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Methane Carboxylation Using Electrochemically Activated Carbon Dioxide

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Abstract

Direct synthesis of CH_3COOH from CH_4 and 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 CO_2, our strategy sought to first activate CO_2 to produce CO (through electrochemical CO_2 reduction) and O_2 (through water oxidation), followed by oxidative CH_4 carbonylation catalyzed by Rh single atom catalysts supported on zeolite. The net result was CH_4 carboxylation with 100% atom economy. CH_3COOH was obtained at a high selectivity (>80%) and good yield (*ca*. 3.2 mmol/g_{cat} in 3 h). Isotope labelling experiments confirmed that CH_3COOH is produced through the coupling of CH_4 and CO_2. This work represents the first successful integration of CO/O_2 production with oxidative carbonylation reaction. The result is expected to inspire more carboxylation reactions utilizing preactivated CO_2 that take advantage of both products from the reduction and oxidation processes, thus achieving high atom efficiency in the synthesis.

Graphical Abstract

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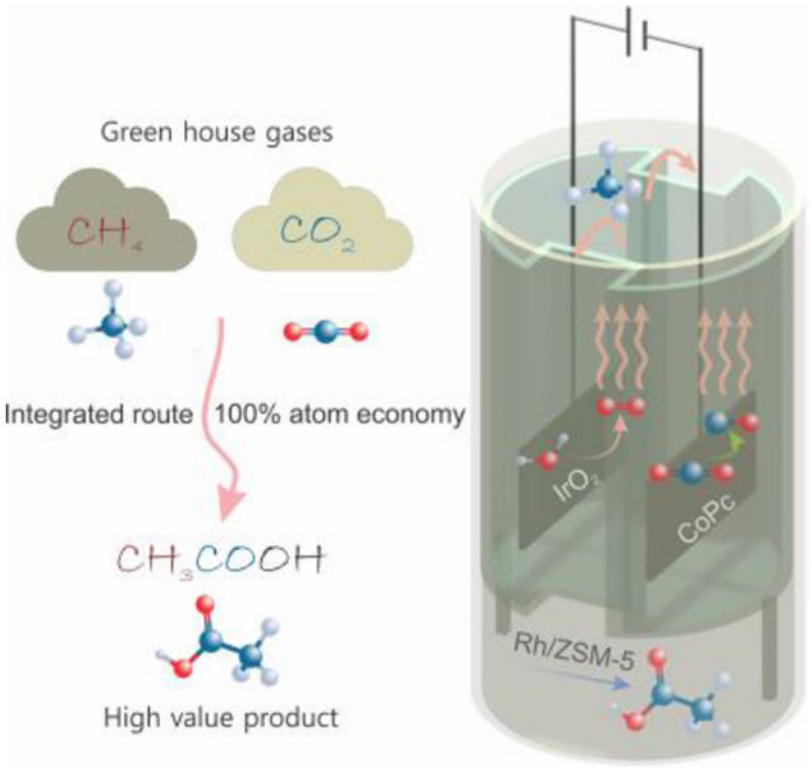

Direct synthesis of CH_3COOH from CH_4 and CO_2 is made possible. The process first activates CO_2 by electrochemistry, producing CO and O_2. It is followed by oxidative CH_4 carbonylation catalyzed by Rh single atom catalysts. The net result is CH_4 carboxylation with 100% atom economy.

Keywords

electrochemistry; catalysis; acetic acid synthesis; methane carboxylation; CO_2 utilization

As an abundant natural resource, methane (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 CH_4, its large-scale industrial utilization has been limited to first reforming it to produce syngas (CO and H_2), followed by subsequent processes often broadly referred to as the Fischer-Tropsch transformation to form liquid hydrocarbons.[1] Consider the production of CH_3COOH 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.[2] 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).[3] 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 CO as a precursor. Moreover, they both use CH_3OH as the other precursor, the synthesis of which (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.[4] While exciting progress has been made toward this direction, the process still relies on pre-synthesized toxic CO as a carbonylation precursor, whose industrial synthesis requires SMR.

