Metal Hydroxide Assisted Integrated Direct Air Capture and Conversion to Methane with Ni/Al2O3 catalysts

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Metal Hydroxide Assisted Integrated Direct Air Capture and Conversion to Methane with Ni/Al_2O_3 catalysts

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Methods to synthesize sustainable and renewable methane are becoming of growing interest to relieve humankind from its reliance on fossil and finite natural gas reserves. Metal hydroxide salts are able to capture CO_2 from dilute sources including ambient air in the form of carbonate and bicarbonate salts. We report herein the direct conversion of such inorganic carbonate salts into methane in yields of up to 100% utilizing both Ni/Al_2O_3 and $Ni/CaAl_2O_4$ catalysts. This conversion is achieved in 48 hours with 50 bar of hydrogen at a relatively moderate temperature of 225°C under batch conditions. Water was also shown to improve the conversion of the carbonate salt to methane and the Ni/Al_2O_3 catalyst retained 99% of its activity in the alkaline media after five consecutive hydrogenation cycles. Remarkably, the metal hydroxide was also regenerated during the reaction and was reused to capture CO_2 for subsequent reactions. Compared to the conventional sequential approach involving the capture of CO_2 followed by the release of CO_2 and its hydrogenation to methane in the Sabatier reaction, the integrated route presented here can offer a number of energetic and economic benefits that could pave the way for a robust carbon capture and conversion process.

A number of carbon capture technologies are being developed as strategies to limit unabated climate change from continuing.[1] Carbon Capture and Sequestration (CCS) captures CO_2 from various sources including flue gases, industrial exhausts as well as the atmosphere and stores it underground in suitable geological formation or through reaction with appropriate minerals (mineralization).[2–4] Carbon Capture and Utilization (CCU), on the other hand, captures CO_2 from these same sources and proposes to use the CO_2 either as such or as a feedstock for numerous products including fuels, chemicals and plastics.[5–7] Both CCS and CCU rely on CO_2 capture processes that differ depending on parameters such as the CO_2 source, CO_2 concentration and purity. In CCU, capture and utilization/recycling have for the most part been conducted as two distinct operations that follow a sequential pathway, where CO_2 is first captured in a capture media. The captured CO_2 is then released from this capture media in an energy intensive desorption/regeneration step. Subsequently, the obtained CO_2 is compressed to be used as is, sequestered, and/or transformed into fuels and materials. The CO_2 desorption step is an endothermic process and often the energy intensive step in the overall process. It is only recently that scientists started looking into the possibility of combining capture and utilization. The integrated carbon capture and utilization (ICCU) protocols pursued by our group and others should reduce the overall energy needs of the process and lower both operational and capital expenses through process intensification. ICCU of CO_2 leads to value-added products such as methanol, formate, formamide, dimethyl ether, carbon monoxide and methane.[8–14] Methane in particular is the main component of natural gas that constitutes a large proportion of the energy consumed around the world, accounting for example for 34% of the primary energy consumption in the United States.[15] Thus, providing new pathways to synthesize methane from CO_2 and green hydrogen, where the CO_2 is captured from point sources and the atmosphere would lead to green methane, while allowing for the continued use of the vast infrastructure already in place for natural gas distribution. Carbon recycling would reduce the environmental impact of natural gas/methane and allow it to become increasingly renewable and carbon neutral.

Most of the routes currently proposed to produce methane from CO_2 rely on the sequential CCU approach described above where CO_2 is first captured and then released in an energy demanding step from the capture media at a high concentration before being

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hydrogenated to methane at 300-400 °C following the well-established Sabatier reaction.

In contrast to that approach, combining carbon dioxide capture with methane synthesis in an integrated process is a relatively novel concept. It has previously been reported by Heldebrant et al.[16] in a system utilizing primary and secondary amines to capture CO_2 and then convert the captured product to methane using heterogeneous ruthenium catalysts and hydrogen. Amines have been well studied as carbon capture agents, especially in homogenous systems.[17–19] However, amines have volatility and toxicity issues and often suffer from oxidative degradation.[20–23] Thus, precautions need to be taken when amines are used for the capture of CO_2, especially from air. This system also utilized ruthenium metal to catalyse the reaction. However, earth abundant metals, like nickel have also been shown to perform methanation reactions.[24–27]

Capturing CO_2 with metal hydroxides to form bicarbonate or carbonate salts has also been researched and circumvents some of the issues with amine based systems including the discussed volatility and degradation concerns.[28,29] Recently, it was reported by Prakash et al. that bicarbonate salts can be hydrogenated to methanol over a $Cu/ZnO/Al_2O_3$ catalyst.[30] Using this catalyst, the paper also showed that CO_2 can be captured from air by a metal hydroxide solution in ethylene glycol and directly converted to methanol with a yield of 97%. This example of integrated capture and conversion inspired us to explore the possibility of using a similar approach to obtain other products beside methanol; in this case methane, in high yields.

