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**DOI**

[10.1021/acssuschemeng.0c07162](https://doi.org/10.1021/acssuschemeng.0c07162)

**Publication date**

2021

**Document Version**

Accepted author manuscript

**Published in**

ACS Sustainable Chemistry and Engineering

**Citation (APA)**

Kosaka, F., Liu, Y., Chen, S. Y., Mochizuki, T., Takagi, H., Urakawa, A., & Kuramoto, K. (2021). Enhanced Activity of Integrated CO<sub>2</sub> Capture and Reduction to CH<sub>4</sub> under Pressurized Conditions toward Atmospheric CO<sub>2</sub> Utilization. *ACS Sustainable Chemistry and Engineering*, 9(9), 3452-3463. <https://doi.org/10.1021/acssuschemeng.0c07162>

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# ***Enhanced Activity of Integrated CO<sub>2</sub> Capture and Reduction to CH<sub>4</sub> under Pressurized Conditions Towards Atmospheric CO<sub>2</sub> Utilization***

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KEYWORDS: CO<sub>2</sub> capture, CO<sub>2</sub> utilization, CO<sub>2</sub> reduction, dual functional catalyst, direct air capture, methanation,

## ABSTRACT

Direct conversion of dilute CO<sub>2</sub> contained in power plant or industrial exhaust gas and the atmosphere into high-concentration hydrocarbons without a need of separate CO<sub>2</sub> capture and purification processes is one of the awaited technologies in envisioned low-carbon societies. In this study, we investigated the performance of integrated CO<sub>2</sub> capture and reduction to CH<sub>4</sub> over Ni-based dual functional catalysts promoted with Na, K and Ca. Ni/Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> exhibited the highest activity for integrated CO<sub>2</sub> (5% CO<sub>2</sub>) capture and reduction, achieving high CO<sub>2</sub> conversion (>96%) and CH<sub>4</sub> selectivity (>93%). In addition, very low concentration CO<sub>2</sub> (100 ppm CO<sub>2</sub>) was successfully converted to 11.5% CH<sub>4</sub> at the peak point (>1000 times higher concentration than that of the supplied CO<sub>2</sub>) over Ni/Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The Ni-based dual functional catalyst exhibited a high CO<sub>2</sub> conversion exceeding 90%, even when 20% O<sub>2</sub> was present during CO<sub>2</sub> capture. Furthermore, an increased operation pressure had positive impacts on both CO<sub>2</sub> capture and CH<sub>4</sub> formation, and these advantageous effects were also observed when CO<sub>2</sub> concentration was at the level of atmospheric CO<sub>2</sub> (100–400 ppm). As pressure increased from 0.1 to 0.9 MPa, CH<sub>4</sub> production capacity with 400 ppm CO<sub>2</sub> was enhanced from 111 to 160  $\mu\text{mol g}_{\text{cat}}^{-1}$ . The approach in combination with the efficient catalyst shows encouraging promises for CO<sub>2</sub> utilization, enabling direct air capture-conversion to value-added chemicals.

## INTRODUCTION

The aim to establish a low-carbon society has inspired the development of new technologies allowing one to reduce CO<sub>2</sub> emissions and improve energy efficiency by capturing CO<sub>2</sub> contained in power plant/industrial exhaust gas or even in the atmosphere and converting it into useful fuels and chemicals.<sup>1–5</sup> Such carbon capture and utilization processes (CCU) can be made even greener when coupled with reduction by H<sub>2</sub> produced by large-scale electrolysis of water using surplus or renewable source-derived electricity.<sup>3,6,7</sup> For example, CO<sub>2</sub> can be hydrogenated to form CH<sub>4</sub> according to the well-known Sabatier reaction (Eq. 1).<sup>7–10</sup>

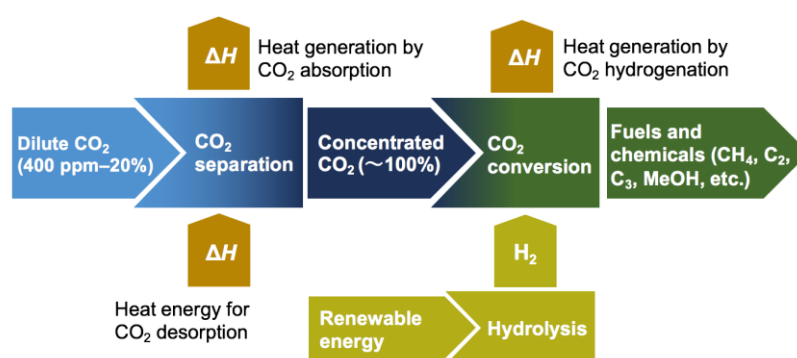


CO<sub>2</sub> methanation has attracted much attention as a means of effective CO<sub>2</sub>/H<sub>2</sub> utilization and has been implemented in several pilot plants, e.g., Audi e-gas has been running a 6-MW demonstration plant since 2013.<sup>6</sup> In a conventional CCU process, flue gas with a low CO<sub>2</sub> content is passed through a CO<sub>2</sub> capture and separation unit to afford a CO<sub>2</sub>-rich (~100%) feedstock suitable for subsequent utilization processes such as hydrogenation.<sup>1</sup> CO<sub>2</sub> can be separated from flue gas by absorption, physisorption, or gas separation membranes using amines, aqueous hydroxides, alkali carbonates, metal-organic frameworks, zeolites, and carbon-based materials as capture agents.<sup>11–17</sup> Despite the efforts made to improve the efficiency and energy cost of CO<sub>2</sub> capture and separation technologies,<sup>11–17</sup> CO<sub>2</sub> capture and separation from flue gas remains energy-consuming and costly, e.g., much thermal energy is consumed during CO<sub>2</sub> desorption.<sup>18</sup>

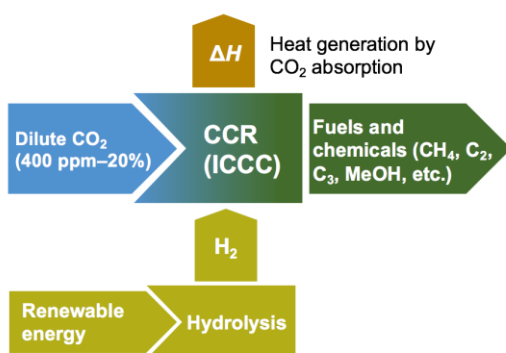
In the past years, the need to decrease the energy cost and increase the efficiency of CO<sub>2</sub>

utilization has inspired the development of technologies allowing CO<sub>2</sub> contained in power plant/industrial exhaust gas or even in the atmosphere to be directly converted into high-concentration hydrocarbons or syngas without a separate CO<sub>2</sub> capture and separation process (Figure 1a).<sup>19–37</sup> These technologies convert dilute CO<sub>2</sub> directly into high concentrations of hydrocarbons in a single process. Such single-process methods are denoted as CO<sub>2</sub> capture and reduction (CCR) or integrated CO<sub>2</sub> capture and conversion (ICCC) (Figure 1b).

### (a) Conventional two-step CCU process

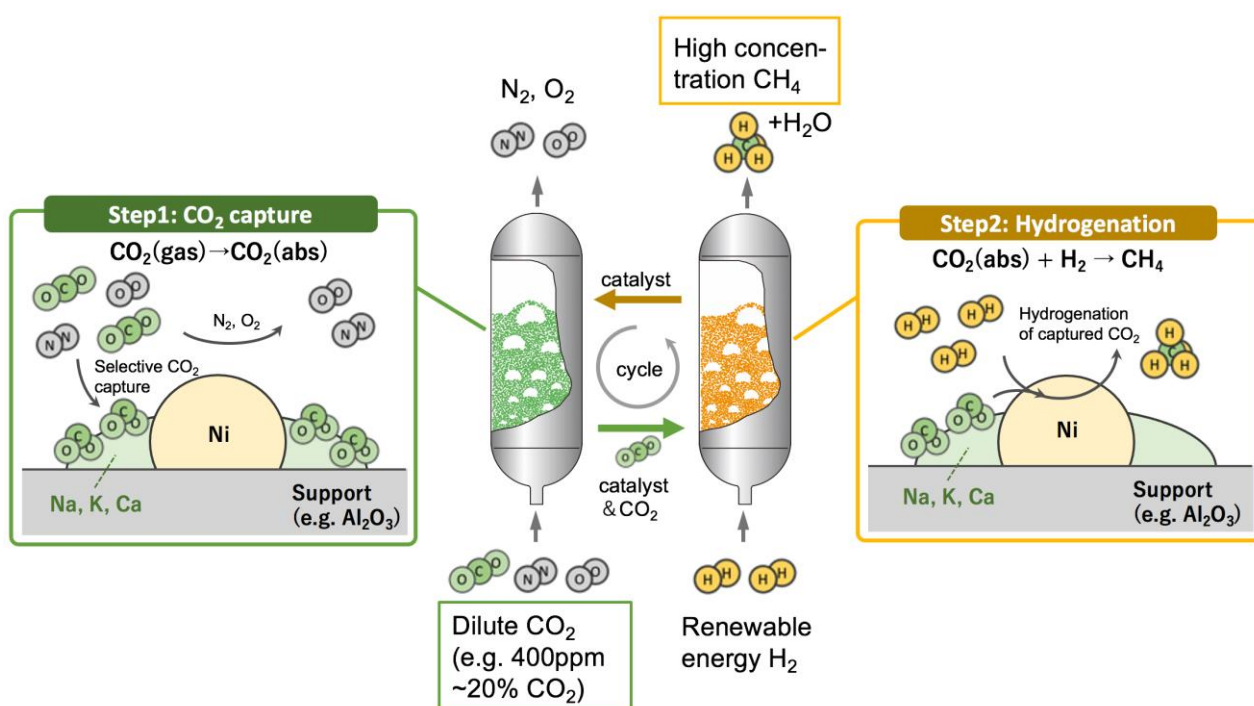
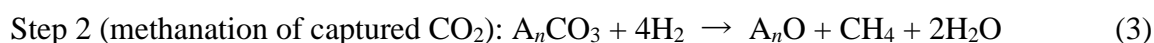


### (b) Integrated CO<sub>2</sub> capture and reduction (CCR, ICCC) process



**Figure 1.** Conceptual diagram of (a) a conventional two-step CCU process and (b) an integrated process for the direct capture and reduction of dilute CO<sub>2</sub> into hydrocarbons over dual-functional catalysts.

The integrated CO<sub>2</sub> capture and conversion technology follows two reaction steps for CO<sub>2</sub> methanation as exemplified by the use of fluidized bed reactors as shown in Figure 2 and Eqs. 2–3. Below, alkaline/alkaline-earth metal oxides and carbonates are shown as representative material for CO<sub>2</sub> capture and formed after the capture, respectively. They can be different such as hydroxides and formates depending on the choice of constituting materials of catalyst<sup>28</sup>.



**Figure 2.** Conceptual diagram of the integrated process for the direct capture of dilute CO<sub>2</sub> into hydrocarbons over dual-functional catalysts using the circulating fluidized-bed reactor.

