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# Continuous direct air capture and conversion tandem system applicable to a wide range of CO<sub>2</sub> concentrations†

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The concentrations of CO<sub>2</sub> emitted from different CO<sub>2</sub> sources vary significantly. Thus, processes capable of accommodating a broad range of CO<sub>2</sub> concentrations, from 0.04% (air) to 10% (power plants), must be developed to achieve carbon neutrality. In this study, we developed a two-step CO<sub>2</sub> capture and hydrogenation system by employing Rb-oxide-incorporated zeolites as CO<sub>2</sub> adsorbents and Ni/CeO<sub>2</sub> or Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> as catalysts for CO<sub>2</sub> hydrogenation. This process is suitable for continuous operation over a temperature swing of 40–200 °C. Notably, this system can operate at low temperatures (below 200 °C) using a simple temperature-swing process in the presence of O<sub>2</sub>. Compared with more than 100 previously reported systems that can convert CO<sub>2</sub> including O<sub>2</sub> to green fuels such as CO or CH<sub>4</sub>, the proposed system achieved the best CO<sub>2</sub> conversions to CH<sub>4</sub> and CO.

Keywords: Direct air capture (DAC); Zeolite sorbent; Temperature swing adsorption (TSA); Methanation; Reverse water-gas shift (RWGS).

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## 1 Introduction

Anthropogenic greenhouse gas emissions are critical in causing global warming.<sup>1,2</sup> To mitigate global warming and achieve a carbon-neutral society, the amount of CO<sub>2</sub> emitted from energy- and industry-related sources must be significantly reduced.<sup>3,4</sup> One of the most promising strategies for mitigating anthropogenic CO<sub>2</sub> emissions is to convert CO<sub>2</sub> into chemical fuels, such as methane or methanol, and value-added chemicals *via* syngas using green H<sub>2</sub> produced *via* water electrolysis using renewable energy sources such as wind and solar power.<sup>5,6</sup> Large-scale production of green H<sub>2</sub> using water electrolysis has already been initiated at sites such as the Shell Energy and Chemicals Park Rheinland in Germany.<sup>7</sup> These efforts highlight the increasing demand for practical CO<sub>2</sub> capture and utilization (CCU) technologies utilizing green H<sub>2</sub>. However, in CCU technologies, CO<sub>2</sub> needs to be captured from emission sources (such as power, refinery, chemical, steel, and ceramic plants) and stored prior to chemical transformation.<sup>8</sup> Although liquid amine

scrubbing is a commonly employed CO<sub>2</sub> capture and storage (CCS) technology in industry,<sup>9</sup> it is hindered by high costs, significant energy requirements for solvent regeneration, and the need for large-scale plants.<sup>10</sup>

CO<sub>2</sub> needs to be captured from emission sources (such as power, refinery, chemical, steel, and ceramic plants) and stored prior to chemical transformation.<sup>8</sup> Although liquid amine scrubbing is a commonly employed CO<sub>2</sub> capture and storage (CCS) technology in the industry,<sup>9</sup> it is hindered by high costs, significant energy requirements for solvent regeneration, and the need for large-scale plants.<sup>10</sup>

Recently, unsteady-state CO<sub>2</sub> hydrogenation processes, known as CO<sub>2</sub> capture and reduction (CCR) and integrated CO<sub>2</sub> capture and conversion, have emerged as alternative technologies in which the need for CCS is avoided.<sup>11,12</sup> In 2016, Urakawa *et al.*<sup>13</sup> and Farrauto *et al.*<sup>14</sup> separately published their works on CCR. Unlike conventional methods, CCR does not require large amounts of thermal energy for CO<sub>2</sub> separation and purification.<sup>15</sup> Furthermore, this process is theoretically applicable to the utilization of O<sub>2</sub>-containing CO<sub>2</sub> emitted from industries such as power plants and is advantageous for practical use.<sup>16</sup>

Dual-functional materials (DFMs) in which alkali or alkaline earth metals for CO<sub>2</sub> capture are combined with transition metals for CO<sub>2</sub> hydrogenation are widely used in CCR operations. Selective CH<sub>4</sub> and CO formation has been reported in various CCR studies (Table S1†). However, the

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reported CCR processes cannot be integrated with effluent streams released from various industrial processes because these are performed by changing the gas conditions stepwise (Fig. 1a). To address this, Urakawa *et al.* proposed a two-reactor parallel-type system for continuous CCR,<sup>13</sup> whereas we developed a two-reactor parallel-type system for the continuous production of green fuels, such as CH<sub>4</sub><sup>17,18</sup> and CO,<sup>19,20</sup> from a CO<sub>2</sub> + O<sub>2</sub>/N<sub>2</sub> mixture by alternating the feeds of CO<sub>2</sub> + O<sub>2</sub>/N<sub>2</sub> and H<sub>2</sub> to the DFMs in the two reactors (Fig. 1b).

Our system can continuously capture low-concentration CO<sub>2</sub> (below 1%) from a mixture of O<sub>2</sub> and convert it into green fuels. However, continuous CCR is not applicable to high-concentration CO<sub>2</sub> emissions that are similar to exhaust gas emissions from thermal power plants and other industrial sources because of the limited CO<sub>2</sub> capacity of DFMs<sup>21</sup> compared with zeolite sorbents.<sup>22,23</sup> For example, less than 30% high-concentration inlet CO<sub>2</sub> (10%) can be converted even when one of the highest-activity DFMs available is used under optimized conditions (Fig. S1 and ESI† Text S1). This is because materials such as CaO—one of the most effective basic metal oxides used in DFMs—store CO<sub>2</sub> *via* a bulk diffusion mechanism, in which CO<sub>2</sub> must pass through CaCO<sub>3</sub> crystals to reach the unreacted CaO core.<sup>24</sup> Only surface carbonates are consumed during the reaction, while bulk carbonates remain inaccessible.<sup>25</sup> Consequently, this limitation restricts their applicability to dilute CO<sub>2</sub> streams. To effectively convert both diluted and high-concentration CO<sub>2</sub> (such as from thermal power plants and other industrial sources), it becomes essential to employ materials offering a range of adsorption site strengths and affinities. In contrast to DFMs, CO<sub>2</sub> can also be physically adsorbed onto sorbents like zeolites, enabling CO<sub>2</sub> adsorption and desorption under mild temperature swing conditions.<sup>26,27</sup> However, removing the thermodynamic equilibrium constraint imposed by low temperatures to ensure high CO<sub>2</sub> conversion appears to be an insurmountable dilemma in continuous CCR. Accordingly, our central motivation was to overcome the limitation of CCR and

expand the application to a wide range of CO<sub>2</sub> concentrations, from direct air capture (DAC) to flue gas, while maintaining high performance.

In this study, we developed a novel system in which tandem CO<sub>2</sub> capture and hydrogenation are achieved by combining Rb-loaded zeolites (Rb-zeolites) as CO<sub>2</sub> adsorbents with CO<sub>2</sub> hydrogenation catalysts (Fig. 1c, and a detailed explanation of these three unsteady-state CO<sub>2</sub> hydrogenation processes is provided in ESI† Text S2). For CO<sub>2</sub> capture, zeolites were used as typical economically viable solid adsorbents. Unlike liquid and solid amines, zeolites do not produce toxic degradation products.<sup>28</sup> In addition, zeolites show greater stability than metal–organic frameworks (MOFs), which are also well-known solid adsorbents.<sup>29,30</sup> For CO<sub>2</sub> hydrogenation, Ni/CeO<sub>2</sub><sup>31–33</sup> and Cu/ZnO/Al<sub>2</sub>O<sub>3</sub><sup>34–36</sup> were used as typical catalysts for methanation and reverse water-gas shift (RWGS) reactions, respectively. Ni/CeO<sub>2</sub><sup>37–40</sup> and Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>,<sup>41–44</sup> easily prepared by a simple method, are promising catalysts for the tandem system toward practical implementation. The sorbents were filled upstream in two parallel reactors. The catalyst was filled downstream in a single reactor. The system was based on continuous temperature swing adsorption (TSA) and catalytic reactions. Initially, a CO<sub>2</sub> + O<sub>2</sub>/N<sub>2</sub> mixture was fed into the Rb-zeolite sorbent (denoted as Z) to capture CO<sub>2</sub> (eqn (1)). After this mixture changed to pure H<sub>2</sub> gas and the sorbent temperature was increased, the captured CO<sub>2</sub> and H<sub>2</sub> were simultaneously desorbed by applying heat (eqn (2)). Desorbed CO<sub>2</sub> and H<sub>2</sub> flowed to the bottom reactor, and the methanation or RWGS reaction proceeded using the catalysts (eqn (3) and (4)).