A careful examination of the molecular structure of CH_3COOH reveals that it would be possible to prepare it by directly coupling CH_4 and 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 using density functional theory (DFT).[5] It has been found that the direct route of CH_3COOH synthesis through CH_4 and CO_2 coupling is thermodynamically unfavorable under practical conditions.[6] Experimental demonstrations of direct CH_4 carboxylation using CO_2 as a source have been scarce, and the few existing catalytic systems suffer poor controls over the product selectivity.[7] 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_4 *or* CO_2, albeit under very different conditions.[4a, 4b, 8] It is, therefore, conceivable to take advantage of these recent developments in the two separate subfields and enable direct synthesis of CH_3COOH using CH_4 and CO_2 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_2 reduction and oxidative CH_4 carbonylation, and achieved atomically efficient synthesis of CH_3COOH with high selectivity.

Among the two precursors, CH_4 and CO_2, 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_2) has been intensely studied and extensively reported in the literature.[8c, 9] For instance, electrochemical CO_2 reduction reaction (CO_2RR) is one of the most published research topics lately. Among the various products, CO can be obtained from CO_2RR with a high selectivity (>90%) and yield.[10] Nevertheless, this important feedstock has been rarely utilized after its generation from CO_2RR.[9c, 11] Skrydstrup *et al.* demonstreated the coupling of CO production from CO_2RR and Pd-catalysed carbonylation reactions in a seminal work.[11] However, organic solvents (*e.g.*, N,N-dimethylformamide) and sacraficial reagents (*e.g.*, triethylamine) were employed to faciliatate the counter reaction for CO_2RR. As a result, the products on the anodes were not utilized and valuable reagents were sacrificed, making it an unsustainable way of valorizing CO_2. Broadly speaking, oxidative carbonylation has been recognized as a promising strategy for CO_2 utilization without sacraficing the counter reaction but has not been achieved yet.[9c] Thus, we demonstrated the first example of integrating CO/O_2 production with oxidative carbonylation herein. When coupled with H_2O oxidation at the counter electrode, the reaction can produce CO and O_2 in stoichiometry. The mixture ($CO:O_2 = 2:1$) can then be utilized to activate CH_4 for the production of CH_3COOH 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_4 by CO_2 in an integrated fashion. For this body of work, commercially available cobalt(II) phthalocyanine (CoPc) complexes[10b, 12] and IrO_2[13] were chosen as the catalysts for CO_2RR and oxygen evolution reaction (OER), respectively, as shown in Figure 1, **right** (also see the reactor setup in Figure S1 in Supporting Information, SI). The former was chosen for its easy access and high selectivity toward CO as well as its tolerence of O_2 with pressurized CO_2 and high stability, and the latter was selected for its high activitiy and stability toward H_2O oxidation. With a constant current density of 11.1 mA/cm^2, 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_2 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_2 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 ($CO:O_2$) was stable throughout the reaction. The partial pressures of CO and O_2 (P_{CO} and P_{O2}) reached *ca.* 4 bar and 2 bar, respectively, at 22 h. Pressumably due to the competitive O_2 reduction reaction, the faradaic efficiency for CO_2RR was relatively low (*ca.* 30%), which was comparable with that under a similar volume fraction of O_2 in previous reports.[14] As will be further discussed later in this *Communication*, the yield of H_2 was *ca.* 0.6 bar under this condition. Because previous literature has shown that such pressures are suitable for CH_4 carbonylation reactions,[4a] we employed 22 h as the reaction time for CO_2RR for the remainder of this study.

