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# Methane Carboxylation Using Electrochemically Activated Carbon Dioxide

Yucheng Yuan, Yuhan Zhang, Haoyi Li, Muchun Fei, Hongna Zhang, John Santoro, and Dunwei Wang\*

**Abstract:** Direct synthesis of  $\text{CH}_3\text{COOH}$  from  $\text{CH}_4$  and  $\text{CO}_2$  is an appealing approach for the utilization of two potent greenhouse gases that are notoriously difficult to activate. In this *Communication*, we report an integrated route to enable this reaction. Recognizing the thermodynamic stability of  $\text{CO}_2$ , our strategy sought to first activate  $\text{CO}_2$  to produce  $\text{CO}$  (through electrochemical  $\text{CO}_2$  reduction) and  $\text{O}_2$  (through water oxidation), followed by oxidative  $\text{CH}_4$  carbonylation catalyzed by Rh single atom catalysts supported on zeolite. The net result was  $\text{CH}_4$  carboxylation with 100% atom economy.  $\text{CH}_3\text{COOH}$  was obtained at a high selectivity (>80%) and good yield (ca.  $3.2 \text{ mmol g}^{-1}_{\text{cat}}$  in 3 h). Isotope labelling experiments confirmed that  $\text{CH}_3\text{COOH}$  is produced through the coupling of  $\text{CH}_4$  and  $\text{CO}_2$ . This work represents the first successful integration of  $\text{CO}/\text{O}_2$  production with oxidative carbonylation reaction. The result is expected to inspire more carboxylation reactions utilizing preactivated  $\text{CO}_2$  that take advantage of both products from the reduction and oxidation processes, thus achieving high atom efficiency in the synthesis.

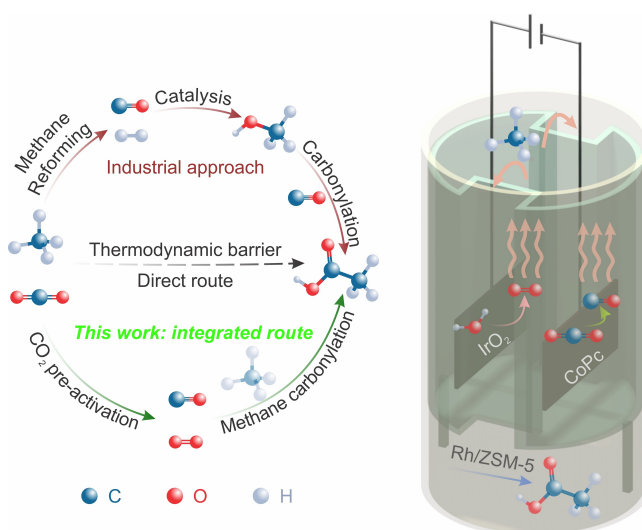
As an abundant natural resource, methane ( $\text{CH}_4$ ) is an appealing feedstock for producing high-value hydrocarbons such as liquid fuels and other chemicals. However, due to the notorious difficulties in selectively activating the C–H bonds in  $\text{CH}_4$ , its large-scale industrial utilization has been limited to first reforming it to produce syngas ( $\text{CO}$  and  $\text{H}_2$ ), followed by subsequent processes often broadly referred to as the Fischer–Tropsch transformation to form liquid hydrocarbons.<sup>[1]</sup> Consider the production of  $\text{CH}_3\text{COOH}$  as one example, which is widely used in food industry and medicinal applications as well as a precursor for the synthesis of various chemicals, including vinyl acetate

