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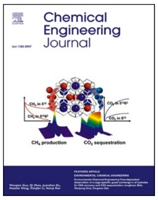

Short communication

Combined capture and reduction of CO_2 to methanol using a dual-bed packed reactor

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ABSTRACT

Recently, carbon capture and reduction (CCR) technology has gained interest to directly convert CO_2 to value-added products without requiring purification of CO_2 and its subsequent transportation. CCR to methanol in one dual function material (DFM) poses mechanistic and kinetic challenges. To counteract this, a process combining Na/Al_2O_3 as a capture component and $Cu/ZnO/Al_2O_3$ (CZA) as methanol synthesis catalyst was developed to allow CCR to methanol. With a 5 vol% CO_2 flow for capture and subsequent H_2 stream combined with a temperature swing, a methanol selectivity of 26 % was achieved at 9 bar. Further investigation found that Na/Al_2O_3 significantly increased methanol yield, while a stacked configuration of Na/Al_2O_3 followed by CZA significantly outperformed a mixed configuration of the two catalysts. With further investigation of operation at higher pressure and surface mechanism, an effective CCR to methanol process using two affordable yet readily available catalysts can be realized.

1. Introduction

With increasing momentum towards a carbon neutral future [1], the development of carbon dioxide (CO_2) capture, utilization, and storage (CCUS) technologies is crucial to facilitate the transition. Such technology captures CO_2 either from waste streams of chemical processes or directly from air (known as direct air capture (DAC) [2]) and either stores it [3] or converts it to value-added products generally via a catalytic hydrogenation reaction, known as carbon capture and utilization (CCU) [4–6]. Out of the potential products that can be formed from CCU, methanol is of high interest due to its importance as a fuel and commodity chemical [7,8], even having potential to liberate humanity's reliance on fossil fuels [1]. To minimize challenges regarding purification and transportation of captured CO_2, an approach can be taken where CO_2 capture and hydrogenation can be performed in one reactor, known as carbon capture and reduction (CCR). However, to the best of our knowledge, publications concerning CCR to methanol using heterogeneous catalysts is inexistant.

In a combined CCR process, two possible design approaches can be taken. The first is to implement a true dual function material (DFM) where CO_2 capture and reduction to methanol are both performed on one catalyst. This approach was previously investigated for CCR to methane [9–14] and CO [15–18]. In the case of methanol synthesis, addition of a common CO_2 capture component such as Na or K on the industrial standard $Cu/ZnO/Al_2O_3$ (CZA) catalyst [19] is expected to result in negative effects on catalytic activity due to promoted RWGS activity [20]. The second, more practical approach is to combine two different catalysts in one reactor to induce the bifunctionality. Publications using this dual-bed reactor method are currently available for the conversion of syngas to low carbon olefins and aromatics [21], production of ethanol from dimethyl ether and syngas [22], CO_2 capture and methanation [23,24] and the oxidation of ethane to ethylene [25]. When considering CCR to methanol, one component would generally act as a CO_2 sorbent in addition to CZA for subsequent reduction. Na/Al_2O_3 especially shows promising performance as a CO_2 sorbent while maintaining a relatively low cost due to the lack of a transition metal [26].

Fig. 1 shows a CCR to methanol process that can be achieved by stacking (i.e. sequentially placing) a Na/Al_2O_3 bed with that of CZA.

In the CCR process, the reactor is first fed with CO_2 to enable exothermic CO_2 capture following Equation (1) to result in Na_2CO_3.

