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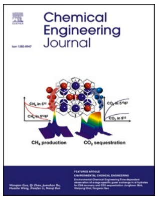

Direct and continuous conversion of flue gas CO_2 into green fuels using dual function materials in a circulating fluidized bed system

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ABSTRACT

Carbon capture and utilization (CCU) technologies, such as CO_2 methanation, generally require energy-intensive CO_2 capture and separation processes prior to catalytic CO_2 conversion. In contrast, integrated CO_2 capture and reduction (CCR) technologies that use dual function materials (DFM) can directly convert low-concentration CO_2 in flue gas or atmosphere into high-concentration CH_4 or CO. In this study, we demonstrate a circulating fluidized bed (CFB) approach to enable continuous operation of CCR. In the CFB approach, the DFM ($Na/Ni/Al_2O_3$) circulates between two bubbling fluidized beds to enable steady-state cyclic operation of (1) selective capture of CO_2 in flue gas/air and (2) hydrogenation of the captured CO_2. We succeeded in the continuous synthesis of CH_4 with high CO_2 capture efficiency (>88 %) and high H_2 conversion (>85 %) yielding mainly CH_4 (selectivity > 99 %) as the product at high concentration (>20 % CH_4) using 2 % CO_2/N_2 as the model flue gas.

1. Introduction

Carbon capture and utilization (CCU), such as CO_2 hydrogenation to gaseous and liquid fuels and value-added chemicals, has attracted significant attention as an efficient technology towards a carbon neutral society[1–3]. In addition, CO_2 methanation (Eq. (1)) has gained attention as a CCU technology to produce synthetic natural gas from CO_2 and H_2[4–7].

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (1)$$

To produce CH_4 from CO_2 contained in flue gas or air, low-concentration CO_2 often coexisting with O_2 and N_2 needs to be first treated to obtain high-purity CO_2 using CO_2 capture and separation technology such as amine absorption. Subsequently, CH_4 is synthesized from high-purity CO_2 and H_2 using a solid catalyst[4–7]. However, amine absorption and other CO_2 purification technologies are energy-intensive because of the significant thermal energy required for CO_2 desorption in a temperature swing process[8].

To reduce the overall energy requirement of CCU, integrated CO_2 capture and reduction using dual function materials (DFM) has been proposed[9,10]. The process has been called as CO_2 capture and reduction (CCR) or integrated CO_2 capture and utilization (ICCU), which has the advantage of not requiring energy-intensive CO_2 capture processes such as amine absorption. DFM includes alkaline or alkaline earth components for CO_2 capture (e.g., Na or Ca) and CO_2 hydrogenation (e.g., Ni or Ru for methanation). The two reaction steps involved are (i) selective CO_2 capture inside or on DFM from low-concentration CO_2 and (ii) hydrogenation of the captured CO_2, which are performed alternately.

$$\text{Step (i): } A_nO + CO_2 \rightarrow A_nCO_3 \quad (2)$$

$$\text{Step (ii): } A_nCO_3 + 4H_2 \rightarrow A_nO + CH_4 + 2H_2O \quad (3)$$

where, A = e.g. Li, Na, K, Ca, or Mg; and n = 1 or 2. The CCR concept was proposed by Farrauto group[9] and Urakawa group[10]. They demonstrated selective CO_2 capture from low-concentration CO_2 and its conversion into CH_4[9] and CO[10] in a fixed bed reactor using Ru/Ca/Al_2O_3[9] and FeCrCu/K/MgO-Al_2O_3[10] as DFM, respectively. Later, different research groups reported the development of various CCR catalysts[11–21], including several review papers in recent years [22–26]. To date, all studies have focused on evaluating the initial potential of DFMs and on the development of novel DFMs using small amounts of catalysts (approximately 50–1000 mg).