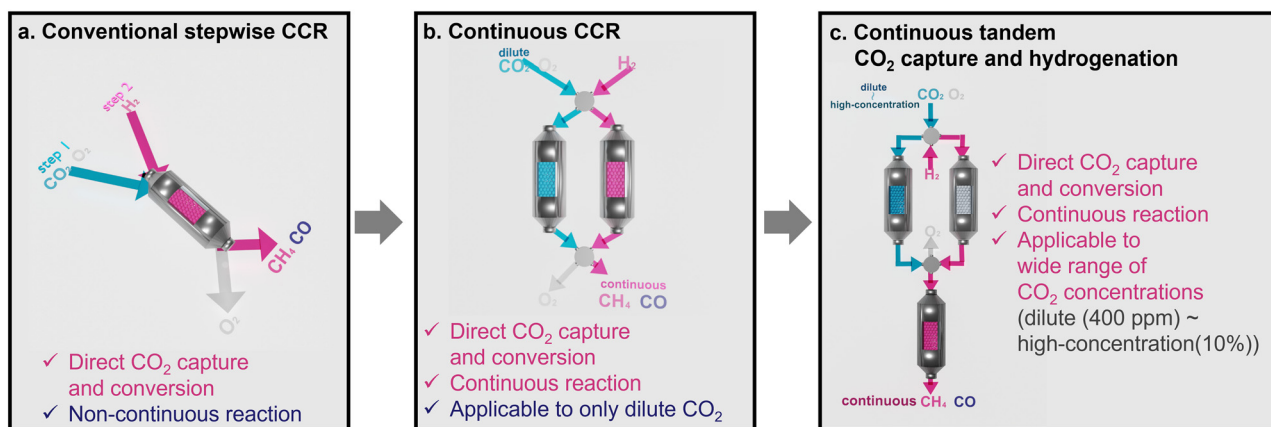
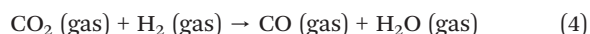
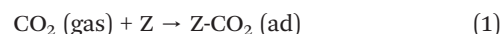


Fig. 1 Conceptual diagram of (a) conventional stepwise CCR, (b) continuous CCR, and (c) continuous tandem CO<sub>2</sub> capture and hydrogenation processes.



This new process is suitable for continuous operation under temperature-swing cycling in the low-temperature range (between 40 and 200 °C) in the presence of O<sub>2</sub>. Compared with more than 100 reported CCR processes, this novel process exhibited high inlet CO<sub>2</sub> conversion.

## 2 Results and discussion

### 2.1 Screening and optimizing sorbents and catalysts

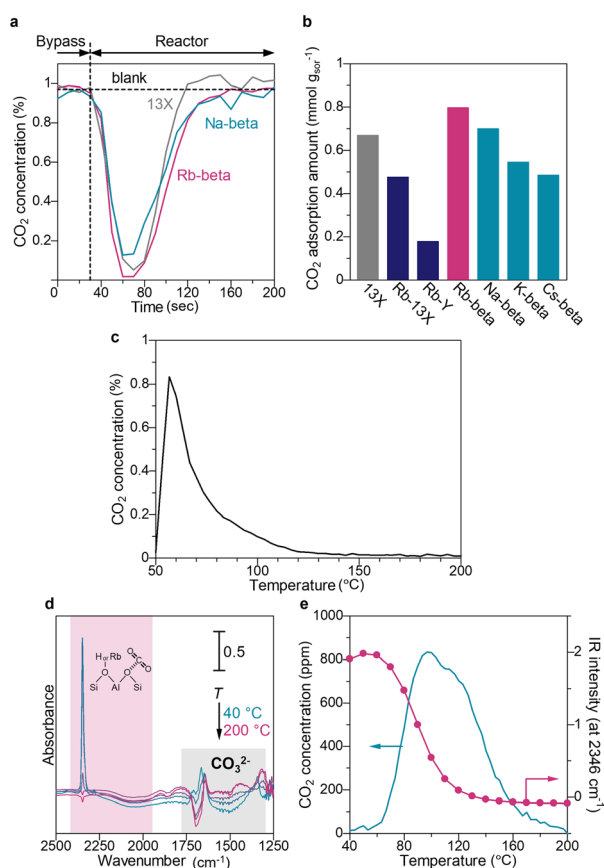
First, we examined the CO<sub>2</sub> adsorption properties of zeolite sorbents at 50 °C using a fixed-bed continuous-flow system (Fig. S2†). The breakthrough curve obtained from the CO<sub>2</sub> adsorption measurements is shown in Fig. 2a, and the CO<sub>2</sub> adsorption amount determined from the breakthrough curve is presented in Fig. 2b. Among Rb-zeolites (such as Rb-13X, Rb-Y, and Rb-beta) and alkali-metal-loaded beta zeolites (such

as Rb-, Na-, K-, and Cs-beta), Rb-beta exhibited the highest amount of CO<sub>2</sub> adsorption. Similarly, we investigated the CO<sub>2</sub> adsorption properties of bare beta zeolite (H-beta) as a reference for comparison with Rb-beta (Fig. S3†). The introduction of Rb<sup>+</sup> cations increased the CO<sub>2</sub> adsorption capacity, suggesting that the framework oxygen atoms became more electron-rich due to the presence of the basic alkali metal cations.<sup>45</sup> This result is consistent with previous reports.<sup>46,47</sup> It is considered that physisorbed CO<sub>2</sub>, which interacts weakly with the framework oxygen atoms, was more effectively stabilized within the zeolite structure.

Subsequently, we performed temperature-programmed desorption (TPD) measurements of CO<sub>2</sub> to explore the CO<sub>2</sub> desorption properties of Rb-beta (Fig. 2c). CO<sub>2</sub> desorption from Rb-beta was observed over the temperature range of 50–150 °C, and the total amount of desorbed CO<sub>2</sub> (0.8 mmol g<sup>-1</sup>) was close to the CO<sub>2</sub> adsorption amount (0.8 mmol g<sup>-1</sup>). This indicated that adsorbed CO<sub>2</sub> at 50 °C was completely desorbed after heating to 150 °C. To investigate zeolite structure, Fig. S4† shows XRD patterns of alkali-metal-loaded beta zeolite samples. XRD peaks of alkali-metal-loaded beta zeolites closely resembled those of H-beta, indicating that the zeolite framework remained intact after immobilizing alkali metals.

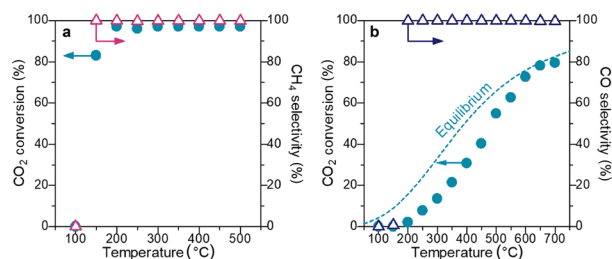
To elucidate the mechanism underlying CO<sub>2</sub> adsorption and desorption, *operando* Fourier transform infrared (FTIR) spectroscopy was performed during the TPD of CO<sub>2</sub> on Rb-beta. A schematic of the setup is shown in Fig. S5.† Prior to the experiment, the infrared (IR) disk was heated under He at 400 °C for 30 min and then cooled to 40 °C. To record the background spectrum, 1% CO<sub>2</sub>/He was fed to the sample at 40 °C for 5 min and purged under He. A strong band at 2275 cm<sup>-1</sup> assigned to the physically adsorbed CO<sub>2</sub> on zeolite<sup>48,49</sup> and two weak broad bands at 1720 and 1280 cm<sup>-1</sup> assigned to the carbonate species<sup>50,51</sup> were observed before heating (Fig. 2d). These results indicated that physically adsorbed CO<sub>2</sub> was the main adsorbed species and carbonate was a minor species. As the temperature increased from 60 to 160 °C, the band intensity for the physically adsorbed CO<sub>2</sub> sharply decreased, accompanied by CO<sub>2</sub> formation at the outlet of the IR cell (Fig. 2e). This indicated that the physical adsorption and desorption of CO<sub>2</sub> were responsible for the adsorption/desorption of CO<sub>2</sub> on Rb-beta.