Converting inorganic carbonates and bicarbonates to methane has been previously reported in flow systems.[31–33] However, these systems often utilize temperatures above 500 °C raising their energetic costs. Some of the previous accounts using flow reactor conditions have been performed with earth abundant metals, like nickel. However, current ICCU with heterogeneous catalysts more commonly utilize rare-earth catalysts, such as ruthenium and iridium.[10,16]

The Direct Air Capture of carbon dioxide (DAC) utilizing a hydroxide salt and the subsequent conversion of the obtained metal carbonate salt to methane is a process of importance. It would circumvent the volatility problems of amine-based sorbents and could be designed in such a way to avoid base deactivation as the choice of solvent should be less constrained.[34] Current attempts in utilizing this technology typically use bifunctional solid materials composed of an alkali metal containing species and a catalyst. The alkali metal species on the surface reacts with CO_2 to form a carbonate/bicarbonate salt. This salt is then decomposed to form CO_2 again before the reaction occurs.[24,35–37] As the catalysts used are generally air sensitive, this means that the catalyst in these bifunctional materials need to be regenerated under hydrogen during each adsorption/conversion cycle. This consumes part of the hydrogen and is rather energy intensive. At the same time, a large amount of catalyst is also tied up in the adsorbent material during the adsorption period, which could be capital intensive, especially if the catalyst is based on precious metals. Thus, it could be advantageous to decouple the capture and conversion steps. In the first step, CO_2 is captured with a strong base in the form of a carbonate/bicarbonate salt. In a second, separate but adjacent, step this salt is converted to methane over a catalyst. In doing so, the catalyst is always in the hydrogenation mode and does not require regeneration in each recurring adsorption/conversion cycle. It should allow for a more efficient use of the catalyst and reduce the amount of catalyst needed and therefore cost of the overall process.

Herein, we report the direct hydrogenative conversion of potassium bicarbonate and carbonate to methane at relatively low temperatures and the concurrent regeneration of the hydroxide base utilizing both Ni/Al_2O_3 and $Ni/CaAl_2O_4$ catalysts. This reaction can also be undertaken with carbonate and bicarbonate salts synthesized directly from the atmospheric air using an alkali metal hydroxide thus decoupling capture and conversion. The catalyst can then be easily separated from the base after the reaction and both components be used again in subsequent reaction cycles (Figure 1). Interestingly, the reaction does not consume more hydrogen as compared to the simple hydrogenation of CO_2 to methane with the added benefit of regenerating the base that can be reused for subsequent CO_2 capture (Figure 2, Sabatier reaction).

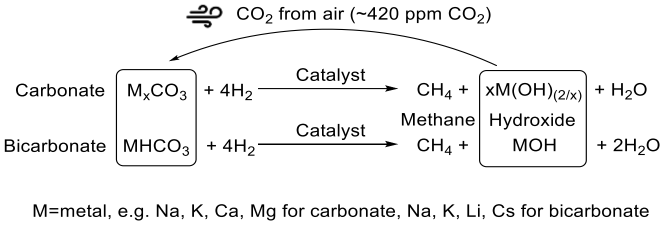

Figure 1. Direct air capture of CO_2 with a metal hydroxide and hydrogenation of the obtained carbonate/bicarbonate to methane with concurrent recycling of the base.

$$CO_2 + 4H_2 \xrightarrow{\text{Catalyst}} CH_4 + 2H_2O$$

Figure 2. Hydrogenation of CO_2 to methane (Sabatier reaction).

