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Continuous CO₂ capture and reduction to CO by circulating transition-metal-free dual-function material in fluidized-bed reactors

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ABSTRACT

To mitigate global warming and achieve a sustainable society, innovative technologies for efficient CO₂ utilization are required. Integrated CO₂ capture and reduction (CCR) using dual-function materials (DFMs) is favorable owing to its potentially low energy consumption, capital investment, and processing costs. Although numerous studies have focused on catalytic science, continuous and steady-state CCR operations have not been sufficiently addressed from an engineering perspective. In this study, a circulating fluidized bed (CFB) system is investigated for continuous CCR to syngas (CO + H₂). In the CFB system, transition-metal-free DFM (Na/Al₂O₃) particles are circulated between two bubbling fluidized-bed reactors. The DFM captures CO₂ in one reactor (CO₂ capture reactor) and reduces the captured CO₂ to CO by the reaction with H₂ in the other reactor (H₂ reactor). The effluent gas concentrations from both reactors reach steady state and are maintained for over 8 h. For the product gas from the H₂ reactor, the CO₂ conversion and CO selectivity exceed 80 % and 99 %, respectively. However, the H₂ conversion is <20 %, indicating a potential challenge for the CFB system for integrated CCR. Furthermore, this study confirms that the H₂/CO ratio for syngas can be controlled by adjusting the experimental conditions (particularly, the H₂ flow rate). Consequently, the CFB system can be modified to facilitate the interaction between H₂ gas and the DFM particles.

1. Introduction

The Intergovernmental Panel on Climate Change (IPCC), in its sixth report, concluded that anthropogenic emissions of greenhouse gases (GHGs) have unequivocally caused global warming [1]. Global net emissions of the primary GHG, carbon dioxide, have continually increased and reached 59 GtCO₂-eq in 2019; more than 60 % of the CO₂ emissions were found to originate from fossil fuels and industry [2]. The development of innovative technologies for carbon dioxide capture, utilization, and storage (CCUS) is essential for controlling global warming and achieving a sustainable society. CCUS technologies generally require a series of operations such as CO₂ capture, desorption, purification, compression, and transportation before CO₂ utilization, including conversion or storage [3–8]. The utilization of CO₂ is preferable to its storage from the perspective of exploiting CO₂ as a carbon source to produce fuels and value-added chemicals.

Recently, various studies have been conducted to investigate the viability of integrated CO₂ capture and utilization (ICCU) or CO₂ capture and reduction (CCR), wherein CO₂ is captured by an adsorbent and directly converted into the desired product without being desorbed. The advantage of CCR is that the operations between CO₂ capture and utilization are eliminated; thus, energy consumption and costs for capital investment and processing can be substantially reduced. Techniques for CO₂ capture using amine solutions have been combined with thermocatalytic [9–11] and electrocatalytic [12,13] CO₂ conversion. Although such gas–liquid absorption techniques are industrially established for CO₂ capture, amine solutions are typically unstable under heating conditions exceeding 100 °C and generate emissions of harmful thermal degradation products [14–16]. This limits the scope of CO₂ conversion reactions to those with sufficient reaction rates at extremely low temperatures. In contrast, the integration of CO₂ conversion with CO₂ capture using solid adsorbents is feasible at higher temperatures.

Abbreviations: CCR, CO₂ capture and reduction; CCUS, carbon dioxide capture, utilization and storage; CFB, circulating fluidized bed; DFM, dual-function material; DRM, dry reforming of methane; GHG, greenhouse gas; RWGS, reverse water gas shift.

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Consequently, a greater variety of CO₂ conversion reactions, such as methanation, reverse water gas shift (RWGS), and dry reforming of methane (DRM), can be considered.

Dual-function materials (DFMs) which serve as both solid CO₂ sorbents and catalysts for CO₂ conversion have been proposed by pioneer research groups [17,18] and investigated by several researchers thus far. Alkali or alkaline earth metals including Na [19,20], K [21,22], and Ca [23,24] are typically employed as CO₂ sorbents in DFMs. Generally, Ca requires higher regeneration temperatures (>600 °C) to demonstrate its excellent capacity for CO₂ capture, whereas Na and K can be used at lower temperatures with less capacity [25]. Transition metals such as Ni [26–29], Ru [30,31], and Cu [21,22] are used in DFMs as catalysts to convert the captured CO₂ via the desired reaction. Ni is one of the most frequently used catalysts in DFMs because of its relatively low cost and versatile activity in catalyzing methanation, RWGS, and DRM, which are interchangeable depending on the reaction temperature [32,33]. We have previously reported CCR to CH₄ using Ni-based DFMs promoted with Na, K, and Ca [26]. Among the studied DFMs, Na/Ni/Al₂O₃ showed the highest CO₂ conversion exceeding 96 % and CH₄ selectivity exceeding 93 % at 450 °C and 0.1 MPa. By pressurizing from 0.1 to 0.9 MPa, the CH₄ production capacity was enhanced from 111 to 160 mmol/g with a model CO₂ source (400 ppm) to imitate direct air capture. Recently, we have further demonstrated that even transition-metal-free DFMs have remarkable activity against CCR to CO [20]. Na/Al₂O₃ exhibited excellent performance to achieve a CO₂ conversion exceeding 90 % and CO selectivity exceeding 95 % at 450–500 °C and 0.1 MPa. In addition, it showed the potential to produce syngas-like mixture with an H₂/CO molar ratio of 2–3 from atmospheric-level CO₂ (400 ppm). The absence of transition metals could be advantageous in terms of low material cost and environment-friendliness.