We adopted Ni/CeO<sub>2</sub> and Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> as typical catalysts for the methanation and RWGS reactions. The reaction temperatures for these catalysts were optimized by performing steady-state reaction experiments (Fig. 3). When the Ni/CeO<sub>2</sub> catalyst was used, the CO<sub>2</sub> conversion and CH<sub>4</sub> selectivity sharply increased at a temperature of >150 °C (Fig. 3a). The reaction over the temperature range of 200–500 °C resulted in nearly complete conversion of CO<sub>2</sub> to CH<sub>4</sub> (CO<sub>2</sub> conversion ≥ 97.0%, CH<sub>4</sub> selectivity ≥ 99.7%). In the case of the RWGS reaction with the Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst, the CO<sub>2</sub> conversion monotonically increased from 2.0% to 78.1% with the temperature over the range of 100–650 °C (Fig. 3b). Compared with equilibrium conversion, the difference of CO<sub>2</sub> conversion was almost zero at 650 °C. Further increasing the



**Fig. 2** (a) CO<sub>2</sub> adsorption at 50 °C for 200 s under a flow of 0.97% CO<sub>2</sub> (He balance; total flow: 100 mL min<sup>-1</sup>). The flow passed through a bypass line in the first 20 s; (b) Comparison between CO<sub>2</sub> adsorption amounts on zeolite sorbents at 50 °C (determined by conducting the experiment shown in Fig. 1a); (c) CO<sub>2</sub> TPD profiles for Rb-beta under He flow. Conditions: heated at 500 °C under He flow and then cooled to 50 °C under He flow; 1% CO<sub>2</sub>/N<sub>2</sub> mixture was fed into the reactor at 50 °C for 30 min and purged with He for 5 min. The CO<sub>2</sub> TPD experiment was conducted by applying heat under He flow; (d) *operando* FTIR spectroscopy for Rb-beta under CO<sub>2</sub> TPD condition. IR spectra of adsorbed species at temperature intervals of 40 °C; (e) time-resolved trends in the IR intensities of adsorbed CO<sub>2</sub>; concentration of desorbed CO<sub>2</sub>. The background spectrum was recorded before CO<sub>2</sub> capture.





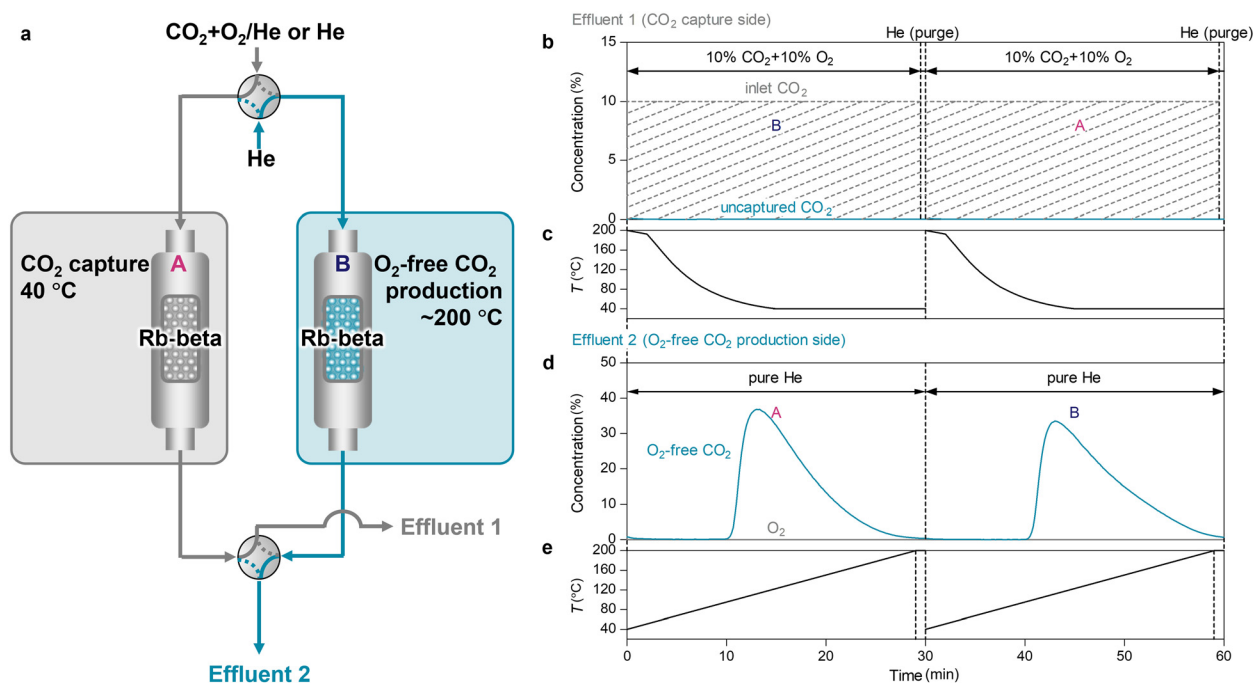
**Fig. 3** (a) CO<sub>2</sub> conversion and CH<sub>4</sub> selectivity with respect to reaction temperature with Ni/CeO<sub>2</sub> catalyst; (b) CO<sub>2</sub> conversion and CO selectivity with respect to reaction temperature with Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst. The dependence of the amount of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> is shown in Fig. S6.†

temperature to 700 °C did not significantly improve CO<sub>2</sub> conversion (79.4%). CO selectivity was high ( $\geq 99.3\%$ ) at a temperature of  $>200$  °C.

## 2.2 Continuous production of O<sub>2</sub>-free CO<sub>2</sub> from CO<sub>2</sub> + O<sub>2</sub> mixture

Prior to the continuous CO<sub>2</sub> capture and hydrogenation using the coupled tandem TSA/catalyst system, we demonstrated the continuous production of O<sub>2</sub>-free CO<sub>2</sub> from a model combustion exhaust gas (10% CO<sub>2</sub> + 10% O<sub>2</sub>/He) using the TSA system. Fig. 4a shows a schematic of the TSA system for O<sub>2</sub>-free CO<sub>2</sub> production from the model combustion exhaust gas. Two reactors containing equal amounts of Rb-beta were

set up in parallel for CO<sub>2</sub> capture and desorption. The CO<sub>2</sub> concentrations in effluents 1 and 2 were monitored by performing FTIR spectroscopy, and the O<sub>2</sub> concentration in effluent 1 was monitored by using mass spectrometry (MS). A gas mixture of CO<sub>2</sub> + O<sub>2</sub>/He was fed into one reactor for 29.5 min for CO<sub>2</sub> capture and then purged with He (0.5 min) to remove the remaining O<sub>2</sub> from the reactor. The other reactor (containing CO<sub>2</sub>-captured Rb-beta) was heated to 200 °C under He to produce O<sub>2</sub>-free CO<sub>2</sub> in effluent 2. The details of this procedure are presented in Fig. S7.† Fig. 4b and d show the typical variations in the CO<sub>2</sub> and O<sub>2</sub> concentrations in effluents 1 and 2 over time, respectively. CO<sub>2</sub> is captured from the CO<sub>2</sub>/O<sub>2</sub> mixture when the reactor is cooled from 200 to 40 °C. During the CO<sub>2</sub>-capture period, the outlet CO<sub>2</sub> concentration (in effluent 1) is below the detection limit, indicating that CO<sub>2</sub> is almost completely removed from the 10% CO<sub>2</sub> + 10% O<sub>2</sub> mixture. Subsequently, two 4-way valves connected to the top and bottom of the tubular reactors are simultaneously switched, and the captured CO<sub>2</sub> is released by heating to 200 °C (5.5 °C min<sup>-1</sup>) under He flow; this results in the formation of O<sub>2</sub>-free CO<sub>2</sub> in effluent 2. The maximum concentration of the liberated CO<sub>2</sub> is ~37%. The amounts of captured CO<sub>2</sub> (12.1 mmol) and produced O<sub>2</sub>-free CO<sub>2</sub> (11.9 mmol) in one cycle, calculated by applying eqn (2) and (3) in ESI† Text S3, are shown in Fig. S10 and S11. Note that the production of CO<sub>2</sub> results in an increase in the total flow rate (from 120 to 167 mL min<sup>-1</sup>) of effluent 2. The CO<sub>2</sub> capture and desorption experiments are performed continuously for



**Fig. 4** (a) Schematic of the two-reactor TSA system for continuous CO<sub>2</sub> capture and O<sub>2</sub>-free CO<sub>2</sub> production; captured gas (100 mL min<sup>-1</sup>, 10% CO<sub>2</sub> + 10% O<sub>2</sub>/He for 29.5 min and then pure He for 0.5 min) and released gas (120 mL min<sup>-1</sup>, pure He for 30 min) were alternately fed into each reactor containing 14 g of Rb-beta; (b) and (d) typical variations in the CO<sub>2</sub> and O<sub>2</sub> concentrations in effluents 1 and 2 over time, respectively; (c) and (e) typical temperature changes in reactor A and B over time, respectively. O<sub>2</sub> concentration in effluent 1 is shown in Fig. S8.† The response curves for the outlet CO<sub>2</sub> over the blank are displayed in Fig. S9.†





seven cycles (Fig. S12†). These results clearly reveal the continuous production of O<sub>2</sub>-free CO<sub>2</sub> from the 10% CO<sub>2</sub>/10% O<sub>2</sub> gas mixture.