To perform oxidative CH_4 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_2 at 550 °C for 3 h (Figure S3).[4a] Diffuse reflectance infrared Fourier transform spectroscopy study of CO (CO-DRIFTS) on the H_2 treated catalyst featured two characteristic peaks at 2114 cm^{-1} and 2048 cm^{-1}, which are attributed to symmetrical and asymmetrical stretching of CO adsorbed onto isolated mononuclear $Rh^I(CO)_2$ species (Figure S4).[4a] Another important note we have taken from the previous report was the reaction conditions, where the optimum ratio between the reactants was $CH_4:CO:O_2$ = 20:5:2. Away from these ratios, further increasing O_2 would lead to overoxidation and poorer selectivity towards CH_3COOH, and reducing it would result in a lower yield. A constraint we faced in our experiments is the ratio between CO and O_2 (2:1), which is fixed as determined by the stoichiometry of CO_2 reduction coupled with H_2O oxidation. We thus sought to observe how varying the partial pressure of CH_4 with a fixed $CO:O_2$ ratio might influence the reactions. As shown in Figure 3a and Figure S5a, when P_{CO} and P_{O2} were fixed at 4 bar and 2 bar, respectively, there was a clear trend of increased CH_3COOH production with the increase of P_{CH4} up to 18 bar, beyond which higher P_{CH4} led to reduced CH_3COOH 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.[4a] Another figure of merit we closely monitored was the selectivity toward CH_3COOH among all liquid products. It is observed in Figure 3a that at 85%, it

is comparable to the benchmark reported previously.[4a, 4b] This selectivity was obtained at P_{CH4} = 18 bar; further increasing CH_4 resulted in reduced selectivity toward CH_3COOH. 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 CH_4, 4 bar CO, and 2 bar O_2) was desired, whereas higher or lower total pressure would lead to reduced CH_3COOH yield. As has been reported before, the influence of the ratios and pressures of reactants on the reaction can be complex,[4a, 4b] 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 CO_2 reduction and CH_4 oxidative carbonylation as described above. Briefly, the process started with loading the reactor with 18 bar CH_4 and 8 bar CO_2, where 6 mg Rh-ZSM-5 (0.5 wt% Rh loading) was dispersed in 4 mL DI H_2O. In the inner reaction chamber, 7 mL electrolyte containing 0.1 M $KHCO_3$ was used; the cathode was CoPc, and the anode was IrO_2, as detailed in the SI. A constant current density of 11.1 mA/cm^2 was first applied for 22 h at room temperature, during which 4 bar CO and 2 bar O_2 were produced. Afterwards, the electrolysis was stopped, and the reactor was brought to 150 °C and maintained at this temperature for 3 h. At the end, *ca.* 3.2 mmol/g_{cat} CH_3COOH 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 CH_4, 4 bar CO, and 2 bar O_2. Possible reasons for the reduced yield include the presence of CO_2 in the reaction medium, the existence of 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 CO_2 and H_2, the following control experiments were performed. As shown in Figure S8, with the addition of 4 bar CO_2 to the standard gases used for thermocatalysis, the yield of CH_3COOH was slightly lower (by 6%). The addition of 0.5 bar H_2, on the other hand, led to a significant decrease of the yield (by 32%). With both 4 bar CO_2 and 0.5 bar 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 H_2, although there appeared to be a synergistic effect between CO_2 and H_2. Future research should focus on enhancing the selectivity of O_2-tolerent CO_2 reaction catalysts to further suppress H_2 production.

Our next task was to prove that the product was indeed the coupling of CH_4 and CO_2. For this purpose, we employed $^{13}CO_2$ as an isotope label for product analysis using ^{13}C nuclear magnetic resonance (^{13}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 $(^{13}CH_3)_2SO$ (39.4 ppm) in ^{13}C NMR spectrum can be readily distinguished from those of the liquid products, $(CH_3)_2SO$ (30 μL) was added to the collected reaction solution as an internal standard to compare the amounts of isotope-labelled products. Low intensity $^{13}CH_3COOH$ (δ = 21.3 ppm) and $CH_3{}^{13}COOH$

(δ = 180.0 ppm) were detected in the control reactions with unlabeled CO_2 due to the natural abundance (1.1%) of ^{13}C (Figure 4, top). In stark contrast, the peak corresponding to $CH_3{}^{13}COOH$ was much more pronounced in the products of the $^{13}CO_2$-labeled reaction, strongly supporting that the carbonyl group in CH_3COOH is derived from CO_2 (Figure 4, bottom). By comparison, the peak of $^{13}CH_3COOH$ was negligible in the $^{13}CO_2$-labeled reaction products, suggesting that the methyl group is from unlabeled CH_4 (Figure 4, bottom). Furthermore, due to the high selectivity towards the formation of CH_3COOH under the integrated reaction conditions, only small amount of HCOOH and CH_3OH were detected (Figure 4 and Figure S9). Based on these isotope-labelled results, we confirmed that the formation of CH_3COOH was from the product of CH_4 carboxylation with activated CO_2.