As a practical application of CCR using DFM, an alternating gas

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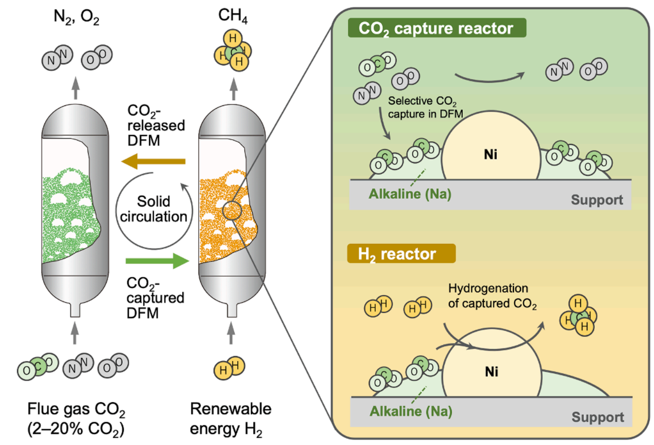

Fig. 1. Schematic for integrated dilute CO_2 capture and reduction into CH_4 using DFM and CFB reactors.

switching system using two (or more than two) packed bed reactors has been proposed (Figure S1(a))[10,27,28]. Very recently, Li *et al.* performed continuous CO synthesis from low concentrations of CO_2 using two fixed-bed reactors, but the concentration of produced CO was still low (approximately 0.3 % CO) which was lower than that of the supplied CO_2 (0.5 %) [28]. In addition, in this mode of operation there are some intrinsic drawbacks such as the inevitable influence of residual gas during the gas switching and the unsteady distribution of product concentration and temperature in the reactors.

Herein, we demonstrate a circulating fluidized bed (CFB) approach as a practical CCR process using nearly 1 kg of $Na/Ni/Al_2O_3$ particles as DFM (Figs. 1 and S1(b)). Low-concentration CO_2 and pure H_2 are supplied at a constant flow rate into the two reactors, namely a CO_2 capture reactor and a H_2 reactor, respectively. DFM particles are fluidized by these gases and circulated between these reactors. Since no gas switching is required, the process can be operated under steady-state to enable continuous CO_2 capture and CH_4 production and no fluctuations in gaseous concentration and temperature distribution in the reactors are expected.

2. Results and discussions

The $Na/Ni/Al_2O_3$ (DFM) efficient for CCR was prepared by the same method as reported previously [29]. In addition, Ni/Al_2O_3 (a conventional CO_2 methanation catalyst) was prepared as a reference using the same method. Figures S2–S5 and Table S1 show the characterization of the samples using X-ray diffraction (XRD), N_2-adsorption, H_2 temperature programmed reduction (H_2-TPR), and CO_2 temperature programmed detection (CO_2-TPD). As shown in the CCR experiments using a fixed bed reactor (i.e. gas switching mode, Figures S6 and S7), the DFM ($Na/Ni/Al_2O_3$) can selectively capture CO_2 from low-concentration CO_2 at the Na site and synthesize CH_4 with high selectivity in H_2 atmosphere.

Fig. 2(a) and S9 show a scheme of the CFB setup for continuous CO_2 capture and CH_4 production experiments using DFM. Two bubbling fluidized beds were used for the CO_2 capture reactor and H_2 reactor, and

