produce synthesis gas and solid carbon. The system consists of three reaction parts (first stage: methanation, second stage: DRM, third stage: carbon capture, in series), utilizing various structured catalysts, as depicted in Figure 2. The catalysts were the spiral-type Ni/CeO_2 and/or Ru/CeO_2 for methanation, the spiral-type Ni/CeO_2-Al_2O_3 for DRM and the wall-type Fe-Co-K

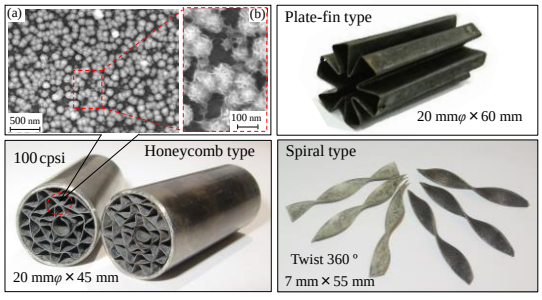

Figure 2 Various structured catalysts used in methanation, DRM and carbon capture

catalyst for carbon capture. All catalysts were prepared on both aluminum substrate and stainless-steel substrate, using the wash-coating and/or the electroless plating. The feeding gas condition was as follows: CO_2 : H_2 : O_2 : N_2 = 20 : 56 : 3 : 21 vol%, with a feeding rate ranging from 1.0 to 10.0 L/min. After reducing each catalyst, reaction was carried out at 25 °C (room temperature) for methanation, 700 °C for DRM, 470 °C for carbon capture.

Results and Discussion

Figure 3 displays typical results from the constructed multi-stage system operating at a feeding gas rate of 2 L/min, highlighting its impressive capability to convert GHG into valuable materials. The CO_2 conversion in methanation zone was approximately 75 % without external heating (at room temp.), and CH_4 was selectively produced with 98% or more. In DRM zone, both CO_2 and CH_4 conversions were 70 % or more, and synthesis gas was produced with H_2/CO= 2.0, which is suitable for the Fischer-Tropsch process. In addition, carbon capture rate was 56 %. From TEM and SEM observations, the captured carbon takes on some fibrous shape with nanotube structures, offering the potential for utilization as functional materials.

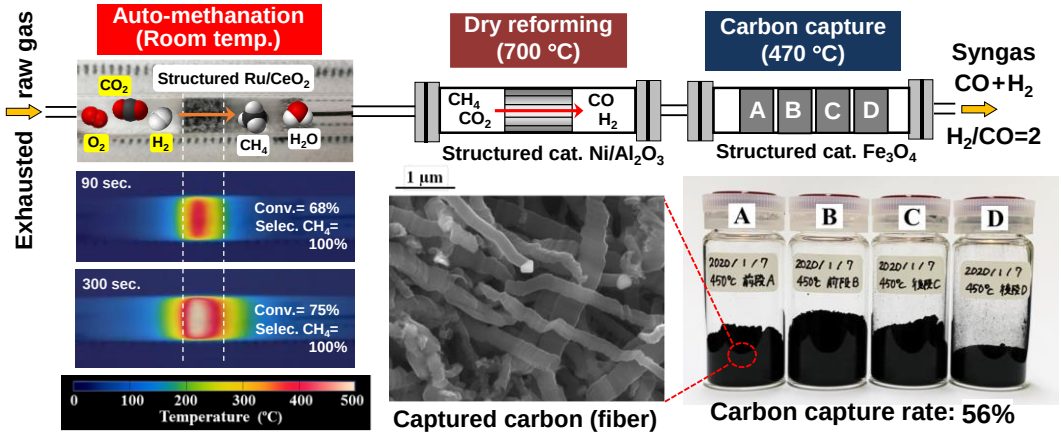

Figure 3 High performance of constructed system for producing syngas and solid carbon from GHG

Figure 4 represents a thermodynamic evaluation of the constructed system using exergy as an index. Methanation process consumes a large amount of hydrogen (H_2/CO_2=2.0-3.0), thereby the system diminished the exergy efficiency. However, by integrating dry reforming and solid carbon capturing processes, such disadvantage of the system was progressively recovered, resulting in the thermodynamic advantage. The system's effectiveness is clearly evident.

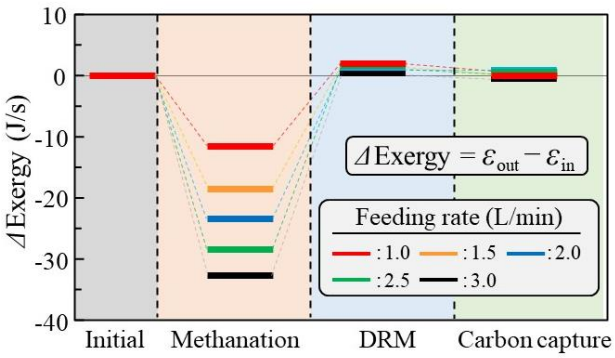

Figure 4 Exergy merit of the multi-stage system

References

1. C. Fukuhara, A. Kamiyama, M. Itoh, N. Hirata, S. Ratchahat, M. Sudoh, R. Watanabe, Chemical Engineering Science, **2020**, *219*, 115589.
2. W. Kawasaki, R. Watanabe, C. Fukuhara, Journal of CO_2 utilization, **2017**, *22*, 91-96.
3. C. Fukuhara, Y. Matsui, M. Tanebayashi, R. Watanabe, Chemical Engineering Journal Advances, **2021**, *5*, 100057.

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