In conclusion, we have demonstrated the direct synthesis of CH_3COOH with high selectivity from two greenhouse gases CH_4 and CO_2 via integrated electrocatalytic CO_2RR and OER by an oxidative CH_4 carbonylation mechanism. While most CO_2RR 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_2O 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_4 and activated CO_2. This study shows that the integrated route is an alternative to the existing processes that require the reforming of CH_4 and the utilization of highly toxic gases such as CO. The result proves the concept of electrocatalytically activating a thermodynamically stable molecule (CO_2) 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_2 reduction by, for examples, O_2-tolerant CO_2RR catalytic systems with high selectivity, and electrolyte-free electrolysis methods.[15] Given the broad utilities of oxidative carbonylation in synthetic chemistry, our reported approach is expected to readily find ready applications.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

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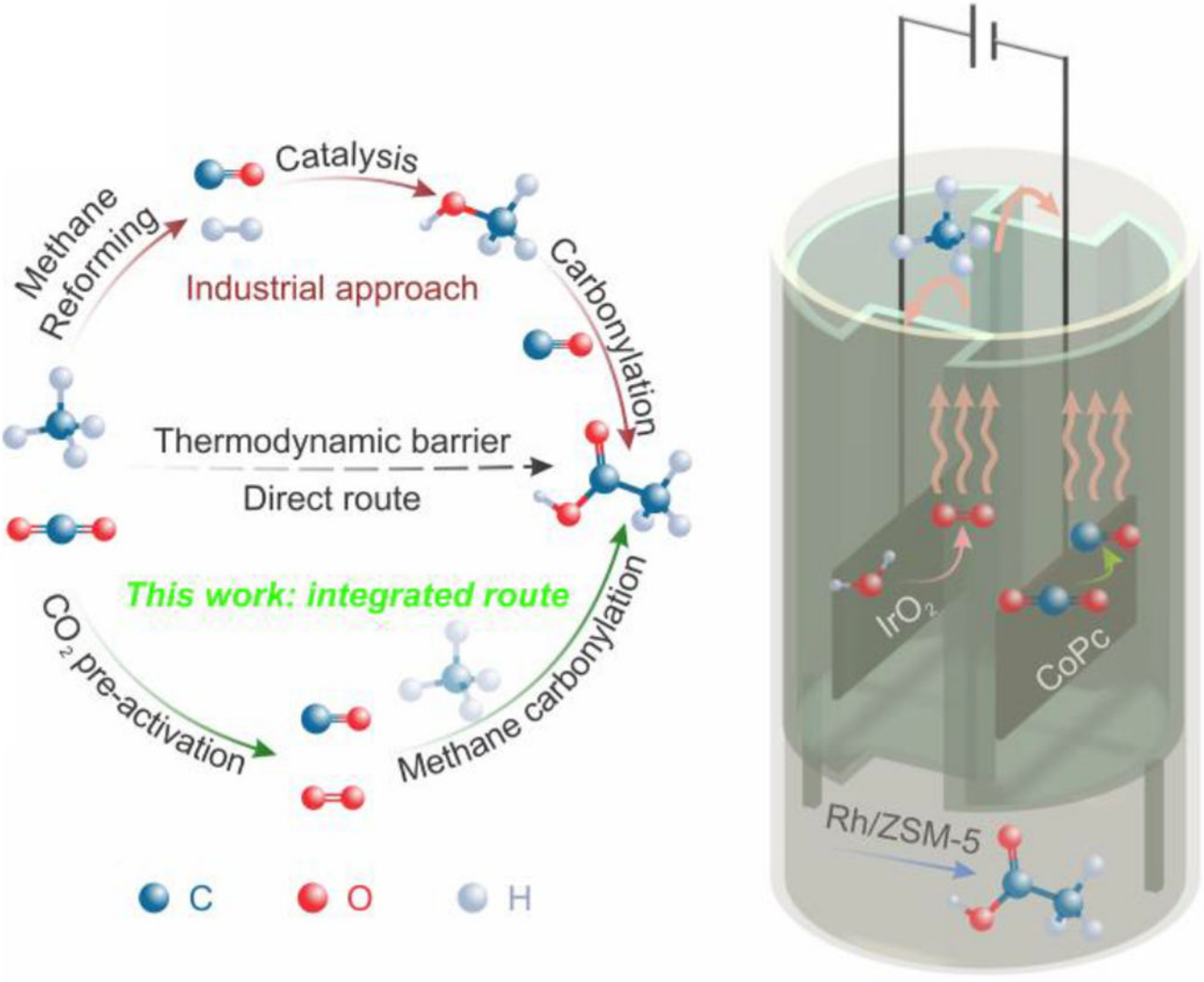