### 2.3 Continuous CO<sub>2</sub> capture and methanation/RWGS reaction using the tandem system

Next, continuous CO<sub>2</sub> capture and methanation were performed using the tandem TSA/methanation system. Unlike DFM designs, the tandem-system design allows individually optimized active sites and reaction conditions for each step. The proposed TSA system converts the model combustion exhaust (10% CO<sub>2</sub> + 10% O<sub>2</sub>) to O<sub>2</sub>-free CO<sub>2</sub>, which undergoes methanation under H<sub>2</sub> in the reactor (containing Ni/CeO<sub>2</sub>) downstream at 300 °C (Fig. 5a). Note that H<sub>2</sub> is expected to act as an inert gas, similar to He, because the Rb-beta sorbent does not promote hydrogenation. First, the CO<sub>2</sub> + O<sub>2</sub> mixture is fed into one reactor of the TSA system for 29.5 min for CO<sub>2</sub> capture, and then, pure He (0.5 min) is fed to purge the remaining O<sub>2</sub> in the reactor. The other reactor (containing CO<sub>2</sub>-captured Rb-beta) is heated to 200 °C (5.5 °C min<sup>-1</sup>) under pure H<sub>2</sub> for 30 min. The desorbed CO<sub>2</sub> and H<sub>2</sub> are fed into the methanation reactor and converted to CH<sub>4</sub>. The details of this procedure are displayed in Fig. S13.†

Fig. 5b and d show the typical variations in the CH<sub>4</sub>, CO<sub>2</sub>, and O<sub>2</sub> concentrations in effluents 1 and 2 over time, analyzed online by employing an IR gas-cell and MS, respectively. Fig. 5c and e depict the optimized time

variations in the temperatures of the two TSA reactors. During the CO<sub>2</sub>-capture period, the outlet CO<sub>2</sub> concentration (in effluent 1) is below the detection limit, indicating that CO<sub>2</sub> is almost completely removed from the 10% CO<sub>2</sub> + 10% O<sub>2</sub> mixture. Subsequently, two 4-way valves connected to the top and bottom of the tubular reactors are simultaneously switched, and the captured CO<sub>2</sub> is released by heating under H<sub>2</sub>. When CO<sub>2</sub>-captured Rb-beta is heated under H<sub>2</sub>, CH<sub>4</sub> was observed in effluent 2, with a maximum concentration of ~66.3%. The concentration of CO (0.02%) is low, and CO<sub>2</sub> is not present in effluent 2; thus, CH<sub>4</sub> selectivity is ≥99%. Note that the high conversion level of CO<sub>2</sub> and H<sub>2</sub> over the downstream Ni/CeO<sub>2</sub> catalyst results in a significant decrease in the total flow rate (from 120 to 40 mL min<sup>-1</sup>) of effluent 2 (details on the decrease in the total flow rate are shown in ESI† Text S4 and Fig. S14 and S15). The CO<sub>2</sub> capture and desorption/methanation experiments are performed continuously for four cycles (Fig. S16†). Fig. S17 and S18† show the results of condition optimization for the CO<sub>2</sub> capture and desorption/methanation experiments. The effect of the CO<sub>2</sub>-capture temperature (40, 80, 100, and 120 °C) on the CH<sub>4</sub> yield (Fig. S17†) reveals that the lowest temperature (40 °C) produces the highest CH<sub>4</sub> yield, simply because a lower adsorption temperature leads to a larger CO<sub>2</sub> capacity of Rb-beta. The effect of the catalyst amount (Fig. S18†) shows that increasing the catalyst amount (from 2 to 15 g) results in a slight increase in the CH<sub>4</sub> yield (from 85 to 92%) and a large decrease in the space-time-yield of CH<sub>4</sub> (STY<sub>CH<sub>4</sub></sub>) (from 11.9 to 1.8 mmol g<sup>-1</sup> h<sup>-1</sup>).

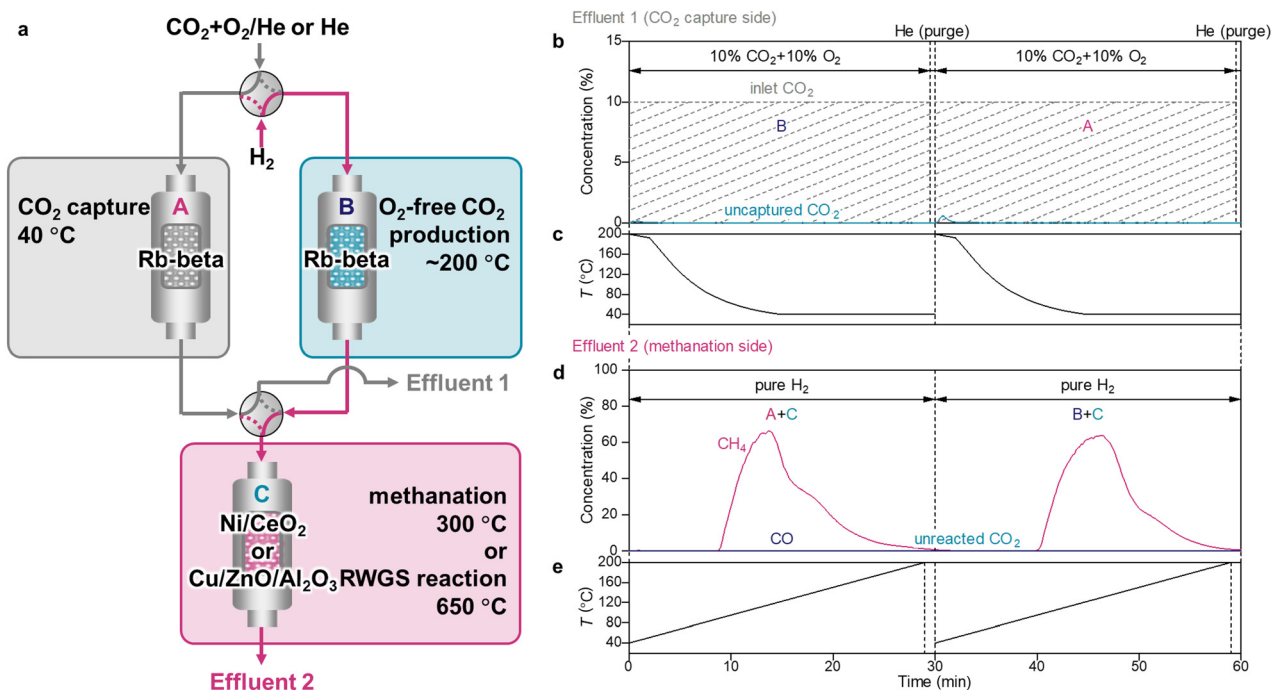


Fig. 5 (a) Schematic of the two-reactor TSA system for continuous CO<sub>2</sub> capture and methanation; captured gas (100 mL min<sup>-1</sup>; 10% CO<sub>2</sub> + 10% O<sub>2</sub>/He for 29.5 min and then pure He for 0.5 min) and hydrogenation gas (120 mL min<sup>-1</sup>; pure H<sub>2</sub> for 30 min) were alternately fed into each reactor containing 14 g of Rb-beta; (b) and (d) typical variations in the CH<sub>4</sub>, CO<sub>2</sub>, and CO concentrations in effluents 1 and 2 over time, respectively; (c) and (e) typical temperature changes in reactor A and B over time, respectively.



A  $\text{CH}_4$  yield of 92% is almost double those in the previously reported catalytic systems for the methanation of a  $\text{CO}_2/\text{O}_2$  mixture using CCR (16 reports and 55 reaction processes presented in Fig. 6a; details are listed in Table S1†). The reaction temperature in our system (300 °C) is the lowest among the reported systems, and the inlet  $\text{CO}_2$  concentration in our system is the highest among the reported systems. Note that the majority of the previously reported CCR systems for  $\text{CH}_4$  production were tested in the absence of  $\text{O}_2$  during the  $\text{CO}_2$ -capture period (10 reports and 100 reaction processes; details are listed in Table S2†). Compared with those systems, our system produces the highest  $\text{CH}_4$  yield.

Under conditions relevant to future practical implementation, gas purging with unreacted gas is expected to be avoided, and recycling of unreacted  $\text{H}_2$  is anticipated to be implemented. Continuous  $\text{CO}_2$  capture and methanation were conducted using the tandem system without gas purging (Fig. S19†). Under these conditions, the effluent gas composition remained nearly unchanged compared to that observed under gas purge conditions (Fig. 5d), suggesting that the effect of transient  $\text{O}_2$  inflow was negligible. This is possibly because oxidized Ni species were readily reduced during the initial introduction of  $\text{H}_2$ , demonstrating that this tandem system exhibits complete  $\text{O}_2$ -tolerance. While the current system shows high performance, future implementation of  $\text{CH}_4/\text{H}_2$  product gas recycling as a reductive gas suggests the potential to further improve  $\text{H}_2$  utilization efficiency.

