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Enhanced Activity of Integrated CO₂ Capture and Reduction to CH₄ under Pressurized Conditions Towards Atmospheric CO₂ Utilization

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ABSTRACT

Direct conversion of dilute CO₂ contained in power plant or industrial exhaust gas and the atmosphere into high-concentration hydrocarbons without a need of separate CO₂ capture and purification processes is one of the awaited technologies in envisioned low-carbon societies. In this study, we investigated the performance of integrated CO₂ capture and reduction to CH₄ over Nibased dual functional catalysts promoted with Na, K and Ca. Ni/Na-γ-Al₂O₃ exhibited the highest activity for integrated CO₂ (5% CO₂) capture and reduction, achieving high CO₂ conversion (>96%) and CH₄ selectivity (>93%). In addition, very low concentration CO₂ (100 ppm CO₂) was successfully converted to 11.5% CH₄ at the peak point (>1000 times higher concentration than that of the supplied CO₂) over Ni/Na- γ -Al₂O₃. The Ni-based dual functional catalyst exhibited a high CO_2 conversion exceeding 90%, even when 20% O_2 was present during CO_2 capture. Furthermore, an increased operation pressure had positive impacts on both CO₂ capture and CH₄ formation, and these advantageous effects were also observed when CO₂ concentration was at the level of atmospheric CO₂ (100-400 ppm). As pressure increased from 0.1 to 0.9 MPa, CH₄ production capacity with 400 ppm CO₂ was enhanced from 111 to 160 μ mol g_{cat}⁻¹. The approach in combination with the efficient catalyst shows encouraging promises for CO₂ 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_2 emissions and improve energy efficiency by capturing CO_2 contained in power plant/industrial exhaust gas or even in the atmosphere and converting it into useful fuels and chemicals.^{1–5} Such carbon capture and utilization processes (CCU) can be made even greener when coupled with reduction by H₂ produced by large-scale electrolysis of water using surplus or renewable source–derived electricity.^{3,6,7} For example, CO_2 can be hydrogenated to form CH₄ according to the well-known Sabatier reaction (Eq. 1).^{7–10}

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{1}$$

CO₂ methanation has attracted much attention as a means of effective CO₂/H₂ utilization and has been implemented in several pilot plants, e.g., Audi e-gas has been running a 6-MW demonstration plant since 2013.⁶ In a conventional CCU process, flue gas with a low CO₂ content is passed through a CO₂ capture and separation unit to afford a CO₂-rich (~100%) feedstock suitable for subsequent utilization processes such as hydrogenation.¹ CO₂ 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.^{11–17} Despite the efforts made to improve the efficiency and energy cost of CO₂ capture and separation technologies,^{11–17} CO₂ capture and separation from flue gas remains energy-consuming and costly, e.g., much thermal energy is consumed during CO₂ desorption.¹⁸

In the past years, the need to decrease the energy cost and increase the efficiency of CO₂

utilization has inspired the development of technologies allowing CO_2 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_2 capture and separation process (Figure 1a).^{19–37} These technologies convert dilute CO_2 directly into high concentrations of hydrocarbons in a single process. Such single-process methods are denoted as CO_2 capture and reduction (CCR) or integrated CO_2 capture and conversion (ICCC) (Figure 1b).



(a) Conventional two-step CCU process

(b) Integrated CO₂ 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_2 into hydrocarbons over dual-functional catalysts.

The integrated CO₂ capture and conversion technology follows two reaction steps for CO₂ 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 CO₂ capture and formed after the capture, respectively. They can be different such as hydroxides and formates depending on the choice of constituting materials of catalyst²⁸.

Step 1 (CO₂ absorption): $A_nO + CO_2 \rightarrow A_nCO_3$ (A = Li, Na, K, Ca, Mg; n = 1 or 2) (2)

Step 2 (methanation of captured CO₂):
$$A_n CO_3 + 4H_2 \rightarrow A_n O + CH_4 + 2H_2 O$$
 (3)



Figure 2. Conceptual diagram of the integrated process for the direct capture of dilute CO_2 into hydrocarbons over dual-functional catalysts using the circulating fluidized-bed reactor.