Owing to the early stages of technological development, most studies have primarily focused on catalytic science by developing novel DFMs. However, the engineering aspects of CCR have not been sufficiently emphasized. Studies on DFMs generally involve a fixed-bed reactor and intermittent alternating operations for CO₂ capture and reduction. Although material development is crucial, the development of novel CCR processes that enable continuous and steady-state operations is essential for industrialization. Continuous operations for CCR to CH₄ [34] and CO [35] have been demonstrated at the lab scale using two isothermal fixed-bed reactors packed with DFMs in parallel. This method enables an apparent steady-state capture and conversion by alternating the feed gases to each reactor. Another approach, namely, a circulating fluidized bed (CFB) system, was employed in our previous study for CCR to CH₄ [36] using approximately 1 kg of the Na/Ni/Al₂O₃ DFM. In the CFB system, DFM particles were continuously circulated between two fluidized-bed reactors instead of exchanging the feed gases. The advantage of this CFB system is that the temperature in each reactor can be controlled separately, and an actual steady state in terms of gas feed, effluent flow, and concentration, can be achieved.

In this study, the concept of continuous CCR to syngas (CO + H₂) is demonstrated by combining our knowledge of transition-metal-free Na/Al₂O₃ DFM [20] and the CFB system [36]. The obtained results are compared with previous results for CCR to CH₄ using a Na/Ni/Al₂O₃ DFM to determine the bottleneck that reduces the overall efficiency. Accordingly, the effects of the operating conditions are investigated to elucidate the characteristics of the CFB system and to maximize its performance for continuous CCR.

2. Materials and methods

2.1. Preparation and characterization of DFM

γ -Al₂O₃ (Neobead MSC#300, Mizusawa Industrial Chemicals, Ltd.) was used as a support for the DFM, and Na₂CO₃ (guaranteed reagent, Fujifilm Wako Pure Chemical Corp.) was used as the precursor. The transition-metal-free Na/Al₂O₃ DFM was prepared by the wet

impregnation of an aqueous solution of Na₂CO₃ on γ -Al₂O₃. The impregnated samples were dried at 110 °C for 12 h and subsequently calcined in air at 550 °C for 4 h. The alkali-metal loading was set to 16 wt % in the carbonate form. The textural properties and crystalline structures of the prepared DFM was characterized by N₂ adsorption–desorption and powder X-ray diffraction (XRD) analyses, similar to our previously reported process [20]. In addition, the minimum fluidization velocity of the sample was experimentally determined from the relationship between the pressure drop in the DFM bed and the gas velocity, as described in the [Supplementary Material](#).

2.2. Continuous CCR to CO in the CFB system

Fig. 1 shows a schematic of the CFB setup. Approximately 600 g of the prepared Na/Al₂O₃ DFM was loaded into the CFB system and continuously circulated in two bubbling fluidized-bed reactors, i.e., the CO₂ capture reactor and H₂ reactors. The CO₂ capture reactor was maintained at 200–500 °C with external heating, and 2 vol% CO₂/N₂ (flow rate = 8 L/min) was supplied to the bottom of the reactor. The Na sites in the DFM selectively captured CO₂ in this reactor. The flow rate of the CO₂-containing gas was sufficiently high to fluidize the DFM particles in the CO₂ capture reactor and to entrain the DFM particles from the reactor to a cyclone through the riser. The entrained DFM particles and the CO₂-lean gas entered the cyclone, where they were separated. The vented CO₂-lean gas was analyzed using a dual-channel micro gas chromatograph (GC) equipped with thermal conductivity detectors (Agilent 490, Agilent Technologies, Inc.) after water vapor was condensed.

