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Continuous CO₂ capture and methanation over Ni–Ca/Al₂O₃ dual functional materials†

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Although Ni–Ca-based dual functional materials (DFMs) have been examined for CO₂ capture and reduction with H₂ (CCR) for the synthesis of CH₄, their performance has generally been investigated using single reactors in an oxygen-free environment. In addition, continuous CCR operations have scarcely been investigated. In this study, continuous CCR for the production of CH₄ was investigated using a double reactor system over Al₂O₃-supported Ni–Ca DFMs in the presence of O₂. We found that a high Ca loading (Ni(10)–Ca(30)/Al₂O₃, 10 wt% Ni, and 30 wt% CaO) was necessary for reaction efficiency under isothermal conditions at 450 °C. The optimized DFM exhibited an excellent performance (46% CO₂ conversion, 45% CH₄ yield, and 97% CH₄ selectivity, respectively) and good stability over 24 h. The structure and CCR activity of Ni(10)–Ca(30)/Al₂O₃ were studied using X-ray diffraction (XRD), scanning transmission electron microscopy (STEM), energy-dispersive X-ray spectrometry (EDS), temperature-programmed desorption (TPD), and temperature-programmed surface reaction (TPSR) techniques.

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Introduction

As a major component of greenhouse gases, CO₂ is a significant contributor to global warming. To reduce CO₂ emissions and establish a low-carbon society, carbon capture and utilization (CCU) strategies, including CO₂ capture and reduction (CCR) using H₂ or hydrocarbons, provide valuable approaches.¹ Among these, CO₂ capture and methanation is an effective protocol for the synthesis of carbon-neutral CH₄.² Alkali and alkaline earth metals are widely used for CO₂ capture, owing to their high capacity for CO₂ uptake and the ability to form metal carbonates. To promote carbonate hydrogenation, transition metals, such as Ru, Pt, Fe, Ni, and Cu are utilized. Thus, dual functional materials (DFMs) consisting of alkali/earth alkaline metal salts and transition metal species have attracted considerable interest in recent years.³

CaO is generally used for CO₂ capture, and Ni is particularly promising owing to its low price.⁴ Therefore, Ni–Ca DFMs hold promise for CO₂ capture and methanation processes. For example, Yang *et al.*⁵ found that CO₂ conversion and CH₄ selectivity were higher with the use of Ni/CaO–Al₂O₃ than with that of Ni/Al₂O₃ as a result of surface coverage by CO₂-derived species on the CaO–Al₂O₃ surface. Alipour *et al.*⁶ reported that

the capacity for CO₂ capture was improved noticeably when CaO, MgO, or BaO was loaded onto a Ni/Al₂O₃ catalyst. Bermejo-Lopez *et al.*⁴ investigated the effect of Ni content in DFMs on CCR using CaO as a sorbent. They established that the maximum CH₄ formation (142 μmol g⁻¹) at 520 °C was achieved using 15Ni15Ca (15 wt% Ni, and 15 wt% CaO). Sun *et al.*⁷ studied the effect of the interactions between the Ni active sites and CaO sorbents on the CCR process. They found that CO₂ conversion and CH₄ selectivity using 1% Ni/CeO₂–CaO, obtained by physical mixing of 1% Ni/CeO₂ and CaO in a mass ratio of 1 : 1, increased significantly to 62% and 84%, respectively, when the distance between the catalytic sites and sorbents was increased to a suitable scale. Although CCR over DFMs aims to utilize diluted CO₂ in air or flue gas, most previous studies on Ni-based DFMs were conducted under O₂-free conditions.^{4–7} Recently, Kuramoto and co-workers⁸ studied the CCR activity of Ni-based DFMs comprising Na, K, or Ca, in the presence of oxygen. They found that when the operational pressure was increased from 0.1 to 0.9 MPa using 400 ppm CO₂, CH₄ production over Ni–Na/Al₂O₃ increased from 111 to 160 μmol g⁻¹. Although pressure elevation effectively enhances the CCR performance, mild reaction conditions are preferable from an economic viewpoint.

Recently, we developed DFMs comprising Na-modified Pt NPs on Al₂O₃ as effective DFMs for CO₂ capture in the presence of O₂ and reduction with H₂ to generate CO.⁹ A continuous CCR operation was achieved using a double reactor system, whereby the valves on the top and bottom were controlled to switch the gas supply. This protocol was proposed by Urakawa *et al.* in the

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first time.¹⁰ In this study, continuous CCR was investigated using Al₂O₃-supported Ni–Ca DFMs. We optimized the loading amounts of Ni and Ca and found that a high Ca loading (Ni = 10 wt% and CaO = 30 wt%, Ni(10)–Ca(30)/Al₂O₃) was optimal for CCR under isothermal conditions at 450 °C. Characterization of the high Ca-content Ni–Ca/Al₂O₃ DFM revealed the formation of a Ca–Al mixed oxide phase derived from the mayenite (Ca₁₂Al₁₄O₃₃) structure.¹¹ The impact of mixed oxide formation on CO₂ adsorption and desorption, as well as on the hydrogenation of adsorbed CO₂ was discussed.