monomer, esters, acetic anhydride, and numerous polymeric materials.<sup>[2]</sup> Two industrial methods prevail in the efforts of synthesizing this important intermediate in bulk quantities, namely the Monsanto process and the Cativa process (Figure 1).<sup>[3]</sup> While different in the catalysts they employ, both processes share many similarities. For instance, the key to both processes is the carbonylation step, which uses  $\text{CO}$  as a precursor. Moreover, they both use  $\text{CH}_3\text{OH}$  as the other precursor, the synthesis of which ( $\text{CO}$  hydrogenation) is in turn enabled by steam methane reforming (SMR). Recognizing the undesired issues of SMR such as high energy intensity and low efficiency, researchers have sought to achieve direct methane carbonylation with the help of molecular oxygen.<sup>[4]</sup> While exciting progress has been made toward this direction, the process still relies on pre-synthesized toxic  $\text{CO}$  as a carbonylation precursor, whose industrial synthesis requires SMR.

A careful examination of the molecular structure of  $\text{CH}_3\text{COOH}$  reveals that it would be possible to prepare it by directly coupling  $\text{CH}_4$  and  $\text{CO}_2$  with 100% atom efficiency (Figure 1). Given the abundance of both molecules in nature and their potent greenhouse effects, such a route would be of great interest. Indeed, several studies have already been carried out to investigate this possibility computationally

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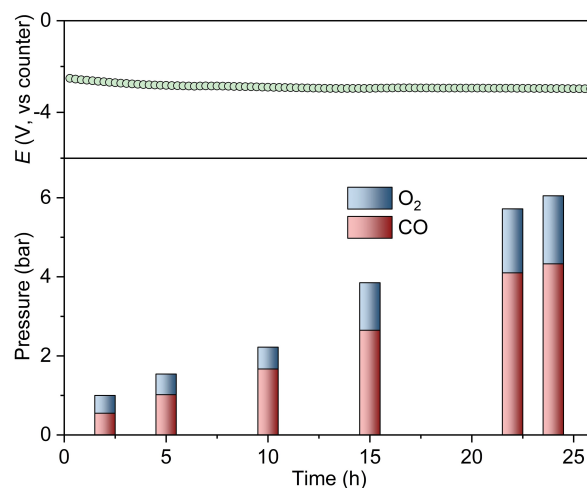
**Figure 1.** Overview of our design. Left: Different routes to synthesize  $\text{CH}_3\text{COOH}$ . Right: Schematic illustration of an integrated route via electrocatalytic conversion of  $\text{CO}_2$  to  $\text{CO}$  and subsequent thermocatalytic methane carbonylation to synthesize  $\text{CH}_3\text{COOH}$ .

using density functional theory (DFT).<sup>[5]</sup> It has been found that the direct route of CH<sub>3</sub>COOH synthesis through CH<sub>4</sub> and CO<sub>2</sub> coupling is thermodynamically unfavorable under practical conditions.<sup>[6]</sup> Experimental demonstrations of direct CH<sub>4</sub> carboxylation using CO<sub>2</sub> as a source have been scarce, and the few existing catalytic systems suffer poor controls over the product selectivity.<sup>[7]</sup> At the heart of the challenge is the need to simultaneously activate two highly stable molecules in a controllable fashion. On the other hand, recent literatures have seen significant efforts and successes to activate CH<sub>4</sub> or CO<sub>2</sub>, albeit under very different conditions.<sup>[4a,b,8]</sup> It is, therefore, conceivable to take advantage of these recent developments in the two separate subfields and enable direct synthesis of CH<sub>3</sub>COOH using CH<sub>4</sub> and CO<sub>2</sub> as the only precursors. It is within this context that we have developed the present work. As shown in Figure 1, we capitalized on recent successes in two different directions, namely selective CO<sub>2</sub> reduction and oxidative CH<sub>4</sub> carbonylation, and achieved atomically efficient synthesis of CH<sub>3</sub>COOH with high selectivity.