In step 1, CO<sub>2</sub> is selectively captured as alkali/alkaline earth metal carbonates inside/on the catalysts, while other gases such as N<sub>2</sub> and O<sub>2</sub> pass through (Eq. 2). In step 2, the catalyst is exposed to H<sub>2</sub> to convert the captured CO<sub>2</sub> into hydrocarbons such as CH<sub>4</sub> (Eq. 3). In the CO<sub>2</sub> reduction reactor (step 2), CO<sub>2</sub> desorption and CO<sub>2</sub> methanation reactions proceed simultaneously. CO<sub>2</sub> desorption is an endothermic reaction, while CO<sub>2</sub> methanation is exothermic. Therefore, the two reactions can be balanced in a single reactor in the CCR process by selecting the appropriate CO<sub>2</sub> absorber and reaction conditions. Large amounts of heat energy, that are otherwise required for conventional CO<sub>2</sub> separation and purification processes, are not needed in this process (Figure S1 and Table S1). Therefore, the CCR process can enhance the efficiency of the CCU process, although detailed quantitative discussions based on process simulations are necessary in the future.

In the CCR process, catalysts need to possess activity for both CO<sub>2</sub> capture and CO<sub>2</sub> reduction and are therefore called dual-functional catalysts. The concept of dual-functional catalysts was proposed in 2015 by Farrauto's group, who used Ru- and Ca-promoted  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for the capture of 5 vol% CO<sub>2</sub> and its reduction by H<sub>2</sub> in a fixed-bed reactor at 320 °C.<sup>23</sup> The authors observed the formation of CH<sub>4</sub> upon switching from CO<sub>2</sub>-containing gas to H<sub>2</sub> and thus demonstrated that a dual-functional catalyst can capture dilute CO<sub>2</sub> and directly convert it into CH<sub>4</sub>.<sup>23</sup> Since then, the group has carried out other pioneering research, developing dual-functional catalysts with Ru, Rh, and Ni as active metal species and Na, K, and Mg as CO<sub>2</sub>-absorbing components.<sup>21,25,31,33,35,37</sup> At the same period, Urakawa's group reported Fe- and Cu-based dual-functional catalysts directly converting dilute CO<sub>2</sub> into concentrated syngas.<sup>19,28</sup> FeCrCu/K/MgO-Al<sub>2</sub>O<sub>3</sub> successfully absorbed 5–10% CO<sub>2</sub>

and converted it into CO with a high selectivity of 90–96% in an H<sub>2</sub> atmosphere at 450–550 °C.<sup>19</sup> The excellent functionality was retained even when O<sub>2</sub> and H<sub>2</sub>O vapor were present in the CO<sub>2</sub>-containing gas stream<sup>19</sup>. Furthermore, they carried out space- and time-resolved *operando* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) studies to elucidate the detailed reaction mechanism of CO<sub>2</sub> capture and reduction<sup>28</sup>. Regarding the utilization of very low CO<sub>2</sub> levels (e.g., atmospheric CO<sub>2</sub> levels of 400 ppm), Veselovskaya et al. reported a direct air capture and methanation process using separately allocated fixed-bed reactors containing a K-based CO<sub>2</sub> capture solid sorbent and methanation catalysts<sup>26,30,36</sup>. However, the future deployment of simpler CO<sub>2</sub> capture and reduction processes using fluidized-bed reactors (Figure 2) requires catalysts with dual functionality.

In this study, we developed Ni-based dual-functional catalysts and studied the effects of operating conditions on direct CO<sub>2</sub> capture and reduction to CH<sub>4</sub> using a fixed-bed reactor. As a well-known CO<sub>2</sub> methanation catalyst, Ni has an advantage over other active metals because of its relatively high natural abundance. Bermejo-López et al. investigated the optimization of active metal (Ni) content in dual-functional catalysts and realized a minor improvement (from 150 to 186  $\mu\text{mol g}_{\text{cat}}^{-1}$  for Ni-Na<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>) by catalyst composition tuning.<sup>34</sup> Obviously, the current challenges is how to enhance CO<sub>2</sub> capture capacity and CH<sub>4</sub> selectivity. Previous bifunctional catalytic CO<sub>2</sub> capture and reduction has been carried out at ambient pressure. Herein, we report significant improvements in these, facilitated by elevated reaction pressures (up to 0.9 MPa) besides tuning an appropriate catalyst composition. This approach is even able to efficiently capture 100-



400 ppm CO<sub>2</sub> and selectively convert it to CH<sub>4</sub>. In addition, we report on the CO<sub>2</sub> capture and reduction performance of the Ni-based catalyst in the presence of O<sub>2</sub> during the CO<sub>2</sub> capture period.

## EXPERIMENTAL

### Preparation of Ni/(Na, K, Ca)/Al<sub>2</sub>O<sub>3</sub> and Ni/Al<sub>2</sub>O<sub>3</sub> catalysts

$\gamma$ -Al<sub>2</sub>O<sub>3</sub> (sample code: JRC-ALO-5, 74–125  $\mu$ m) was supplied by the Catalysis Society of Japan (Japan Reference Catalysts). Na, K, Ca, and Ni precursors (Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, respectively) were purchased from Fujifilm Wako Pure Chemical, Japan.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was impregnated with an aqueous solution (50 mL) containing Na, K, and Ca precursors, dried at 110 °C overnight, and calcined in air at 550 °C for 4 h. The alkali carbonate loading was maintained at 15 wt% against  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The Na-, K-, and Ca-modified  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was impregnated with an aqueous Ni precursor solution (50 mL) as described above, with the Ni loading maintained at 10 wt% against modified  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. As a result, Ni/Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Ni/K- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and Ni/Ca- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> dual-functional catalysts were obtained. Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> prepared by incipient impregnation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (JRC-ALO-5) with an aqueous Ni precursor solution as described above was used as a reference catalyst.

### Catalyst Characterization

Wide-angle XRD patterns were recorded for  $2\theta = 10\text{--}80^\circ$  on a Rigaku SmartLab SE diffractometer at 40 keV and 50 mA using a step size of  $0.02^\circ$  and a scan rate of 2 s per step. Cu  $K_\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) was used as the X-ray source. N<sub>2</sub> adsorption-desorption isotherms were recorded at  $-196^\circ\text{C}$  using a Belsorp max instrument for samples outgassed at  $150^\circ\text{C}$  in high vacuum ( $<10^{-5}$  Torr). Specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method at  $P/P_0 = 0.05\text{--}0.25$ . Pore volume was obtained by accumulation up to  $P/P_0 = 0.95$ . Pore size distribution was

analyzed by a non-linear density functional theory (NLDFT) method using a desorption branch. Temperature-programmed reduction (TPR) and temperature-programmed desorption (TPD) experiments were performed on a Belcat II instrument equipped with a thermal conductivity detector (TCD) and a BELMass mass spectrometer. Prior to H<sub>2</sub>-TPR, the dried samples (~100 mg) were finely packed in a quartz tube and purged with a G1-grade standard of 5.05 vol% H<sub>2</sub>/Ar at a flow rate of 15 mL min<sup>-1</sup> at 50 °C until the TCD and MS signals were stable. Downstream composition was monitored by mass spectrometry and calibrated using standard gases. To enable comparison, the signals were normalized by sample weight. H<sub>2</sub>-TPR-MS profiles were recorded at 50–950 °C and calibrated using a G1-grade standard gas of 1 vol% H<sub>2</sub>/Ar. Prior to CO<sub>2</sub>-TPD-MS measurements, the samples were reduced at 500 °C in a flow of H<sub>2</sub> (50 mL min<sup>-1</sup>) for 1 h. For CO<sub>2</sub> chemisorption, a standard gas of 5 vol% CO<sub>2</sub>/Ar was passed through the reduced samples at 50 °C for 30 min. Physically adsorbed CO<sub>2</sub> was purged by an Ar flow (50 mL min<sup>-1</sup>) until the TCD and MS signals were stable. For to the Ar-TPD-MS measurement, the fresh samples were in situ reduced at 500 °C by a H<sub>2</sub> flow (50 mL min<sup>-1</sup>) for 1 h, followed by purging with an Ar flow (50 mL min<sup>-1</sup>) and cooling to 0 °C. Then, the hydrogen species remained on the reduced samples were gradually desorbed by heating and their amounts were monitored by the Ar-TPD-MS method.

### **CO<sub>2</sub> capture and reduction to CH<sub>4</sub> in a fixed-bed reactor**

Figure S2 shows the experimental setup used for the integrated process of direct CO<sub>2</sub> capture and reduction into CH<sub>4</sub>. Gas flow was automatically controlled using a gas supply system with mass

flow controllers (HM1000, HEMMI) and monitored by a non-dispersive infrared (NDIR) gas analyzer (VA-5000, HORIBA). Each catalyst (1 or 3 g) including the active components and the support was packed in a stainless-steel reactor (I.D.: 9 mm, catalyst bed height: ca. 20 mm), assembled in an electric furnace, and reduced at 500 °C in H<sub>2</sub> for 1 h at atmospheric pressure before the integrated process. Reaction temperature was monitored by placing a thermocouple in a 1/8-inch SUS tube inserted into the reaction tube. The integrated process consisted of the following steps: (i) CO<sub>2</sub> capture for 10 s–100 min, (ii) 5 min N<sub>2</sub> purging to remove unreacted CO<sub>2</sub>, and (iii) reduction of the chemically captured CO<sub>2</sub> with H<sub>2</sub> for 5 min. Steps (i), (ii), and (iii) were performed using 0.01–13 vol% CO<sub>2</sub>/N<sub>2</sub> (or 0.04 vol% CO<sub>2</sub>/20%O<sub>2</sub>/80%N<sub>2</sub>), N<sub>2</sub>, and H<sub>2</sub> as feed gases, respectively. The CO<sub>2</sub> capture and reduction cycle (steps (i–iii)) was repeated five times at 450 °C after H<sub>2</sub>-pretreatment at 500 °C, with the results of the first cycle presented below and the results of the five cycles presented in Figure S3 and Figure S4. During operation, the temperature was maintained at 450 °C and the total gas flow rate was 50–500 NmL min<sup>-1</sup>. Reaction pressure was varied from 0.1 to 0.9 MPa. The composition of the exhaust gas at the outlet was qualitatively and quantitatively analyzed using a BELMass mass spectrometer and an NDIR gas analyzer, respectively. The CH<sub>4</sub> formation ( $q_{\text{CH}_4}$ ), CO formation ( $q_{\text{CO}}$ ), and CO<sub>2</sub> capture ( $C_{\text{CO}_2}$ ) capacities, as well as the CO<sub>2</sub> conversion ( $X_{\text{CO}_2}$ ), the selectivity for CH<sub>4</sub> or CO ( $S_i$ ,  $i = \text{CH}_4$  or CO), and the CO<sub>2</sub> capture efficiency ( $\eta_{\text{CO}_2}$ ) were quantified using Eqs. 4–9, respectively.

$$q_{\text{CH}_4} [\mu\text{mol g}^{-1}] = \frac{1}{W} \int_{t_{\text{H}_2, \text{in}}}^{t_{\text{H}_2, \text{out}}} F_{\text{CH}_4}(t) dt, \quad (4)$$

$$q_{\text{CO}} [\mu\text{mol g}^{-1}] = \frac{1}{W} \int_{t_{\text{H}_2, \text{in}}}^{t_{\text{H}_2, \text{out}}} F_{\text{CO, out}}(t) dt, \quad (5)$$

$$C_{\text{CO}_2} [\mu\text{mol g}^{-1}] = \frac{1}{W} \int_{t_{\text{H}_2, \text{in}}}^{t_{\text{H}_2, \text{out}}} \{F_{\text{CH}_4, \text{out}}(t) + F_{\text{CO}, \text{out}}(t) + F_{\text{CO}_2, \text{out}}(t)\} dt, \quad (6)$$

$$X_{\text{CO}_2} = \frac{q_{\text{CH}_4} + q_{\text{CO}}}{C_{\text{CO}_2}}, \quad (7)$$

$$S_i = \frac{q_i}{q_{\text{CH}_4} + q_{\text{CO}}}, \quad (8)$$

$$\eta_{\text{CO}_2} = \frac{\int_{t_{\text{H}_2, \text{in}}}^{t_{\text{H}_2, \text{out}}} \{F_{\text{CH}_4, \text{out}}(t) + F_{\text{CO}, \text{out}}(t) + F_{\text{CO}_2, \text{out}}(t)\} dt}{F_{\text{CO}_2, \text{in}} \times t_{\text{CO}_2}} \quad (9)$$

where  $W$ ,  $F_{\text{CH}_4, \text{out}}$ ,  $F_{\text{CO}_2, \text{out}}$ ,  $F_{\text{CO}, \text{out}}$ ,  $F_{\text{CO}_2, \text{in}}$ ,  $t_{\text{CO}_2}$ ,  $t_{\text{H}_2, \text{in}}$ , and  $t_{\text{H}_2, \text{out}}$  are the catalyst weight, the molar flow rates of CH<sub>4</sub>, CO<sub>2</sub>, and CO in the outlet gas, the molar flow rate of CO<sub>2</sub> in the inlet gas, the CO<sub>2</sub> supply period, the time of starting H<sub>2</sub> supply, and the time of ending H<sub>2</sub> supply, respectively.