Subsequently, the DFM particles were accumulated in the upper loop seal, preventing the undesired mixing of gases between the two reactors. As N₂ was supplied to the loop seal at a relatively low flow rate of approximately 0.15 L/min, the overflowing DFM particles were continuously entrained to the H₂ reactor. The H₂ reactor was maintained at 500–700 °C with an electric heater, and H₂ was supplied to the bottom of the reactor at a flow rate of 0.4–2.0 L/min. In this reactor, the DFM

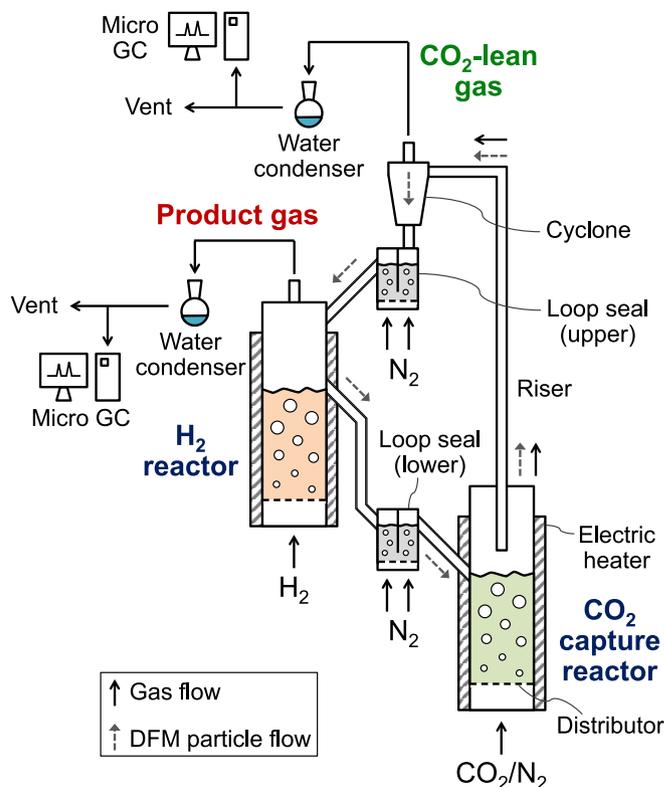


Fig. 1. Schematic of the circulating fluidized bed (CFB) system with Na/Al₂O₃ dual-function material (DFM).

particles were regenerated by releasing the captured carbon, primarily as CO. Subsequently, the DFM particles returned to the CO₂ capture reactor through the lower loop seal. The product gas was vented from the top of the H₂ reactor and analyzed using a micro-GC after water vapor was condensed.

For quantitative analysis, the data obtained from the CO₂ capture reactor was used to calculate the CO₂ capture efficiency (η_{CO_2}) as follows:

$$\eta_{\text{CO}_2} = \left(1 - \frac{C_{\text{CO}_2-\text{R}_{\text{CO}_2,\text{out}}}}{C_{\text{CO}_2-\text{R}_{\text{CO}_2,\text{in}}}}\right) \times 100 \quad (1)$$

where $C_{\text{CO}_2-\text{R}_{\text{CO}_2,\text{in}}}$ and $C_{\text{CO}_2-\text{R}_{\text{CO}_2,\text{out}}}$ represent the CO₂ concentrations in the feed gas stream and the CO₂-lean gas exiting the CO₂ capture reactor, respectively. Using the data obtained from the H₂ reactor, the CO₂ conversion (X_{CO_2}), selectivity for CO or CH₄ (S_{CO} , S_{CH_4}), and H₂ conversion (X_{H_2}) were calculated as follows:

$$X_{\text{CO}_2} = \left(1 - \frac{C_{\text{CO}_2-\text{R}_{\text{H}_2,\text{out}}}}{C_{\text{CO}_2-\text{R}_{\text{H}_2,\text{out}}} + C_{\text{CO}-\text{R}_{\text{H}_2,\text{out}}} + C_{\text{CH}_4-\text{R}_{\text{H}_2,\text{out}}}}\right) \times 100 \quad (2)$$

$$S_{\text{CO}} = \frac{C_{\text{CO}-\text{R}_{\text{H}_2,\text{out}}}}{C_{\text{CO}-\text{R}_{\text{H}_2,\text{out}}} + C_{\text{CH}_4-\text{R}_{\text{H}_2,\text{out}}}} \times 100 \quad (3)$$

$$S_{\text{CH}_4} = \frac{C_{\text{CH}_4-\text{R}_{\text{H}_2,\text{out}}}}{C_{\text{CO}-\text{R}_{\text{H}_2,\text{out}}} + C_{\text{CH}_4-\text{R}_{\text{H}_2,\text{out}}}} \times 100 = 100 - S_{\text{CO}} \quad (4)$$

$$X_{\text{H}_2} = \left(1 - \frac{C_{\text{H}_2-\text{R}_{\text{H}_2,\text{out}}}}{C_{\text{H}_2-\text{R}_{\text{H}_2,\text{out}}} + C_{\text{CO}-\text{R}_{\text{H}_2,\text{out}}} + 4C_{\text{CH}_4-\text{R}_{\text{H}_2,\text{out}}}}\right) \times 100 \quad (5)$$

where $C_{i-\text{R}_{\text{H}_2,\text{out}}}$ represents the concentration of i ($i = \text{CO}_2$, CO, CH₄, or H₂) in the product gas exiting the H₂ reactor.