Results and Discussions

To test the activity of the catalyst for hydrogenation, potassium bicarbonate was used as a model substrate. Ethylene glycol had previously been reported as an optimal solvent for the integrated capture and conversion of CO_2 to methanol. However, ethylene glycol has also been reported to reform and decompose to $CH_4/CO/CO_2$ under the reaction conditions used in our work.[38–40] Indeed, when a blank hydrogenation reaction was performed with only ethylene glycol and the nickel-based catalyst, we observed the formation of $CH_4/CO/CO_2$. Thus, water was used as a solvent to avoid these issues and any additional carbon source in the system. In a first series of experiments, a commercial steam reforming catalyst, $Ni/CaAl_2O_4$ (HiFUEL R110, Alfa Aesar), was utilized for the hydrogenation of bicarbonate salts.[41] Optimization results are presented in Table 1. Temperature was an important parameter for the reaction, as both 170 and 200°C showed very little conversion to methane at 6 and 7%, respectively. Only upon reaching 225°C, did the reaction proceed to methane with a much higher yield of up to

Table 1. Hydrogenation of $KHCO_3$ and K_2CO_3 to methane over $Ni/CaAl_2O_4$

Entry	Salt	Amount of salt (mmol)	H_2 pressure (bar)	Temperature (°C)	Time (hours)	Methane yield (mmol)	Methane yield (%)	Methane productivity $g_{methane}\cdot h^{-1}\cdot kg_{cat}^{-1}$
1	$KHCO_3$	10	50	170	48	0.6	6	0.67
2	$KHCO_3$	10	50	200	48	0.7	7	0.78
3	$KHCO_3$	10	50	225	48	9.7	97	10.8
4	$KHCO_3$	10	40	225	48	5.4	54	6.0
6	$KHCO_3$	10	60	225	48	8.2	82	9.1
7	$KHCO_3$	10	70	225	48	6.3	63	7.0
8	$KHCO_3$	10	50	225	24	2.2	22	4.9
9	$KHCO_3$	10	50	225	72	9.8	98	7.3
10	K_2CO_3	10	50	225	48	5.3	53	5.9
11	$KHCO_3$[a]	10	50	225	48	4.8	48	5.4
12	K_2CO_3[a]	10	50	225	50	0	0	0

Reaction conditions: water (10 mL), H_2 pressure at room temperature, 300 mg $Ni/CaAl_2O_4$. [a] water (0 mL). Methane yields calculated relative to the carbonate as determined by Gas chromatography. Yield calculations ± 5%.

97% with $KHCO_3$. This resulted in the highest methane productivity of 10.8 $g_{methane}\cdot h^{-1}\cdot kg_{cat}^{-1}$, which was calculated using similar methods reported previously.[13,24] Under these conditions, both decreasing or increasing the H_2 pressure below or above 50 bar had a negative effect on the methane yield. Lowering the reaction time from 48 to 24h greatly diminished the methane yield. K_2CO_3 was also hydrogenated to methane, although with a yield that was about half the one observed with $KHCO_3$ after 48h under similar reaction conditions. Interestingly, even in the absence of water, $KHCO_3$ was converted to methane with a yield of 48% compared to no conversion for K_2CO_3.

The $Ni/CaAl_2O_4$ catalyst was subsequently tested over several cycles to assess its reusability and stability. Captured CO_2 was used in the recycling experiments. 4 mmol of KOH was dissolved in water and pure CO_2 was contacted with the salt solution for three hours. The amount of captured CO_2 in the form of a carbonate/bicarbonate mixture was quantified by ^{13}C NMR. After capture, the obtained potassium carbonate/bicarbonate was subjected to hydrogenation using the conditions in entry 3 of Table 1. In the first cycle, 3.23 mmol of methane was obtained from 4 mmol of CO_2 captured. The liquid aqueous solution after reaction was separated from the solid catalyst and subjected to CO_2 capture, capturing 2.75 mmol of CO_2 and demonstrating the regeneration of the KOH base in the hydrogenation process. The obtained aqueous solution was then subjected to hydrogenation in a second cycle using the same catalyst as in the first cycle. After that, the capture/hydrogenation was repeated 3 more times. The results of the recycling studies are shown in Table 2. After five cycles, the amount of base had decreased from the original 4 mmol to 2 mmol. Consequently, while the conversion of CO_2 to methane remained relatively constant in the ~90-100% range after the initial cycle, the lower carbonate content led to a decrease in the amount of methane that can be formed in each cycle. Thus, at some point in the reaction, the base is deactivated or converted to a product that is less able to capture CO_2.