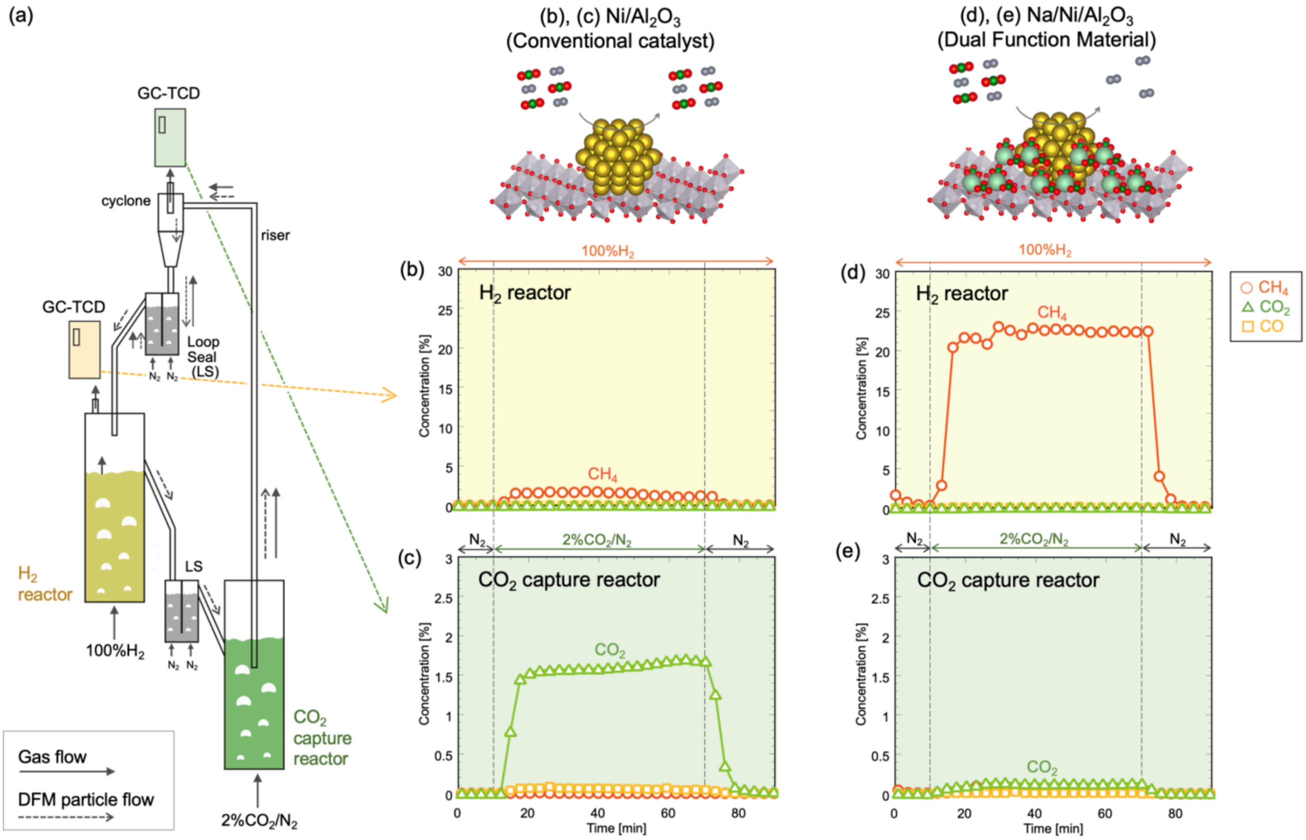

Fig. 2. (a) Scheme of continuous CH_4 production experiments using a CFB system with DFM($Na/Ni/Al_2O_3$). The LS is an important component that carries the DFM solids captured in the cyclone to the next reactor and avoids direct gas flow between the H_2 reactor and the CO_2 capture reactor. (b), (c) conventional CO_2 methanation catalyst (Ni/Al_2O_3) and (d), (e) DFM ($Na/Ni/Al_2O_3$). Reaction products in outlet gas from (b), (d) H_2 reactor at 450 °C and (c), (e) CO_2 capture reactor at 400 °C. 0.89 L min^{-1} of 100 %H_2 and 8 L min^{-1} of 2 %CO_2/N_2 were supplied into the H_2 reactor and the CO_2 capture reactor, respectively (from 10 to 70 min).