In step 1, CO₂ is selectively captured as alkali/alkaline earth metal carbonates inside/on the catalysts, while other gases such as N₂ and O₂ pass through (Eq. 2). In step 2, the catalyst is exposed to H₂ to convert the captured CO₂ into hydrocarbons such as CH₄ (Eq. 3). In the CO₂ reduction reactor (step 2), CO₂ desorption and CO₂ methanation reactions proceed simultaneously. CO₂ desorption is an endothermic reaction, while CO₂ methanation is exothermic. Therefore, the two reactions can be balanced in a single reactor in the CCR process by selecting the appropriate CO₂ absorber and reaction conditions. Large amounts of heat energy, that are otherwise required for conventional CO₂ 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 CO₂ capture and CO₂ 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 γ -Al₂O₃ for the capture of 5 vol% CO₂ and its reduction by H₂ in a fixed-bed reactor at 320 °C.²³ The authors observed the formation of CH₄ upon switching from CO₂-containing gas to H₂ and thus demonstrated that a dual-functional catalyst can capture dilute CO₂ and directly convert it into CH₄.²³ 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 CO₂-absorbing components. ^{21,25,31,33,35,37} At the same period, Urakawa's group reported Fe- and Cu-based dual-functional catalysts directly converting dilute CO₂ into concentrated syngas.^{19,28} FeCrCu/K/MgO-Al₂O₃ successfully absorbed 5–10% CO₂

and converted it into CO with a high selectivity of 90–96% in an H₂ atmosphere at 450–550 °C.¹⁹ The excellent functionality was retained even when O₂ and H₂O vapor were present in the CO₂containing gas stream¹⁹. 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 CO₂ capture and reduction²⁸. Regarding the utilization of very low CO₂ levels (e.g., atmospheric CO₂ 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 CO₂ capture solid sorbent and methanation catalysts^{26,30,36}. However, the future deployment of simpler CO₂ 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 CO₂ capture and reduction to CH₄ using a fixed-bed reactor. As a well-known CO₂ 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 μ mol g_{cat}⁻¹ for Ni-Na₂CO₃/Al₂O₃) by catalyst composition tuning.³⁴ Obviously, the current challenges is how to enhance CO₂ capture capacity and CH₄ selectivity. Previous bifunctional catalytic CO₂ 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_2 and selectively convert it to CH_4 . In addition, we report on the CO_2 capture and reduction performance of the Ni-based catalyst in the presence of O_2 during the CO_2 capture period.

EXPERIMENTAL

Preparation of Ni/(Na, K, Ca)/Al₂O₃ and Ni/Al₂O₃ catalysts

 γ -Al₂O₃ (sample code: JRC-ALO-5, 74–125 µm) was supplied by the Catalysis Society of Japan (Japan Reference Catalysts). Na, K, Ca, and Ni precursors (Na₂CO₃, K₂CO₃, Ca(NO₃)₂·4H₂O, and Ni(NO₃)₂·6H₂O, respectively) were purchased from Fujifilm Wako Pure Chemical, Japan. γ -Al₂O₃ 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 γ -Al₂O₃. The Na-, K-, and Ca-modified γ -Al₂O₃ was impregnated with an aqueous Ni precursor solution (50 mL) as described above, with the Ni loading maintained at 10 wt% against modified γ -Al₂O₃. As a result, Ni/Na- γ -Al₂O₃, Ni/K- γ -Al₂O₃, and Ni/Ca- γ -Al₂O₃ dual-functional catalysts were obtained. Ni/ γ -Al₂O₃ prepared by incipient impregnation of γ -Al₂O₃ (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 $2\theta = 10-80^{\circ}$ on a Rigaku SmartLab SE diffractometer at 40 keV and 50 mA using a step size of 0.02° and a scan rate of 2 s per step. Cu K_{α} radiation ($\lambda =$ 1.5418 Å) was used as the X-ray source. N₂ adsorption-desorption isotherms were recorded at -196 °C using a Belsorp max instrument for samples outgassed at 150 °C in high vacuum (<10⁻⁵ Torr). Specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method at $P/P_0 = 0.05-$ 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 H₂-TPR, the dried samples (~100 mg) were finely packed in a quartz tube and purged with a G1-grade standard of 5.05 vol% H₂/Ar at a flow rate of 15 mL min⁻¹ 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. H₂-TPR-MS profiles were recorded at 50-950 °C and calibrated using a G1-grade standard gas of 1 vol% H₂/Ar. Prior to CO₂-TPD-MS measurements, the samples were reduced at 500 °C in a flow of H₂ (50 mL min⁻¹) for 1 h. For CO₂ chemisorption, a standard gas of 5 vol% CO₂/Ar was passed through the reduced samples at 50 °C for 30 min. Physically adsorbed CO₂ was purged by an Ar flow (50 mL min⁻¹) 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 H₂ flow (50 mL min⁻¹) for 1 h, followed by purging with an Ar flow (50 mL min⁻¹) 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.