It has been previously reported that calcium present in $Ni/CaAl_2O_4$ can interact with metal carbonates to form calcium carbonate, which is less soluble and could be a contributing factor to the loss of capture regeneration over the course of the five reactions.[36,37] The relevant reactions are shown in Figure 3. Having a decreased amount of potassium hydroxide with an increased

Table 2. Recycling experiments of the $Ni/CaAl_2O_4$ catalyst and KOH base for methane production over 5 absorption/hydrogenation cycles

Cycle	Amount of CO_2 captured (mmol)	Conversion to methane (mmol)	Conversion to methane (%)	Capture regeneration (%)[a]
1	4.03	3.23	80.1	-
2	2.75	2.70	98.2	68.2
3	2.4	2.25	93.8	87.3
4	2.24	2.07	92.0	93.8
5	2.05	1.98	96.6	91.1

Reaction conditions: water (10 mL), 50 bar H_2 pressure at room temperature, 300 mg $Ni/CaAl_2O_4$, 48 hours, initial amount of KOH: 4 mmol. Methane yields calculated relative to the carbonate as determined by Gas chromatography. Yield calculations ± 5%. [a] compared to CO_2 absorption in previous cycle.

Table 3. Hydrogenation of metal bicarbonate and carbonate to methane over Ni/Al_2O_3 (25 wt% Ni)

Salt	Amount (mmol)	Hydrogen pressure (bar)	Temperature (°C)	Time (hours)	Water (mL)	Methane yield (mmol)	Methane yield (%)	Methane productivity $g_{methane}\cdot h^{-1}\cdot kg_{cat}^{-1}$
$KHCO_3$	10	50	225	48	10	10	100	11.1
K_2CO_3	10	50	225	48	10	10	100	11.1
$K_2{}^{13}CO_3$	10	50	225	48	10	10	100	11.1
K_2CO_3	20	50	225	48	10	11	55	12.3
Na_2CO_3	10	50	225	48	10	10	100	11.1
Li_2CO_3	10	50	225	48	10	9.1	91	10.1
Cs_2CO_3	10	50	225	48	10	10	100	11.1
$CaCO_3$	10	50	225	48	10	0.5	5	0.6
$CaCO_3/K_2CO_3$[a]	10	50	225	48	10	1.5	15	1.7

Reaction conditions: water (10 mL), 50 bar H_2 pressure at room temperature, 300 mg Ni/Al_2O_3 [a] 9.0 mmol $CaCO_3$ and 1.0 mmol K_2CO_3. Methane yields calculated relative to the carbonate as determined by Gas chromatography. Yield calculations ± 5%.

amount of calcium hydroxide in the solution negatively effects the CO_2 capture step after the reaction. It has been reported that potassium hydroxide is able to capture CO_2 much faster than calcium hydroxide.[18] This is consistent with our results where potassium peaks are present in the XRD of the catalyst after the reaction as shown in Figure S1.

$$CaAl_2O_4 + K_2CO_3 \longrightarrow 2KAlO_2 + CaCO_3$$

$$CaAl_4O_7 + K_2CO_3 + 2KOH + 7H_2O \longrightarrow 4KAl(OH)_4 + CaCO_3$$

$$Ca_3Al_2O_6 + 3K_2CO_3 + 2H_2O \longrightarrow 2KAlO_2 + 3CaCO_3 + 4KOH$$

$$Ca_{12}Al_{14}O_{33} + 12K_2CO_3 + 5H_2O \longrightarrow 14KAlO_2 + 12CaCO_3 + 10KOH$$

Figure 3. Depiction of a possible deactivation pathways on the catalyst surface for $Ni/CaAl_2O_4$.[42-43]