$$Na_2O + CO_2 \rightleftharpoons Na_2CO_3 \tag{1}$$

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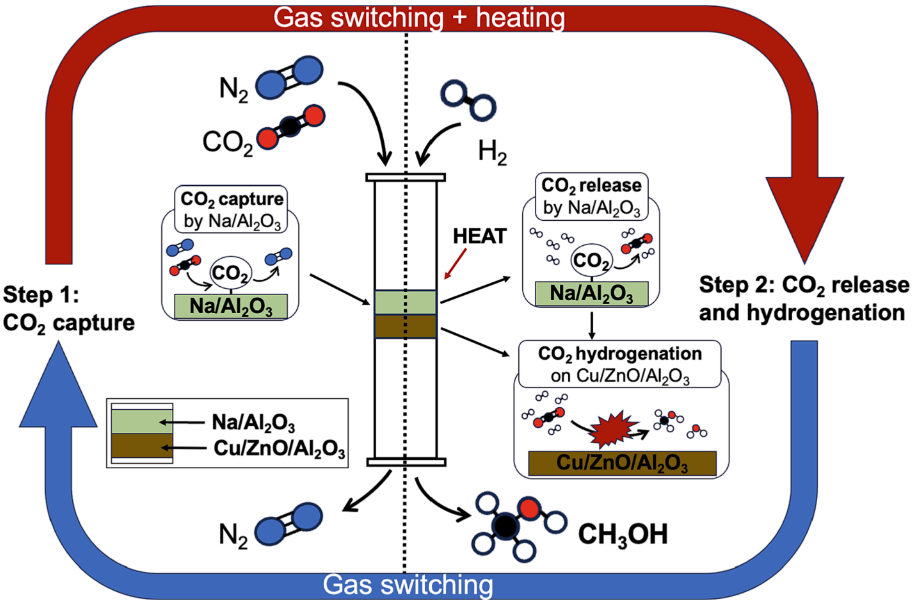

Fig. 1. Conceptual diagram of integrated CO_2 capture and conversion to methanol and other products using a dual-bed reactor.

After purging the excess CO_2 with an inert such as N_2, the reactor is fed with H_2 and heated to allow and promote endothermic CO_2 release via the reverse of Equation (1) and subsequent conversion of CO_2 to take place. Previous CO_2-TPD studies have confirmed the occurance of CO_2 desorption from Na/Al_2O_3 under inerts [27]. We believe that the addition of a different gas environment such as H_2 would provide similar or superior CO_2 desorption performance. CO_2 release can further be promoted by heating the reactor [26]. The desorbed CO_2 then travels together with (renewable) H_2 to the CZA bed, where methanol synthesis can take place. CO_2 hydrogenation to methanol undergoes two key reaction paths. One is the exothermic direct hydrogenation of CO_2 to methanol (shown in Equation (2), and the other an endothermic RWGS side reaction to CO (shown in Equation (3) followed by CO hydrogenation (shown in Equation (4).

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + 2H_2O \tag{2}$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \tag{3}$$

$$CO + H_2 \rightleftharpoons CH_3OH \tag{4}$$

Operation at higher pressures in CCR to methanol are desired to increase CO_2 capture capacity [27] and to increase CO_2 conversion and methanol selectivity, provided a high H_2/CO_2 ratio is also achieved [7,8].

In this study, an initial CCR to methanol process was developed using a combination of Na/Al_2O_3 and CZA. In order to gain an initial understanding, the study focused on the nature of Na/Al_2O_3 during CO_2 capture and release, followed by the operating conditions and configurations of Na/Al_2O_3 and CZA.

2. Experimental

2.1. Preparation of catalysts

Na/Al_2O_3 (16 wt%) was synthesized using an impregnation method, following protocol from Sasayama *et al.* with precursors purchased from the same chemical suppliers [18]. $Cu/ZnO/Al_2O_3$ (40 wt% Cu, 40 wt% ZnO) was synthesized using a co-precipitation method [28]. A mixture of 12.2 g $Cu(NO_3)_2{\cdot}3H_2O$ (Fujifilm Wako Pure Chemical Corp.), 14.6 g $Zn(NO_3)_2{\cdot}6H_2O$ (Fujifilm Wako Pure Chemical Corp.), and 7.4 g