## RESULTS AND DISCUSSION

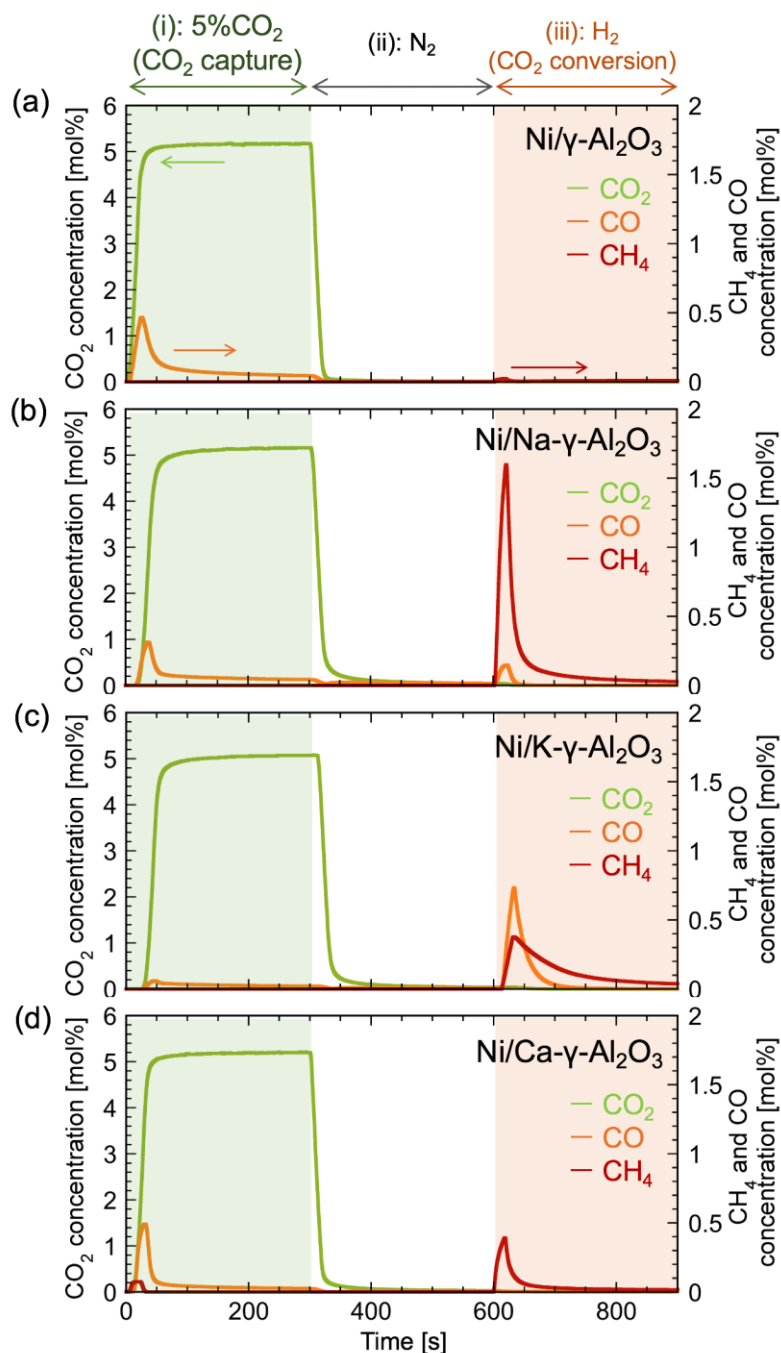
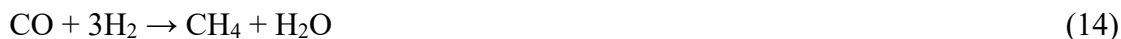
### Screening of catalysts under atmospheric pressure

Figure 3 shows the performance of the integrated CO<sub>2</sub> capture and reduction process over dual functional catalysts (Ni/Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Ni/K- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and Ni/Ca- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) examined at 450 °C under atmospheric pressure, in comparison to a reference catalyst (Ni/Al<sub>2</sub>O<sub>3</sub>). As aforementioned, this process can be divided into three steps: (i) chemical capture of CO<sub>2</sub> over Ni/Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> corresponding to Eqs. (10)–(12),



(ii) purging with N<sub>2</sub> for 5 min to eliminate gaseous and weakly sorbed CO<sub>2</sub>, and (iii) hydrogenation

of the captured CO<sub>2</sub> in the H<sub>2</sub> flow (Eqs. (1), (13) and (14)).



**Figure 3.** Performances of (a) Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (b) Ni/Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (c) Ni/K- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and (d) Ni/Ca- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for integrated CO<sub>2</sub> capture and reduction into CH<sub>4</sub> at 450 °C and atmospheric pressure compared to Ni/Al<sub>2</sub>O<sub>3</sub> as a reference catalyst. The gas flow (total flow rate = 500 mL min<sup>-1</sup>) was stepwise switched from 5% CO<sub>2</sub> in N<sub>2</sub> to N<sub>2</sub> (at 300 s) and H<sub>2</sub> (at 600 s). Catalyst weight: 1g.

In Eqs. (10)-(12), sodium oxide and hydroxide were assumed as the CO<sub>2</sub> capture components and formation of sodium carbonate and bicarbonate was assumed as resulting components although the actual chemical states of captured CO<sub>2</sub> need to be verified<sup>38-40</sup>. In step (i), a small amount of CO was formed (Figure 3), possibly through the reduction of CO<sub>2</sub> by surface-adsorbed hydrogen (Eq. 15), particularly in the cases of Ni/γ-Al<sub>2</sub>O<sub>3</sub> and Ni/Ca-γ-Al<sub>2</sub>O<sub>3</sub>.

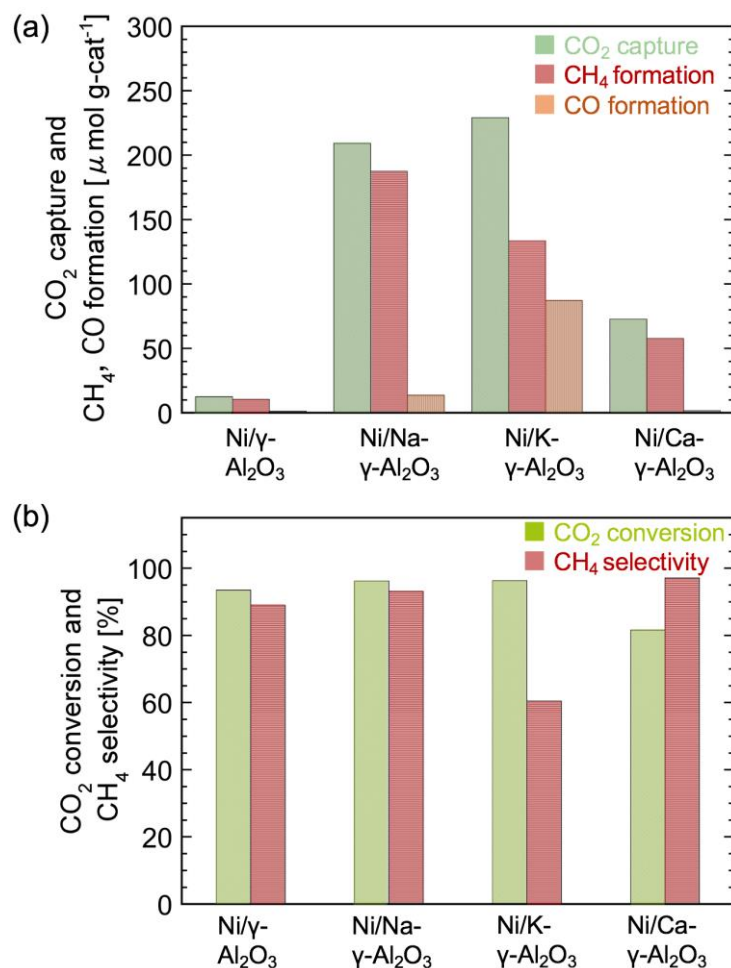


In step (ii), a fast decrease in CO<sub>2</sub> content due to the N<sub>2</sub> purge was observed for Ni/γ-Al<sub>2</sub>O<sub>3</sub> and Ni/Ca-γ-Al<sub>2</sub>O<sub>3</sub>. Delayed CO<sub>2</sub> content decay was observed for Ni/Na-γ-Al<sub>2</sub>O<sub>3</sub> and Ni/K-γ-Al<sub>2</sub>O<sub>3</sub>, indicating that Na- and K- promotion enhanced the CO<sub>2</sub>-catalyst interaction. In step (iii), negligible CH<sub>4</sub> formation was observed for conventional CH<sub>4</sub> methanation catalyst, Ni/γ-Al<sub>2</sub>O<sub>3</sub>, because of its small CO<sub>2</sub> capture capacity, which was ascribed to minor CO<sub>2</sub> adsorption (as opposed to absorption) during the CO<sub>2</sub> capture process. In contrast, large amounts of CH<sub>4</sub> and CO were produced over dual-functional catalysts. A large amount of CH<sub>4</sub> was formed over Ni/Na-γ-Al<sub>2</sub>O<sub>3</sub>, with a small amount of CO produced in the reduction phase. On the other hand, similar amounts of CO and CH<sub>4</sub> were generated over Ni/K-γ-Al<sub>2</sub>O<sub>3</sub>. Ni/Ca-γ-Al<sub>2</sub>O<sub>3</sub> selectively afforded CH<sub>4</sub>, albeit in a smaller amount than the Na-promoted catalyst. Although the CO<sub>2</sub> capture efficiency was <5% (Figure S5), we found that it could be improved, as detailed later. To focus on the effects of different catalysts and reaction conditions, such as the CO<sub>2</sub> concentration and pressure, sufficiently long CO<sub>2</sub> capture periods were generally used for the purpose of this study. It should be noted that the CH<sub>4</sub> concentration in the

outlet gas can be enhanced by increasing the ratio of the catalyst weight to the gas flow rate, as shown in Figure S12, and as described in previous literature<sup>29</sup>, in which >60% CH<sub>4</sub> was obtained when employing a relatively large catalyst amount and a slow gas flow rate. In this study, a relatively high gas flow rate of 500 mL min<sup>-1</sup> was generally used to improve the response of the gas analysis for the unsteady-state reaction, and to focus on the effects of the catalyst and reaction conditions (i.e., the pressure and CO<sub>2</sub> concentration).