CO2 capture and reduction to CH4 in a fixed-bed reactor

Figure S2 shows the experimental setup used for the integrated process of direct CO₂ capture and reduction into CH₄. 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 H₂ 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) CO₂ capture for 10 s–100 min, (ii) 5 min N₂ purging to remove unreacted CO₂, and (iii) reduction of the chemically captured CO₂ with H₂ for 5 min. Steps (i), (ii), and (iii) were performed using 0.01-13 vol% CO₂/N₂ (or 0.04 vol% CO₂/20%O₂/80%N₂), N₂, and H₂ as feed gases, respectively. The CO₂ capture and reduction cycle (steps (i-iii)) was repeated five times at 450 °C after H₂pretreatment 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⁻¹. 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 CH₄ formation (q_{CH_4}) , CO formation (q_{CO}) , and CO₂ capture (C_{CO_2}) capacities, as well as the CO₂ conversion (X_{CO2}), the selectivity for CH₄ or CO (S_i , $i = CH_4$ or CO), and the CO₂ capture efficiency (η_{CO_2}) were quantified using Eqs. 4–9, respectively.

$$q_{\rm CH_4} \, [\mu {\rm mol} \, {\rm g}^{-1}] = \frac{1}{W} \int_{{\rm t}_{{\rm H}_2, \, {\rm in}}}^{{\rm t}_{{\rm H}_2, \, {\rm out}}} F_{\rm CH_4}(t) dt, \tag{4}$$

$$q_{\rm CO} \, [\mu {\rm mol} \, {\rm g}^{-1}] = \frac{1}{W} \int_{{\rm tH}_{2,\,\rm in}}^{{\rm tH}_{2,\,\rm out}} F_{\rm CO,\,\rm out}(t) dt, \tag{5}$$

$$C_{\rm CO_2} \, [\mu {\rm mol} \, {\rm g}^{-1}] = \frac{1}{W} \int_{{\rm tH}_2, \, {\rm in}}^{{\rm tH}_2, \, {\rm out}} \{ F_{\rm CH_4, {\rm out}}(t) + F_{\rm CO, \, {\rm out}}(t) + F_{\rm CO_2, {\rm out}}(t) \} dt, \tag{6}$$

$$X_{\rm CO_2} = \frac{q_{\rm CH_4} + q_{\rm CO}}{C_{\rm CO_2}},\tag{7}$$

$$S_i = \frac{q_i}{q_{\rm CH_4} + q_{\rm CO}},\tag{8}$$

$$\eta_{\rm CO_2} = \frac{\int_{t_{\rm H_2,\,in}}^{t_{\rm H_2,\,out}} \{F_{\rm CH_4,out}(t) + F_{\rm CO,\,out}(t) + F_{\rm CO_2,out}(t)\}dt}{F_{\rm CO_2,in} \times t_{\rm CO_2}}$$
(9)

where W, $F_{CH_4,out}$, $F_{CO_2,out}$, $F_{CO_2,in}$, t_{CO_2} , $t_{H_2,in}$, and $t_{H_2,in}$ are the catalyst weight, the molar flow rates of CH₄, CO₂, and CO in the outlet gas, the molar flow rate of CO₂ in the inlet gas, the CO₂ supply period, the time of starting H₂ supply, and the time of ending H₂ supply, respectively.

RESULTS AND DISCUSSION

Screening of catalysts under atmospheric pressure

Figure 3 shows the performance of the integrated CO₂ capture and reduction process over dual functional catalysts (Ni/Na- γ -Al₂O₃, Ni/K- γ -Al₂O₃, and Ni/Ca- γ -Al₂O₃) examined at 450 °C under atmospheric pressure, in comparison to a reference catalyst (Ni/Al₂O₃). As aforementioned, this process can be divided into three steps: (i) chemical capture of CO₂ over Ni/Na- γ -Al₂O₃ corresponding to Eqs. (10)–(12),

$$Na_2O + CO_2 \rightarrow Na_2CO_3, \tag{10}$$

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O, \tag{11}$$

$$NaOH + CO_2 \rightarrow NaHCO_3, \tag{12}$$

(ii) purging with N₂ for 5 min to eliminate gaseous and weakly sorbed CO₂, and (iii) hydrogenation

of the captured CO_2 in the H₂ flow (Eqs. (1), (13) and (14)).

$$CO_2 + H_2 \rightarrow CO + H_2O$$
 (13)

(14)

 $\mathrm{CO} + 3\mathrm{H}_2 \rightarrow \mathrm{CH}_4 + \mathrm{H}_2\mathrm{O}$



Figure 3. Performances of (a) Ni/ γ -Al₂O₃, (b) Ni/Na- γ -Al₂O₃, (c) Ni/K- γ -Al₂O₃, and (d) Ni/Ca- γ -Al₂O₃ for integrated CO₂ capture and reduction into CH₄ at 450 °C and atmospheric pressure compared to Ni/Al₂O₃ as a reference catalyst. The gas flow (total flow rate = 500 mL min⁻¹) was stepwise switched from 5% CO₂ in N₂ to N₂ (at 300 s) and H₂ (at 600 s). Catalyst weight: 1g.