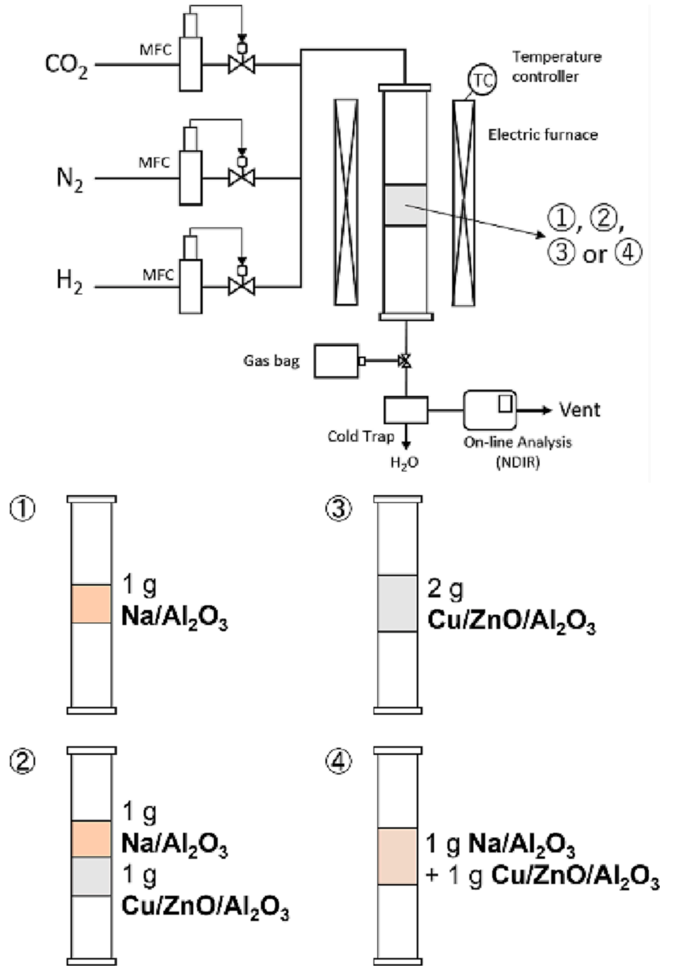

Fig. 2. Schematic of the experimental setup used during this study, as well the various configurations of catalyst beds.

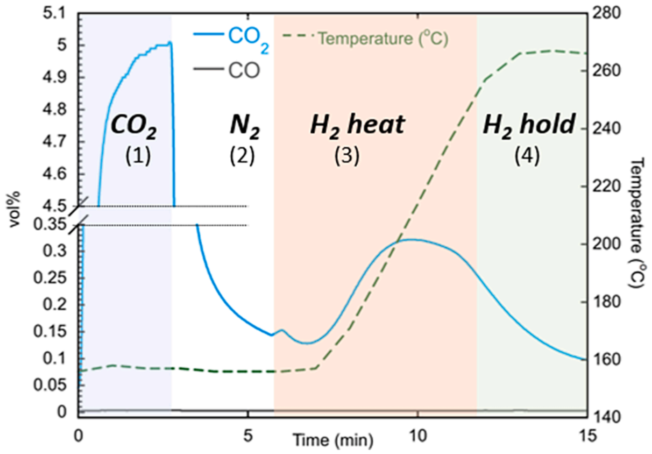

Fig. 3. CO_2 concentration profile during CO_2 capture and its release under H_2 with a temperature ramp of 20 °C/min at a H_2 flow rate of 100 mL/min (p = 1 bar).

$Al_2(NO_3)_3 \cdot 9H_2O$ (Fujifilm Wako Pure Chemical Corp.) was dissolved in 200 mL of distilled water to form a mixed metal nitrate solution. Subsequently, a mixed alkali solution of 2 M NaOH and 0.5 M Na_2CO_3 was added dropwise to the mixed nitrate solution at room temperature while stirring strongly to reach a pH of around 9.5. The resulting suspension was further aged at 70 °C for 3 h under continuous stirring. The precipitate obtained by filtration was then added to a beaker containing 800 mL of distilled water. After washing while stirring at room temperature for 3 h, the precipitate was filtered, dried overnight at 110 °C, and calcined in air at 450 °C for 3 h.