Figure 4 quantifies CH<sub>4</sub> and CO formed in step (iii) and the amount of captured CO<sub>2</sub> based on Eqs. 4–6. The CO<sub>2</sub> capture and CH<sub>4</sub> formation capacities of Ni/γ-Al<sub>2</sub>O<sub>3</sub> equaled 12.7 and 10.6 μmol g<sub>cat</sub><sup>-1</sup>, respectively. In the case of Ni/Na-γ-Al<sub>2</sub>O<sub>3</sub>, the respective values (209 and 186 μmol g<sub>cat</sub><sup>-1</sup>) were one order of magnitude higher, and a small amount of CO was also formed (13.8 μmol g<sub>cat</sub><sup>-1</sup>). The selectivity for CH<sub>4</sub> reached 93%. Although the CO<sub>2</sub> capture capacity of Ni/K-γ-Al<sub>2</sub>O<sub>3</sub> exceeded that of Ni/Na-γ-Al<sub>2</sub>O<sub>3</sub>, the CH<sub>4</sub> selectivity of the former was as low as 61% because of the formation of large amounts of CO. This finding demonstrates that the hydrogenation ability and selectivity of Ni are affected by the type of promoter used for CO<sub>2</sub> capture, which agrees with the previous literature where potassium on Ni catalysts enhances CO selectivity.<sup>41</sup> Ni/Ca-γ-Al<sub>2</sub>O<sub>3</sub> was ineffective for capturing large amounts of CO<sub>2</sub>, possibly because of the high stability of CaCO<sub>3</sub>.<sup>42</sup> CO<sub>2</sub> release from CaCO<sub>3</sub> generally requires a high temperature of about 700°C, which is incompatible with the temperature range of CO<sub>2</sub> methanation.<sup>42</sup> Considering the above results, we mainly focused on the characterization and performance of Ni/Na-γ-Al<sub>2</sub>O<sub>3</sub> under pressurized conditions.





**Figure 4.** (a) CO/CH<sub>4</sub> production capacities and CO<sub>2</sub> capture capacities of Ni/Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Ni/K- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Ni/Ca- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 450 °C and atmospheric pressure and (b) corresponding CO<sub>2</sub> conversion ( $X_{\text{CO}_2}$ ) and CH<sub>4</sub> selectivity ( $S_{\text{CH}_4}$ ).

## Characterization

The structural properties of Ni/Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were examined by wide-angle XRD, N<sub>2</sub> adsorption-desorption, H<sub>2</sub>-TPR, Ar-TPD, and CO<sub>2</sub>-TPD (Figures S6–S10). Figure S6 shows that no Ni species were detected in Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, indicating that Ni species were well dispersed on the  $\gamma$ -

Al<sub>2</sub>O<sub>3</sub> framework. In contrast, the XRD pattern of fresh Ni/Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> featured a weak peak at  $2\theta = 29.2^\circ$  corresponding to the (200) plane of Na<sub>2</sub>CO<sub>3</sub> and a series of NiO peaks. The NiO crystallite size was calculated as 25.3 nm by the Scherrer equation using the width at half height of the NiO (111) peak. Figure S7 shows the N<sub>2</sub> adsorption-desorption isotherms of as-prepared and reduced (at 500 °C) Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni/Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as well as the corresponding pore size distributions. All samples featured type-IV isotherms with an H<sub>1</sub> hysteresis loop associated with the mesoporous structure of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

The reducibility and basicity of Ni/Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were examined by H<sub>2</sub>-TPR and CO<sub>2</sub>-TPD, respectively (Figures S8 and S9). For Ni/Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, NiO reduction was observed at lower temperatures ( $\sim 500$  °C, denoted as  $\beta'$ ) than for Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. This behavior suggested that the reduction of NiO was facilitated by the presence of Na, presumably because of the weak metal-support interaction of NiO and the Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface. Figure S9 shows that the desorption of CO<sub>2</sub> from Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was observed at 50–300 °C, with the corresponding peak centered at  $\sim 135$  °C. The CO<sub>2</sub> uptake of this reference catalyst was determined as 0.12 mmol g<sup>-1</sup>. In contrast, Ni/Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> featured two strong signals centered at 166 and 630 °C, which were ascribed to the desorption of chemisorbed CO<sub>2</sub> and the thermal decomposition of Na<sub>2</sub>CO<sub>3</sub>, respectively. The CO<sub>2</sub> uptake of this catalyst (1.10 mmol g<sup>-1</sup>) significantly exceeded that of the reference. Thus, the co-existence of Ni and Na was concluded to increase the number of catalytic sites for CO<sub>2</sub> chemisorption.

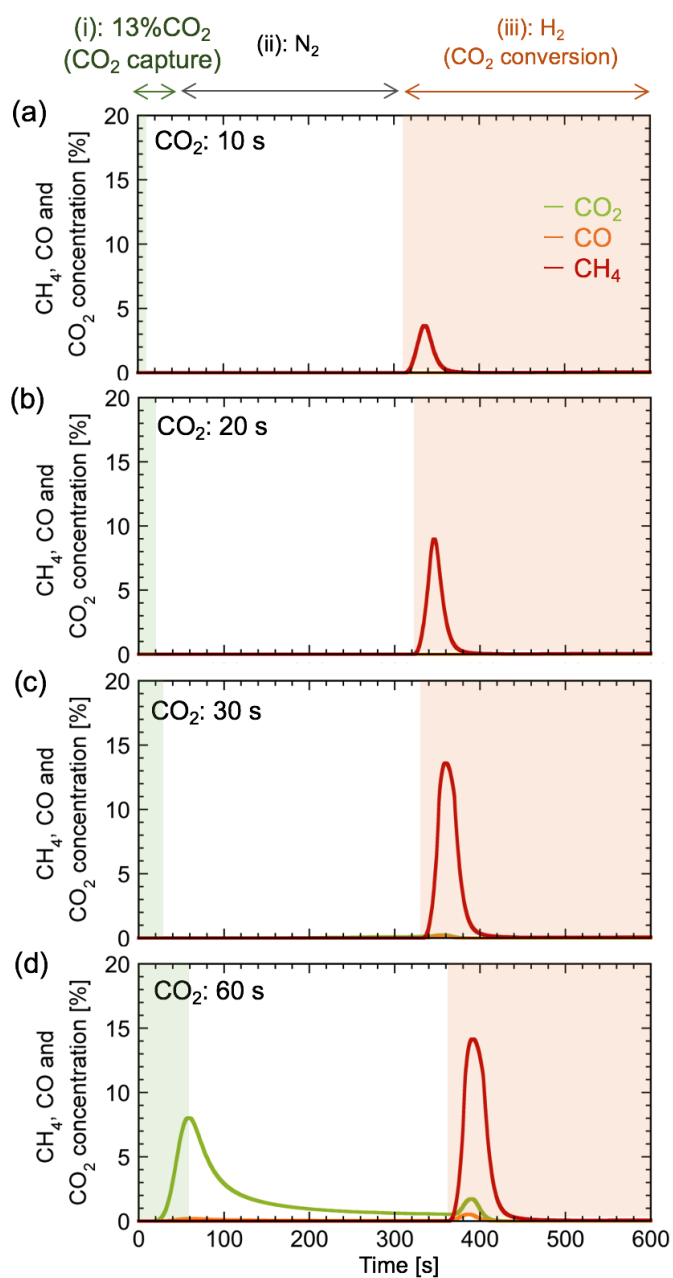
To elucidate the CO formation mechanism during the CO<sub>2</sub> capture step, we carried out the temperature-programmed desorption of the reduced catalysts in the Ar atmosphere (Figure S10).

The Ar-TPD-MS data can be employed to estimate the amount of hydrogen species adsorbed on the reduced samples. The results show that the amount of hydrogen adsorbed on the reduced catalysts is in the order of Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> > Ni/Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> > Ni/Ca- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to Ni/K- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, which is the same as the order of CO formation amount during the CO<sub>2</sub> capture step (Figure 3). It can be concluded based on these trends that the formation of the CO during the CO<sub>2</sub> capture step is related to the hydrogenation of CO<sub>2</sub> by the hydrogen adsorbed on the reduced catalysts.

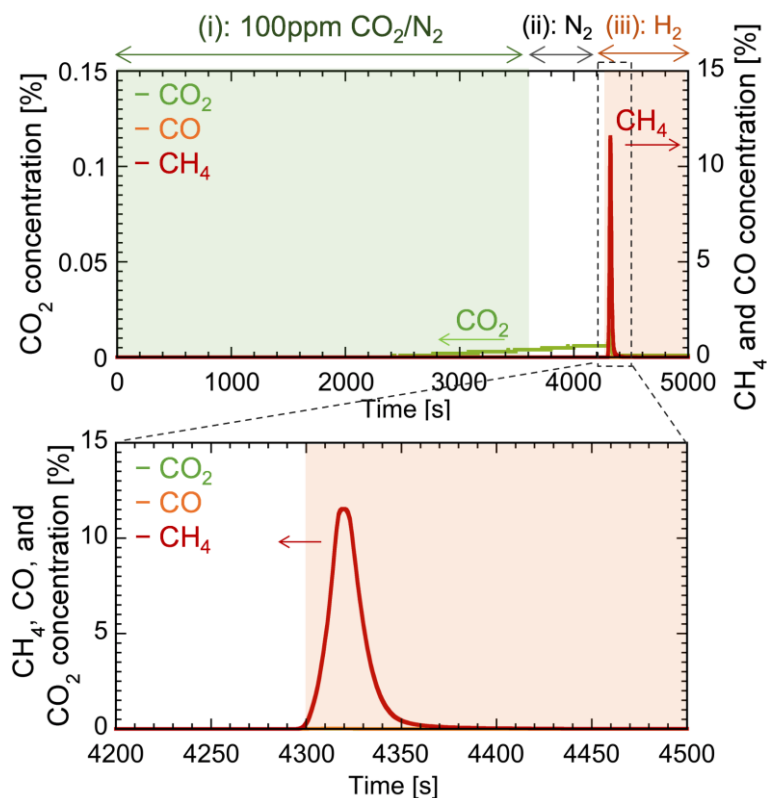
### **Feasibility study of integrated CO<sub>2</sub> capture and reduction over Ni/Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>**

Figure 5 shows the effect of the CO<sub>2</sub> capture period (10–60 s) on the integrated CO<sub>2</sub> capture and reduction performance over Ni/Na-Al<sub>2</sub>O<sub>3</sub>. When the CO<sub>2</sub> (13% CO<sub>2</sub>) supply period was <30 seconds, the CO<sub>2</sub> concentration in the outlet gas was particularly low, and the majority of the supplied CO<sub>2</sub> was captured in the catalyst. Figure S13 shows the effect of the CO<sub>2</sub> supply period on the CO<sub>2</sub> capture efficiency, the CO<sub>2</sub> conversion, and the CH<sub>4</sub> selectivity. More specifically, the CO<sub>2</sub> capture efficiency was high when the CO<sub>2</sub> supply period was appropriate, and the efficiency decreased when the CO<sub>2</sub> supply period was too long due to the fact that the CO<sub>2</sub> capture capacity of the catalyst was saturated. Furthermore, it was found that the CO<sub>2</sub> conversion and CH<sub>4</sub> selectivity were improved when the hydrogenation of CO<sub>2</sub> was carried out, under the condition that the CO<sub>2</sub> absorption capacity of the catalyst was not saturated. These results may suggest that strongly-absorbed CO<sub>2</sub> exists in the early stages, while weakly-absorbed CO<sub>2</sub> exists in the near-saturation stages, and that these different CO<sub>2</sub> species may exhibit different activities for hydrogenation. In

addition, Figure 6 shows the gas concentration in the outlet when 100 ppm CO<sub>2</sub> was supplied at a rate of 500 mL min<sup>-1</sup> for 1 h, followed by a supply of 50 mL min<sup>-1</sup> of H<sub>2</sub>, and using a Ni/Na-Al<sub>2</sub>O<sub>3</sub> catalyst (3 g). In this case, 100 ppm CO<sub>2</sub> was successfully converted to 11.5% CH<sub>4</sub> at the peak point (>1000 times higher concentration than that of the supplied CO<sub>2</sub>). These results indicate that the approach employed herein can efficiently convert dilute CO<sub>2</sub> into highly concentrated hydrocarbons without the requirement for CO<sub>2</sub> separation and purification.