Experimental

DFM preparation

Ni–Ca/Al₂O₃ DFMs were synthesized using the wetness impregnation method. The γ -Al₂O₃ support was obtained by calcination of boehmite (γ -AlOOH, Sasol Chemicals) at 900 °C for 3 h. An appropriate amount of aqueous Ca(NO₃)₂·H₂O (AR 98.5%, FUJIFILM Wako Pure Chemical Corporation) was stirred for 3 h with calcined γ -Al₂O₃ for impregnation (Ca: 6, 20, 30, 40, and 50 wt%). The resultant suspension of Al₂O₃ and Ca(NO₃)₂ was then evaporated at 50 °C using a vacuum pump, followed by drying at 100 °C overnight. The Ca/Al₂O₃ support was obtained after calcination at 600 °C for 2 h. Next, Ca–Al₂O₃ was impregnated with Ni(NO₃)₂·6H₂O (AR > 99%, FUJIFILM Wako Pure Chemical Corporation) (Ni: 1, 5, 10, and 15 wt%) as follows. A Ca/Al₂O₃ suspension in Ni precursor solution was stirred at room temperature for 30 min, and then the mixture was evaporated, dried, and calcined, as described for the Ca–Al₂O₃ support preparation procedure. Finally, Ni–Ca/Al₂O₃ DFMs with varying Ca loadings were obtained, denoted as Ni(*x*)–Ca(*y*)/Al₂O₃ (where *x* and *y* are the loadings of Ni and Ca, respectively).

For the synthesis of Ca₁₂Al₁₄O₃₃, mixed aqueous solutions of Ca(NO₃)₂·H₂O and γ -AlOOH in a molar ratio of 12 : 7 were continuously stirred at room temperature for 3 h and then evaporated at 50 °C using a vacuum pump, followed by drying at 100 °C overnight. The dried powder was calcined at 1050 °C for 2 h to obtain Ca₁₂Al₁₄O₃₃. Finally, Ni/Ca₁₂Al₁₄O₃₃ was obtained using the above-described procedure for the synthesis of Ni–Ca/Al₂O₃ DFMs.

Characterization

Powder X-ray diffraction (XRD) measurements were carried out on a Rigaku MiniFlex II/AP diffractometer with Cu K α radiation. High-Angle Annular Dark Field Scanning Transmission Electron Microscopy (HAADF-STEM) images were recorded on a FEI Titan G2 microscope equipped with an energy dispersive X-ray (EDX) analyzer. The specific surface area was calculated using Brunauer–Emmett–Teller (BET) theory over the range $P/P_0 = 0.1$ – 0.3 . Temperature programmed desorption of carbon dioxide (CO₂ TPD) was performed on a vertical quartz fixed-bed flow reactor connected with a mass spectrometer (Microtrac BEL Corp.). A 100 mg of sample was put on quartz wool in the middle of the reactor. The reactor set in an electric tube furnace and purged under N₂ flow (95 mL min^{−1}) for 30 min at 450 °C, and then cool down the sample to room temperature. Next, the

1% CO₂/N₂ (100 mL min^{−1}) mixed gases fed into the reactor for 30 min and then flowed N₂ for 15 min. After that, the TPD profile was obtained by heating the sample from 30 to 650 °C in N₂ flow with elevating temperature by 10 °C min^{−1}. Temperature program surface reaction (TPSR) was performed on the same equipment as described for TPD measurement. First, sample with 100 mg was put on quartz wool in the middle of the reactor. The reactor set in an electric tube furnace and pretreatment under 10% H₂/N₂ flow (100 mL min^{−1}) for 30 min at 450 °C. The sample was cooled down to room temperature in subsequently. Next, 1% CO₂/10% O₂/N₂ (100 mL min^{−1}) flow was fed into the reactor for 30 min and then flowed N₂ for 15 min. Finally, TPSR profile was obtained by heating the sample from 30 to 650 °C by 10 °C min^{−1} with 5% H₂/N₂ flow (100 mL min^{−1}).

Continuous CCR operation

CCR was performed in continuous separated fixed-bed flow reactors (Fig. 1). The similar reaction system has been developed in our previous study.⁹ Two vertical quartz reactors were utilized (reactors A and B), and 100 mg of the sample was placed on quartz wool in the middle of the reactor. Two sides of the tube were filled with sea sand. Both reactors were equipped with the same DFM and placed in an electric tube furnace. Reactors were heated to 500 °C under N₂ flow (90 mL min^{−1}), followed by the introduction of 10% H₂/N₂ (100 mL min^{−1}) for pretreatment over 20 min at 500 °C. The two timer-control 4-way valves were switched simultaneously to continuously collect the effluent gases containing uncaptured CO₂ (effluent 1) and generated CO and CH₄, and desorbed CO₂ (effluent 2) from each outlet line. The compositions of effluents 1 and 2 were monitored employing Fourier transform infrared (FTIR) spectroscopy (JASCO FT/IR-4600) using gas cells. The background spectrum was acquired once the temperature decreased to 450 °C after H₂ pretreatment followed by N₂ purging. Next, 100 mL min^{−1} of 1% CO₂/10% O₂/N₂ was fed to reactor A for 30 s, and then the gas feed was switched to 100 mL min^{−1} of pure H₂ for 30 s. Reactor B underwent reverse treatment; thus, 100 mL min^{−1} of pure H₂ was fed into reactor B for 30 s, and then the gas was switched to 100 mL min^{−1} of 1% CO₂/10% O₂/N₂ for 30 s. CCR was also conducted using a single reactor for comparison. Thus, only one reactor was equipped with a DFM (100 mg) and the other reactor was filled with pure sea sand. The subsequent steps implemented for the single reactor were the same as those described for the continuous operation of the double reactor system. The CO₂ capture amount (q_{CO_2}), amount of generated CO and CH₄ (denoted as q_{CO} , q_{CH_4} , respectively), selectivity for CO (Sel_{CO}), and conversion of captured CO₂ ($\text{Conv}_{\text{capCO}_2}$) were calculated as follows:

$$q_{\text{CO}_2} (\text{mmol g}^{-1}) = \frac{\int_0^{t_a} [F_{\text{CO}_2}^{\text{in}}(t) - F_{\text{CO}_2}^{\text{out}}(t)] dt}{m} \quad (1)$$

$$q_{\text{CO}} (\mu\text{mol g}^{-1}) = \frac{\int_0^{t_{\text{H}}} F_{\text{CO}}^{\text{out}}(t) dt}{m} \quad (2)$$