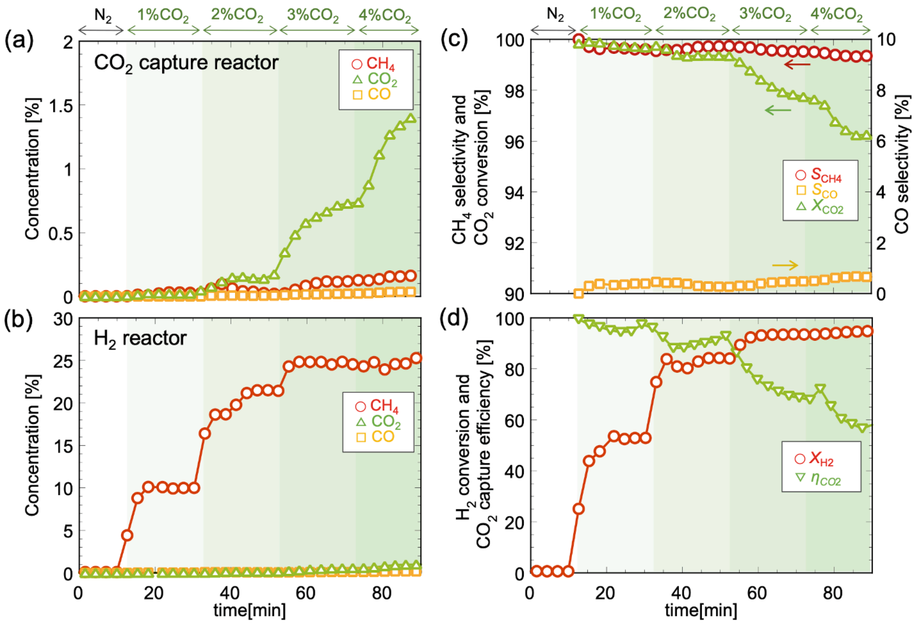

Fig. 3. Effects of CO_2 concentration (1 %–4% CO_2) for continuous CH_4 production using CFB reactors with $Na/Ni/Al_2O_3$. Reaction products in outlet gas from (a) CO_2 capture reactor at 400 °C and (b) H_2 reactor at 450 °C. 0.89 L min^{-1} of 100 %H_2 and 8 L min^{-1} of x%CO_2/N_2 ($x = 1$–4) were supplied into the H_2 reactor and the CO_2 capture reactor, respectively. (c) CH_4 and CO selectivities, and CO_2 conversion in the H_2 reactor, and (d) H_2 conversion in the H_2 reactor and CO_2 capture efficiency in the CO_2 reactor.

DFM particles were circulated between the reactors through a cyclone and loop seals. x%CO_2/N_2 ($x = 1$–4) and 100 % H_2 were supplied into the reactors from the bottom, respectively. The DFM selectively captures CO_2 from the x% CO_2/N_2 in the CO_2 capture reactor, and the CO_2-captured DFM flows upward through a riser. In the cyclone, the CO_2-lean gas is vented, and the DFM particles pass through a 1st loop seal (LS) to the H_2 reactor, where the captured CO_2 in the DFM and H_2 react to form CH_4. LS is an important component that carries the DFM solids captured in the cyclone to the next reactor and avoids direct gas flow from riser to the H_2 reactor. The DFM that released CO_2 returns to the CO_2 capture reactor through the 2nd LS and captures CO_2 again. By means of the catalyst circulation with CFB approach, CO_2 capture and its hydrogenation (Fig. 1) can be performed continuously and in a steady state without gas switching.

Fig. 2(b)-(e) show the reaction products (CO_2, CO, and CH_4) from the CO_2 capture reactor (Fig. 2(c) and (e)) and the H_2 reactor (Fig. 2(b) and (d)) using DFM ($Na/Ni/Al_2O_3$) and conventional catalyst (Ni/Al_2O_3). First, 100 % N_2 was fed to the CO_2 capture reactor and 100 % H_2 was fed to the H_2 reactor for a sufficient time until the reactor temperature and outlet gas concentration became stable. Thereafter, 2 % CO_2/N_2 was fed to the CO_2 capture reactor for 1 h. After 1 h, the CO_2 feed was stopped and N_2 was fed again. Meanwhile, the H_2 reactor was continuously supplied with 100 % H_2. In Figure S10, H_2 and N_2 concentrations are shown.

First, when Ni/Al_2O_3 was used (Fig. 2(c)), a rapid increase in the CO_2 concentration (up to 1.7 % CO_2) was observed after the CO_2-contaning gas was supplied into the CO_2 capture reactor. Since a small amount of CO_2 can be adsorbed on Ni/Al_2O_3, most of the supplied CO_2 passes through the catalyst and is detected in the outlet gas stream. In contrast, when $Na/Ni/Al_2O_3$ was used (Fig. 2(e)), most entering CO_2 to the reactor was captured and only 0.15 % CO_2 was uncaptured and found in the outlet stream. The results clearly indicate that the following reactions between DFM and CO_2 occur at the Na site, and a significant amount of CO_2 was captured inside the DFM particles.

$$Na_2O + CO_2 \rightarrow Na_2CO_3 \tag{4}$$

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O \tag{5}$$

$$NaOH + CO_2 \rightarrow NaHCO_3 \tag{6}$$

Figures S10(c) and S10(g) show the CO_2 capture efficiency and CO_2 capture amount of Ni/Al_2O_3 and $Na/Ni/Al_2O_3$, respectively. The CO_2 capture efficiency was >88 % with $Na/Ni/Al_2O_3$. The CO_2 capture amount in CFB was approximately 23–25 μmol g-DFM^{-1} (Figure S10 (g)), while the maximum CO_2 capture capacity evaluated in a fixed bed (Figure S7) was several times higher. This is likely due to the lower contact time of the DFM with the CO_2 containing gas under the used conditions in the CFB mode of operation and shows that the CO_2 capture is a kinetically driven process as expected.