Among the two precursors, CH<sub>4</sub> and CO<sub>2</sub>, the latter is difficult to activate because of its thermodynamic stability, whereas the activation of the former is primarily due to the high kinetic barriers. We were, therefore, inspired to first seek to address the thermodynamic challenge. Fortunately, this topic (the activation of CO<sub>2</sub>) has been intensely studied and extensively reported in the literature.<sup>[8c,9]</sup> For instance, electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) is one of the most published research topics lately. Among the various products, CO can be obtained from CO<sub>2</sub>RR with a high selectivity (>90%) and yield.<sup>[10]</sup> Nevertheless, this important feedstock has been rarely utilized after its generation from CO<sub>2</sub>RR.<sup>[9c,11]</sup> Skrydstrup et al. demonstrated the coupling of CO production from CO<sub>2</sub>RR and Pd-catalysed carbonylation reactions in a seminal work.<sup>[11]</sup> However, organic solvents (e.g., N,N-dimethylformamide) and sacrificial reagents (e.g., triethylamine) were employed to facilitate the counter reaction for CO<sub>2</sub>RR. As a result, the products on the anodes were not utilized and valuable reagents were sacrificed, making it an unsustainable way of valorizing CO<sub>2</sub>. Broadly speaking, oxidative carbonylation has been recognized as a promising strategy for CO<sub>2</sub> utilization without sacrificing the counter reaction but has not been achieved yet.<sup>[9c]</sup> Thus, we demonstrated the first example of integrating CO/O<sub>2</sub> production with oxidative carbonylation herein. When coupled with H<sub>2</sub>O oxidation at the counter electrode, the reaction can produce CO and O<sub>2</sub> in stoichiometry. The mixture (CO:O<sub>2</sub>=2:1) can then be utilized to activate CH<sub>4</sub> for the production of CH<sub>3</sub>COOH with 100% atom efficiency. We specifically employed this setup and carefully chose catalysts for the three reactions involved with the goal to demonstrate the feasibility of carboxylation reaction of CH<sub>4</sub> by CO<sub>2</sub> in an integrated fashion. For this body of work, commercially available cobalt(II) phthalocyanine (CoPc) complexes<sup>[10b,12]</sup> and IrO<sub>2</sub><sup>[13]</sup> were chosen as the catalysts for CO<sub>2</sub>RR and oxygen evolution reaction (OER), respectively, as shown in Figure 1, right (also see the reactor setup in Figure S1 in Supporting Information). The former was chosen for its easy

access and high selectivity toward CO as well as its tolerance of O<sub>2</sub> with pressurized CO<sub>2</sub> and high stability, and the latter was selected for its high activity and stability toward H<sub>2</sub>O oxidation. With a constant current density of 11.1 mA cm<sup>-2</sup>, the potential difference between the cathode and anode remained relatively stable at ca. 2.9 V for at least 26 h, indicating the electrochemical system was stable under our experimental conditions (Figure 2, top, see linear sweep voltammetry (LSV) curves of CoPc in Figure S2). The CO and O<sub>2</sub> products were monitored by a gas chromatography equipped with a flame ionization detector (GC-FID) for CO and thermal conductivity detector (GC-TCD) for O<sub>2</sub> quantifications, respectively. The partial pressures of these products were then calculated, and the data are shown in Figure 2 (bottom). It was observed that their ratio (CO:O<sub>2</sub>) was stable throughout the reaction. The partial pressures of CO and O<sub>2</sub> ( $P_{\text{CO}}$  and  $P_{\text{O}_2}$ ) reached ca. 4 bar and 2 bar, respectively, at 22 h. Presumably due to the competitive O<sub>2</sub> reduction reaction, the faradaic efficiency for CO<sub>2</sub>RR was relatively low (ca. 30%), which was comparable with that under a similar volume fraction of O<sub>2</sub> in previous reports.<sup>[14]</sup> As will be further discussed later in this *Communication*, the yield of H<sub>2</sub> was ca. 0.6 bar under this condition. Because previous literature has shown that such pressures are suitable for CH<sub>4</sub> carbonylation reactions,<sup>[4a]</sup> we employed 22 h as the reaction time for CO<sub>2</sub>RR for the remainder of this study.