2.2. Catalytic evaluation

The investigation into the CO_2 capture and release capability of Na/Al_2O_3 and the CCR experiments of Na/Al_2O_3 and CZA were performed in the experimental setup shown in Fig. 2. The setup consists of three mass flow controllers (MFCs) to supply the gases, an electric furnace surrounding the reactor and a valve that can switch the direction of the effluent stream between a continuous gas analyzer (nondispersive infrared spectroscopy (NDIR)) and a gas bag. A thermocouple was inserted into the reactor to monitor the reaction temperature. In the case of investigating the nature of CO_2 capture and release of Na/Al_2O_3, reactor configuration ① shown in Fig. 2 was used, and the valve was set towards analysis using the NDIR. Pre-treatment of Na/Al_2O_3 was performed by heating the reactor to 500 °C at 10 °C/min under 100 mL/min H_2 flow and maintained at 500 °C for 1 h.

The pre-treatment was performed to activate the CO_2 capturing capacity of Na/Al_2O_3 [18]. After completion, the reactor was allowed to cool to 150 °C under N_2. For the CCR experiments, reactor configurations ②, ③, ④ were used depending on the purpose of the experiment. Since pre-treatment of CZA at the same conditions as Na/Al_2O_3 (T = 500 °C) poses potential deactivation of CZA, pre-treatment of all relevant configurations was done by heating the reactor to 260 °C at a heating rate of 10 °C/min under 100 mL/min H_2 flow and maintained at 260 °C for 1 h. The reactor was subsequently allowed to cool to 150 °C under N_2.

All experiments underwent four key steps to simulate CCR: (1) 5 vol % CO_2 was passed at 200 mL/min for 3 min to allow CO_2 capture at 150 °C, (2) the reactor was purged with 200 mL/min N_2 to remove excess CO_2 present after step (1) at 150 °C, (3) 100 mL/min H_2 was passed into the reactor which was heated from 150 °C to 250 °C in the case of Na/Al_2O_3 alone and 230 °C in the CCR experiments with a heating rate of 20 °C/min, and (4) 100 mL/min H_2 was passed for 2 min for Na/Al_2O_3 alone and 6 min for the CCR experiments while keeping the reactor temperature set at the maximum temperature specified in step (3). After steps (1)-(4) were complete, the reactor was cooled under N_2 flow (200 mL/min) to 150 °C to purge the outlet gases formed in steps (3) and (4). Finally, the experimental procedure was repeated from step (1). Four repeated sequences of the steps was performed, and the values shown represent their averages while considering standard deviation. Analysis of the outlet gases were performed using an NDIR for Na/Al_2O_3 alone. For the CCR to methanol experiments, the outlet gases were collected in a gas bag for 10 min upon initiating H_2 flow (step (3)) and analyzed using gas chromatography equipped with a thermal conductivity detector (Agilent 490, Agilent Technologies) and a flame ionization detector (Agilent 7890B, Agilent Technologies).

Calculation of the molar quantity of CO_2 desorbed per gram of Na/Al_2O_3 (n_{CO_2}) was calculated by integrating the CO_2 concentration profile (F_{CO_2}) during a period t_0 to t_1 and dividing by the mass of Na/Al_2O_3 (W), shown in Equation (5).

$$n_{CO_2} = \frac{1}{W}\int_{t_0}^{t_1} F_{CO_2}(t)dt \tag{5}$$

The CO_2 conversion (X_{CO_2}) and the selectivity of each respective outlet product (S_x) were calculated using Equations (6) and (7).

$$X_{CO_2} = \frac{C_{MeOH} + C_{CO} + C_{CH_4}}{C_{MeOH} + C_{CO} + C_{CH_4} + C_{CO_2}} \times 100\,\% \tag{6}$$

$$S_x = \frac{C_x}{C_{MeOH} + C_{CO} + C_{CH_4}} \times 100\,\% \tag{7}$$

Where C is the concentration of component identified in the outlet gas sample bag.

3. Results and discussion

3.1. CO_2 capture and release on Na/Al_2O_3

Since the extent of methanol synthesis is limited by the extent of CO_2 desorption from Na/Al_2O_3, studying its nature was of high importance. Fig. 3 shows the concentration profile plotted during steps (1) to (4) using Na/Al_2O_3 as a CO_2 capture component.