3. Results and discussion

3.1. Characterization of DFM

The characteristics of the prepared DFM are briefly described in this section. Further details are provided in the [Supplementary Material](#). N₂ adsorption–desorption analysis revealed that Na impregnation did not markedly damage the porous structure of the alumina support ([Table S1](#)). In the XRD analysis, the distinct diffraction peaks of $\gamma\text{-Al}_2\text{O}_3$ and extremely small peaks of Na₂CO₃ were detected ([Fig. S1](#)), indicating that the Na sites were well dispersed on the alumina support. As presented in [Fig. S2](#) and [Table S2](#), the relationship between the pressure drop in the DFM bed and the gas velocity was used to determine the minimum fluidization velocities, which were found to be 1.2, 1.1, and 0.99 cm/s at 300, 400, and 500 °C, respectively. Considering the inner diameters of the reactors (approximately 3.8 cm), the minimum fluidization velocities were converted to 0.82, 0.76, and 0.68 L/min at 300, 400, and 500 °C, respectively.

3.2. Demonstration of continuous CCR to CO in the CFB system

The experimental results of continuous CCR in the CFB system using the transition-metal-free Na/Al₂O₃ DFM are presented in [Fig. 2](#). Here, the CO₂ capture reactor was maintained at 400 °C, the temperature and H₂ feed flow rate in the H₂ reactor were set to 500 °C and 0.8 L/min, respectively. [Fig. 2\(a\)](#) shows the concentration profile of the CO₂-lean gas exiting the CO₂ capture reactor. Immediately after the CO₂-containing gas was supplied to the CO₂ capture reactor, the CO₂ concentration gradually increased and remained constant for over 8 h. The dashed line in the figure indicates the feed CO₂ concentration. This indicates that approximately half of the fed CO₂ was continuously captured in the DFM. One or more carbonation reactions listed below

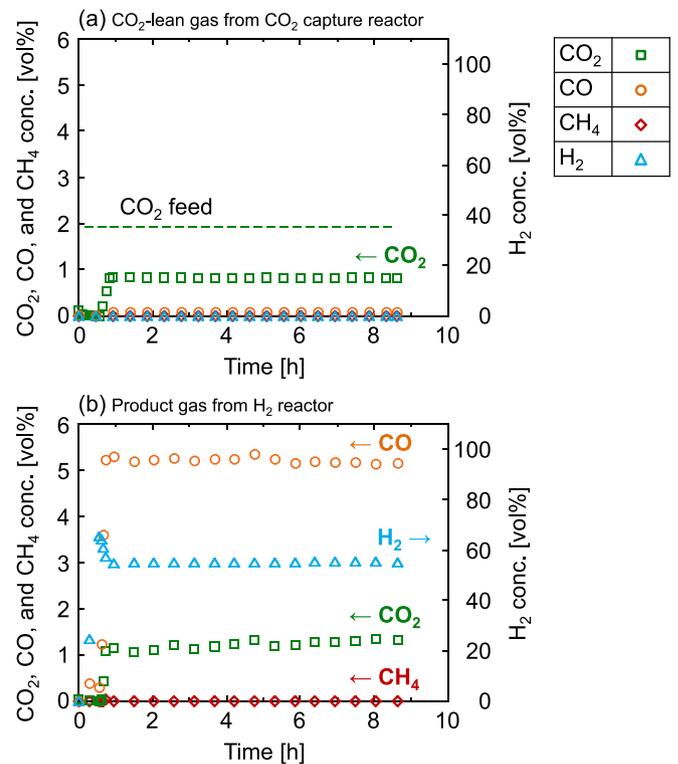
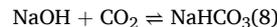
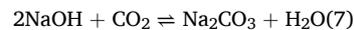
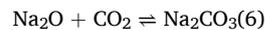


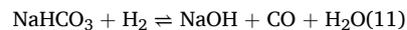
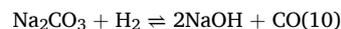
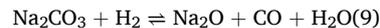
Fig. 2. Concentration profiles of (a) CO₂-lean gas exhausted from the CO₂ capture reactor at 400 °C and 8 L/min flow of 2 vol% CO₂/N₂ and (b) product gas exhausted from the H₂ reactor at 500 °C and 0.8 L/min flow of 100 % H₂.

are considered to contribute to the CO₂ capture.



In addition, H₂ was not detected in the CO₂ capture reactor despite the continuous H₂ supply to the H₂ reactor, indicating that the loop seals successfully prevented the undesired mixing of gases between the two reactors.