Figure 1.

Overview of our design. **Left**: Different routes to synthesize CH_3COOH. **Right**: Schematic illustration of an integrated route via electrocatalytic conversion of CO_2 to CO and subsequent thermocatalytic methane carbonylation to synthesize CH_3COOH.

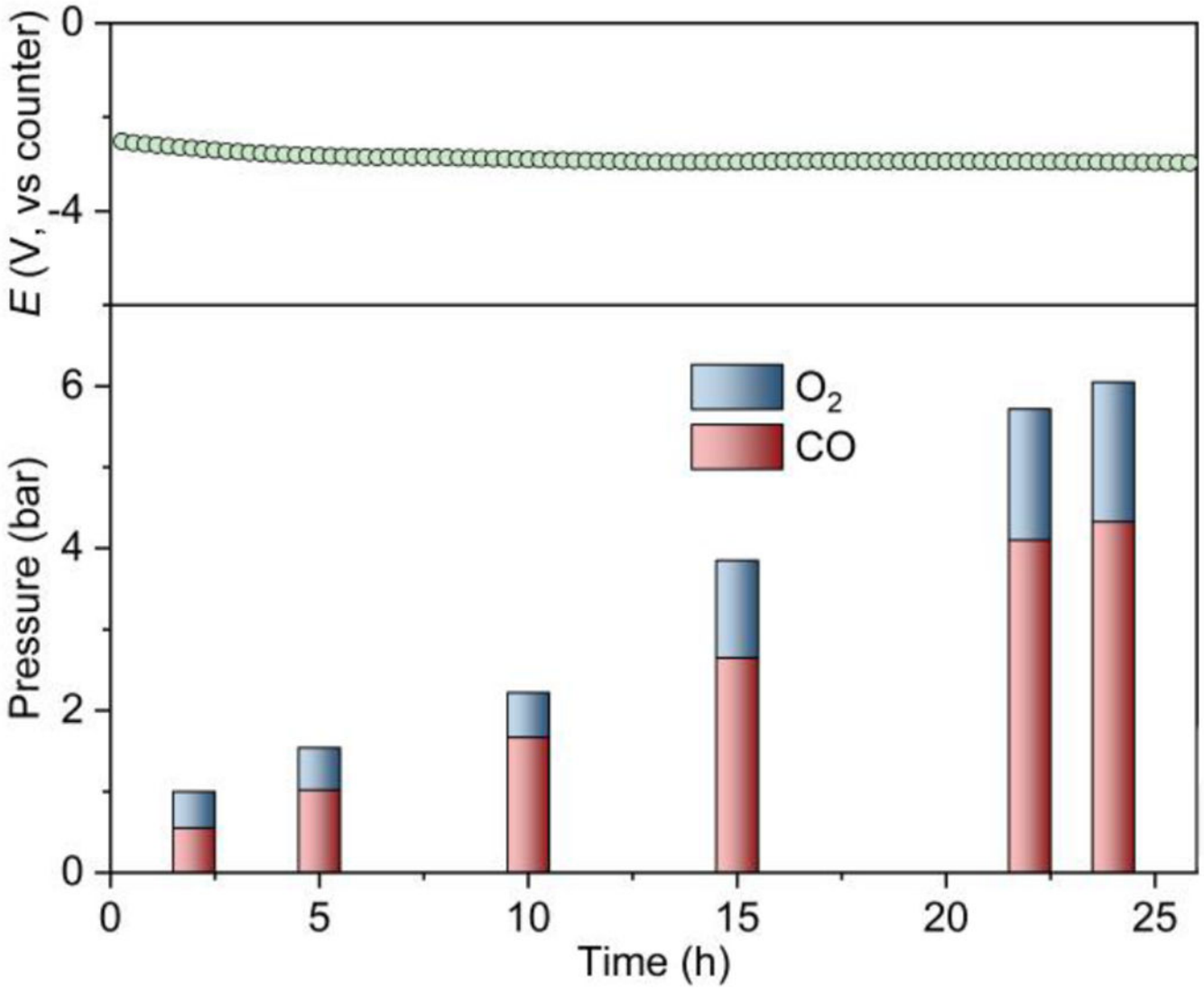

Figure 2.

Electrochemical reduction of CO_2 and the production of CO and O_2. **Top**: Voltage evolution during the electrocatalytic CO_2RR with a constant current of 11.1 mA/cm^2. The data are *iR* corrected. **Bottom**: CO and O_2 pressures at different electrocatalytic