On the other hand, employing $Na/Ni/Al_2O_3$ (Fig. 2(d)), a rapid CH_4 formation was observed after the H_2 reactor when CO_2 was supplied to the CO_2 capture reactor. The CH_4 formation continued stably throughout 1 h of the CO_2 supply. The concentration of produced CH_4 was >20 %. Considering that no gaseous CO_2 was supplied to the H_2 reactor and the concentration of supplied CO_2 into the CO_2 capture reactor was 2 %, it is clear that a high concentration of CH_4 was produced by the reaction of H_2 and CO_2 captured inside the DFM particles by one or more of the following reactions.

$$Na_2CO_3 + 4H_2 \rightarrow Na_2O + CH_4 + 2H_2O \tag{7}$$

$$Na_2CO_3 + 4H_2 \rightarrow 2NaOH + CH_4 + H_2O \tag{8}$$

$$NaHCO_3 + 4H_2 \rightarrow NaOH + CH_4 + 2H_2O \tag{9}$$

In contrast, when Ni/Al_2O_3 was used, the amount of captured CO_2 carried by the catalyst to the H_2 reactor was very small. The supplied H_2 passed through the reactor and mostly remained unreacted, and a low CH_4 concentration of less than 2 % was observed. As the reaction

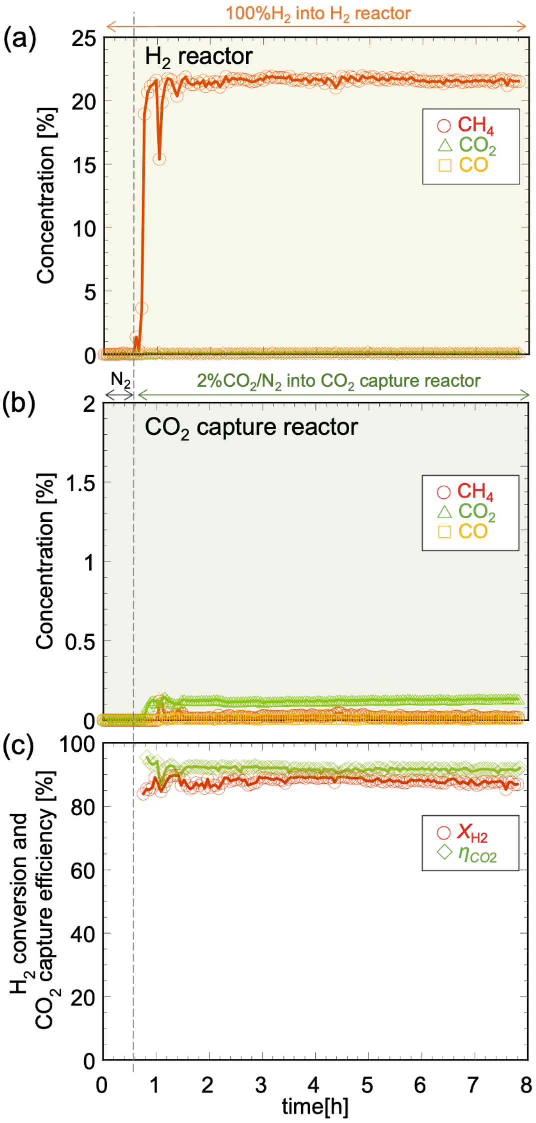

Fig. 4. Reaction products in outlet gas during 7 h stability test for continuous CH_4 production using CFB reactors with $Na/Ni/Al_2O_3$ from (a) CO_2 capture reactor at 400 °C, (b) H_2 reactor at 450 °C. H_2 was fed into the H_2 reactor at a rate of of 0.89 L min^{-1} and 2 %CO_2/N_2 was fed into the CO_2 capture reactor at a rate of of 8 L min^{-1}. (c) H_2 conversion and CO_2 capture efficiency.