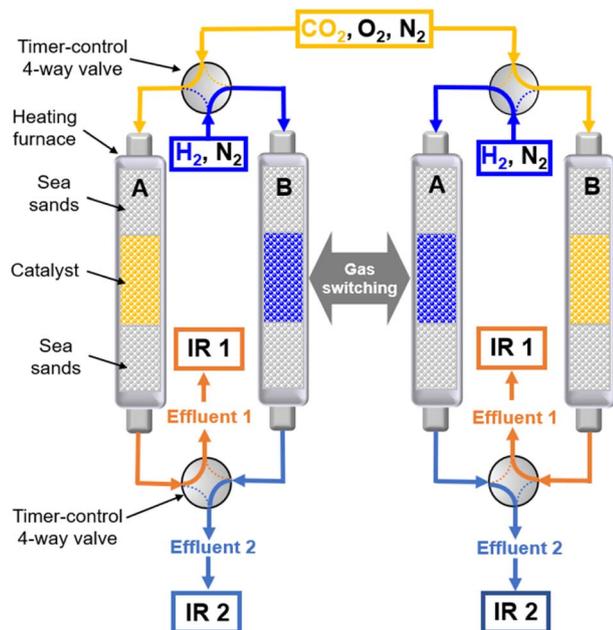


Fig. 1 Diagram of the continuous-operation CCR double reactor system.

$$q_{\text{CH}_4} (\mu\text{mol g}^{-1}) = \frac{\int_0^{t_H} F_{\text{CH}_4}^{\text{out}}(t) dt}{m} \quad (3)$$

$$\text{Sel}_{\text{CO}}(\%) = \frac{q_{\text{CO}}}{q_{\text{CH}_4} + q_{\text{CO}}} \times 100 \quad (4)$$

$$\text{Conv}_{\text{capCO}_2}(\%) = \frac{q_{\text{CO}} + q_{\text{CH}_4}}{q_{\text{CO}_2}} \times 100 \quad (5)$$

where $F_{\text{CO}_2}^{\text{in}}$ and $F_{\text{CO}_2}^{\text{out}}$ are the CO_2 molar flow rates at the column inlet and outlet, respectively; $F_{\text{CO}}^{\text{out}}$ and $F_{\text{CH}_4}^{\text{out}}$ are the CO and CH_4 molar flow rates at the column outlet, respectively; m is the DFM

mass; t_a is the duration of the adsorption stage; t_H denotes the duration of the H_2 reduction process.

Results and discussion

DFMs comprising different loading amounts of Ni and Ca on Al_2O_3 were screened to determine the optimal composition for the continuous CCR system. First, the effect of Ca content was studied, while the Ni loading was kept constant at 10 wt% (CaO: 0, 6, 20, 30, and 40 wt%). As shown in Fig. 2, Ni(10)/ Al_2O_3 without Ca adsorbed a moderate amount of CO_2 ($132 \mu\text{mol g}^{-1}$), but CH_4 production was low ($2 \mu\text{mol g}^{-1}$). The CO_2 capture amount gradually increased from 228 to $390 \mu\text{mol g}^{-1}$ as the Ca content increased from 6 to 40 wt% whereas CH_4 formation was the highest ($153 \mu\text{mol g}^{-1}$) for Ni(10)-Ca(30)/ Al_2O_3 . This result illustrates the importance of optimizing the Ca loading on Ni-Ca/ Al_2O_3 DFMs. The CO_2 conversion, CH_4 yield, and CH_4 selectivity in CCR using Ni(10)-Ca(30)/ Al_2O_3 were 46%, 45%, and 97%, respectively. These values were comparable with those for reported Ni-Ca DFMs (Table S1†). Next, Ni(x)-Ca(30)/ Al_2O_3 containing varying Ni loadings (Ni: 5, 10, and 20 wt%) were also prepared and tested for continuous CCR (Fig. 2). A Ni loading of 10 wt% was found to be optimal for both CO_2 adsorption and CH_4 formation. Thus, the optimal loading amounts of Ca and Ni were 30 and 10 wt%, respectively, for continuous CCR operation under isothermal conditions at 450°C . Furthermore, 30 wt% CaO was loaded onto Ni(10)/ Al_2O_3 and then applied to continuous CCR to investigate the effect of the Ni and Ca loading sequence (Fig. 2). The amounts of CO_2 captured and CH_4 formed over Ca(30)-Ni(10)/ Al_2O_3 were 217 and $64 \mu\text{mol g}^{-1}$, respectively. These values are lower than those for Ni(10)-Ca(30)/ Al_2O_3 (340 and $153 \mu\text{mol g}^{-1}$), suggesting the importance of the loading sequence of Ni and Ca onto Al_2O_3 . Thus, Ni(10)-Ca(30)/ Al_2O_3 was applied in further investigations in this study.

Next, the comparison of continuous CCRs using double and single reactor systems using Ni(10)-Ca(30)/ Al_2O_3 is shown in