To perform oxidative CH<sub>4</sub> carbonylation in the second step, we prepared atomically dispersed rhodium (Rh) catalyst on a zeolite support (0.5 wt % Rh-ZSM-5) following a previous report by Flytzani-Stephanopoulos and treated the as-synthesized catalyst with H<sub>2</sub> at 550 °C for 3 h (Figure S3).<sup>[4a]</sup> Diffuse reflectance infrared Fourier transform spectroscopy study of CO (CO-DRIFTS) on the H<sub>2</sub> treated catalyst featured two characteristic peaks at 2114 cm<sup>-1</sup> and 2048 cm<sup>-1</sup>, which are attributed to symmetrical and asym-

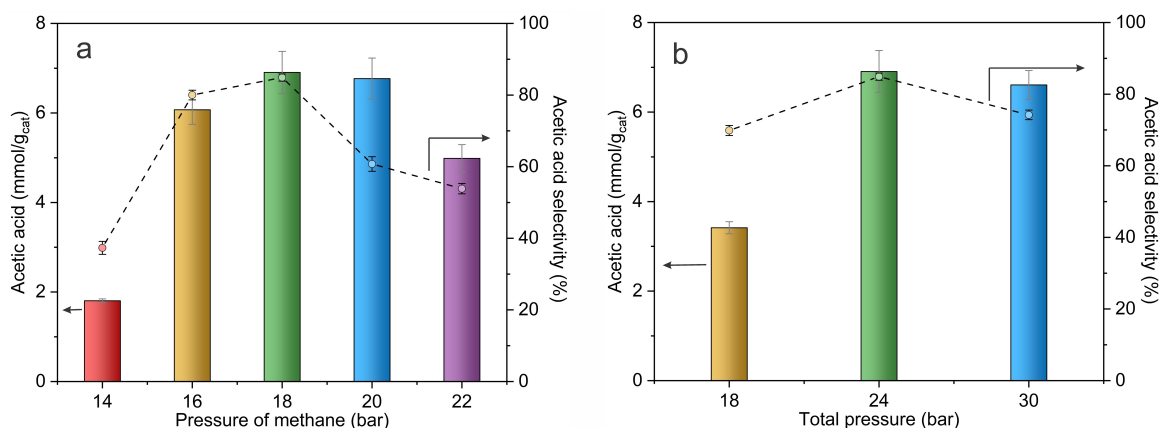


**Figure 2.** Electrochemical reduction of CO<sub>2</sub> and the production of CO and O<sub>2</sub>. Top: Voltage evolution during the electrocatalytic CO<sub>2</sub>RR with a constant current of 11.1 mA cm<sup>-2</sup>. The data are *iR* corrected. Bottom: CO and O<sub>2</sub> pressures at different electrocatalytic CO<sub>2</sub>RR times with an initial CO<sub>2</sub> pressure of 8 bar and CH<sub>4</sub> pressure of 18 bar.