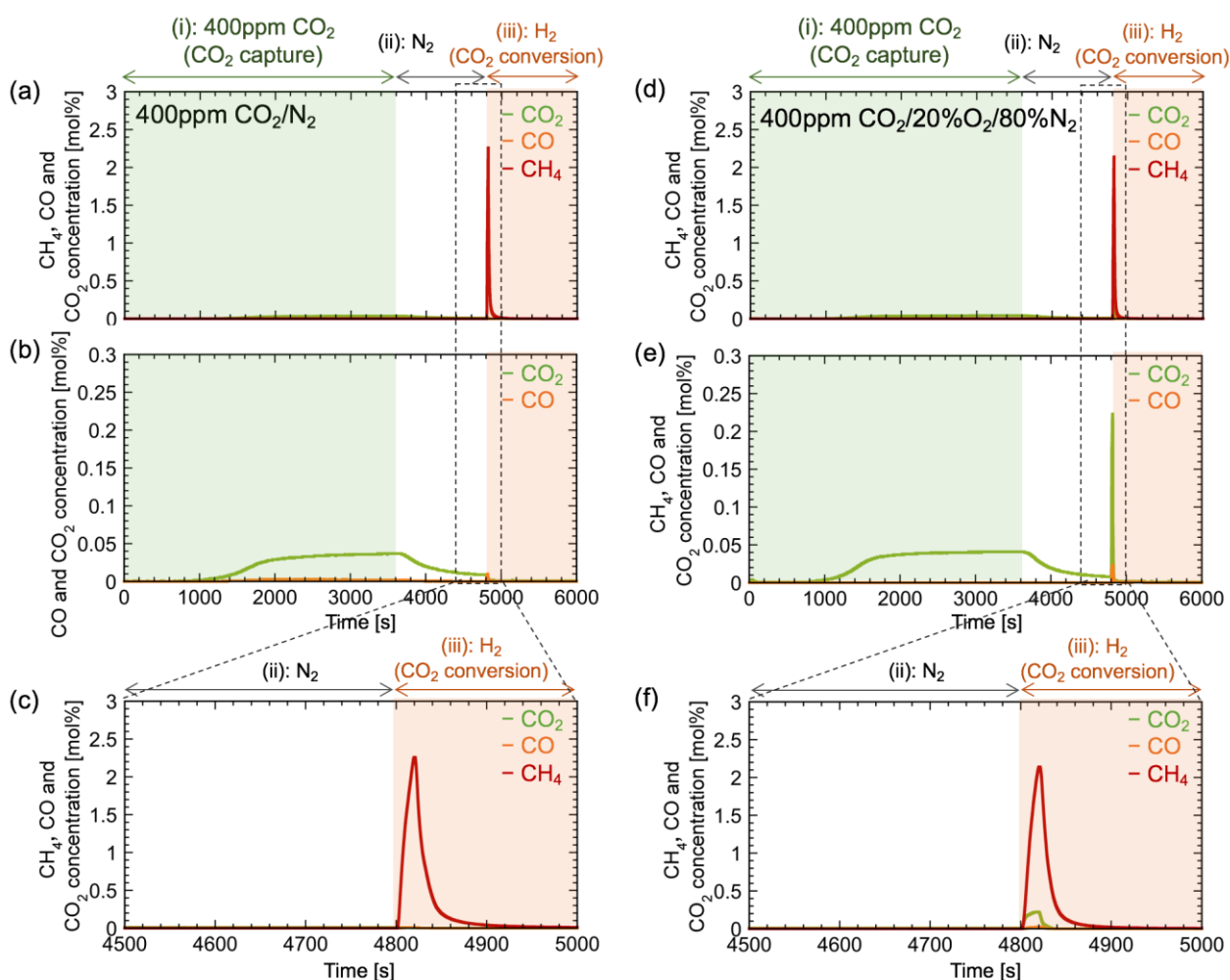
**Figure 5.** Effect of  $\text{CO}_2$  capture period (10–60 s) on the integrated  $\text{CO}_2$  capture and reduction into  $\text{CH}_4$  over  $\text{Ni}/\text{Na-}\gamma\text{-Al}_2\text{O}_3$  under atmospheric pressure. 3 g of catalyst was used, and the gas flow (total flow rate =  $50 \text{ mL min}^{-1}$ ) was switched stepwise from 13%  $\text{CO}_2$  in  $\text{N}_2$  to  $\text{N}_2$  and  $\text{H}_2$ .



**Figure 6.** Evolution of product contents during 100 ppm CO<sub>2</sub> capture and reduction over Ni/Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at atmospheric pressure. The CO<sub>2</sub> capture period lasted for 1 h. 3 g of catalyst was used and the gas flow was switched stepwise from 100 ppm CO<sub>2</sub> in N<sub>2</sub> (total flow rate = 500 mL min<sup>-1</sup>) to N<sub>2</sub> (500 mL min<sup>-1</sup>) and H<sub>2</sub> (50 mL min<sup>-1</sup>).

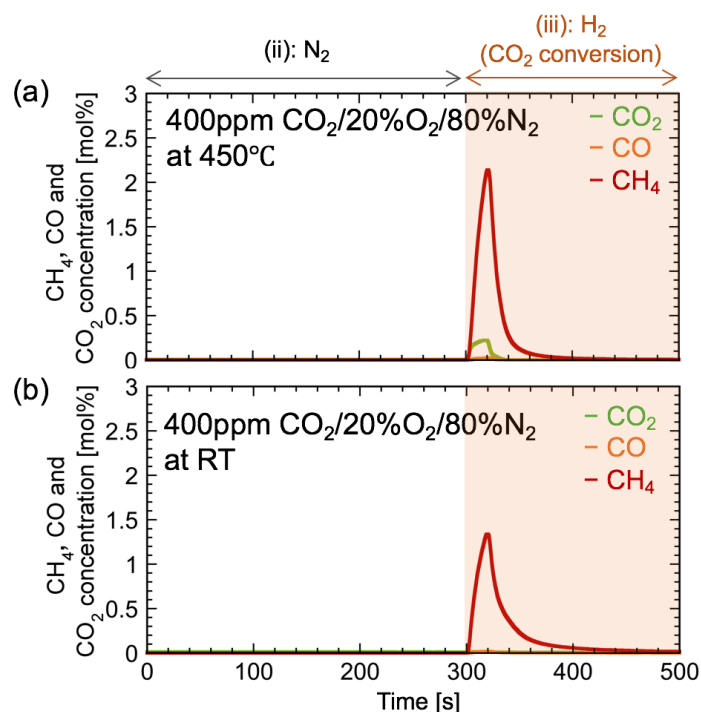
We investigated the CO<sub>2</sub> capture and reduction performance of the Ni/Na-Al<sub>2</sub>O<sub>3</sub> in the presence of O<sub>2</sub> during the CO<sub>2</sub> capture period for atmospheric CO<sub>2</sub> utilization. Figure 7 shows the effect of O<sub>2</sub> during the CO<sub>2</sub> capture period on the CO<sub>2</sub> capture and reduction performance on Ni/Na-Al<sub>2</sub>O<sub>3</sub>. Although unreacted CO<sub>2</sub> formation under H<sub>2</sub> atmosphere increased for 400 ppm CO<sub>2</sub>/20%O<sub>2</sub> (Figure 7(e) and 7(f)), the CH<sub>4</sub> formation amount was comparably high and the CH<sub>4</sub> selectivity was over 90% (Figure 7(f)). This result differs from the previous literature<sup>37</sup> that points the limitations of Ni during CO<sub>2</sub> capture in an O<sub>2</sub>-containing atmosphere. However, the relatively high temperature of 450 °C and the difference in catalyst preparation may have influenced the Ni reactivation rate in

the H<sub>2</sub> atmosphere and the O<sub>2</sub> tolerance of the catalyst. Subsequently, this may have resulted in high performance under O<sub>2</sub>-containing conditions in this study. Figure S14 shows the five cycles of CO<sub>2</sub> capture and CO<sub>2</sub> reduction using 400 ppm CO<sub>2</sub>/20% O<sub>2</sub>. The high CH<sub>4</sub> formation activity in the first cycle was maintained during several cycles, and the degradation of the catalyst exposed to O<sub>2</sub> was comparable to the degradation of the catalyst with 5% CO<sub>2</sub>/N<sub>2</sub> for CO<sub>2</sub> capture (Figure S3(b)).



**Figure 7.** Effect of O<sub>2</sub> in CO<sub>2</sub> capture period on the integrated CO<sub>2</sub> capture and reduction into CH<sub>4</sub> over Ni-Na/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 450 °C under atmospheric pressure. (a)-(c) 400 ppm CO<sub>2</sub>/N<sub>2</sub> and (d)-(f) 400 ppm CO<sub>2</sub>/20%O<sub>2</sub>/80%N<sub>2</sub> for CO<sub>2</sub> capture. The gas flow (total flow rate = 200 mL min<sup>-1</sup>) was stepwise switched from 400ppm CO<sub>2</sub> to N<sub>2</sub> (at 3600 s) and H<sub>2</sub> (at 4800 s). Catalyst weight: 1g.

Furthermore, we investigated the effect of CO<sub>2</sub> capture temperature in the presence of O<sub>2</sub> on the CH<sub>4</sub> formation performance. As shown in Figure 8, unreacted CO<sub>2</sub> release was almost negligible when the CO<sub>2</sub> capture temperature was lowered. In our future work, we consider using a circulating fluidized bed to realize a continuous process, as illustrated in Figure 2. Therefore, it is possible to operate the CO<sub>2</sub> capture reactor at a lower temperature compared to the CO<sub>2</sub> reduction reactor. The results suggest that a high CH<sub>4</sub> selectivity can be achieved and the oxidation of the earth's abundant Ni catalysts can be prevented by optimizing the CO<sub>2</sub> capture reactor temperature in the circulating fluidized bed for atmospheric CO<sub>2</sub> capture.