We demonstrated continuous  $\text{CO}_2$  capture and the RWGS reaction using a system similar to that described in the previous subsection; in this system, a commercial  $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$  catalyst was used as the RWGS catalyst (catalyst amount = 10 g) (Fig. S20†). When Rb-beta was heated from 40 to 200 °C, CO was formed with a maximum concentration of ~41.0%,  $\text{CO}_2$  was desorbed with a maximum concentration of ~11.2%, and almost no  $\text{CH}_4$  was detected (CO selectivity  $\geq 99\%$ ). In addition, no  $\text{CO}_2$  was detected in effluent 1 using gas-cell IR, indicating that almost all the supplied  $\text{CO}_2$  was captured by Rb-beta. Given the CO production per unit time (a detailed explanation is presented in ESI† Text S5 and Fig. S21), the conversion of inlet  $\text{CO}_2$  to CO (denoted as the CO yield) was 85%, indicating that a

considerable amount of the supplied high-concentration  $\text{CO}_2$  in the presence of  $\text{O}_2$  was continuously converted to CO. This reaction was repeated several times and maintained for at least 2 h (six cycles; Fig. S22†). Furthermore, the amount of  $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$  included in this RWGS system was optimized from 0.2 to 14 g (Fig. S23†). When the catalyst amount was between 1 to 15 g, the CO yield was over 85% and the maximum CO production rate was  $20.1 \text{ mmol g}^{-1} \text{ h}^{-1}$ . When the catalyst amount was decreased to 0.2 g, the CO yield decreased by 45% but the space-time-yield of CO ( $\text{STY}_{\text{CO}}$ ) increased to  $55.5 \text{ mmol g}^{-1} \text{ h}^{-1}$ . Thus, increasing the catalyst amount from 0.2 to 1 g resulted in a sharp increase in the CO yield (from 45% to 85%), but further increasing the amount from 1 to 15 g resulted in limited change (from 85% to 81%). Additionally, increasing the catalyst amount from 0.2 to 15 g significantly decreased the  $\text{STY}_{\text{CO}}$  from 55.5 to  $1.5 \text{ mmol g}^{-1} \text{ h}^{-1}$ .

The system was compared with previously reported systems (10 reports and 30 reaction processes in Fig. 6b; details are listed in Table S3†). The majority of the previously reported CCR systems for CO production were evaluated at low inlet  $\text{CO}_2$  concentrations (below 1%). Our system demonstrated the RWGS process with a high CO yield (85%) at a high inlet  $\text{CO}_2$  concentration (10%). Notably, many of the previously studied CCR systems aimed at CO production were tested in the absence of  $\text{O}_2$  during  $\text{CO}_2$  capture (as detailed in Table S4;† 10 reports and 100 reaction processes). Compared with systems with the same inlet  $\text{CO}_2$  concentration (10%), our system demonstrated approximately twice the CO yield.

For example, in Fischer-Tropsch (FT),<sup>52</sup> methanol ( $\text{MeOH}$ ),<sup>53</sup> and ethanol ( $\text{EtOH}$ ) syntheses<sup>54</sup> from syngas, the  $\text{H}_2/\text{CO}$  ratio of the syngas significantly affects the selectivity and yield of the product. Similar to the aforementioned methanation system, the  $\text{H}_2$  input was optimized (Fig. 7). When the  $\text{H}_2$  flow time was reduced from 30 to 20 min in one cycle, the  $\text{H}_2$  conversion slightly increased from 9.8% to 15% and the  $\text{H}_2/\text{CO}$  ratio changed from 9.1 to 3.7, which is closer to the ideal value of 2.0 for FT, MeOH, and EtOH syntheses, while retaining a high CO yield (93%) (see ESI† Text S5 for details). Furthermore, syngas is an environment-friendly alternative gaseous fuel for internal combustion during engine operations, and  $\text{H}_2$ -rich syngas ( $\text{H}_2/\text{CO} \geq 3.0$ ) has been reported to improve thermal efficiency;<sup>55</sup> this continuous RWGS process also has the potential to provide industrially valuable syngas. This technique is effective for continuous  $\text{CO}_2$  capture and methanation. A decrease in the  $\text{H}_2$  flow time improved the  $\text{H}_2$  utilization efficiency ( $\text{H}_2$  conversion increased from 38% to 58%; Fig. S24; see ESI† Text S6 for details).

In this chapter, we demonstrated that the developed tandem system is effective for the ambient-pressure conversion of  $\text{CO}_2$  in model combustion exhaust into  $\text{CH}_4$  and CO *via* methanation and RWGS reaction. Because this system does not require a pressure swing adsorption (PSA) unit, it has the potential to operate all reactors under

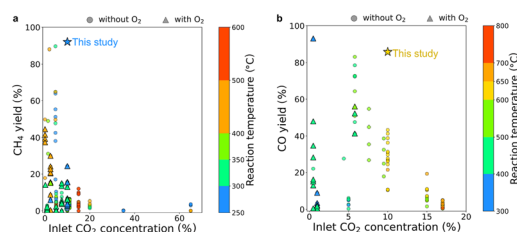
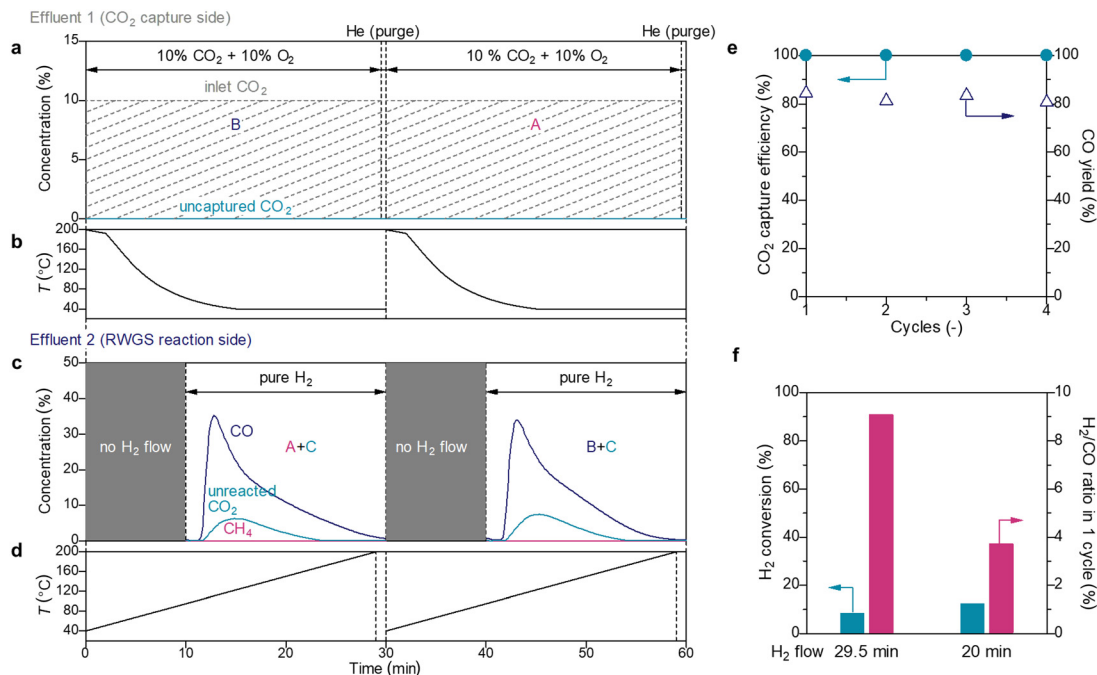


Fig. 6 Performance of (a) methanation and (b) RWGS reaction processes in the proposed system and previously reported systems for exhaust or atmospheric  $\text{CO}_2$  conversion (references are listed in Tables S1–S4†).