[Fig. 2\(b\)](#) shows the concentration profile of the product gas exiting the H₂ reactor. The CO concentration plateaued above 5 vol% and was maintained for approximately 8 h. The captured CO₂ in the DFM was reduced to CO via the following RWGS-like reactions.



The formation of CH₄ was almost negligible, and the captured CO₂ was selectively reduced to CO. However, more than 1 vol% of CO₂ was detected, indicating that a fraction of the captured CO₂ was released from the DFM without being converted into CO. The molar ratio of unreacted H₂ to the produced CO is an important factor in the direct utilization of the product gas as syngas. Although the practically feasible H₂/CO ratio for Fischer–Tropsch or methanol syntheses is 2–3, the steady-state value was approximately 11 in the present study. The inclusion of CO₂ in CO + H₂ syngas can be beneficial, as considered in industrial syngas-to-methanol processes. However, for brevity and better process controllability, the discussion in this section focuses on the H₂/CO ratio without CO₂. Methods to improve the H₂/CO ratio are discussed in [Section 3.4](#).

The outputs from both reactors were stable over 8 h, and CCR was

expected to be repeated for more than 100 cycles during this operation, assuming the similar circulation rate of 320 cm³/min (approximately 3 min for one cycle) to our previous result [36]. Herein, one cycle of circulation in the CFB system is represented by the DFM particles passing once through the CO₂ capture reactor and H₂ reactor (Refer to Table S3 for details). The textural properties and crystalline structures of the as-prepared and used DFM samples were compared (Table S1 and Fig. S1). No obvious degradation of DFM was observed during its use in the CFB system. Although a considerably longer stability test is necessary, the Na/Al₂O₃ DFM can enable steady-state operation.

3.3. Identifying bottlenecks of CCR in the CFB system

To identify possible bottlenecks of CCR to CO in the CFB system, the abovementioned experimental results are further discussed in comparison with our previous results [36] obtained for CCR to CH₄ by circulating the Na/Ni/Al₂O₃ DFM in an identical setup. The previous results for similar experimental conditions are shown in Fig. S3. Based on the concentration profiles of the two DFMs, the CO₂ capture efficiency (η_{CO_2}) in the CO₂ capture reactor and the CO₂ conversion (X_{CO_2}), selectivity to CO or CH₄ (S_{CO} , S_{CH_4}), and H₂ conversion (X_{H_2}) were calculated and compared (Table 1). The Na/Ni/Al₂O₃ DFM captured more than 85 % of CO₂ from the feed stream (2 vol% CO₂/N₂) in the CO₂ capture reactor, whereas the Na/Al₂O₃ DFM captured only 56 %. However, in previously reported experiments using a typical fixed-bed reactor setup, the Na/Al₂O₃ DFM exhibited a comparable CO₂ capture performance to that of the Na/Ni/Al₂O₃ DFM [20,26]. The reason for this difference is clarified through a further discussion of the H₂ reactor.

In the H₂ reactor, the Na/Al₂O₃ DFMs exhibited an excellent CO selectivity of >99 %, and the formation of CH₄ was negligible. CO₂ conversion was greater than 80 % in the absence of transition metals. The detailed reaction mechanism of the transition-metal-free DFM is currently under investigation and will be reported in the near future. Nevertheless, the CO₂ conversion using Na/Al₂O₃ was lower than that using Na/Ni/Al₂O₃, indicating that additional CO₂ was released from the DFM without being converted into products. The H₂ conversion using Na/Al₂O₃ was only one-tenth of that using Na/Ni/Al₂O₃. Although the nature of the reaction is different (RWGS vs. methanation) and the required H₂ amount differs depending on the amount of captured CO₂, the results indicate that the reaction rate of Na/Al₂O₃ in CO₂ reduction should be lower than that of Na/Ni/Al₂O₃.

In summary, the low reaction rate of Na/Al₂O₃ in CO₂ reduction is considered a bottleneck that limits the overall reaction efficiency of the CFB system. Only a fraction of the captured CO₂ is reduced to form CO in the H₂ reactor, implying that Na/Al₂O₃ is not sufficiently regenerated for the subsequent CO₂ capture. Therefore, the Na/Al₂O₃ particles, which retain CO₂, flow back into the CO₂ reactor, resulting in less CO₂ capture. Nevertheless, because the reaction behaviors in the two fluidized-bed reactors affect each other, this bottleneck should be carefully examined by changing the experimental conditions in both reactors.

Table 1

Comparison of CO₂ capture efficiency (η_{CO_2}), CO₂ conversion (X_{CO_2}), selectivity to CO or CH₄ (S_{CO} , S_{CH_4}), and H₂ conversion (X_{H_2}) with the two DFMs.