In Eqs. (10)-(12), sodium oxide and hydroxide were assumed as the CO₂ capture components and formation of sodium carbonate and bicarbonate was assumed as resulting components although the actual chemical states of captured CO₂ need to be verified^{38–40}. In step (i), a small amount of CO was formed (Figure 3), possibly through the reduction of CO₂ by surface-adsorbed hydrogen (Eq. 15), particularly in the cases of Ni/ γ -Al₂O₃ and Ni/Ca- γ -Al₂O₃.

$$2Ni-H_{ad} + CO_2 \rightarrow 2Ni + CO + H_2O, \tag{15}$$

In step (ii), a fast decrease in CO₂ content due to the N₂ purge was observed for Ni/ γ -Al₂O₃ and Ni/Ca- γ -Al₂O₃. Delayed CO₂ content decay was observed for Ni/Na- γ -Al₂O₃ and Ni/K- γ -Al₂O₃, indicating that Na- and K- promotion enhanced the CO₂-catalyst interaction. In step (iii), negligible CH₄ formation was observed for conventional CH₄ methanation catalyst, Ni/ γ -Al₂O₃, because of its small CO₂ capture capacity, which was ascribed to minor CO₂ adsorption (as opposed to absorption) during the CO₂ capture process. In contrast, large amounts of CH₄ and CO were produced over dual-functional catalysts. A large amount of CH₄ was formed over Ni/Na- γ -Al₂O₃, with a small amount of CO produced in the reduction phase. On the other hand, similar amounts of CO and CH₄ were generated over Ni/K- γ -Al₂O₃. Ni/Ca- γ -Al₂O₃ selectively afforded CH₄, albeit in a smaller amount than the Na-promoted catalyst. Although the CO₂ 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 CO₂ concentration and pressure, sufficiently long CO₂ capture periods were generally used for the purpose of this study. It should be noted that the CH₄ 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 literature²⁹, in which >60% CH₄ 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⁻¹ 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 CO₂ concentration).

Figure 4 quantifies CH₄ and CO formed in step (iii) and the amount of captured CO₂ based on Eqs. 4-6. The CO₂ capture and CH₄ formation capacities of Ni/γ-Al₂O₃ equaled 12.7 and 10.6 μ mol g_{cat}⁻¹, respectively. In the case of Ni/Na- γ -Al₂O₃, the respective values (209 and 186 μ mol g_{cat} ⁻¹) were one order of magnitude higher, and a small amount of CO was also formed (13.8 μ mol g_{cat} ⁻¹). The selectivity for CH₄ reached 93%. Although the CO₂ capture capacity of Ni/K- γ -Al₂O₃ exceeded that of Ni/Na-y-Al₂O₃, the CH₄ 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 CO₂ capture, which agrees with the previous literature where potassium on Ni catalysts enhances CO selectivity.⁴¹ Ni/Ca-y-Al₂O₃ was ineffective for capturing large amounts of CO₂, possibly because of the high stability of CaCO₃.⁴² CO₂ release from CaCO₃ generally requires a high temperature of about 700°C, which is incompatible with the temperature range of CO₂ methanation.⁴² Considering the above results, we mainly focused on the characterization and performance of Ni/Na-y-Al₂O₃ under pressurized conditions.



Figure 4. (a) CO/CH₄ production capacities and CO₂ capture capacities of Ni/Na- γ -Al₂O₃, Ni/K- γ -Al₂O₃, Ni/Ca- γ -Al₂O₃, and Ni/Al₂O₃ at 450 °C and atmospheric pressure and (b) corresponding CO₂ conversion (*X*_{CO2}) and CH₄ selectivity (*S*_{CH4}).

Characterization

The structural properties of Ni/Na- γ -Al₂O₃ and Ni/ γ -Al₂O₃ were examined by wide-angle XRD, N₂ adsorption-desorption, H₂-TPR, Ar-TPD, and CO₂-TPD (Figures S6–S10). Figure S6 shows that no Ni species were detected in Ni/ γ -Al₂O₃, indicating that Ni species were well dispersed on the γ -

Al₂O₃ framework. In contrast, the XRD pattern of fresh Ni/Na- γ -Al₂O₃ featured a weak peak at 2 θ = 29.2° corresponding to the (200) plane of Na₂CO₃ 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 N₂ adsorption-desorption isotherms of as-prepared and reduced (at 500 °C) Ni/ γ -Al₂O₃ and Ni/Na- γ -Al₂O₃ as well as the corresponding pore size distributions. All samples featured type-IV isotherms with an H₁ hysteresis loop associated with the mesoporous structure of γ -Al₂O₃.