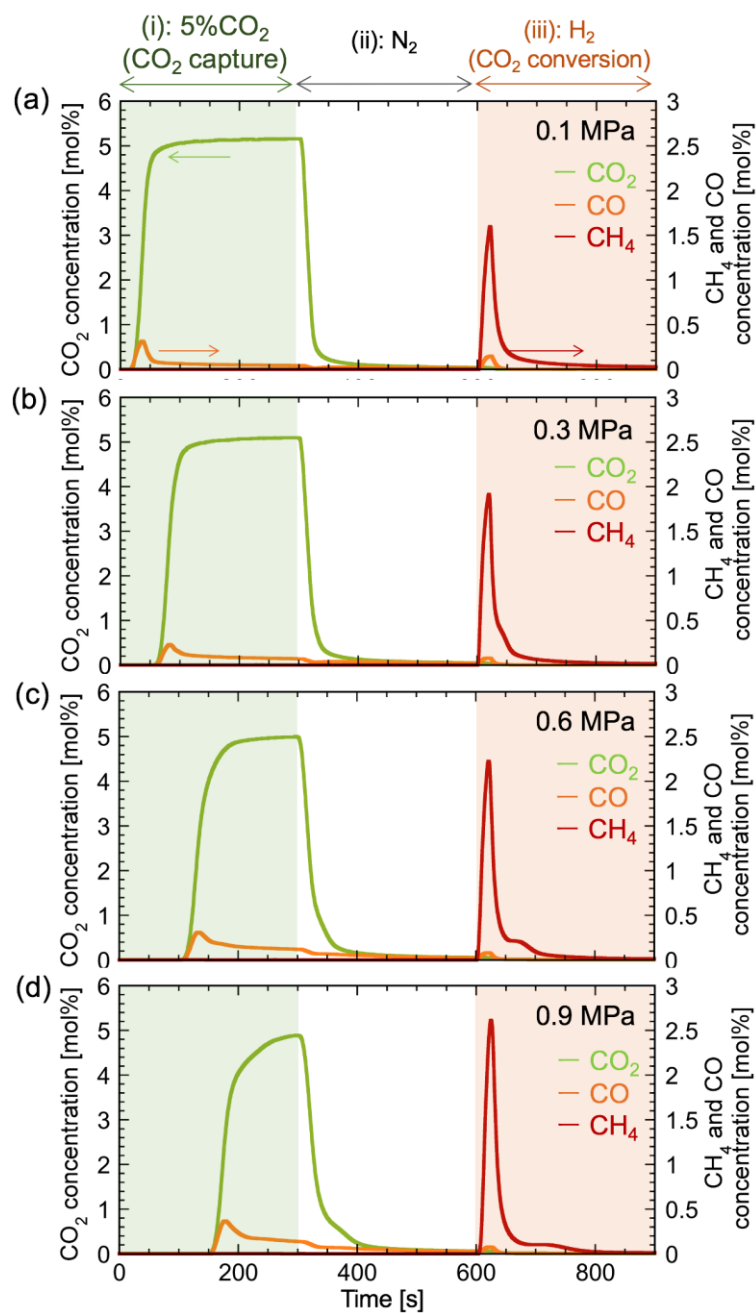


**Figure 8.** Effect of CO<sub>2</sub> capture temperature on the integrated CO<sub>2</sub> capture and reduction into CH<sub>4</sub> over Ni-Na/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> under atmospheric pressure. CO<sub>2</sub> capture (400ppm CO<sub>2</sub>/20%O<sub>2</sub>/80%N<sub>2</sub>) was performed at (a) 450 °C and (b) room temperature (20–25 °C), and then, reduction of the captured CO<sub>2</sub> by H<sub>2</sub> (300 s ~) was performed at 450 °C. Catalyst weight: 1g.

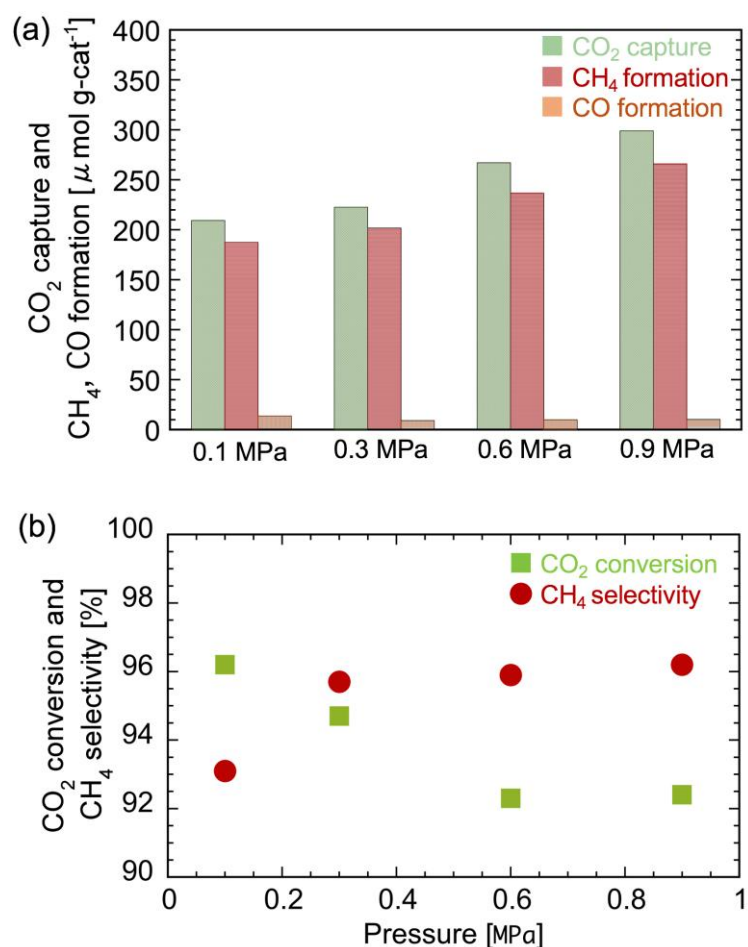


### **Enhanced capture and reduction of 5% CO<sub>2</sub> to CH<sub>4</sub> over Ni/Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> under pressure**

As shown in Figure 3, Ni/Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> showed the highest activity for integrated CO<sub>2</sub> capture and reduction into CH<sub>4</sub> at atmospheric pressure. Therefore, this catalyst was used to examine the effects of pressure (0.1–0.9 MPa) and CO<sub>2</sub> content (5% and 100–400 ppm) relevant for direct air capture on the efficiency of CO<sub>2</sub> capture and reduction into CH<sub>4</sub>. Figure 9 presents the effects of pressure, revealing that high pressure favored CH<sub>4</sub> formation. A transient and peaky response of the CH<sub>4</sub> signal was observed at all pressures, indicating that Ni/Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> can provide a fast response during CO<sub>2</sub> reduction even under pressure.



**Figure 9.** Effect of pressure (0.1–0.9 MPa) on the integrated CO<sub>2</sub> capture and reduction into CH<sub>4</sub> over Ni-Na/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The gas flow (total flow rate = 500 mL min<sup>-1</sup>) was stepwise switched from 5% CO<sub>2</sub> in N<sub>2</sub> to N<sub>2</sub> (at 300 s) and H<sub>2</sub> (at 600 s). Catalyst weight: 1g.

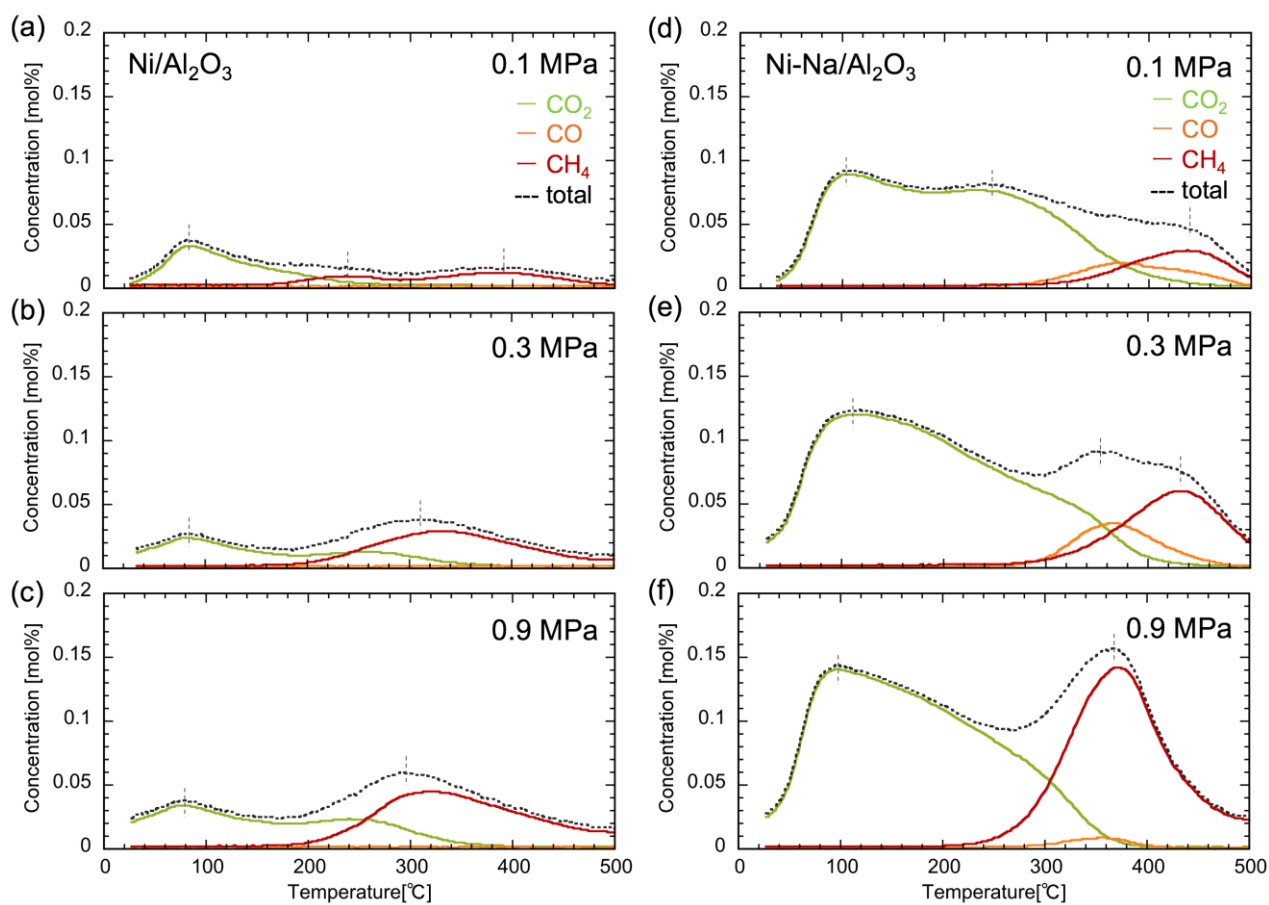


**Figure 10.** Effect of pressure on (a) CO<sub>2</sub> capture and CH<sub>4</sub> formation over Ni-Na/γ-Al<sub>2</sub>O<sub>3</sub> and (b) corresponding CO<sub>2</sub> conversion ( $X_{\text{CO}_2}$ ) and CH<sub>4</sub> selectivity ( $S_{\text{CH}_4}$ ).