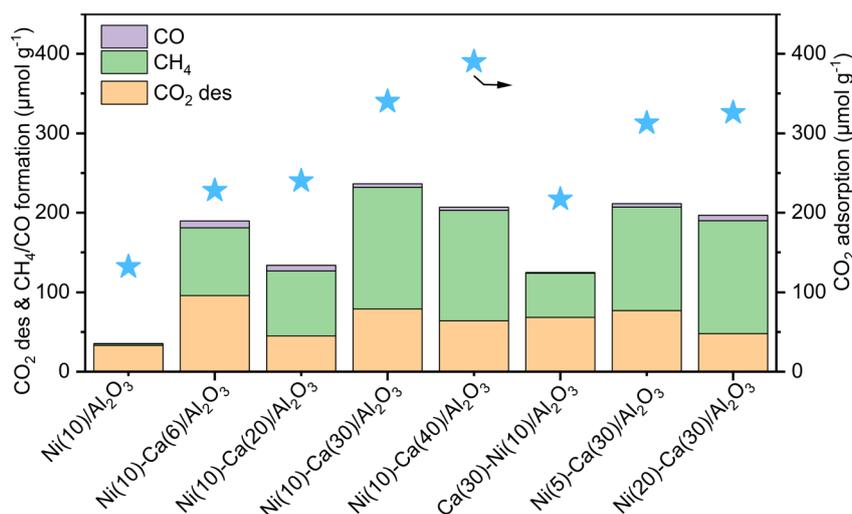


Fig. 2 Effluent gas compositions for continuous CCR operation over Ni(x)-Ca(y)/ Al_2O_3 with varying Ca and Ni loadings. Conditions: 100 mg sample for each reactor, 450°C , 100 mL min^{-1} of 1% $\text{CO}_2/10\% \text{ O}_2/\text{N}_2$ for 30 s, then switched to 100 mL min^{-1} of H_2 for 30 s.



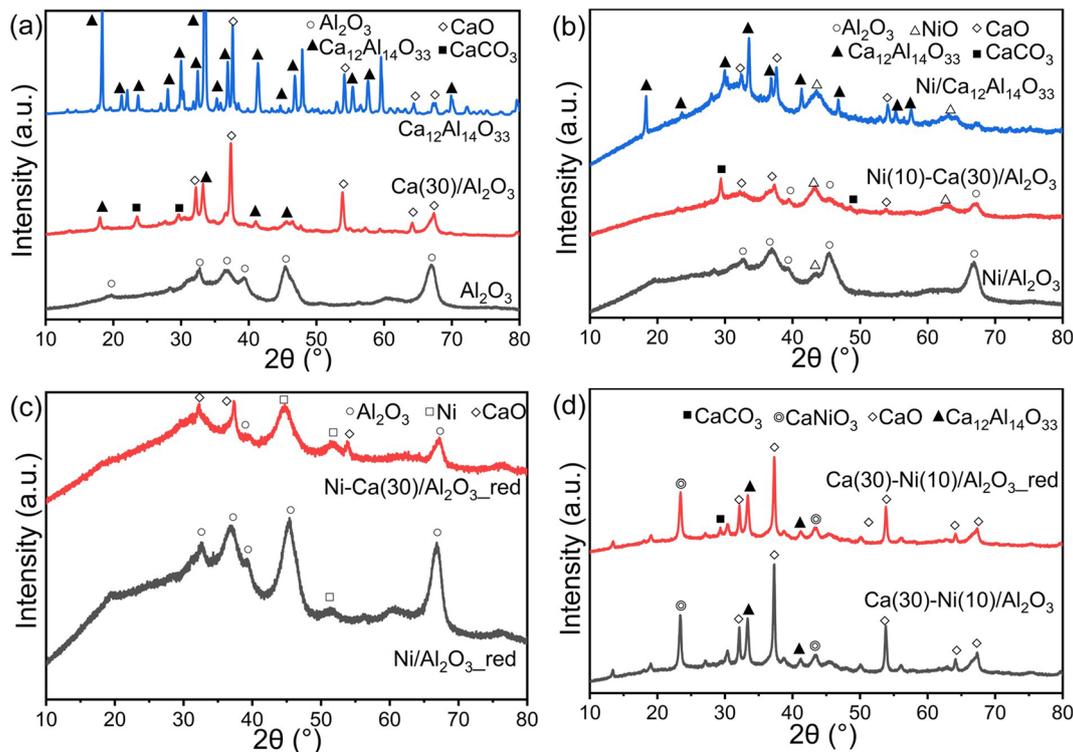


Fig. 3 XRD patterns of (a) Al_2O_3 , $\text{Ca}(30)/\text{Al}_2\text{O}_3$, and $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ without Ni loading; (b) calcined $\text{Ni}(10)/\text{Al}_2\text{O}_3$, $\text{Ni}(10)-\text{Ca}(30)/\text{Al}_2\text{O}_3$ and $\text{Ni}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$; (c) reduced $\text{Ni}(10)/\text{Al}_2\text{O}_3$ and $\text{Ni}(10)-\text{Ca}(30)/\text{Al}_2\text{O}_3$; (d) calcined and reduced $\text{Ca}(30)-\text{Ni}(10)/\text{Al}_2\text{O}_3$.

Fig. S1.† The effluent concentration profiles of uncaptured CO_2 , generated CH_4 and CO , and desorbed CO_2 during continuous CCR are shown in Fig. S1a.† The concentration of uncaptured

CO_2 ranged from 1100 to 2200 ppm. The highest concentration of formed CH_4 was 4600 ppm, with a selectivity of 97%, and the amount of CO formed was <150 ppm. The concentration of