The delay in the increase of CO_2 concentration up to its feed concentration (5 vol%) indicated successful capture of CO_2 on the Na/Al_2O_3 surface following Equation (1). Upon purging with N_2 (step (2)), the CO_2 concentration rapidly decreased, leaving adsorbed CO_2 on the catalyst surface. Upon heating the reactor at 20 °C/min (step (3)) an increase in CO_2 concentration was observed between 7 and 14 min. The maximum release of CO_2 was observed at approximately 10 min with a CO_2 flow rate of 0.67 mL/min at approximately 200 °C, in-line with the temperature range used for current industrial CO_2 hydrogenation to methanol processes. In addition, a total of 0.1 mmol of CO_2/g-Na/Al_2O_3 was desorbed in the 7 to 14 min period following Equation (5). This quantity

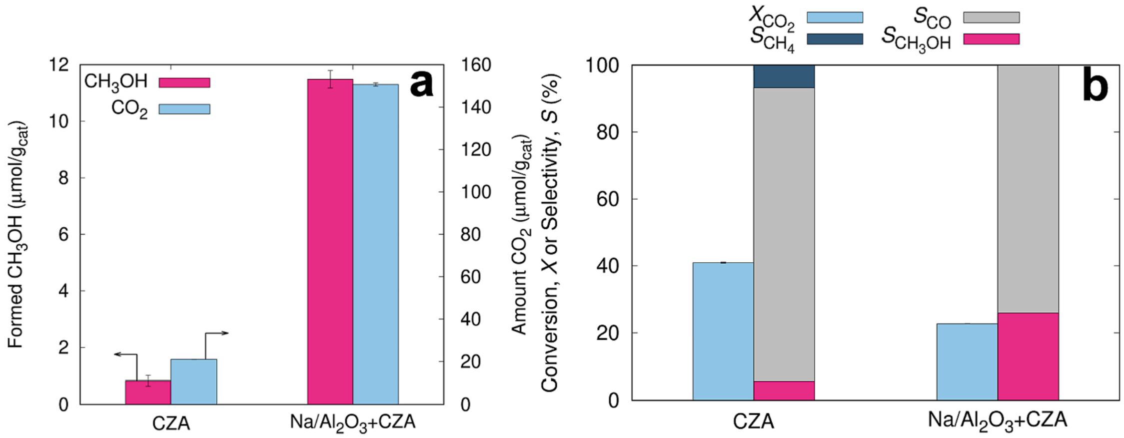

Fig. 4. Comparison in CCR-to-methanol performance between CZA alone and Na/Al$_2$O$_3$ stacked with CZA in terms of (a) molar quantity of methanol and CO$_2$ in the gas bag sample per gram of CZA and Na/Al$_2$O$_3$, respectively and (b) CO$_2$ conversion and methanol, CO and CH$_4$ selectivity (reaction conditions: p = 9 bar, H$_2$ flow rate = 100 mL/min with heating rate of 20 °C/min to 230 °C).

of CO$_2$ desorption was in line with that of the captured CO$_2$ obtained from our previous study [18]. Assuming that the surface cosists of only γ-Al$_2$O$_3$ and CO$_2$ sorption forms monolayer adsorption [29], this amount of captured CO$_2$ corresponds to a CO$_2$ surface coverage of 34.1 %, indicating a relatively good use of the catalyst surface. Using the results obtained in Fig. 3 as a basis, a temperature ramp rate of 20 °C/min and a temperature range of 150–230 °C was chosen for CCR testing with the addition of CZA. To suppress RWGS as much as possible, the reactor was not heated beyond 230 °C.

3.2. CCR to methanol

Investigation and optimization of CCR to methanol using Na/Al$_2$O$_3$ and CZA was initiated using the knowledge gained from the previous section. Fig. 4 shows the difference in CCR performance between CZA alone (configuration ③ in Fig. 2) and Na/Al$_2$O$_3$ stacked with CZA (configuration ② in Fig. 2) on (a) the molar quantity of methanol and CO$_2$ in the gas sampling bag per gram of CZA and Na/Al$_2$O$_3$, respectively, and (b) catalytic performance upon reaction at 9 bar.