Figure 10(a) shows that high pressure increased the efficiencies of CO<sub>2</sub> capture and CO<sub>2</sub> reduction to CH<sub>4</sub> over Ni-Na-γ-Al<sub>2</sub>O<sub>3</sub> while suppressing CO formation. Specifically, as pressure increased from ambient to 0.9 MPa, the CO<sub>2</sub> capture capacity increased from 209 to 299 μmol g<sub>cat</sub><sup>-1</sup> (43% increase), while CH<sub>4</sub> formation capacity increased from 188 to 266 μmol g<sub>cat</sub><sup>-1</sup> (41% increase). Figure 10(b) shows the effects of pressure on CO<sub>2</sub> conversion and CH<sub>4</sub> selectivity for Ni-Na-Al<sub>2</sub>O<sub>3</sub>. A high CO<sub>2</sub> conversion and a CH<sub>4</sub> selectivity of >92% were maintained despite the large CO<sub>2</sub> capture capacity under pressurized conditions. With increasing pressure, CH<sub>4</sub> selectivity increased

from 93 to 96%. These results suggest that high pressures positively affect the CO<sub>2</sub> capture and conversion performance of Ni/Na-Al<sub>2</sub>O<sub>3</sub>.

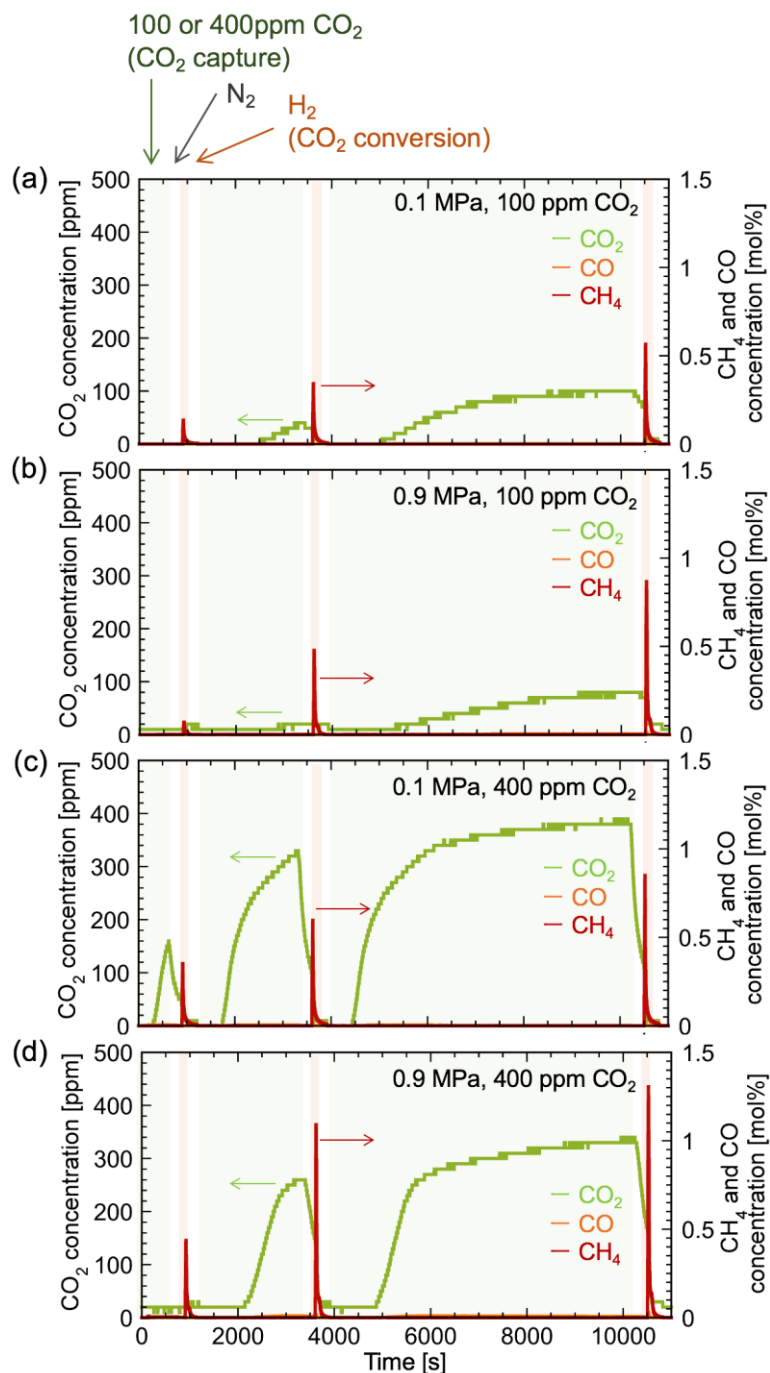
To investigate the influence of pressure on direct CO<sub>2</sub> capture and reduction, we examined the TPR of CO<sub>2</sub>-loaded Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni/Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 0.1–0.9 MPa. Prior to these experiments, the samples were reduced at 500 °C for 1 h, subjected to room-temperature CO<sub>2</sub> capture for 1 h, and then purged with a flow of H<sub>2</sub> for 30 min. TPR was performed from room temperature to 500 °C at a heating rate of 10 °C min<sup>-1</sup>, and the outgas was quantitatively analyzed by the NDIR detector (Figure 11). For Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the amounts of CO<sub>2</sub>, CO, and CH<sub>4</sub> were small, which was ascribed to the small amount of physically and chemically adsorbed CO<sub>2</sub> on Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Although CH<sub>4</sub> was observed at a relatively low temperature (~200 °C) because of the high methanation activity of Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the effect of pressure on CO<sub>2</sub> capture capacity was also small for this catalyst. On the other hand, enhanced CO<sub>2</sub> desorption and CH<sub>4</sub>/CO formation were observed for Ni/Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. In addition, the signals of CO<sub>2</sub> and CH<sub>4</sub> (but not of CO) gained intensity with increasing pressure. High pressures favored the complete hydrogenation of CO<sub>2</sub> to CH<sub>4</sub> (Eq. 1) but hindered the hydrogenation of CO<sub>2</sub> to CO (Eq. 13), especially at 0.9 MPa. This could be attributed to the advantageous pressure-dependency of the CO<sub>2</sub> methanation reaction (as predicted by Le Chatelier's principle). As pressure increased from atmospheric level to 0.9 MPa, no shift of the CO<sub>2</sub> desorption peak around 100 °C was observed, whereas the CH<sub>4</sub> formation peak shifted from 440 to 370 °C. This suggests that under pressurized conditions, the partial pressure of H<sub>2</sub> increases to accelerate the desorption of CO<sub>2</sub> and its conversion to CH<sub>4</sub>.



**Figure 11.** TPR profiles of CO<sub>2</sub>-loaded catalysts [(a–c) Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and (d–f) Ni-Na/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>] recorded at pressures of 0.1–0.9 MPa. Catalyst weight: 1g.

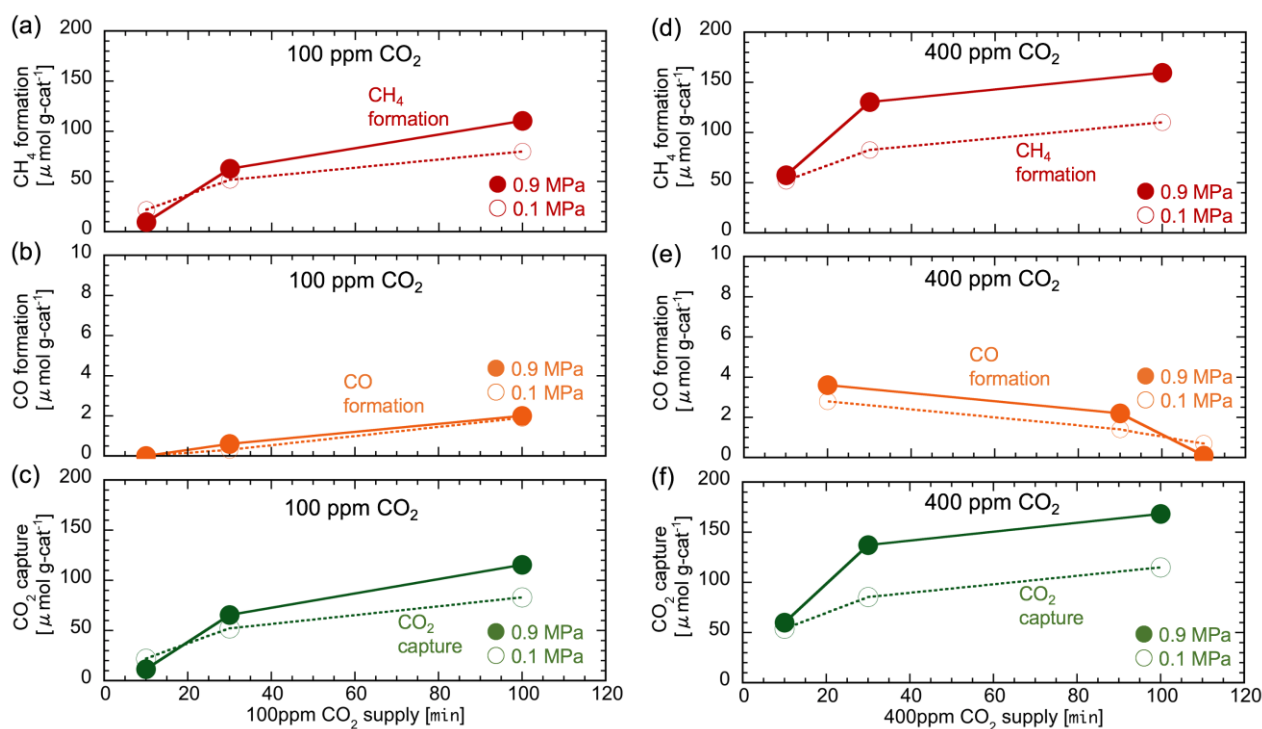
### Enhanced capture and reduction of 100 and 400 ppm CO<sub>2</sub> to CH<sub>4</sub> over Ni-Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> under pressure

Furthermore, we investigated the performance of Ni-Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for the integrated process at CO<sub>2</sub> levels relatively close to (400 ppm) and much lower than (100 ppm) that of atmospheric air (Figure 12).



**Figure 12.** Evolution of product contents during dilute CO<sub>2</sub> capture and reduction on Ni-Na/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at variable pressures ((a), (c) 0.1 MPa atm and (b), (d) 0.9 MPa) and CO<sub>2</sub> levels ((a), (b) 100 ppm and (c), (d) 400 ppm CO<sub>2</sub> diluted with N<sub>2</sub>). The CO<sub>2</sub> capture period lasted for 10, 30, or 100 min, and the total flow rate equaled 500 mL min<sup>-1</sup>. Catalyst weight: 1g.