metrical stretching of CO adsorbed onto isolated mononuclear  $\text{Rh}^{\text{I}}(\text{CO})_2$  species (Figure S4).<sup>[4a]</sup> Another important note we have taken from the previous report was the reaction conditions, where the optimum ratio between the reactants was  $\text{CH}_4:\text{CO}:\text{O}_2=20:5:2$ . Away from these ratios, further increasing  $\text{O}_2$  would lead to overoxidation and poorer selectivity towards  $\text{CH}_3\text{COOH}$ , and reducing it would result in a lower yield. A constraint we faced in our experiments is the ratio between CO and  $\text{O}_2$  (2:1), which is fixed as determined by the stoichiometry of  $\text{CO}_2$  reduction coupled with  $\text{H}_2\text{O}$  oxidation. We thus sought to observe how varying the partial pressure of  $\text{CH}_4$  with a fixed  $\text{CO}:\text{O}_2$  ratio might influence the reactions. As shown in Figure 3a and Figure S5a, when  $P_{\text{CO}}$  and  $P_{\text{O}_2}$  were fixed at 4 bar and 2 bar, respectively, there was a clear trend of increased  $\text{CH}_3\text{COOH}$  production with the increase of  $P_{\text{CH}_4}$  up to 18 bar, beyond which higher  $P_{\text{CH}_4}$  led to reduced  $\text{CH}_3\text{COOH}$  yield. We note that there should be additional room for further optimization with regard to the yield as normalized to the catalyst loading. For instance, Flytzani-Stephanopoulos et al. have shown that the catalyst performance could be readily improved by repeating the impregnation process multiple times.<sup>[4a]</sup> Another figure of merit we closely monitored was the selectivity toward  $\text{CH}_3\text{COOH}$  among all liquid products. It is observed in Figure 3a that at 85%, it is comparable to the benchmark reported previously.<sup>[4a,b]</sup> This selectivity was obtained at  $P_{\text{CH}_4}=18$  bar; further increasing  $\text{CH}_4$  resulted in reduced selectivity toward  $\text{CH}_3\text{COOH}$ . The last set of parameters we have varied was the total pressure. It is seen in Figure 3b and Figure S5b that a total pressure of 24 bar (18 bar  $\text{CH}_4$ , 4 bar  $\text{CO}$ , and 2 bar  $\text{O}_2$ ) was desired, whereas higher or lower total pressure would lead to reduced  $\text{CH}_3\text{COOH}$  yield. As has been reported before, the influence of the ratios and pressures of reactants on the reaction can be complex,<sup>[4a,b]</sup> and fully understanding the mechanism and optimizing the reaction would be a significant undertaking that is beyond the scope of this present work. Nevertheless, it is important to note that our results

indeed lay the groundwork for future research to further understand and optimize the process.

Guided by this set of parameters achieved through model reactions, we next carried out a 2-step process as shown in Figure 1, right by combining the  $\text{CO}_2$  reduction and  $\text{CH}_4$  oxidative carbonylation as described above. Briefly, the process started with loading the reactor with 18 bar  $\text{CH}_4$  and 8 bar  $\text{CO}_2$ , where 6 mg Rh-ZSM-5 (0.5 wt % Rh loading) was dispersed in 4 mL DI  $\text{H}_2\text{O}$ . In the inner reaction chamber, 7 mL electrolyte containing 0.1 M  $\text{KHCO}_3$  was used; the cathode was CoPc, and the anode was  $\text{IrO}_2$ , as detailed in the Supporting Information. A constant current density of  $11.1 \text{ mA cm}^{-2}$  was first applied for 22 h at room temperature, during which 4 bar  $\text{CO}$  and 2 bar  $\text{O}_2$  were produced. Afterwards, the electrolysis was stopped, and the reactor was brought to  $150^\circ\text{C}$  and maintained at this temperature for 3 h. At the end, *ca.*  $3.2 \text{ mmol g}^{-1}_{\text{cat}}$   $\text{CH}_3\text{COOH}$  with a selectivity of 83% was detected (Figure S6). The yield was approximately 46% of what was obtained if the reaction was carried out in a single step with 18 bar  $\text{CH}_4$ , 4 bar  $\text{CO}$ , and 2 bar  $\text{O}_2$ . Possible reasons for the reduced yield include the presence of  $\text{CO}_2$  in the reaction medium, the existence of  $\text{H}_2$  byproducts as a result of the hydrogen evolution reaction (*ca.* 0.6 bar, Figure S7). To assess the influence of the oxidative carbonylation by the presence of  $\text{CO}_2$  and  $\text{H}_2$ , the following control experiments were performed. As shown in Figure S8, with the addition of 4 bar  $\text{CO}_2$  to the standard gases used for thermocatalysis, the yield of  $\text{CH}_3\text{COOH}$  was slightly lower (by 6%). The addition of 0.5 bar  $\text{H}_2$ , on the other hand, led to a significant decrease of the yield (by 32%). With both 4 bar  $\text{CO}_2$  and 0.5 bar  $\text{H}_2$  added, a 52% yield reduction was observed. It is important to note that no significant change to the product selectivity was measured in all these experiments. Taken together, we concluded that the key culprit for the decreased yield of the integrated experiment was due to the presence of  $\text{H}_2$ , although there appeared to be a synergistic effect between  $\text{CO}_2$  and  $\text{H}_2$ . Future research should focus on