The reducibility and basicity of Ni/Na- γ -Al₂O₃ were examined by H₂-TPR and CO₂-TPD, respectively (Figures S8 and S9). For Ni/Na- γ -Al₂O₃, NiO reduction was observed at lower temperatures (~500 °C, denoted as β ^{*}) than for Ni/ γ -Al₂O₃. 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- γ -Al₂O₃ surface. Figure S9 shows that the desorption of CO₂ from Ni/ γ -Al₂O₃ was observed at 50–300 °C, with the corresponding peak centered at ~135 °C. The CO₂ uptake of this reference catalyst was determined as 0.12 mmol g⁻¹. In contrast, Ni/Na- γ -Al₂O₃ featured two strong signals centered at 166 and 630 °C, which were ascribed to the desorption of chemisorbed CO₂ and the thermal decomposition of Na₂CO₃, respectively. The CO₂ uptake of this catalyst (1.10 mmol g⁻¹) significantly exceeded that of the reference. Thus, the co-existence of Ni and Na was concluded to increase the number of catalytic sites for CO₂ chemisorption.

To elcidate the CO formation mechanism during the CO₂ 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/ γ -Al₂O₃ > Ni/Na- γ -Al₂O₃ > Ni/Ca- γ -Al₂O₃ to Ni/K- γ -Al₂O₃, which is the same as the order of CO formation amount during the CO₂ capture step (Figure 3). It can be concluded based on these trends that the formation of the CO during the CO₂ capture step is related to the hydrogenation of CO₂ by the hydrogen adsorbed on the reduced catalysts.

Feasibility study of integrated CO₂ capture and reduction over Ni/Na-γ-Al₂O₃

Figure 5 shows the effect of the CO₂ capture period (10–60 s) on the integrated CO₂ capture and reduction performance over Ni/Na-Al₂O₃. When the CO₂ (13% CO₂) supply period was <30 seconds, the CO₂ concentration in the outlet gas was particularly low, and the majority of the supplied CO₂ was captured in the catalyst. Figure S13 shows the effect of the CO₂ supply period on the CO₂ capture efficiency, the CO₂ conversion, and the CH₄ selectivity. More specifically, the CO₂ capture efficiency was high when the CO₂ supply period was appropriate, and the efficiency decreased when the CO₂ supply period was too long due to the fact that the CO₂ capture capacity of the catalyst was saturated. Furthermore, it was found that the CO₂ conversion and CH₄ selectivity were improved when the hydrogenation of CO₂ was carried out, under the condition that the CO₂ absorption capacity of the catalyst was not saturated. These results may suggest that stronglyabsorbed CO₂ exists in the early stages, while weakly-absorbed CO₂ exists in the near-saturation stages, and that these different CO₂ species may exhibit different activities for hydrogenation. In addition, Figure 6 shows the gas concentration in the outlet when 100 ppm CO_2 was supplied at a rate of 500 mL min⁻¹ for 1 h, followed by a supply of 50 mL min⁻¹ of H₂, and using a Ni/Na-Al₂O₃ catalyst (3 g). In this case, 100 ppm CO_2 was successfully converted to 11.5% CH₄ at the peak point (>1000 times higher concentration than that of the supplied CO_2). These results indicate that the approach employed herein can efficiently convert dilute CO_2 into highly concentrated hydrocarbons without the requirement for CO_2 separation and purification.



Figure 5. Effect of CO₂ capture period (10–60 s) on the integrated CO₂ capture and reduction into CH₄ over Ni/Na- γ -Al₂O₃ under atmospheric pressure. 3 g of catalyst was used, and the gas flow (total flow rate = 50 mL min⁻¹) was switched stepwise from 13% CO₂ in N₂ to N₂ and H₂.



Figure 6. Evolution of product contents during 100 ppm CO₂ capture and reduction over Ni/Na- γ -Al₂O₃ at atmospheric pressure. The CO₂ capture period lasted for 1 h. 3 g of catalyst was used and the gas flow was switched stepwise from 100 ppm CO₂ in N₂ (total flow rate = 500 mL min⁻¹) to N₂ (500 mL min⁻¹) and H₂ (50 mL min⁻¹).

We investigated the CO₂ capture and reduction performance of the Ni/Na-Al₂O₃ in the presence of O₂ during the CO₂ capture period for atmospheric CO₂ utilization. Figure 7 shows the effect of O₂ during the CO₂ capture period on the CO₂ capture and reduction performance on Ni/Na-Al₂O₃. Although unreacted CO₂ formation under H₂ atmosphere increased for 400 ppm CO₂/20%O₂ (Figure 7(e) and 7(f)), the CH₄ formation amount was comparably high and the CH₄ selectivity was over 90% (Figure 7(f)). This result differs from the previous literature³⁷ that points the limitations of Ni during CO₂ capture in an O₂-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 H₂ atmosphere and the O₂ tolerance of the catalyst. Subsequently, this may have resulted in high performance under O₂-containing conditions in this study. Figure S14 shows the five cycles of CO₂ capture and CO₂ reduction using 400 ppm CO₂/20% O₂. The high CH₄ formation activity in the first cycle was maintained during several cycles, and the degradation of the catalyst exposed to O₂ was comparable to the degradation of the catalyst with 5% CO₂/N₂ for CO₂ capture (Figure S3(b)).