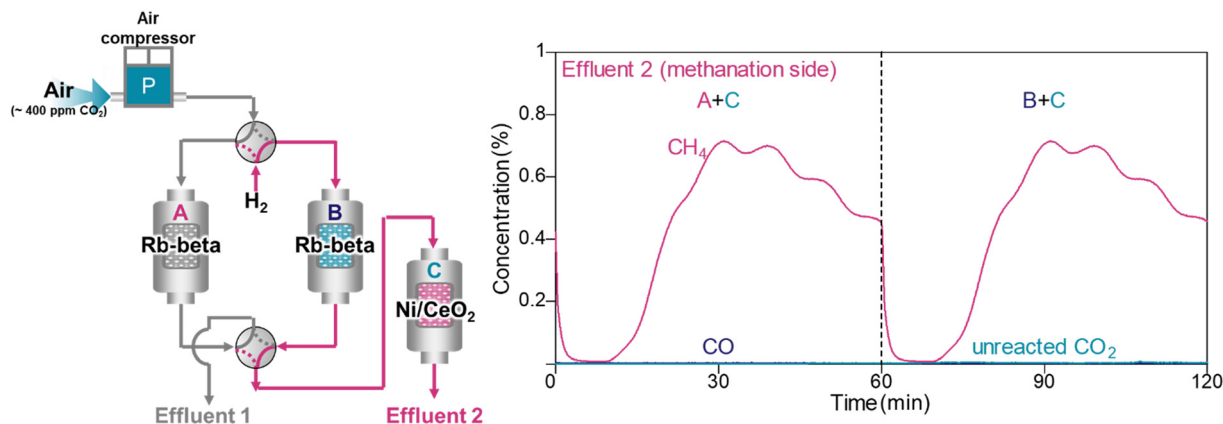
**Fig. 7** Continuous CO<sub>2</sub> capture and methanation; captured gas (100 mL min<sup>-1</sup>; 10% CO<sub>2</sub> + 10% O<sub>2</sub>/He for 29.5 min and then pure He for 0.5 min) and hydrogenation gas (120 mL min<sup>-1</sup>; pure H<sub>2</sub> for 20 min) were alternately fed into each reactor containing 14 g of Rb-beta. (a) and (c) typical variations in the CH<sub>4</sub>, CO<sub>2</sub>, and CO concentrations in effluents 1 and 2 over time, respectively; (b) and (d) typical temperature changes in reactors a and b over time, respectively; (e) changes in the CO<sub>2</sub> capture efficiency and CO yield during cyclic test; (f) comparison of H<sub>2</sub> conversion and ratio of effluent CO to H<sub>2</sub> in one cycle between the conditions depicted in Fig. S20a† (H<sub>2</sub> flow for 29.5 min) and those in Fig. 7a (H<sub>2</sub> flow for 20 min).

uniform pressurized conditions. This tandem system with conventional MeOH or FT synthesis catalysts such as Cu/ZnO/Al<sub>2</sub>O<sub>3</sub><sup>56–58</sup> and Fe-based catalysts,<sup>59,60</sup> which operate under elevated pressure, could enable the direct synthesis of methanol and liquefied petroleum gas (LPG) from CO<sub>2</sub> in model combustion exhaust streams.

## 2.4 Continuous direct air capture and methanation

Next, we broadened the applicability of the proposed system for continuous CH<sub>4</sub> production from ambient CO<sub>2</sub> (Fig. 8).

For ambient CO<sub>2</sub> capture and methanation, a high flow rate (500 mL min<sup>-1</sup>) of air was fed into one TSA reactor for 60 min, whereas a low flow rate (10 mL min<sup>-1</sup>) of pure H<sub>2</sub> was fed to the other TSA reactor (containing CO<sub>2</sub>-captured Rb-beta) for 60 min. The H<sub>2</sub> and desorbed CO<sub>2</sub> from the other TSA reactor were subsequently fed into the downstream methanation reactor (containing Ni/CeO<sub>2</sub>). When CO<sub>2</sub>-captured Rb-beta was heated under H<sub>2</sub>, the desorbed CO<sub>2</sub> underwent methanation on the downstream Ni/CeO<sub>2</sub> catalyst to produce a high concentration of CH<sub>4</sub>. The maximum CH<sub>4</sub> concentration was 0.7%, and the average CH<sub>4</sub> concentration



**Fig. 8** Schematic and typical variations in the CH<sub>4</sub>, CO, and unreacted CO<sub>2</sub> amounts in effluent 2 over time for continuous direct air capture and methanation. Conditions: 14 g of Rb-beta for each upper reactor and temperature swing from 40 to 200 °C (heating rate = 20 °C min<sup>-1</sup>); 15 g of Ni/CeO<sub>2</sub> for the bottom reactor, 300 °C, and 500 mL min<sup>-1</sup> air for 60 min and switched to 10 mL min<sup>-1</sup> H<sub>2</sub> for another 60 min.



was  $\sim 0.4\%$ . The results highlight the production of 10 times enriched  $\text{CH}_4$  from atmospheric  $\text{CO}_2$ . As shown in our previous study,<sup>61</sup> the enrichment methodology is simply based on the difference in the flow rates for  $\text{CO}_2$  capture (500  $\text{mL min}^{-1}$ ) and reduction (10  $\text{mL min}^{-1}$ ). As shown in Fig. S25,<sup>†</sup> the proposed methanation method is also applicable to high concentrations (40%) of  $\text{CO}_2$ . The 40%  $\text{CO}_2$  + 10%  $\text{O}_2$  mixture undergoes methanation, and the  $\text{CH}_4$  yield is  $\sim 70\%$ . These results demonstrate that the proposed methanation system can be applied to a wide range of  $\text{CO}_2$  concentrations.

## 2.5 Energy efficiency

To assess the energy requirements of the two processes, we analyzed the energy efficiency ( $\eta$ ) and fuel production efficiency (FPE) of the tandem methanation and CCR systems.<sup>62</sup> The  $\eta$  for  $\text{CO}_2$  conversion reactions was calculated using the following equation:<sup>63</sup>

$$\eta (\%) = \frac{\Delta H_R (\text{kJ mol}^{-1}) \cdot X_{\text{CO}_2} \cdot r_{\text{CO}_2, \text{in}} (\text{mol s}^{-1})}{P (\text{kW})}$$

where  $r_{\text{CO}_2, \text{in}}$  represents the molar flow rate of  $\text{CO}_2$  at the inlet of the reactor, and  $\Delta H_R$  is the reaction enthalpy ( $-165 \text{ kJ mol}^{-1}$  for the methanation process at 298 K). The calculated  $\eta$  values for the two systems are plotted as a function of time elapsed in Fig. 9a. The  $\eta$  for CCR is 46% at the beginning of the reaction but declines exponentially owing to the limited  $\text{CO}_2$  capacity of the DFM. In contrast, the  $\eta$  for tandem methanation is significantly higher than that for CCR, owing to the lower total thermal input and greater  $\text{CH}_4$  production. The system performances are compared in Fig. 9b. The advantages of tandem methanation over CCR are evident in terms of the  $\text{CH}_4$  yield,  $\text{CH}_4$  selectivity,  $\text{CH}_4$  production per

gram of the catalyst + adsorbent (to ensure a fair comparison between the two systems), and  $\eta$ . Note that the  $\eta$  for tandem methanation exceeds 100%. This is because only the power input is considered in the overall energy input and output and the net energy flow of the reactants and products is ignored.

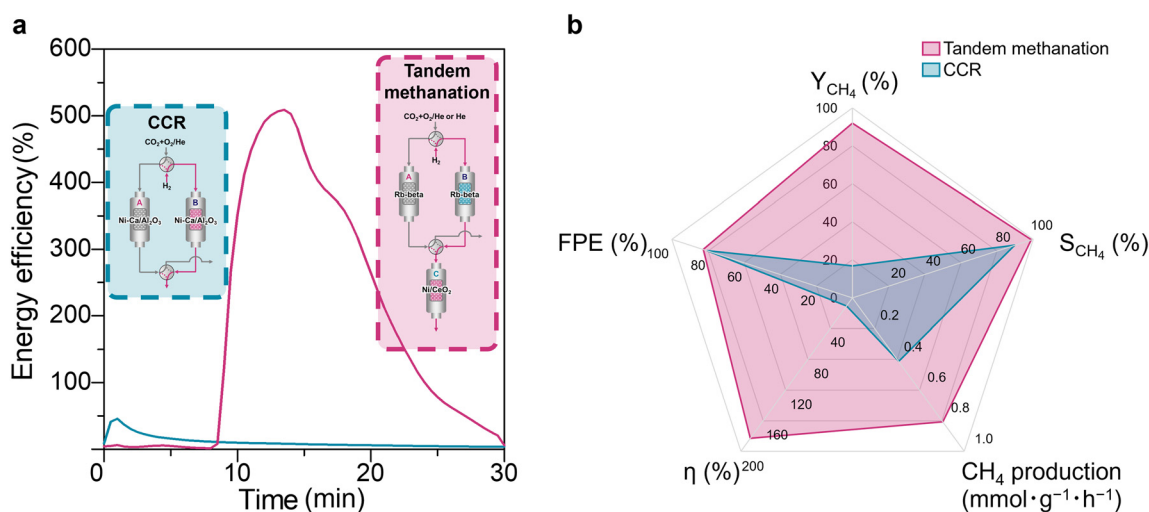
We also compared the FPEs of the two systems. The FPE for the methanation reaction is defined as the ratio of the energy output in the form of methane (not considering unreacted  $\text{H}_2$  at the exit) to the total energy input. The output energy is estimated based solely on the low heating value of  $\text{CH}_4$  ( $\text{LHV}_{\text{CH}_4}$ ), because the condensation heat of the produced water is typically not recovered. The energy input includes both the thermal input and the feed gas ( $\text{H}_2$ ), which possesses a heating value and contributes energy to the process. Therefore, the FPE is calculated as