DFM	CO ₂ capture reactor η_{CO_2} [%]	H ₂ reactor			
		X_{CO_2} [%]	S_{CO} [%]	S_{CH_4} [%]	X_{H_2} [%]
Na/Al ₂ O ₃	55.7 ± 2.3	82.0 ± 4.9	99.6 ± 0.5	0.4 ± 0.5	8.1 ± 0.6
Na/Ni/Al ₂ O ₃ [36]	>85	>99	<1	>99	>85

3.4. Effect of operating conditions in the H₂ reactor on overall CCR behavior

To overcome the bottleneck and enhance the CCR performance, the effect of the operating conditions in the H₂ reactor on the overall reaction behavior was investigated. Fig. 3 presents the experimental results for different H₂ flow rates and temperatures in the H₂ reactor. The flow rates relative to the minimum fluidization velocity at 500 °C (u/u_{mf}) are shown in the legend. The temperatures shown in the figure represent the values measured in the experiments.

Initially, the effects of the H₂ flow rate were evaluated. Fig. 3(a) shows the increase in the CO₂ capture efficiency with the H₂ flow rate, despite no change in the operating conditions of the CO₂ capture reactor. This suggests that the bottleneck in the H₂ reactor was mitigated by increasing the H₂ flow rate. The increase in the CO₂ capture efficiency was drastic when changing the H₂ flow rate from 0.4 to 0.8 L/min and was stabilized above 0.8 L/min. Similarly, the CO₂ conversion in the H₂ reactor improved when the H₂ flow rate was increased from 0.4 to 0.8 L/min, particularly at lower temperatures, whereas no significant difference was observed between 0.8 and 1.6 L/min (Fig. 3(b)). The increase in CO₂ conversion indicates a decrease in the proportion of unreacted CO₂ in the product gas in the H₂ reactor.

The marked change in performance upon increasing the H₂ flow from 0.4 to 0.8 L/min can be understood in terms of the minimum fluidization velocity, which coincides with this flow rate range (Section 3.1). Particularly, the fixed DFM bed changes to a fluidized bed in this range, resulting in a more efficient interaction and reaction between the flowing H₂ gas and DFM particles retaining CO₂. Consequently, the DFM particles are regenerated by releasing or reacting with the captured CO₂ at an H₂ flow rate of 0.8 L/min. The more effectively regenerated DFM particles return to the CO₂ capture reactor and can capture more CO₂. As shown in Fig. 3(c), particularly above the minimum fluidization velocity, the H₂ conversion at 1.6 L/min was lower than that at 0.8 L/min, indicating that the excess H₂ supply flowed out unreacted. As observed in Fig. 3(d), the H₂/CO ratio at 1.6 L/min was higher than that at 0.8 L/min. The excess H₂ resulted in higher concentrations of the unreacted H₂ and lower concentrations of the produced CO in the product gas. This is the reason for higher H₂/CO ratios with higher H₂ flow rates. On the other hand, the CO selectivity approached 99 % and was unaffected in the investigated H₂ flow rate range.

Subsequently, the effects of reaction temperature in the H₂ reactor were examined. Fig. 3(a)–(c) show that the CO₂ capture efficiency, CO₂ conversion, and H₂ conversion increase with increasing temperature. Higher hydrogenation temperatures favor endothermic CO formation reactions (Eqs. (9)–(11)) in terms of both thermodynamics and kinetics; therefore, these interrelated characteristics improved with increasing temperature. Particularly, the H₂/CO ratio decreased with increasing temperature and approached 6 at 0.8 L/min and the highest temperature in the H₂ reactor. Although the H₂/CO ratio was still as high as that of practical syngas, this experimental result confirmed that the H₂/CO ratio could be controlled depending on the operating conditions. However, the CO selectivity was not affected by the temperature in the H₂ reactor or the H₂ flow rate in the studied range.

Therefore, the CFB system shows better CCR performance at H₂ flow rates that are slightly higher than the minimum fluidization velocity and at higher temperatures. Nonetheless, the originally white DFM particles gradually turned gray as the temperature increased above 600 °C (data not shown). This could be attributed to the deposition of carbon by coking reactions, which may decrease the activity of the DFM. Further investigation is necessary to determine the optimum temperature for balancing the reaction efficiency and durability of the DFM.

3.5. Effect of operating conditions in the CO₂ reactor on overall behavior

Furthermore, the effects of the operating conditions of the CO₂ capture reactor on the overall reaction behavior were investigated.