A successful CCR to methanol process was achieved and performance improved significantly with the addition of Na/Al$_2$O$_3$, displaying a quantity of methanol approximately 14 times higher compared to CZA alone. Furthermore, the quantity of CO$_2$ present in the gas bag increased from 21 µmol to 150 µmol upon addition of Na/Al$_2$O$_3$, demonstrating higher CO$_2$ capture capacity and thus a higher quantity available for methanol synthesis. Similar trends were observed in the catalytic performance data shown in Fig. 4b, where methanol selectivity increased from 5.7 % for CZA alone to 26 % for Na/Al$_2$O$_3$ and CZA. CO dominated the outlet stream in the case of CZA alone with a selectivity of 87.5 %, likely due to the decomposition of ZnCO$_3$ to CO. Generally, the decomposition of carbonates are favored at temperatures above 500 °C [30]. However, under a H$_2$-rich environment this decomposition of ZnCO$_3$ can occur at lower temperatures [30]. By adding Na/Al$_2$O$_3$, the CO$_2$ adsorption capacity was greatly increased, allowing higher quantities of CO$_2$ to enter the CZA phase for reaction. The CO$_2$ conversion was higher than the values obtained from previous thermodynamic studies [7,8,31] since the reaction was performed under non-stoichiometric ratio of H$_2$/CO$_2$ with a significant excess of H$_2$. The H$_2$/CO$_2$ ratio in the gas sampling bag was above 180 in all experiments, resulting in an environment favourable for CO$_2$ hydrogenation.

Fig. 5 shows the effect of reactor pressure on CO$_2$ conversion, methanol selectivity and quantity formed during CCR for the stacked configuration of Na/Al$_2$O$_3$ and CZA (configuration ② in Fig. 2). Tests were performed at 1, 3, 6 and 9 bar.

Methanol selectivity increased accordingly with increasing pressure; from 1 % at 1 bar to 26 % at 9 bar. The low reactor pressure resulted in a thermodynamically and kinetically challenging environment for methanol synthesis to take place despite successful capture of CO$_2$ [7,8,31]. The setup used during the study shown in Fig. 2 limited the maximum reactor pressure to 10 bar. However, learning from the trends seen in Fig. 5 breakthrough improvements in methanol selectivity and CO$_2$ conversion can be expected if the experiment were carried out at pressures close to the operating conditions of the current industrial CO$_2$ hydrogenation to methanol process (p = 60–100 bar) [7]. Using the results obtained in Fig. 5, all remaining experiments regarding CCR to methanol were performed at a reactor pressure of 9 bar.

Fig. 6 compares the CCR performance to methanol between a stacked configuration and mixed configuration of Na/Al$_2$O$_3$ and CZA (configurations ② and ④ in Fig. 2) at a reactor pressure of 9 bar.

Upon mixing the two catalysts the performance worsened significantly compared to the stacked configuration, with methanol selectivity being over 22 % lower despite a comparable CO$_2$ conversion at around 20 %. Similar results were obtained in literature when considering CO$_2$ methanation, where the mixed configuration of capture component and methanation catalyst resulted in higher CO selectivity [32]. The reason for the decrease in performance likely stems from the oxidizing nature of CO$_2$ where the Cu component in CZA becomes mildly oxidized upon

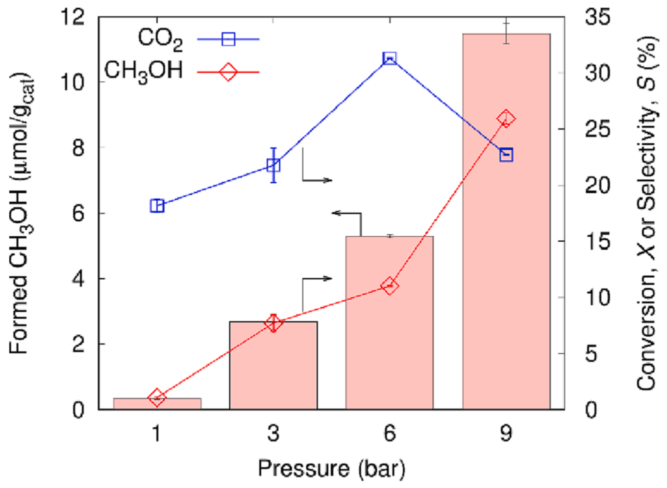

Fig. 5. Effect of reactor pressure on CO$_2$ conversion, methanol selectivity and quantity of formed methanol in the gas sampling bag per gram of CZA for a stacked Na/Al$_2$O$_3$ and CZA configuration on (reaction conditions: p = 1, 3, 6, 9 bar, H$_2$ flow rate = 100 mL/min with heating rate of 20 °C/min to 230 °C).