$$\begin{aligned} \text{FPE} (\%) &= \frac{\text{Output energy}}{\text{Input energy}} \\ &= \frac{\text{LHV}_{\text{CH}_4} (\text{kJ mol}^{-1}) \cdot r_{\text{CH}_4} (\text{mol s}^{-1})}{P (\text{kW}) + \text{LHV}_{\text{H}_2} (\text{kJ mol}^{-1}) \times (r_{\text{H}_2, \text{in}} - r_{\text{H}_2, \text{out}}) (\text{mol s}^{-1})} \end{aligned}$$

where  $P$  is the thermal input,  $r_{\text{CH}_4}$  is the mole of  $\text{CH}_4$  production,  $r_{\text{H}_2, \text{in}} - r_{\text{H}_2, \text{out}} = (n_{\text{H}_2, \text{in}} - n_{\text{H}_2, \text{out}})/\Delta t$  is the rate of  $\text{H}_2$  consumption, and  $\text{LHV}_{\text{H}_2}$  and  $\text{LHV}_{\text{CH}_4}$  are the LHV of the converted hydrogen and methane ( $242$  and  $801 \text{ kJ mol}^{-1}$ ), respectively. As depicted in Fig. 9b, tandem methanation yields a high FPE of 83%, whereas CCR exhibits an FPE of 80%.

## 3 Conclusions

In summary, we developed a new method for the continuous production of  $\text{O}_2$ -free  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{CO}$  from the atmosphere and a simulated exhaust gas ( $\text{CO}_2/\text{O}_2/\text{He}$  mixture). The



**Fig. 9** (a) Typical variations in the energy efficiencies of CCR and tandem methanation system over time. Conditions: 14 g of Rb-beta for each upper reactor and temperature swing from 40 to 200 °C (heating rate = 20 °C min<sup>-1</sup>); 15 g of Ni/CeO<sub>2</sub> for the bottom reactor, 300 °C, and 500 mL min<sup>-1</sup> air for 60 min and switched to 10 mL min<sup>-1</sup> H<sub>2</sub> for another 60 min; (b) comparison of the  $\text{CH}_4$  yield ( $Y_{\text{CH}_4}$ ),  $\text{CH}_4$  selectivity ( $S_{\text{CH}_4}$ ),  $\text{CH}_4$  production, energy efficiency ( $\eta$ ), and fuel production efficiency (FPE) between the CCR and tandem methanation system. Parameters explaining energy efficiency, such as  $\eta$  and FPE, are detailed in ESI<sup>†</sup> Text S7.





developed process is suitable for continuous operation over a low-temperature swing of 40–200 °C on a Rb-beta sorbent combined with a methanation system at 300 °C and a RWGS system (for syngas synthesis) at 650 °C. The results of this study revealed that the developed process is almost twice as effective as CCR for CO<sub>2</sub> capture and hydrogenation. We also provided evidence that the energy efficiency of the tandem methanation process based on the overall energy input and output is comparatively high because of the low power input required to operate the system and the high CH<sub>4</sub> production. This approach is promising for CO<sub>2</sub> utilization *via* direct air and post-combustion gas capture and conversion to green fuels. In the future, we expect that our flexible process, in combination with efficient catalysts, will contribute to a carbon-neutral society.

## 4 Methods

### 4.1 Sorbent and catalyst preparation

Beta (Si/Al = 5, Mitsui Mining & Smelting Co., Ltd.), 13X (Si/Al = 1.25, Junsei Chemical Co., Ltd.), and Na-Y zeolites (Si/Al = 2.75, JRC-Z-Y5.5, Tosoh Corporation) were used as sorbents and supports. To prepare Rb-loaded zeolite sorbents, Rb species were immobilized on the zeolites using the conventional impregnation method. An appropriate amount of a Rb<sub>2</sub>CO<sub>3</sub> aqueous solution (AR > 99%, FUJIFILM WAKO Pure Chemical Corporation) was incorporated into the zeolites. After being stirred for 3 h at 25 °C, the suspension was evaporated by using a vacuum pump at 50 °C and dried overnight at 100 °C. The solid produced was then calcined at 200 °C for 1 h to obtain the desired Rb-zeolites. Other alkali-metal-loaded zeolite sorbents were prepared by employing the same approach using K<sub>2</sub>CO<sub>3</sub> (AR: 99.0%, Tokyo Chemical Industry Co., Ltd.) and Cs<sub>2</sub>CO<sub>3</sub> (AR > 99%, FUJIFILM WAKO Pure Chemical Corporation) as precursors.

### 4.2 Characterization

CO<sub>2</sub> adsorption measurements were performed by using a fixed-bed flow reactor (Fig. S1†). The zeolite sorbents (50 mg) were placed on quartz wool in the middle of a reactor, which was then placed in an electric tube furnace. The zeolite sorbents were heated to 500 °C under pure He flow (100 mL min<sup>-1</sup>), maintained for 30 min to remove the CO<sub>2</sub> and water vapor included in the zeolites, and cooled to 40 °C. The gas emitted from the reactor outlet was directly connected to a homemade IR gas cell to monitor the CO<sub>2</sub> concentration by performing IR measurements. In the first 30 s, before the CO<sub>2</sub> concentration stabilized, a flow of 1% CO<sub>2</sub>/He was passed through the bypass line and then the feed was switched to the reactor. The CO<sub>2</sub> adsorption amount was calculated from the difference in CO<sub>2</sub> concentrations between the blank and zeolites. Due to the high absorbance of CO<sub>2</sub> in gas-cell IR measurements, fluctuations in the ambient CO<sub>2</sub> concentration can lead to slight variations in the measured values. To evaluate the reproducibility, each sample was measured three times. The resulting deviation in CO<sub>2</sub>

concentration was within approximately ±0.05%, corresponding to an error margin of about ±0.04 mmol g<sub>sor</sub><sup>-1</sup> in the calculated CO<sub>2</sub> adsorption amount. The TPD of CO<sub>2</sub> was also performed using the homemade IR gas cell. The zeolite (100 mg) was pretreated in He atmosphere at 500 °C for 30 min and then cooled to 50 °C. Next, the 1% CO<sub>2</sub>/N<sub>2</sub> (100 mL min<sup>-1</sup>) mixed gas was fed into the reactor for 30 min and then He was flowed for 15 min. The TPD profile was obtained by heating the sample from 30 to 200 °C at a rate of 20 °C min<sup>-1</sup> under He flow. *Operando* FTIR measurements were performed during the TPD of CO<sub>2</sub> using a JASCO FT/IR-4600 spectrometer equipped with a mercury-cadmium-telluride detector and a flow-type quartz IR cell connected to a flow system (total flow rate = 100 mL min<sup>-1</sup>; Fig. S2†). The effluent gas was simultaneously monitored by performing FTIR spectroscopy (JASCO FT/IR-4600) using a homemade gas cell. A sample pellet (40 mg; diameter: 20 mm) was introduced into a quartz cell equipped with a CaF window. The sample pellet was pretreated at 200 °C for 30 min under He flow and cooled to 40 °C, and the 1% CO<sub>2</sub>/He mixture was fed into the reactor for 5 min. Subsequently, the system was purged with He for 10 min and the background spectrum was recorded. Temperature-resolved measurements were performed from 40 to 200 °C. The *operando* IR measurements were performed by monitoring the desorption of CO<sub>2</sub> in the outlet gas mixture.