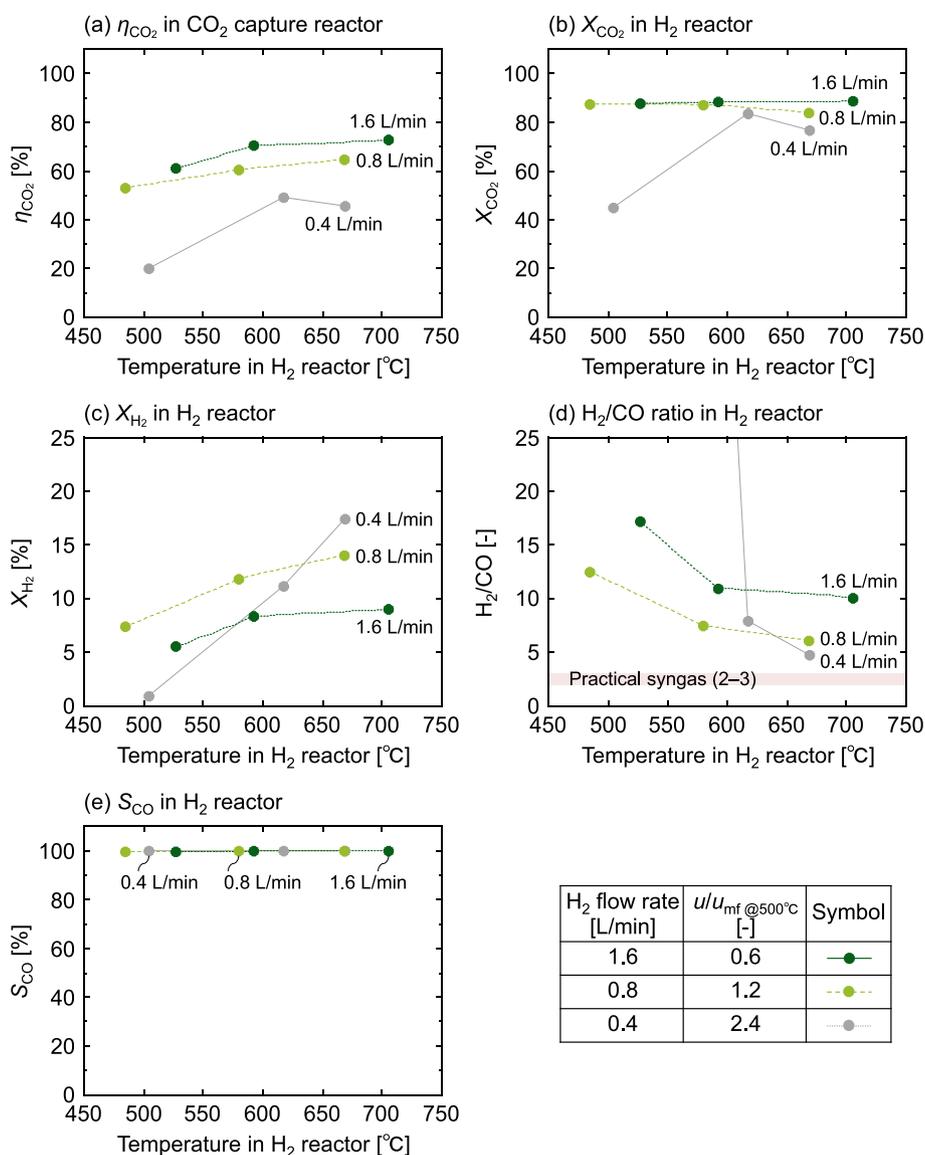


Fig. 3. Effect of H₂ flow rate and temperature in the H₂ reactor on (a) CO₂ capture efficiency in the CO₂ capture reactor and on (b) CO₂ and (c) H₂ conversion, (d) H₂/CO ratio, and (e) selectivity of CO in the H₂ reactor.

Because the feed flow rate to the CO₂ capture reactor is a critical engineering factor that can disrupt the smooth circulation of DFM particles, only the effect of temperature was studied. Fig. 4 depicts the experimental results wherein the H₂ flow rate and temperature in the H₂ reactor were set to 0.8 L/min and 500 °C, respectively, based on the abovementioned discussion. The CO₂ capture efficiency slightly increased upon decreasing the temperature in the CO₂ capture reactor, because exothermic CO₂ capture reactions (Eqs. (6)–(8)) thermodynamically favor lower temperatures.

As the CO₂ capture efficiency increased, additional CO₂ was introduced into the H₂ reactor by the DFM particles, thereby increasing the H₂ conversion. Consequently, the H₂/CO ratio was decreased. The CO₂ conversion in the H₂ reactor decreased slightly with increasing temperature in the CO₂ capture reactor, whereas the CO selectivity remained constant. This trend suggests that a greater inflow of CO₂ (as captured in the DFM) into the H₂ reactor increased the proportion of desorbed CO₂ that was not reduced to CO. To suppress the decrease in CO₂ conversion, the reaction efficiency must be improved in terms of kinetics by catalyst engineering in the H₂ reactor (Section 3.3).