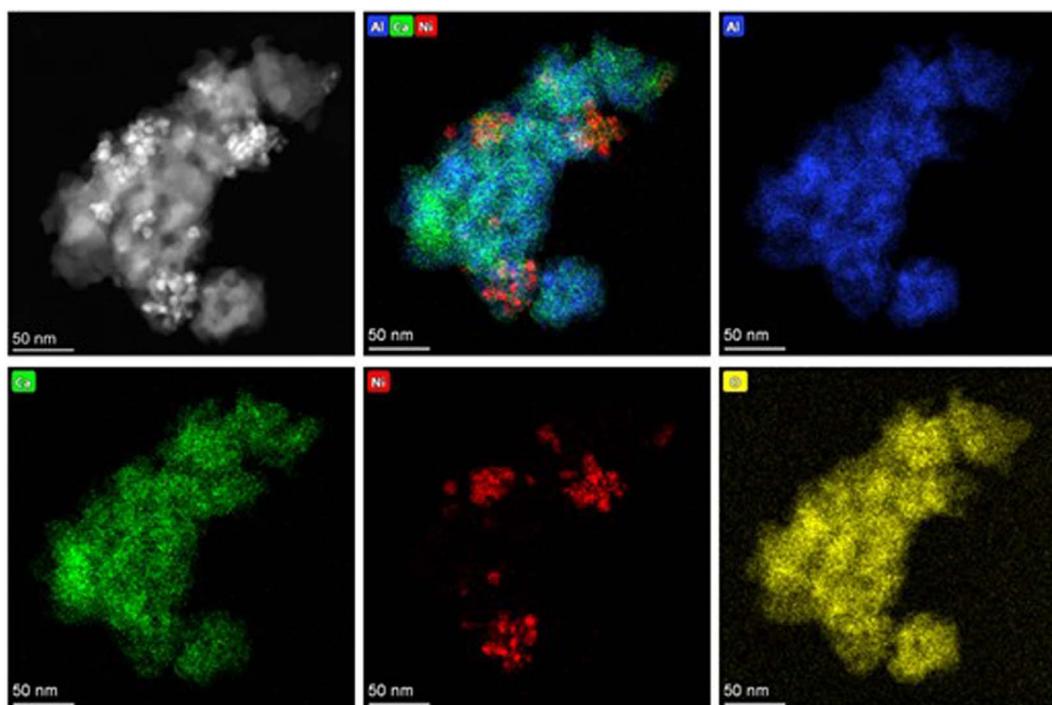


Fig. 4 STEM images and EDS mapping of (a) $\text{Ni}(10)/\text{Al}_2\text{O}_3$ and (b) $\text{Ni}(10)-\text{Ca}(30)/\text{Al}_2\text{O}_3$.



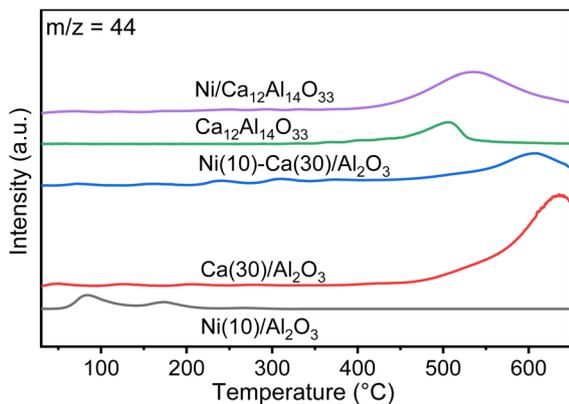


Fig. 5 CO₂ TPD profiles for Ni(10)/Al₂O₃, Ca(30)/Al₂O₃, Ni(10)–Ca(30)/Al₂O₃, Ca₁₂Al₁₄O₃₃, and Ni(10)/Ca₁₂Al₁₄O₃₃. Conditions: 100 mg of DFM, N₂ pretreatment at 450 °C for 30 min, followed by cooling down to room temperature and capture using 1% CO₂/N₂ (100 mL min⁻¹), and then an increase in temperature to 650 °C under pure N₂ (100 mL min⁻¹).

desorbed CO₂ ranged from 1300 to 2300 ppm. In the single reactor system containing Ni(10)–Ca(30)/Al₂O₃ (Fig. S1b†), the concentration of uncaptured CO₂ (100–7500 ppm) was higher than that in the double reactors. The desorbed CO₂ in the single reactor ranged from 200 to 2700 ppm, whereas the highest concentrations of CH₄ (680 ppm) and CO (40 ppm) were considerably lower than those in the double reactors. These results indicate that CO₂ capture and methanation efficiency were significantly improved using a double reactor system.

Fig. 3a shows XRD patterns of Al₂O₃ and Ca(30)/Al₂O₃ without Ni. Peaks at 19.6°, 31.9°, 37.6°, 39.5°, 45.8°, 60.5°, and 66.8° were observed for the Al₂O₃ support, assignable to the γ -Al₂O₃ phase (JCPDS No. 50-0741). For Ca(30)/Al₂O₃, peaks arising from the CaO (JCPDS No. 37-1497) and CaCO₃ (JCPDS No. 17-0763) phases were observed. In addition, the diffraction pattern of Ca₁₂Al₁₄O₃₃ (mayenite, JCPDS No. 48-1882) appeared, and the γ -Al₂O₃ phase almost disappeared, suggesting that γ -Al₂O₃ was possibly converted to Ca₁₂Al₁₄O₃₃. A pure Ca₁₂Al₁₄O₃₃ phase was also synthesized using calcium nitrate and boehmite as precursors in