Figure 7. Effect of O₂ in CO₂ capture period on the integrated CO₂ capture and reduction into CH₄ over Ni-Na/ γ -Al₂O₃ at 450 °C under atmospheric pressure. (a)-(c) 400 ppm CO₂/N₂ and (d)-(f) 400 ppm CO₂/20%O₂/80%N₂ for CO₂ capture. The gas flow (total flow rate = 200 mL min⁻¹) was stepwise switched from 400ppm CO₂ to N₂ (at 3600 s) and H₂ (at 4800 s). Catalyst weight: 1g.

Furthermore, we investigated the effect of CO_2 capture temperature in the presence of O_2 on the CH_4 formation performance. As shown in Figure 8, unreacted CO_2 release was almost negligible when the CO_2 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_2 capture reactor at a lower temperature compared to the CO_2 reduction reactor. The results suggest that a high CH_4 selectivity can be achieved and the oxidation of the earth's abundant Ni catalysts can be prevented by optimizing the CO_2 capture reactor temperature in the circulating fluidized bed for atmospheric CO_2 capture.



Figure 8. Effect of CO₂ capture temperature on the integrated CO₂ capture and reduction into CH₄ over Ni-Na/ γ -Al₂O₃ under atmospheric pressure. CO₂ capture (400ppm CO₂/20%O₂/80%N₂) was performed at (a) 450 °C and (b) room temperature (20–25 °C), and then, reduction of the captured CO₂ by H₂ (300 s ~) was performed at 450 °C. Catalyst weight: 1g.

Enhanced capture and reduction of 5% CO2 to CH4 over Ni/Na-y-Al2O3 under pressure

As shown in Figure 3, Ni/Na- γ -Al₂O₃ showed the highest activity for integrated CO₂ capture and reduction into CH₄ at atmospheric pressure. Therefore, this catalyst was used to examine the effects of pressure (0.1–0.9 MPa) and CO₂ content (5% and 100–400 ppm) relevant for direct air capture on the efficiency of CO₂ capture and reduction into CH₄. Figure 9 presents the effects of pressure, revealing that high pressure favored CH₄ formation. A transient and peaky response of the CH₄ signal was observed at all pressures, indicating that Ni/Na- γ -Al₂O₃ can provide a fast response during CO₂ reduction even under pressure.



Figure 9. Effect of pressure (0.1–0.9 MPa) on the integrated CO₂ capture and reduction into CH₄ over Ni-Na/ γ -Al₂O₃. The gas flow (total flow rate = 500 mL min⁻¹) was stepwise switched from 5% CO₂ in N₂ to N₂ (at 300 s) and H₂ (at 600 s). Catalyst weight: 1g.



Figure 10. Effect of pressure on (a) CO₂ capture and CH₄ formation over Ni-Na/ γ -Al₂O₃ and (b) corresponding CO₂ conversion (X_{CO2}) and CH₄ selectivity (S_{CH4}).

Figure 10(a) shows that high pressure increased the efficiencies of CO₂ capture and CO₂ reduction to CH₄ over Ni/Na- γ -Al₂O₃ while suppressing CO formation. Specifically, as pressure increased from ambient to 0.9 MPa, the CO₂ capture capacity increased from 209 to 299 µmol g_{cat}⁻¹ (43% increase), while CH₄ formation capacity increased from 188 to 266 µmol g_{cat}⁻¹ (41% increase). Figure 10(b) shows the effects of pressure on CO₂ conversion and CH₄ selectivity for Ni/Na-Al₂O₃. A high CO₂ conversion and a CH₄ selectivity of >92% were maintained despite the large CO₂ capture capacity under pressurized conditions. With increasing pressure, CH₄ selectivity increased from 93 to 96%. These results suggest that high pressures positively affect the CO₂ capture and conversion performance of Ni/Na-Al₂O₃.