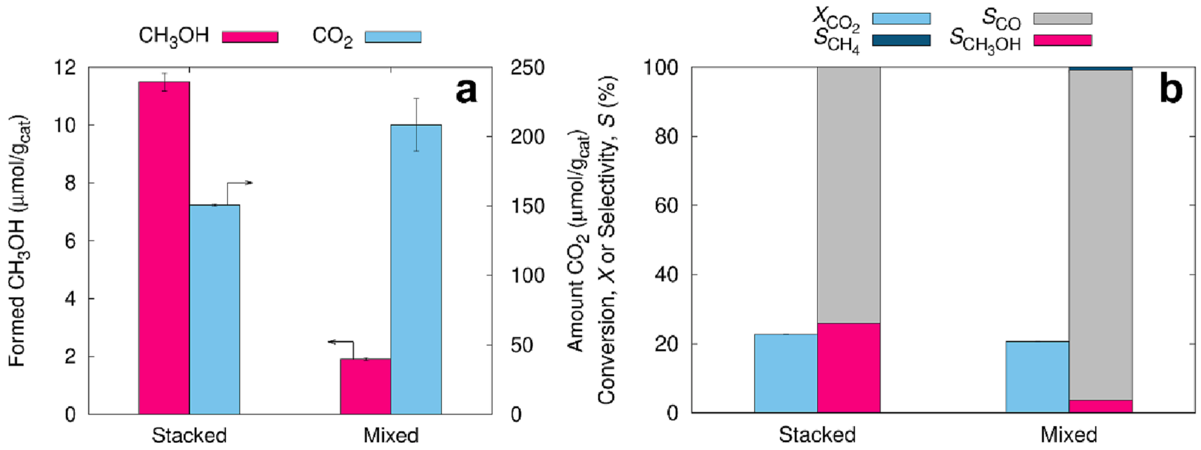

Fig. 6. Effect of a stacked and mixed configuration of Na/Al_2O_3 and CZA on CCR performance to methanol in terms of (a) molar quantity of methanol and CO_2 in the gas bag sample per gram of CZA and Na/Al_2O_3 respectively and (b) CO_2 conversion and methanol, CO and CH_4 selectivity (reaction conditions: p = 9 bar, H_2 flow rate = 100 mL/min with heating rate of 20 °C/min to 230 °C).

exposure, requiring reduction for activity towards hydrogenation to methanol [7,8]. When Na/Al_2O_3 and CZA are sequentially placed,upon switching to H_2 flow H_2 is expected to reach the CZA bed earlier than CO_2. This induces a time difference between the formation of active Cu sites for methanol synthesis and CO_2 desorption from Na/Al_2O_3. On the other hand, in a mixed configuration, this time difference cannot be attained, resulting in hindered formation of the Cu active sites by the presence of an oxidative molecule (CO_2) and thus a higher risk of CO formation. The configuration in which Na/Al_2O_3 and CZA is placed therefore had a significant effect on the catalytic performance for CCR to methanol.

4. Conclusion

Successful carbon capture and reduction to methanol utilizing Na/Al_2O_3 and CZA was achieved, kickstarting the potential for further investigation. In this study, it was found that higher pressure significantly improved methanol selectivity, reaching 26 % at 9 bar. Na/Al_2O_3 is a crucial component to add to CZA in a stacked configuration to result in a higher CO_2 capture capacity and methanol selectivity and molar quantity in the outlet stream. A higher quantity of captured CO_2 while maintaining a high H_2/CO_2 ratio and increasing reactor pressure would increase CCR performance further. Nevertheless, the use of two relatively accessible and affordable catalysts yielded methanol from a diluted stream of CO_2. Although precise mechanistic effects are yet to be investigated, the potential of a combined carbon capture and reduction process to methanol in one reactor is realized.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2023.144227.

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