a suitable stoichiometric ratio and calcination at 1050 °C. The XRD patterns indicated that the prepared sample largely comprised Ca₁₂Al₁₄O₃₃ (Fig. 3a) and a very small amount of CaO. This verified the formation of the Ca₁₂Al₁₄O₃₃ structure over Ca(30)/Al₂O₃. Fig. 3b shows the XRD patterns of Ni-loaded Al₂O₃, Ca(30)/Al₂O₃, and Ca₁₂Al₁₄O₃₃. For calcined Ni(10)/Al₂O₃, in addition to the Al₂O₃ peaks, a peak appeared at 43.3°, which was attributed to the (200) facet of NiO (JCPDS No. 47-1049). A comparison of the XRD patterns of Ni(10)/Al₂O₃ and Ni(10)–Ca(30)/Al₂O₃ revealed that the intensity of the NiO peak was higher for the latter, indicating that Ca-loaded Al₂O₃ promoted NiO crystal growth. Notably, the Ca₁₂Al₁₄O₃₃ phase was not detected after Ni loading, whereas the CaO and CaCO₃ phases were still present in Ni(10)–Ca(30)/Al₂O₃. For Ni(10)/Ca₁₂Al₁₄O₃₃, the diffraction peaks assignable to the Ca₁₂Al₁₄O₃₃ phase decreased dramatically, and a new phase did not appear. These results suggest that Ni loading likely induced the transformation of the Ca₁₂Al₁₄O₃₃ phase to amorphous structures. After H₂ reduction at 500 °C, the Ni metal phase (JCPDS No. 04-0850) appeared in both Ni(10)/Al₂O₃ and Ni(10)–Ca(30)/Al₂O₃ (Fig. 3c), indicating that NiO was converted to Ni metal under H₂ flow. When 10 wt% of Ni was supported on Al₂O₃ first, followed by the introduction of 30 wt% of CaO onto Ni/Al₂O₃ Ca(30–Ni(10)/Al₂O₃), a diffraction pattern indicative of CaNiO₃ (ID: mvc-3998) was observed with peaks assignable to CaO, CaCO₃, and Ca₁₂Al₁₄O₃₃ phases (Fig. 3d). The CaNiO₃ phase was maintained after H₂ treatment at 500 °C, and peaks attributable to Ni metal did not appear, suggesting that Ca–Ni composite oxides are difficult to reduce to Ni metal at CCR operation temperature (450 °C). The formation of CaNiO₃ possibly led to a decrease in the amount of Ni active species, resulting in the inferior CCR performance of Ca(30)–Ni(10)/Al₂O₃ compared to that of Ni(10)–Ca(30)/Al₂O₃.

The specific surface areas of Ni(10)/Al₂O₃, Ni(10)–Ca(30)/Al₂O₃, and Ca(30)/Al₂O₃ were 154, 37, and 34 m² g⁻¹, respectively. Ni(10)–Ca(30)/Al₂O₃ and Ca(30)/Al₂O₃ have similar specific surface areas, which are appreciably lower than that of Ni(10)/Al₂O₃. This is possibly due to the structural transformation of γ -Al₂O₃ to Ca₁₂Al₁₄O₃₃ phase. The similar surface area values were (20–40 m² g⁻¹) obtained in the solid-phase

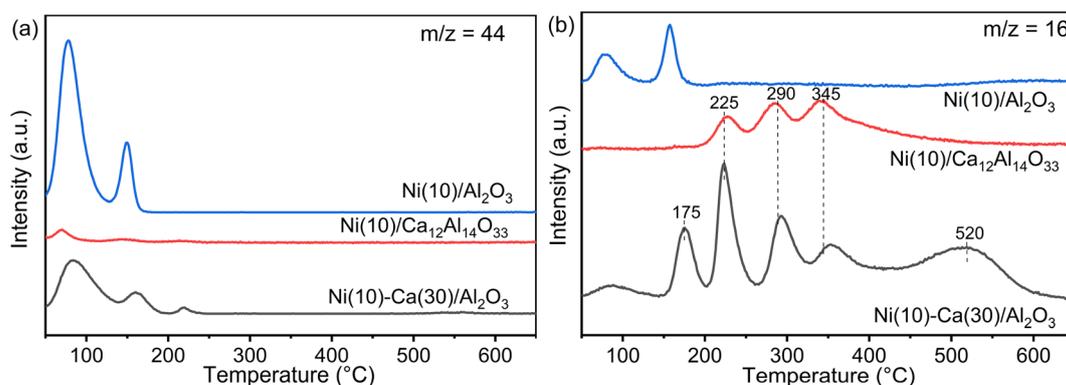


Fig. 6 TPSR profiles of (a) CO₂ and (b) CH₄ for Ni(10)/Al₂O₃, Ni(10)–Ca(30)/Al₂O₃, and Ni(10)/Ca₁₂Al₁₄O₃₃. Conditions: 100 mg of DFM, H₂ pretreatment at 450 °C for 30 min, followed by cooling to room temperature and capture under 1% CO₂/10% O₂/N₂ (100 mL min⁻¹), and then an increase in temperature to 650 °C under 5% H₂/N₂ (100 mL min⁻¹).



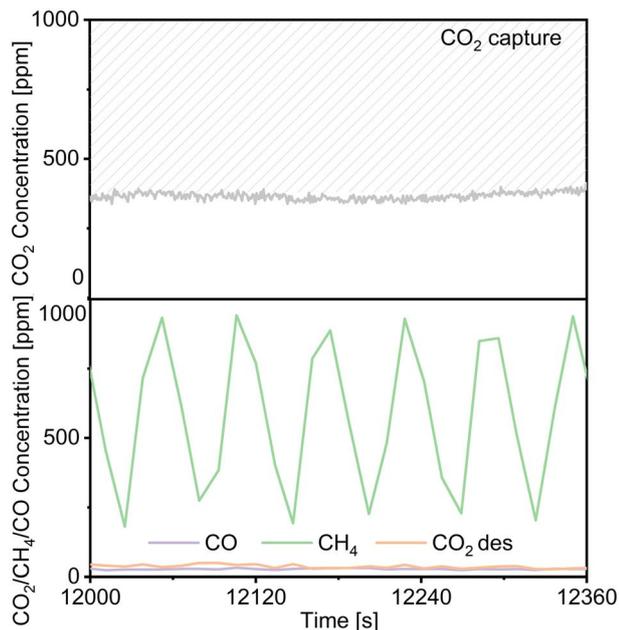


Fig. 7 Effluent gas composition during continuous CCR operation over Ni(10)–Ca(30)/Al₂O₃ using a decreased CO₂ concentration of 1000 ppm in the gas mixture. Conditions: 100 mg of DFM, 450 °C, 100 mL min⁻¹ of 0.1% CO₂/10% O₂/N₂ for 30 s, switched to 100 mL min⁻¹ of H₂ for 30 s.

synthesis of Ca₁₂Al₁₄O₃₃ in the previous literature.¹² The morphology and distribution of the Ni nanoparticles on Ni(10)/Al₂O₃ and Ni(10)–Ca(30)/Al₂O₃ were characterized using STEM and EDS mapping (Fig. S2† and 4). In the case of Ni(10)/Al₂O₃, the Ni nanoparticles were dispersed on Al₂O₃ with an average size of 6.9 nm (Fig. S2†), whereas for Ni(10)–Ca(30)/Al₂O₃, the Ni nanoparticles were aggregated and the particle size increased (Fig. 4), which is consistent with the XRD results.