To investigate the influence of pressure on direct CO₂ capture and reduction, we examined the TPR of CO₂-loaded Ni/γ-Al₂O₃ and Ni/Na-γ-Al₂O₃ at 0.1–0.9 MPa. Prior to these experiments, the samples were reduced at 500 °C for 1 h, subjected to room-temperature CO₂ capture for 1 h, and then purged with a flow of H₂ for 30 min. TPR was performed from room temperature to 500 °C at a heating rate of 10 °C min⁻¹, and the outgas was quantitatively analyzed by the NDIR detector (Figure 11). For Ni/y-Al₂O₃, the amounts of CO₂, CO, and CH₄ were small, which was ascribed to the small amount of physically and chemically adsorbed CO₂ on Ni/ γ -Al₂O₃. Although CH₄ was observed at a relatively low temperature (~200 °C) because of the high methanation activity of Ni/y-Al₂O₃, the effect of pressure on CO₂ capture capacity was also small for this catalyst. On the other hand, enhanced CO₂ desorption and CH₄/CO formation were observed for Ni/Na-γ-Al₂O₃. In addition, the signals of CO₂ and CH₄ (but not of CO) gained intensity with increasing pressure. High pressures favored the complete hydrogenation of CO₂ to CH₄ (Eq. 1) but hindered the hydrogenation of CO₂ to CO (Eq. 13), especially at 0.9 MPa. This could be attributed to the advantageous pressuredependency of the CO₂ methanation reaction (as predicted by Le Chatelier's principle). As pressure increased from atmospheric level to 0.9 MPa, no shift of the CO2 desorption peak around 100 °C was observed, whereas the CH₄ formation peak shifted from 440 to 370 °C. This suggests that under pressurized conditions, the partial pressure of H₂ increases to accelerate the desorption of CO₂ and its conversion to CH₄.



Figure 11. TPR profiles of CO₂-loaded catalysts $[(a-c) Ni/\gamma-Al_2O_3 \text{ and } (d-f) Ni-Na/\gamma-Al_2O_3]$ recorded at pressures of 0.1–0.9 MPa. Catalyst weight: 1g.

Enhanced capture and reduction of 100 and 400 ppm CO₂ to CH₄ over Ni/Na-γ-Al₂O₃ under

pressure

Furthermore, we investigated the performance of Ni/Na- γ -Al₂O₃ for the integrated process at CO₂ 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 CO₂ capture and reduction on Ni-Na/ γ -Al₂O₃ at variable pressures ((a), (c) 0.1 MPa atm and (b), (d) 0.9 MPa) and CO₂ levels ((a), (b)100 ppm and (c), (d) 400 ppm CO₂ diluted with N₂). The CO₂ capture period lasted for 10, 30, or 100 min, and the total flow rate equaled 500 mL min⁻¹. Catalyst weight: 1g.

As shown in Figure 12, elevated pressure promoted CH₄ formation. As described in the previous section, the CH₄ concentration in the outlet gas can be further improved for practical application by optimizing the gas flow rate. For both 100 and 400 ppm CO₂, the amounts of CH₄ formed at 0.9 MPa exceeded those observed at atmospheric pressure. In addition, CH₄ formation was promoted by extending the CO₂ capture period from 10 to 100 min, as also follows from enhanced CO₂ capture at higher pressures. In the case of 100 ppm CO₂ and 0.1 MPa (Figure 12(a)), CO₂ was observed in the outlet gas after 15 min of CO₂ supply, which indicated the concomitant saturation of Ni/Na- γ -Al₂O₃. On the other hand, saturation proceeded slowly at 0.9 MPa (Figure 12(b)). This result indicates that the CO₂ absorption capacity of the dual-functional catalyst increased with increasing pressure and, more importantly, the catalyst was able to efficiently capture CO₂ at low levels.



Figure 13. Effect of pressure on (a), (d) CH₄ formation, (b), (e) CO formation, and (c), (f) CO₂

capture performances with 100 ppm and 400 ppm CO₂ of Ni-Na/γ-Al₂O₃.

Figure 13 summarizes the effects of pressure on CH₄ formation, CO formation, and CO₂ capture performances. For Ni/Na- γ -Al₂O₃, the amounts of produced CH₄ and captured CO₂ increased with increasing pressure and CO₂ capture period. CO formation was insignificant, and CO₂ conversion and CH₄ selectivity exceeded 96% under all conditions. Figure S15 shows CO₂ capture efficiency for 100 and 400 ppm CO₂ capture and reduction. As indicated, a relatively high CO₂ capture efficiency was obtained when an appropriate CO₂ capture period was employed.