CO_2RR times with an initial CO_2 pressure of 8 bar and CH_4 pressure of 18 bar.

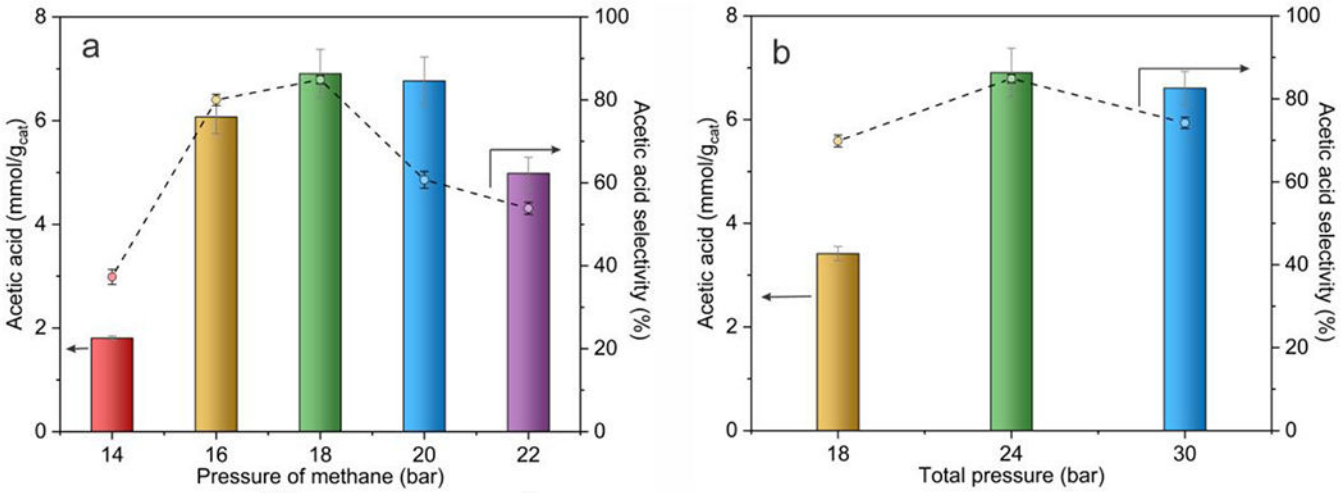

Figure 3.

Influence of pressures of CH_4, CO, and O_2 on the yield of CH_3COOH. Reaction conditions: 16 mg of catalyst, 3-5 bar of CO, 1.5-2.5 bar of O_2, 11 mL of water, 3 h of reaction at 150 °C. (a) Dependence on the pressure of CH_4 when P_{CO} is fixed at 4 bar and P_{O2} is fixed at 2 bar. (b) Dependence on the total pressure with P_{CH4}:P_{CO}:P_{O2} is fixed at 9:2:1. The CH_3COOH selectivity represents that of all liquid products.