**Figure 3.** Influence of pressures of  $\text{CH}_4$ ,  $\text{CO}$ , and  $\text{O}_2$  on the yield of  $\text{CH}_3\text{COOH}$ . Reaction conditions: 16 mg of catalyst, 3–5 bar of  $\text{CO}$ , 1.5–2.5 bar of  $\text{O}_2$ , 11 mL of water, 3 h of reaction at  $150^\circ\text{C}$ . a) Dependence on the pressure of  $\text{CH}_4$  when  $P_{\text{CO}}$  is fixed at 4 bar and  $P_{\text{O}_2}$  is fixed at 2 bar. b) Dependence on the total pressure with  $P_{\text{CH}_4}:P_{\text{CO}}:P_{\text{O}_2}$  is fixed at 9:2:1. The  $\text{CH}_3\text{COOH}$  selectivity represents that of all liquid products.

enhancing the selectivity of O<sub>2</sub>-tolerant CO<sub>2</sub> reaction catalysts to further suppress H<sub>2</sub> production.

Our next task was to prove that the product was indeed the coupling of CH<sub>4</sub> and CO<sub>2</sub>. For this purpose, we employed <sup>13</sup>C as an isotope label for product analysis using <sup>13</sup>C nuclear magnetic resonance (<sup>13</sup>C NMR) (Figure 4). Both isotope-labelled and control experiments were carried out under the same conditions as detailed in the previous paragraph. Since the chemical shift of (<sup>13</sup>CH<sub>3</sub>)<sub>2</sub>SO (39.4 ppm) in <sup>13</sup>C NMR spectrum can be readily distinguished from those of the liquid products, (CH<sub>3</sub>)<sub>2</sub>SO (30 μL) was added to the collected reaction solution as an internal standard to compare the amounts of isotope-labelled products. Low intensity <sup>13</sup>CH<sub>3</sub>COOH (δ=21.3 ppm) and CH<sub>3</sub><sup>13</sup>COOH (δ=180.0 ppm) were detected in the control reactions with unlabeled CO<sub>2</sub> due to the natural abundance (1.1 %) of <sup>13</sup>C (Figure 4, top). In stark contrast, the peak corresponding to CH<sub>3</sub><sup>13</sup>COOH was much more pronounced in the products of the <sup>13</sup>CO<sub>2</sub>-labeled reaction, strongly supporting that the carbonyl group in CH<sub>3</sub>COOH is derived from CO<sub>2</sub> (Figure 4, bottom). By comparison, the peak of <sup>13</sup>CH<sub>3</sub>COOH was negligible in the <sup>13</sup>CO<sub>2</sub>-labeled reaction products, suggesting that the methyl group is from unlabeled CH<sub>4</sub> (Figure 4, bottom). Furthermore, due to the high selectivity towards the formation of CH<sub>3</sub>COOH under the integrated reaction conditions, only small amount of HCOOH and CH<sub>3</sub>OH were detected (Figure 4 and Figure S9). Based on these isotope-labelled results, we confirmed that the formation of CH<sub>3</sub>COOH was from the product of CH<sub>4</sub> carboxylation with activated CO<sub>2</sub>.