CO₂ TPD measurements were conducted to explore the CO₂ desorption properties of Ni(10)/Al₂O₃, Ca(30)/Al₂O₃, Ni(10)–Ca(30)/Al₂O₃, Ca₁₂Al₁₄O₃₃, and Ni(10)/Ca₁₂Al₁₄O₃₃ (Fig. 5). Ni(10)/Al₂O₃ gave rise to two desorption peaks at 80 and 160 °C, possibly arising from the physical adsorption of CO₂ onto the surface of Al₂O₃. In contrast, the TPD profiles for Ni(10)–Ca(30)/Al₂O₃ and Ca(30)/Al₂O₃ displayed a dominant CO₂ desorption peak during the temperature increase from 400 to 600 °C. A similar desorption peak was observed for Ni(10)/Ca₁₂Al₁₄O₃₃ and Ca₁₂Al₁₄O₃₃, implying that this CO₂ desorption was derived from adsorbed CO₂ over Ca–Al mixed oxides.

TPSR measurements were conducted using Ni(10)/Al₂O₃, Ni(10)–Ca(30)/Al₂O₃, and Ni(10)/Ca₁₂Al₁₄O₃₃ to obtain insights into the formation of CH₄ through the reduction of adsorbed CO₂ with H₂ (Fig. 6). Fig. 6a shows the CO₂ desorption peaks during reduction with H₂. Compared to the CO₂ TPD profiles (Fig. 5), the temperature for the CO₂ desorption peaks over Ni(10)/Al₂O₃ was similar to that of the CO₂ adsorption peaks, while for Ni(10)–Ca(30)/Al₂O₃ and Ni(10)/Ca₁₂Al₁₄O₃₃, the CO₂ desorption peaks were nearly absent at temperatures above 400 °C. Fig. 6b shows the CH₄ (*m/z* = 16) formation profiles. For Ni(10)/Al₂O₃, the CH₄ formation temperature was similar to that of CO₂ desorption, implying that once the adsorbed CO₂ species were desorbed, the desorbed CO₂ was converted to CH₄ through reduction with H₂. For Ni(10)–Ca(30)/Al₂O₃ and Ni(10)/Ca₁₂Al₁₄O₃₃, the CH₄ formation peaks were clearly observed at 225, 290, and 345 °C, being lower than the temperature range for CO₂ desorption in their CO₂ TPD profiles. This strongly indicates that the adsorbed CO₂ species were directly converted to CH₄. Additional CH₄ formation peaks were observed at 175 and 520 °C for Ni(10)–Ca(30)/Al₂O₃. The CH₄ formation peak below 200 °C resulted from the activity of Ni supported on Al₂O₃, and the peak at 520 °C possibly appeared due to the Ni supported on calcium oxide or carbonate species. Considering the CCR operation temperature of 450 °C, the Ni species

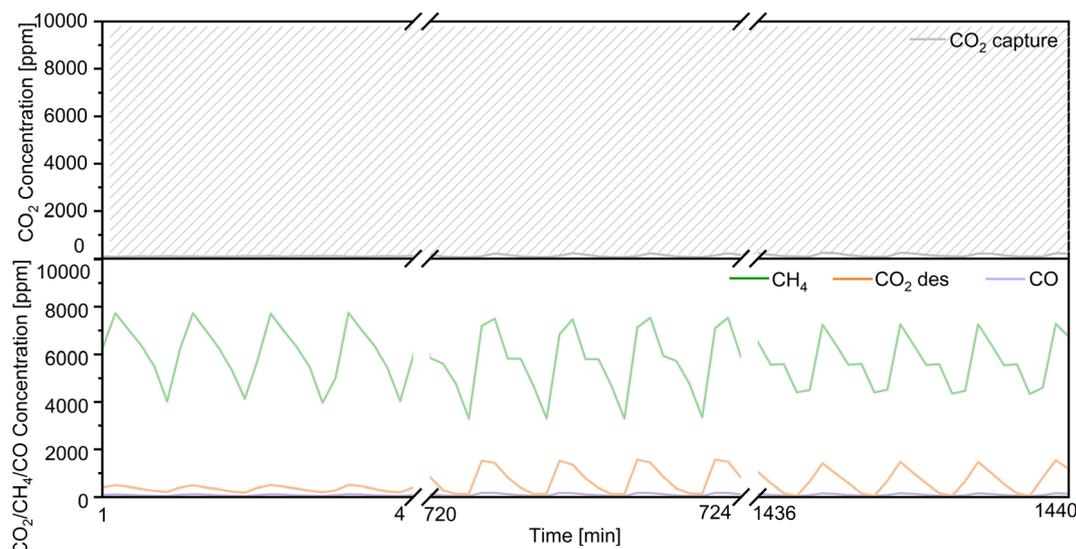


Fig. 8 Long-term continuous CCR operation using the double reactor system for 24 h. Conditions: 300 mg of Ni(10)–Ca(30)/Al₂O₃ for each reactor, 450 °C, 100 mL min⁻¹ of 1% CO₂/10% O₂/N₂ for 30 s, switched to 100 mL min⁻¹ of H₂ for 30 s.



supported on amorphous Ca–Al mixed oxides most likely played the dominant role in the reaction. The performance of Ni/Ca₁₂Al₁₄O₃₃ in continuous CCR verified this hypothesis, whereby high CO₂ capture and CH₄ formation concentrations were obtained (Fig. S3†).