products of the H_2 reactor with $Na/Ni/Al_2O_3$, the concentrations of CO_2 and CO were very low (less than 0.15 %), while the CH_4 selectivity was over 99 %, and almost all the CO_2 released from the DFM was converted to CH_4. As shown in Figure S10(e), the H_2 concentration in the outlet gas of the H_2 reactor was low, less than 15 %, indicating that H_2 conversion in the H_2 reactor was very high (Figure S10(g)) in comparison with the previous continuous CCR study using fixed bed reactors and gas switching[28]. These results indicate that by optimizing the H_2 and CO_2 feeds, CFB can be used to perform efficient and continuous CO_2 capture and hydrogenation with high CO_2 capture efficiency and H_2 utilization. Although a relatively large amount of N_2 was detected from H_2 reactor in this lab-scale test due to the N_2 contamination from the LS (Figure S10 (a) and S10(e)), the N_2 contamination can be reduced to a very small level on a practical scale by optimizing the LS and improving the catalyst performance (i.e., CO_2 capture capacity of DFM). Note that O_2 was not added to 2 % CO_2/N_2 considering the safety aspects in the initial demonstration phase of CFB. Nevertheless, the stability of the catalyst in the presence of O_2 was investigated using a fixed bed reactor. In the presence of O_2, $Na/Ni/Al_2O_3$ showed relatively high CO_2 capture and CH_4 formation performance for 50 cycles at 400 °C (Figure S8). In the future, with a construction of a safely designed system, we aim at evaluating the effects of O_2 on CCR performance using CFB.

Fig. 3 shows the effects of the CO_2 concentration (1–4 %) on CCR performance using CFB.

With a CO_2 feed of less than 2 % (Fig. 3a), the CO_2 concentration at the outlet of the reactor was low ($>$0.2 %), indicating that most of the supplied CO_2 was captured by the DFM. In contrast, when the CO_2 feed was$>$3 %, the CO_2 concentration from the outlet gas increased, showing a decline in the CO_2 capture efficiency, indicating that the rate of CO_2 capture by the DFM was not sufficient in comparison with the CO_2 supply rate. This once again highlights the importance of kinetics in the CO_2 capture process and condition optimization. As for the products from the H_2 reactor, CH_4 formation was selective (Fig. 3(c)) and the CH_4 concentration increased with an increase in supplied CO_2 concentration (Fig. 3(b)) because the amount of CO_2 carried by DFM from the CO_2 capture reactor increased, at higher molar flow rate of CO_2 or indicating the pressure dependency on the CO_2 capture rate. On the other hand, at higher CO_2 feed concentration the H_2 concentration decreased and the H_2 conversion increased monotonically (Fig. 3(d)). However, there was a gradual increase in the amount of unreacted CO_2. These results indicate that the delicate balance among the DFM circulation rate, capture and reduction rates, H_2 and CO_2 flow rates is important for efficient CO_2 capture and conversion. The development of high-performance DFM and fully optimized operating conditions of the CFB such as gas flow rate, operating pressure, and solid circulation likely lead to even greater success in the direct and continuous conversion of dilute CO_2.

Finally, the stability of steady-state CO_2 capture and CH_4 production with CFB was studied by performing a continuous CCR test for 7 h, and the DFM before and after the reaction was characterized. Considering the DFM circulation rate of 320 cm^3 min^{-1} (approximately 3 min for one cycle), CO_2 capture and hydrogenation were repeated for approximately 140 cycles for 7 h. Fig. 4 shows the outlet gas concentrations from the CO_2 and H_2 reactors, H_2 conversion, and CO_2 capture efficiency.

Rapid CH_4 production was observed with the CO_2 supply, followed by stable CH_4 production for the next 7 h without any indication of deactivation. CH_4 was produced with high selectivity at CO_2 conversion. The H_2 conversion and CO_2 capture efficiency were both above 85 %. Fig. 5 shows the XRD patterns and scanning electron microscope (SEM) images of DFM before and after the reaction. The XRD patterns show that the Ni peak became sharper (coarsening of Ni particles) as the reaction time increased, but the change was not significant enough to affect the CH_4 selectivity. No change in the appearance of the DFM particles was observed from the SEM images. Although the circulation of the DFM particles in the CFB may cause attrition and cracking, no obvious changes were observed in this study, probably because of the high mechanical strength of the Al_2O_3 particles.