In conclusion, we have demonstrated the direct synthesis of CH<sub>3</sub>COOH with high selectivity from two greenhouse gases CH<sub>4</sub> and CO<sub>2</sub> via integrated electrocatalytic CO<sub>2</sub>RR and OER by an oxidative CH<sub>4</sub> carboxylation mechanism. While most CO<sub>2</sub>RR studies have overlooked the counter reactions, we have presented the direct utilization of the overall products to synthesize a meaningful compound

under industrially relevant conditions. The reaction is atomically efficient, with H<sub>2</sub>O being the only other chemical that is directly involved in the reaction which is recovered at the end of the catalytic cycle. Isotope studies confirm the coupling reaction between CH<sub>4</sub> and activated CO<sub>2</sub>. This study shows that the integrated route is an alternative to the existing processes that require the reforming of CH<sub>4</sub> and the utilization of highly toxic gases such as CO. The result proves the concept of electrocatalytically activating a thermodynamically stable molecule (CO<sub>2</sub>) and directly using the products without the need of separation or transportation of the intermediates. This proof-of-concept work makes it possible to take advantage of parallel efforts in CO<sub>2</sub> reduction by, for examples, O<sub>2</sub>-tolerant CO<sub>2</sub>RR catalytic systems with high selectivity, and electrolyte-free electrolysis methods.<sup>[15]</sup> Given the broad utilities of oxidative carbonylation in synthetic chemistry, our reported approach is expected to find ready applications.

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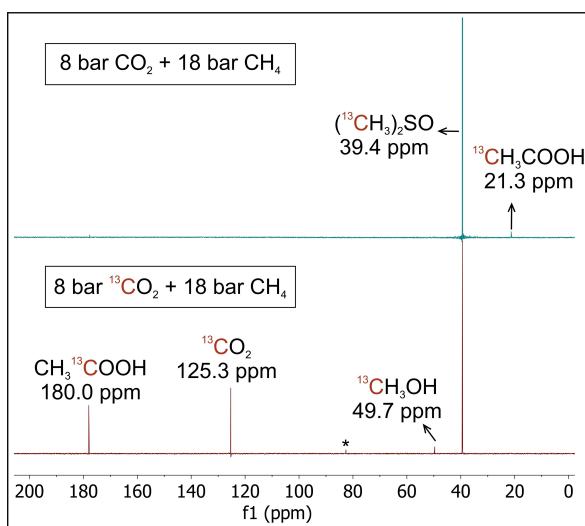
### Conflict of Interest

The authors declare no conflict of interest.

### Data Availability Statement

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

**Keywords:** Acetic Acid Synthesis · CO<sub>2</sub> Utilization · Catalysis · Electrochemistry · Methane Carboxylation



**Figure 4.** <sup>13</sup>C NMR spectra of the liquid products by reactions using CO<sub>2</sub> (top) and <sup>13</sup>CO<sub>2</sub> (bottom). \* indicates CH<sub>2</sub>(OH)<sub>2</sub>.

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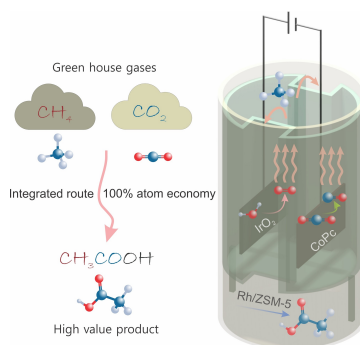
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## Communications

## Carbon Dioxide Utilization

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Methane Carboxylation Using Electrochemically Activated Carbon Dioxide



Direct synthesis of  $\text{CH}_3\text{COOH}$  from  $\text{CH}_4$  and  $\text{CO}_2$  is made possible. The process first activates  $\text{CO}_2$  by electrochemistry, producing  $\text{CO}$  and  $\text{O}_2$ . It is followed by oxidative  $\text{CH}_4$  carbonylation catalyzed by Rh single atom catalysts. The net result is  $\text{CH}_4$  carboxylation with 100% atom economy.