Regarding the utilization of low-concentration CO₂, we decreased the flow rate of CO₂ in the mixed gases from 1% CO₂/10% O₂/N₂ to 0.1% CO₂/10% O₂/N₂ (100 mL min⁻¹) over Ni(10)–Ca(30)/Al₂O₃. As shown in Fig. 7, the concentration of uncaptured CO₂ was approximately 350 ppm. The highest concentration of produced CH₄ was 965 ppm; the concentrations of both the produced CO and desorbed CO₂ were below 30 ppm. The conversion of captured CO₂ and the selectivity for CH₄ were 94% and 95%, respectively, indicating that Ni(10)–Ca(30)/Al₂O₃ favored the conversion of low concentrations of CO₂. A long-term CCR operation experiment was also conducted using 300 mg of Ni(10)–Ca(30)/Al₂O₃ with flowing 1% CO₂/10% O₂/N₂ for 24 h (Fig. 8). Initially, the produced CH₄ concentration ranged from 3200 to 7800 ppm. After 24 h, the highest concentration of CH₄ was 7400 ppm. The highest CO and uncaptured CO₂ concentrations were below 150 and 250 ppm, respectively, for all the reaction times. The desorbed CO₂ concentration ranged from 0 to 1500 ppm in the whole reaction process. Meanwhile, after reaction for 24 h, the CO₂ conversion and CH₄ yield were stable at 60% and 59%, respectively. These results indicate that the Ni(10)–Ca(30)/Al₂O₃ DFM not showed obvious deterioration in the CCR performance for at least 24 h, which exhibited a good durability. The effect of 20% water vapor on continuous CCR operation over Ni(10)–Ca(30)/Al₂O₃ was investigated to evaluate the potential for application to real natural gas power plant effluent (Fig. S4†). The uncaptured CO₂ concentration was maintained between 1000 and 2000 ppm; however, the maximum concentration of formed CH₄ decreased to 2700 ppm. Therefore, water removal from exhaust gas is necessary for real-world applications.

Conclusion

Continuous CO₂ capture and methanation reactions over Ni–Ca based DFMs were studied using double reactors in the presence of oxygen. The utilization of a double reactor system increased the amounts of CO₂ captured and CH₄ produced when compared to the performance of a single reactor system. A relatively high Ca loading (30 wt%) in the DFM was found to be the most effective for continuous CCR operation under isothermal conditions at 450 °C; thus, the Ni(10)–Ca(30)/Al₂O₃ sample displayed an excellent activity and good durability, maintaining its high CCR performance for at least 24 h. The XRD results revealed that a high Ca loading on Al₂O₃ induced the formation of Ca₁₂Al₁₄O₃₃. Subsequent Ni loading resulted in the transformation of Ca₁₂Al₁₄O₃₃ into amorphous structures, which was responsible for the favorable performance of Ni(10)–Ca(30)/Al₂O₃, as indicated by TPD and TPSR measurements. The order of Ca and Ni introduction also affected the structure of the Ni–Ca DFM and its CCR performance, and better results were obtained when Ni was introduced last.

Conflicts of interest

There are no conflicts to declare.

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References

- 1 S. Sun, H. Sun, P. T. Williams and C. Wu, *Sustainable Energy Fuels*, 2021, **5**, 4546–4559.
- 2 J. Lin, C. Ma, Q. Wang, Y. Xu, G. Ma, J. Wang, H. Wang, C. Dong, C. Zhang and M. Ding, *Appl. Catal., B*, 2019, **243**, 262–272.
- 3 I. S. Omodolor, H. O. Otor, J. A. Andonegui, B. J. Allen and A. C. Alba-Rubio, *Ind. Eng. Chem. Res.*, 2020, **59**, 17612–17631.
- 4 A. Bermejo-Lopez, B. Pereda-Ayo, J. A. Gonzalez-Marcos and J. R. Gonzalez-Velasco, *J. CO₂ Util.*, 2019, **34**, 576–587.
- 5 W. Yang, Y. Feng and W. Chu, *Int. J. Chem. Eng.*, 2016, **2016**, 1–8.
- 6 Z. Alipour, M. Rezaei and F. Meshkani, *J. Ind. Eng. Chem.*, 2014, **20**, 2858–2863.
- 7 H. Sun, Y. Wang, S. Xu, A. I. Osman, G. Stenning, J. Han, S. Sun, D. Rooney, P. T. Williams, F. Wang and C. Wu, *Fuel*, 2021, **286**, 119308.
- 8 F. Kosaka, Y. Liu, S. Y. Chen, T. Mochizuki, H. Takagi, A. Urakawa and K. Kuramoto, *ACS Sustainable Chem. Eng.*, 2021, **9**, 3452–3463.
- 9 L. Li, S. Miyazaki, S. Yasumura, K. W. Ting, T. Toyao, Z. Maeno and K. Shimizu, *ACS Catal.*, 2022, **12**, 2639–2650.
- 10 L. F. Bobadilla, J. M. Riesco-García, G. Penelás-Pérez and A. Urakawa, *J. CO₂ Util.*, 2016, **14**, 106–111.
- 11 A. R. Keshavarz and M. Soleimani, *Res. Chem. Intermed.*, 2018, **44**, 1485–1503.
- 12 C. Sriwong, C. Phrompet, W. Tuichai, A. Karaphun, K. Kurosaki and C. Ruttanapun, *Sci. Rep.*, 2022, **10**, 11077.