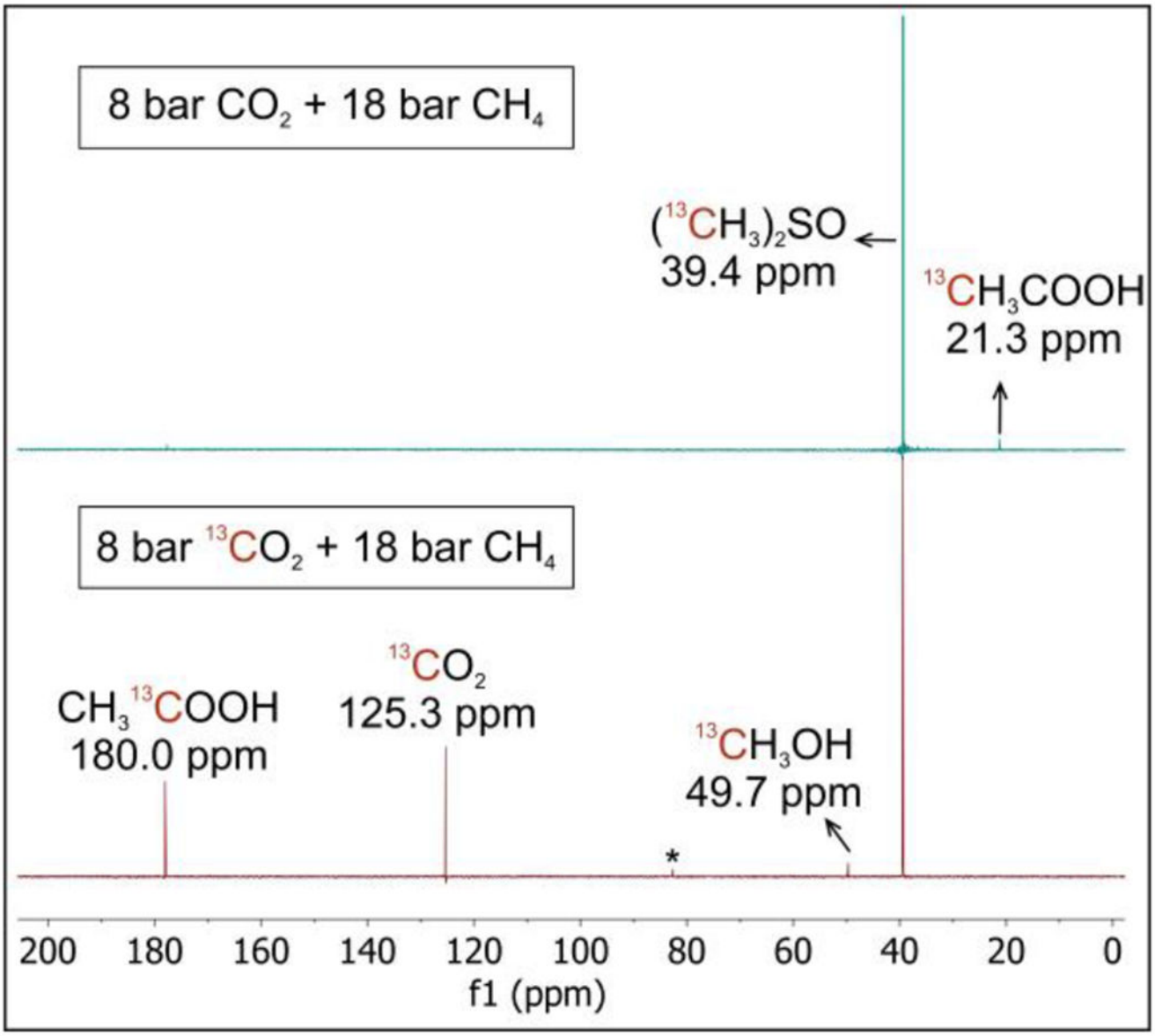

Figure 4.

^{13}C NMR spectra of the liquid products by reactions using CO_2 (**top**) and $^{13}CO_2$ (**bottom**).

* indicates $CH_2(OH)_2$.