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Catalyst	CO ₂ concentration [%]	CO_2 capture [µmol g _{cat} ⁻¹]	CH_4 formation $[\mu mol \ g_{cat}^{-1}]$	CO ₂ conversion [%]	CH ₄ selectivity [%]	Temperature [°C]	Pressure [MPa]	Ref.
Ni/K-γ-Al ₂ O ₃	5% CO ₂ /N ₂	229	134	96	61	450	0.1	This work
Ni/Ca-γ-Al ₂ O ₃	5% CO ₂ /N ₂	73	58	82	97	450	0.1	This work
Ni/Na-γ-Al ₂ O ₃	5% CO ₂ /N ₂	209	188	96	93	450	0.1	This work
	5% CO ₂ /N ₂	299	266	92	96	450	0.9	This work
	400 ppm CO ₂ /N ₂	168	159	97	98	450	0.9	This work
	100 ppm CO ₂ /N ₂	116	111	98	98	450	0.9	This work
Ni-CaO/Al ₂ O ₃	25% CO ₂ /Ar,	171	142	-	_	520	0.1	34
Ni- Na ₂ CO ₃ /Al ₂ O ₃	25% CO ₂ /Ar,	215	186	_	-	400	0.1	34
Ni-Na ₂ O/Al ₂ O ₃	7.5% CO ₂ /N ₂	398	276	71	_	320	0.1	37
Ni-K/ZrO ₂ , Ni-La/ZrO ₂	4.7% CO ₂ /He	-	_	51 32	98 99	350	0.1	20

Table 1. Integrated CO_2 capture and reduction performances of Ni-based dual-functional catalysts reportedpreviously and those described in the present work. All experiments were conducted in a fixed-bed reactor.

Table 1 compares the integrated CO₂ capture and reduction performances of previously reported Nibased dual functional catalysts and those described herein, revealing that pressure elevation increased the efficiency of 5% CO₂ capture by Ni/Na- γ -Al₂O₃ from 209 to 299 μ mol g_{cat}⁻¹. Furthermore, for 400 and 100 ppm CO₂, pressurization allowed the amount of produced CH₄ to be increased to 159 and 111 μ mol g_{cat}⁻¹, respectively. These values are higher than or comparable to those of previous studies of alkali- or alkaline-promoted Ni/ γ -Al₂O₃ and Ni/ZrO₂ catalysts, which were examined by the relatively high concentration of the CO₂ mixture gas (4.7–25% CO₂) under atmospheric pressure. Thus, the investigated dual-functional catalysts could successfully capture CO₂ within a wide content range (100 ppm to 5%) and simultaneously convert it into CH₄ with very high CO₂ conversion and CH₄ selectivity. The results indicate that pressure significantly affects the activity of dualfunctional catalysts for integrated CO₂ capture and reduction, suggesting that pressure elevation is an effective way of improving the efficiency of CO₂ utilization.

CONCLUSIONS

Herein, we investigated the effects of pressure on the performance of Ni-based dual-functional catalysts for integrated CO₂ capture and reduction to CH₄. Specifically, Ni/Na-γ-Al₂O₃, Ni/K-γ-Al₂O₃, and Ni/Ca- γ -Al₂O₃ were prepared as dual-functional catalysts, and Ni/ γ -Al₂O₃ was prepared as a reference catalyst. Among these catalysts, Ni/Na-γ-Al₂O₃ showed the highest activity for integrated CO₂ capture (5 vol% CO₂ absorption) and conversion into CH₄, achieving high CO₂ conversion (>96%) and CH₄ selectivity (>93%). It was found that the CO₂ capture efficiency was particularly high when an appropriate CO₂ supply period was employed. In addition, very low concentration CO₂ (100 ppm CO₂) was successfully converted to 11.5% CH₄ (>1000 times higher concentration than that of the supplied CO₂) over Ni/Na-γ-Al₂O₃. Furthermore, we investigated the CO₂ capture and reduction performance in the presence of O₂ during the CO₂ capture period for atmospheric CO₂ utilization. Although the formation of unreacted CO₂ under H₂ atmosphere increased slightly in the presence of O₂ during CO₂ capture, the amount of CH₄ formation was comparably high. Moreover, CO₂ conversion was over 90% on Ni/Na-Al₂O₃. By lowering the CO₂ capture temperature, unreacted CO₂ release was almost negligible and CH₄ selectivity was further improved. Both CO₂ capture and CH₄ formation were favored by high pressure, e.g., as pressure increased from 0.1 to 0.9 MPa, CO₂ capture capacity increased from 209 to 299 µmol g_{cat}⁻¹, while CH₄ productivity increased from 188 to 266 μ mol g_{cat}⁻¹. In addition, the effect of pressure on catalyst performance was also investigated at very low CO₂ levels of 100 and 400 ppm, and high pressure was found to positively affect both CO₂ capture and CH₄ formation. These results suggest that high pressure enhances the CO₂ absorption and CH₄ formation capacities of dual-functional catalysts and allows for efficient integrated CO₂ capture and reduction into CH₄ even at atmospheric levels of CO₂. The approach, in combination with the efficient catalyst, is promising for CO₂ 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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Synopsis: High pressure promoted the integrated capture and reduction (to CH₄) of dilute CO₂ over a Ni-based Al₂O₃-supported catalys