As shown in Figure 12, elevated pressure promoted CH<sub>4</sub> formation. As described in the previous section, the CH<sub>4</sub> concentration in the outlet gas can be further improved for practical application by optimizing the gas flow rate. For both 100 and 400 ppm CO<sub>2</sub>, the amounts of CH<sub>4</sub> formed at 0.9 MPa exceeded those observed at atmospheric pressure. In addition, CH<sub>4</sub> formation was promoted by extending the CO<sub>2</sub> capture period from 10 to 100 min, as also follows from enhanced CO<sub>2</sub> capture at higher pressures. In the case of 100 ppm CO<sub>2</sub> and 0.1 MPa (Figure 12(a)), CO<sub>2</sub> was observed in the outlet gas after 15 min of CO<sub>2</sub> supply, which indicated the concomitant saturation of Ni/Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. On the other hand, saturation proceeded slowly at 0.9 MPa (Figure 12(b)). This result indicates that the CO<sub>2</sub> absorption capacity of the dual-functional catalyst increased with increasing pressure and, more importantly, the catalyst was able to efficiently capture CO<sub>2</sub> at low levels.



**Figure 13.** Effect of pressure on (a), (d) CH<sub>4</sub> formation, (b), (e) CO formation, and (c), (f) CO<sub>2</sub>

capture performances with 100 ppm and 400 ppm CO<sub>2</sub> of Ni-Na/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

Figure 13 summarizes the effects of pressure on CH<sub>4</sub> formation, CO formation, and CO<sub>2</sub> capture performances. For Ni-Na/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the amounts of produced CH<sub>4</sub> and captured CO<sub>2</sub> increased with increasing pressure and CO<sub>2</sub> capture period. CO formation was insignificant, and CO<sub>2</sub> conversion and CH<sub>4</sub> selectivity exceeded 96% under all conditions. Figure S15 shows CO<sub>2</sub> capture efficiency for 100 and 400 ppm CO<sub>2</sub> capture and reduction. As indicated, a relatively high CO<sub>2</sub> capture efficiency was obtained when an appropriate CO<sub>2</sub> capture period was employed.



**Table 1.** Integrated CO<sub>2</sub> capture and reduction performances of Ni-based dual-functional catalysts reported previously and those described in the present work. All experiments were conducted in a fixed-bed reactor.

Catalyst	CO <sub>2</sub> concentration [%]	CO <sub>2</sub> capture [ $\mu\text{mol g}_{\text{cat}}^{-1}$ ]	CH <sub>4</sub> formation [ $\mu\text{mol g}_{\text{cat}}^{-1}$ ]	CO <sub>2</sub> conversion [%]	CH <sub>4</sub> selectivity [%]	Temperature [°C]	Pressure [MPa]	Ref.
Ni/K- $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	5% CO <sub>2</sub> /N <sub>2</sub>	229	134	96	61	450	0.1	This work
Ni/Ca- $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	5% CO <sub>2</sub> /N <sub>2</sub>	73	58	82	97	450	0.1	This work
Ni/Na- $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	5% CO <sub>2</sub> /N <sub>2</sub>	209	188	96	93	450	0.1	This work
	5% CO <sub>2</sub> /N <sub>2</sub>	299	266	92	96	450	0.9	This work
	400 ppm CO <sub>2</sub> /N <sub>2</sub>	168	159	97	98	450	0.9	This work
	100 ppm CO <sub>2</sub> /N <sub>2</sub>	116	111	98	98	450	0.9	This work
Ni-CaO/Al <sub>2</sub> O <sub>3</sub>	25% CO <sub>2</sub> /Ar,	171	142	–	–	520	0.1	<sup>34</sup>
Ni-Na <sub>2</sub> CO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	25% CO <sub>2</sub> /Ar,	215	186	–	–	400	0.1	<sup>34</sup>
Ni-Na <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	7.5% CO <sub>2</sub> /N <sub>2</sub>	398	276	71	–	320	0.1	<sup>37</sup>
Ni-K/ZrO <sub>2</sub> , Ni-La/ZrO <sub>2</sub>	4.7% CO <sub>2</sub> /He	–	–	51 32	98 99	350	0.1	<sup>20</sup>

Table 1 compares the integrated CO<sub>2</sub> capture and reduction performances of previously reported Ni-based dual functional catalysts and those described herein, revealing that pressure elevation increased the efficiency of 5% CO<sub>2</sub> capture by Ni/Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> from 209 to 299  $\mu\text{mol g}_{\text{cat}}^{-1}$ . Furthermore, for 400 and 100 ppm CO<sub>2</sub>, pressurization allowed the amount of produced CH<sub>4</sub> to be increased to 159 and 111  $\mu\text{mol g}_{\text{cat}}^{-1}$ , respectively. These values are higher than or comparable to those of previous studies of alkali- or alkaline-promoted Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni/ZrO<sub>2</sub> catalysts, which were examined by the relatively high concentration of the CO<sub>2</sub> mixture gas (4.7–25% CO<sub>2</sub>) under atmospheric pressure. Thus, the investigated dual-functional catalysts could successfully capture CO<sub>2</sub> within a wide content range (100 ppm to 5%) and simultaneously convert it into CH<sub>4</sub> with very high CO<sub>2</sub> conversion and CH<sub>4</sub> selectivity. The results indicate that pressure significantly affects the activity of dual-functional catalysts for integrated CO<sub>2</sub> capture and reduction, suggesting that pressure elevation is an effective

way of improving the efficiency of CO<sub>2</sub> utilization.

## CONCLUSIONS

Herein, we investigated the effects of pressure on the performance of Ni-based dual-functional catalysts for integrated CO<sub>2</sub> capture and reduction to CH<sub>4</sub>. Specifically, Ni/Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Ni/K- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and Ni/Ca- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were prepared as dual-functional catalysts, and Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was prepared as a reference catalyst. Among these catalysts, Ni/Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> showed the highest activity for integrated CO<sub>2</sub> capture (5 vol% CO<sub>2</sub> absorption) and conversion into CH<sub>4</sub>, achieving high CO<sub>2</sub> conversion (>96%) and CH<sub>4</sub> selectivity (>93%). It was found that the CO<sub>2</sub> capture efficiency was particularly high when an appropriate CO<sub>2</sub> supply period was employed. In addition, very low concentration CO<sub>2</sub> (100 ppm CO<sub>2</sub>) was successfully converted to 11.5% CH<sub>4</sub> (>1000 times higher concentration than that of the supplied CO<sub>2</sub>) over Ni/Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Furthermore, we investigated the CO<sub>2</sub> capture and reduction performance in the presence of O<sub>2</sub> during the CO<sub>2</sub> capture period for atmospheric CO<sub>2</sub> utilization. Although the formation of unreacted CO<sub>2</sub> under H<sub>2</sub> atmosphere increased slightly in the presence of O<sub>2</sub> during CO<sub>2</sub> capture, the amount of CH<sub>4</sub> formation was comparably high. Moreover, CO<sub>2</sub> conversion was over 90% on Ni/Na-Al<sub>2</sub>O<sub>3</sub>. By lowering the CO<sub>2</sub> capture temperature, unreacted CO<sub>2</sub> release was almost negligible and CH<sub>4</sub> selectivity was further improved. Both CO<sub>2</sub> capture and CH<sub>4</sub> formation were favored by high pressure, e.g., as pressure increased from 0.1 to 0.9 MPa, CO<sub>2</sub> capture capacity increased from 209 to 299  $\mu\text{mol g}_{\text{cat}}^{-1}$ , while

CH<sub>4</sub> productivity increased from 188 to 266 μmol g<sub>cat</sub><sup>-1</sup>. In addition, the effect of pressure on catalyst performance was also investigated at very low CO<sub>2</sub> levels of 100 and 400 ppm, and high pressure was found to positively affect both CO<sub>2</sub> capture and CH<sub>4</sub> formation. These results suggest that high pressure enhances the CO<sub>2</sub> absorption and CH<sub>4</sub> formation capacities of dual-functional catalysts and allows for efficient integrated CO<sub>2</sub> capture and reduction into CH<sub>4</sub> even at atmospheric levels of CO<sub>2</sub>. The approach, in combination with the efficient catalyst, is promising for CO<sub>2</sub> utilization, thus enabling direct air capture-conversion to value-added chemicals.

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The manuscript was written through contributions from all authors. All authors have approved the final version of the manuscript.

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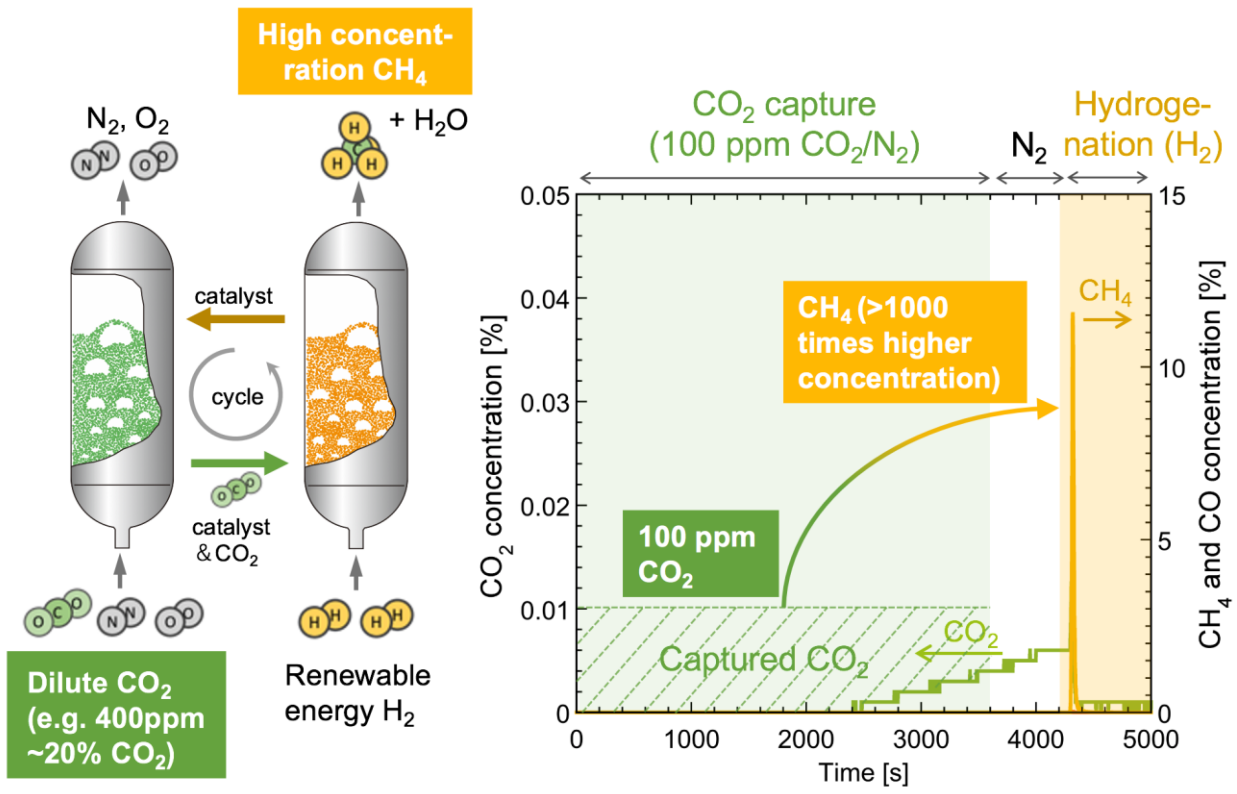
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**Graphical Abstract**



Synopsis: High pressure promoted the integrated capture and reduction (to CH<sub>4</sub>) of dilute CO<sub>2</sub> over a Ni-based Al<sub>2</sub>O<sub>3</sub>-supported catalys