To limit the base deactivation due to the composition of the $Ni/CaAl_2O_4$ catalyst, a Ni/Al_2O_3 catalyst was synthesized containing 25% nickel by weight as confirmed by X-Ray Fluorescence (XRF) (please see SI). Table 3 shows the results for the hydrogenation of metal carbonates and bicarbonates utilizing this catalyst. The yield for $KHCO_3$ was similar to the one obtained with $Ni/CaAl_2O_4$ (100% vs 97% on $Ni/CaAl_2O_4$). However, the yield of methane when utilizing potassium carbonate was greatly improved from 53% with $Ni/CaAl_2O_4$ to 100% with 25%Ni/Al_2O_3. This also led to a corresponding increase in methane productivity from 5.9 to 11.1 $g_{methane}\cdot h^{-1}\cdot kg_{cat}^{-1}$ from the $Ni/CaAl_2O_4$ to Ni/Al_2O_3. This difference is most likely due to the K_2CO_3 interacting with the calcium in the former $Ni/CaAl_2O_4$ catalyst and thus deactivating the catalyst. Due to the absence of calcium in Ni/Al_2O_3 this reaction is not possible. The productivity with Ni/Al_2O_3 was further improved to 12.3 $g_{methane}\cdot h^{-1}\cdot kg_{cat}^{-1}$ when 20 mmol of potassium carbonate was used instead of 10 mmol, although at a lower overall methane yield of only 55%. Other carbonate salts, like sodium carbonate and cesium carbonate can also be utilized resulting in quantitative yields as well. Calcium carbonate performed significantly worse than the aforementioned carbonate salts with a 5% yield of methane. In an attempt to increase the yield with calcium carbonate, a small portion of potassium carbonate was added. This was done in the hope that the resulting potassium hydroxide would leach the calcium carbonate and create potassium carbonate. However, this seemingly did not occur as the methane yield remained relatively low at 15%. When a ^{13}C-labelled potassium carbonate salt was used in the reaction, the result was the formation of ^{13}C-methane as determined by NMR and shown in Figure S12 and S13.

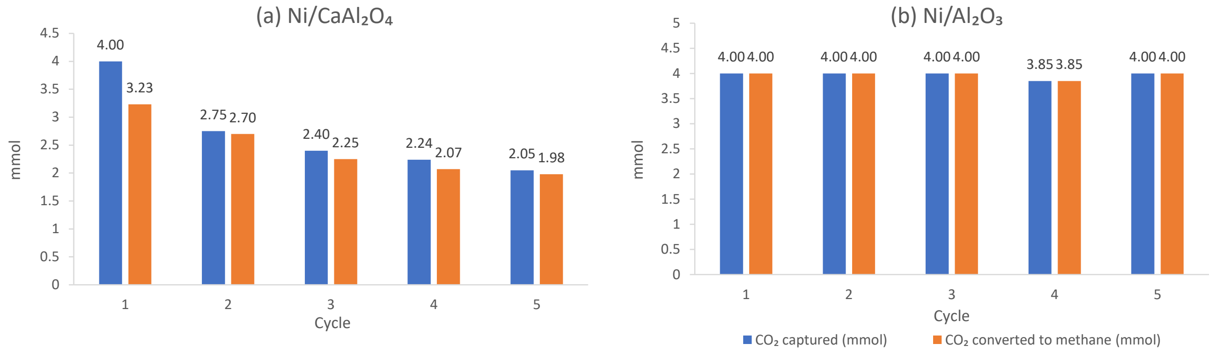

Figure 4. Recycling studies of potassium hydroxide/carbonate for methane production using (a) $Ni/CaAl_2O_4$ and (b) Ni/Al_2O_3.

Table 4. Recycling studies of the Ni/Al_2O_3 catalyst and the KOH base for methane production over 5 absorption/hydrogenation cycles

Cycle	Amount CO_2 captured (mmol)	Conversion to methane (mmol)	Conversion to methane (%)	Capture regeneration (%)[a]
1	4.0	4.0	100	-
2	4.0	4.0	100	100
3	4.0	4.0	100	100
4	3.85	3.85	100	96.3
5	4.0	4.0	100	103.9

Reaction conditions: capture solution (10 mL), 50 bar H_2 pressure at room temperature, 300 mg Ni/Al_2O_3, 4 mmol KOH. Methane yields calculated relative to the carbonate as determined by Gas chromatography. Yield calculations ± 5%. [a] compared to CO_2 absorption in previous cycle.

The stability of the Ni/Al_2O_3 catalyst was then tested over five absorption/hydrogenation cycles using a similar procedure as employed with $Ni/CaAl_2O_4$ but starting with 4 mmol of KOH. In this case, the reactivity remained consistent and 99% of the catalyst activity was retained at the end of five cycles. Again, CO_2 captured by the KOH regenerated during the hydrogenation step was utilized in the form of carbonate in the subsequent cycle. There was no decrease in catalytic activity and only a slight loss in base activity after five cycles as shown in Figure 4b. This was a clear improvement over the system based on $Ni/CaAl_2O_4$. As shown in the XRD (Figure S2), there is less of an accumulation of potassium on the catalyst surface after the reaction. This means that the catalyst surface is less affected over the course of the reaction. The support in the $Ni/CaAl_2O_4$ also deteriorates over the course of the reaction, whereas the alumina in Ni/Al_2O_3 is relatively unaffected by the reaction as shown in Figure S2. The $Ni/CaAl_2O_4$ has potassium peaks in the XRD after the reaction. This also corresponds to the grossite ($CaAl_4O_7$) peaks in the XRD disappearing as compared to the XRD of the catalyst before reaction.