3. Conclusion

We demonstrated the CFB approach, where DFM is circulated between two bubbling fluidized beds to enable continuous CO_2 capture and CH_4 production with CO_2 capture efficiencies and H_2 conversion of

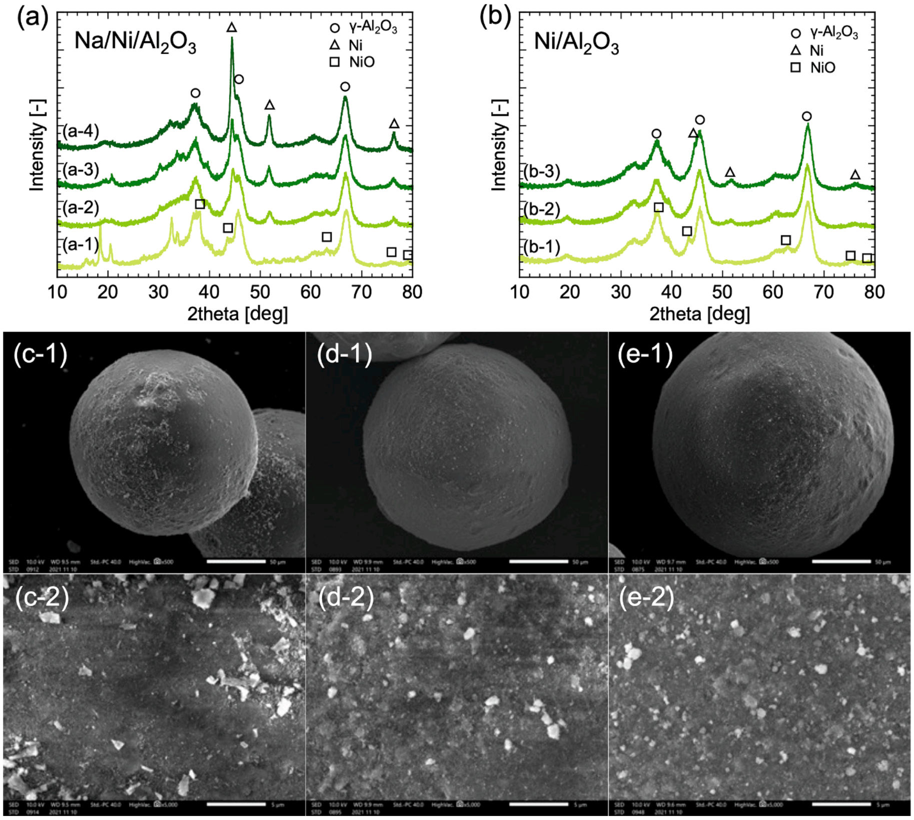

Fig. 5. Wide-angle XRD patterns of (a) $Na/Ni/Al_2O_3$, and (b) Ni/Al_2O_3. (a-1) fresh $Na/Ni/Al_2O_3$, (a-2) after reduction (and before reaction), (a-3) after 3 h of CFB reaction, (a-4) after>20 h of CFB reaction. (b-1) fresh Ni/Al_2O_3, (a-2) after reduction (and before reaction), (a-3) after 1 h of CFB reaction. (c)-(e) SEM images of $Na/Ni/Al_2O_3$. (c) before reaction (after reduction), (d) after 3 h of CFB operation, (e) after>20 h of CFB operation.

over 85 %. This approach may provide promising technological solutions to directly utilize CO_2 contained in flue gas or air for CCU with minimized CAPEX and OPEX by combining CO_2 capture and conversion processes operated under a steady-state manner.

Author contributions

F. K., A.U., and K. K. conceived the project. F. K., M. K., and K. K. designed the CFB setup. F. K. conducted the experiments and analysed the data. S. C. helped to characterize the DFM. A.U. and K. K. guided the work and edited the manuscript. T. S., Y. L., S. C., T. M., and M. K. contributed to discussions and manuscript. All authors have given approval to the final version of the manuscript.

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.cej.2022.138055.

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