### 4.3 Continuous CO<sub>2</sub> capture and O<sub>2</sub>-free CO<sub>2</sub> production using two parallel reactors

Continuous CO<sub>2</sub> capture and O<sub>2</sub>-free CO<sub>2</sub> production were performed using a system similar to that in a previous study.<sup>61</sup> CO<sub>2</sub> was continuously separated by using two fixed-bed flow reactors (Fig. S7†), and the response curves for CO<sub>2</sub> were obtained using a blank test (Fig. S9†). Two vertical quartz reactors (A and B) containing the same sorbent powder (14 g) were placed on quartz wool in the middle of the reactor in an electric tube furnace. The sorbents were pretreated under pure He flow (100 mL min<sup>-1</sup>) at 400 °C. Subsequently, continuous CO<sub>2</sub> capture and O<sub>2</sub>-free CO<sub>2</sub> production were achieved. Two timer-controlled 4-way valves were switched simultaneously to feed a simulated exhaust gas (100 mL min<sup>-1</sup>; 10% CO<sub>2</sub> + 10% O<sub>2</sub>/He for 29.5 min and He for 0.5 min) and an O<sub>2</sub>-free CO<sub>2</sub> gas (120 mL min<sup>-1</sup>; He for 30 min); when the simulated exhaust gas was fed to reactor A, the O<sub>2</sub>-free CO<sub>2</sub> gas was fed to reactor B. Effluent gases containing uncaptured CO<sub>2</sub> from reactor A and B (with O<sub>2</sub> and He) were continuously fed into effluent 1. The produced O<sub>2</sub>-free CO<sub>2</sub> in reactors A and B (with He) was continuously fed into effluent 2. The effluent gas was simultaneously monitored by performing FTIR spectroscopy (JASCO FT/IR-4600) using a gas cell and a mass spectrometer (BELMass, MicrotracBEL Corp.). The CO<sub>2</sub> concentration was calculated using the calibration curve for the CO<sub>2</sub> concentration and the IR peak area in the range of 2395–2235 cm<sup>-1</sup> for ≤1% CO<sub>2</sub> and 3760–3662 cm<sup>-1</sup> for >1% CO<sub>2</sub>. The CO<sub>2</sub> capture efficiency and the yield of O<sub>2</sub>-free CO<sub>2</sub> were calculated as follows:



$$\text{CO}_2 \text{ capture efficiency } [\%] = \frac{\int_0^t [F_{\text{CO}_2}^{\text{in}} - F_{\text{CO}_2}^{\text{out}(1)}(t)] dt}{\int_0^t F_{\text{CO}_2}^{\text{in}}(t) dt} \times 100;$$

$$\text{Yield of O}_2 \text{ free CO}_2 [\%] = \frac{\int_0^t F_{\text{CO}_2}^{\text{out}(2)}(t) dt}{\int_0^t F_{\text{CO}_2}^{\text{in}}(t) dt} \times 100,$$

where  $F_{\text{CO}_2}^{\text{in}}$ ,  $F_{\text{CO}_2}^{\text{out}(1)}$ , and  $F_{\text{CO}_2}^{\text{out}(2)}$  are the  $\text{CO}_2$  molar flow rates at the column inlet and the outlets of effluents 1 and 2, respectively, and  $t$  denotes the duration of one cycle.

#### 4.4 Continuous $\text{CO}_2$ capture and methanation/RWGS reaction using the combined system with two parallel reactors for TSA and a single reactor for hydrogenation

Continuous  $\text{CO}_2$  capture and hydrogenation (such as the methanation and RWGS reactions) were performed using homemade reactors (Fig. 1c; detailed procedure is shown in Fig. S13†). Two vertical quartz reactors (A and B) containing the Rb-beta sorbent powder (14 g), same as those used for  $\text{O}_2$ -free  $\text{CO}_2$  production, were placed on quartz wool in the middle of the reactor in an electric tube furnace. For the methanation and RWGS reactions, Ni/CeO<sub>2</sub> and Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> (commercial, Alfa Aesar) were added to the bottom reactor (C). The sorbents were pretreated under He flow for 30 min at 400 °C. Ni/CeO<sub>2</sub> was pretreated with  $\text{H}_2$  for 30 min at 400 °C. Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> was pretreated with  $\text{H}_2$  for 30 min at 500 °C. After these pretreatments, continuous  $\text{CO}_2$  capture and hydrogenation were performed. Similar to the continuous  $\text{O}_2$ -free  $\text{CO}_2$  production system, 1%  $\text{CO}_2$  + 10%  $\text{O}_2$ /He or pure He (for purging) and pure  $\text{H}_2$  were alternately flowed to each Rb-beta under cooling and heating. The produced  $\text{O}_2$ -free  $\text{CO}_2$  and  $\text{H}_2$  were fed into a hydrogenation catalyst (in reactor C). Effluent 1 contained the uncaptured  $\text{CO}_2$ ,  $\text{O}_2$ , and He. Effluent 2 contained the produced  $\text{CH}_4$ , CO, and unreacted  $\text{CO}_2$ . The produced  $\text{H}_2\text{O}$  was trapped before the gas concentrations were analyzed using cold trap equipment. The gas compositions in effluents 1 and 2 ( $\text{CO}_2$ , CO, and  $\text{CH}_4$ ) were analyzed online by using an FTIR spectrometer (JASCO FT/IR-4600) with a gas cell. The  $\text{STY}_{\text{CH}_4}$ ,  $\text{STY}_{\text{CO}}$ ,  $\text{CH}_4$ , and CO yields and  $\text{H}_2$  conversion are calculated as follows:

$$\text{STY}_{\text{CH}_4} \text{ or } \text{STY}_{\text{CO}} [\text{mmol g}^{-1} \text{ h}^{-1}] = \frac{\int_0^t F_{\text{CH}_4 \text{ or CO}}^{\text{out}}(t) dt}{m_{\text{cat}} \times t};$$

$$\text{CH}_4 \text{ or CO yield } [\%] = \frac{\int_0^t F_{\text{CH}_4 \text{ or CO}}^{\text{out}}(t) dt}{\int_0^t F_{\text{CO}_2}^{\text{in}}(t) dt} \times 100,$$

$$\text{H}_2 \text{ conversion } [\%] = \frac{\int_0^t F_{\text{CO}}^{\text{out}}(t) dt + 4 \int_0^t F_{\text{CH}_4}^{\text{out}}(t) dt}{\int_0^t F_{\text{H}_2}^{\text{in}}(t) dt} \times 100$$

where  $F_{\text{CH}_4}^{\text{out}}$  and  $F_{\text{CO}}^{\text{out}}$  are the  $\text{CH}_4$  and CO molar flow rates, respectively, at the column outlet of effluent 2,  $F_{\text{CO}_2}^{\text{in}}$  and  $F_{\text{H}_2}^{\text{in}}$  are the  $\text{CO}_2$  and  $\text{H}_2$  molar flow rates at the column inlet, and  $m_{\text{cat}}$  is the catalyst mass.  $\text{H}_2$  conversion was calculated based

on the stoichiometric consumption primarily associated with the formation of CO and  $\text{CH}_4$ . To determine the CO and  $\text{CH}_4$  molar flow rates, the peak area values around 2250–2001 and 3031–2994  $\text{cm}^{-1}$  were used, respectively. The power consumption ( $P$ ) for reactor heating, which represents the thermal input, was measured using an electrical power consumption analyser (ELPA, EC-05EB).

#### 4.5 Continuous CCR to $\text{CH}_4$ system

Continuous  $\text{CO}_2$  capture and reduction to  $\text{CH}_4$  using the combined two parallel reactors were performed using homemade reactors (Fig. S14†). Two vertical quartz reactors (A and B), each containing the Ni-Ca/Al<sub>2</sub>O<sub>3</sub> sieves, were placed on quartz wool in the middle of an electric tube furnace. Each Ni-Ca/Al<sub>2</sub>O<sub>3</sub> was pretreated with  $\text{H}_2$  for 30 min at 500 °C. After these pretreatments, continuous CCR was performed. 1%  $\text{CO}_2$  + 10%  $\text{O}_2$ /He and pure  $\text{H}_2$  were alternately flowed to each Ni-Ca/Al<sub>2</sub>O<sub>3</sub> under isothermal conditions. Effluent 1 contained the uncaptured  $\text{CO}_2$ ,  $\text{O}_2$ , and He. Effluent 2 contained the produced  $\text{CH}_4$ , CO, and unreacted  $\text{CO}_2$ . The produced  $\text{H}_2\text{O}$  was trapped before the gas concentrations were analyzed using cold trap equipment. The gas compositions in effluents 1 and 2 ( $\text{CO}_2$ , CO, and  $\text{CH}_4$ ) were analyzed online by using an FTIR spectrometer (JASCO FT/IR-4600) with a gas cell.

### Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

### Author contributions

S. Miy. wrote the manuscript draft and conducted the majority of the experiments, including validation and methodology development (writing – original draft, investigation, validation, methodology). A. A. supervised the project and contributed to manuscript revision (supervision, writing – review & editing). Y. M. and H. S. F. assisted with catalyst preparation and performed catalytic activity trials (investigation, validation). S. Min. and T. T. provided valuable insights into the experimental work and contributed to data visualization and manuscript revision (visualization, writing – review & editing). K. S. designed and supervised the overall project and secured funding (supervision, conceptualization, writing – review & editing, funding acquisition).

### Conflicts of interest

There are no conflicts to declare.

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