Figures 4a and 4b compare the recyclability of the $Ni/CaAl_2O_4$ and Ni/Al_2O_3 catalysts and how these catalysts performed over five absorption/hydrogenation cycles. The graphs show that the system with $Ni/CaAl_2O_4$ exhibits both catalytic deactivation and base loss. In contrast, the system with Ni/Al_2O_3 only exhibits a marginal loss of base. In the case of Ni/Al_2O_3 the recycling studies showed that both the catalyst and the base can perform well over these capture/hydrogenation cycles.

Table 5 shows that the direct capture of CO_2 from the air and its conversion to methane is also possible in high yields. 5 mmol of KOH was used in 10 mL of water to capture 3.53 mmol of CO_2 from air in the form of a bicarbonate/carbonate mixture. This salt was then converted quantitatively to methane over Ni/Al_2O_3 in 48h. To confirm that the base was regenerated, a titration with CO_2 as the acid was performed with the aqueous solution after reaction. The titration resulted in 3.5 mmol of CO_2 being captured demonstrating that the base had therefore been fully regenerated during the hydrogenation reaction.

Table 5. Direct air capture and conversion to methane utilizing a KOH base and Ni/Al_2O_3 catalyst

Amount of KOH (mmol)	Amount CO_2 captured (mmol)	Conversion to methane (mmol)	Conversion to methane (%)
5	3.53	3.53	100

Reaction conditions: capture solution (10 mL), 48 hours, 50 bar H_2 pressure at room temperature, 300 mg Ni/Al_2O_3. Methane yields calculated relative to the carbonate as determined by Gas chromatography. Yield calculations ± 5%.

While the ICCU route described in this report holds promise, it should be noted that it is still at an early stage (technology readiness level (TRL) of about 3) and will require much more development before becoming practical on a larger scale. A continuous process would for example be preferable to the batch approach used here. Shortening of the reaction time by employing improved or different and more active catalysts should also be pursued to improve throughput, productivity, and reduce the energy required to maintain the reactor temperature. To reduce the energy needed for hydrogen compression reaction at a lower pressure, if possible, would be advantageous as well.

The process is also only as green as the feedstock and energy used to run it. As the process matures, care should thus be taken in using renewable sources of energy for all parts of the process including CO_2 capture, hydrogen generation, the hydrogenation reaction, product separation, etc. As for any other proposed low carbon process, a life cycle analysis should also validate the "greenness" of the approach in terms of greenhouse gas emissions, carbon footprint and overall environmental impacts. To be sustainable in the long run CO_2 captured from the atmosphere would be an ideal source for this route. A lot of the DAC technologies such as the one based on metal hydroxides as the capturing media rely on fans to push air through the capturing media.[44-45] Minimizing pressure drop through this aqueous media during CO_2 adsorption through proper equipment design and engineering is thus also a crucial aspect to reduce the energy needs of the fans and the entire ICCU process. Although less efficient for DAC, pools of hydroxides could potentially also be employed to eliminate the need for fans.

Spays of capturing media have been proposed as well to reduce the pressure drop.

Conclusions

We have shown here that the conversion of carbonate salts of potassium and sodium directly to methane can be achieved in high yield and selectivity over heterogeneous catalysts. Because this process is performed in an aqueous solution, it does not suffer from base deactivation that was for instance observed in the homologous methanol synthesis from carbonates, which is carried out in ethylene glycol. High degree of recycling of both the catalyst and base was demonstrated. Thus, this reaction has the potential deliver large number of CO_2 absorption/hydrogenation cycles. Direct air capture of CO_2 and conversion to methane was also achieved with KOH as the base, demonstrating that the synthesis of methane can be effectively performed with atmospheric CO_2. This opens a pathway to potentially synthesize renewable methane with a lower or even neutral carbon footprint through an anthropogenic carbon cycle analogous to nature's own photosynthetic cycle. This is also a three-phase reaction system (solid, liquid, gas) that can offer some advantages. The capture media can be easily separated from the catalyst and allows for easy access for the media to capture CO_2 again while leaving the catalyst unaffected. The product, methane, is also easy to separate due to its gaseous nature.

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Conflicts of interest

The authors declare no competing financial interest.

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