4. Conclusion

Transition metal-free Na/Al₂O₃ DFM particles were circulated between two fluidized-bed reactors for CCR. In the CO₂ capture reactor, approximately half of the supplied CO₂ was continuously captured by the DFM. Subsequently, the CO₂ captured in the DFM was reduced in the H₂ reactor and a syngas-like mixture of H₂/CO was obtained; the CO₂ conversion and CO selectivity exceeded 80 % and 99 %, respectively. The effluent gas concentrations from both reactors were stable for more than 8 h, indicating the successful demonstration of continuous and steady-state CCR of syngas using the Na/Al₂O₃ DFM in the CFB system. However, the H₂ conversion was less than 20 % under the studied conditions, and H₂/CO was still exceedingly high for the direct use of the product gas as syngas. If the H₂ conversion is successfully improved to produce additional CO, the H₂/CO ratio can fall within the target range. This study confirms that the H₂/CO ratio can be controlled by varying the reaction conditions, such as the H₂ flow rate. Although longer residence time of the feed gas would be beneficial to compensate for the slow reaction kinetics of the transition-metal-free DFM, the gas flow rate should exceed the minimum fluidization velocity in the CFB system. Accordingly, the dimensions and configuration of the CFB system will be

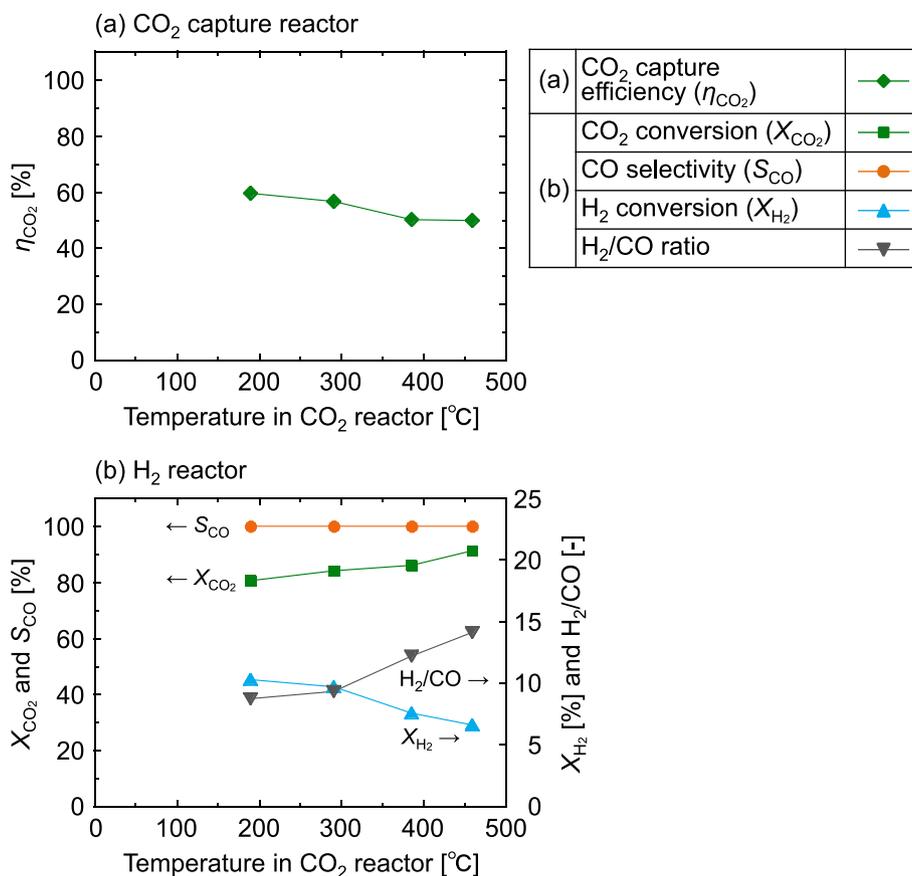


Fig. 4. Effect of temperature in the CO₂ capture reactor on (a) CO₂ capture efficiency in the CO₂ capture reactor and on (b) conversions of CO₂ and H₂, selectivity of CO, and H₂/CO ratio in the H₂ reactor.

effectively upgraded in the near future to enhance the interaction between the reaction gas and DFM particles.

CRediT authorship contribution statement

Tomone Sasayama: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis. **Yuya Ono:** Methodology, Investigation. **Fumihiko Kosaka:** Writing – review & editing, Methodology, Investigation. **Yanyong Liu:** Conceptualization. **Shih-Yuan Chen:** Writing – review & editing. **Takehisa Mochizuki:** Conceptualization. **Koichi Matsuoka:** Writing – review & editing, Supervision, Methodology. **Atsushi Urakawa:** Writing – review & editing, Validation, Supervision. **Koji Kuramoto:** Writing – review & editing, Project administration, Methodology.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2024.128602>.

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