

# Finding a Path to CO<sub>2</sub> Utilization on a Scale that Matters

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## Opportunities and current state of research in CO<sub>2</sub> utilization

Anthropogenic greenhouse gas (GHG) emissions have increased the partial pressure of atmospheric CO<sub>2</sub> to its highest level in the past 3 million years [1]. A rapid emissions drawdown is needed to minimize the risk of triggering climate tipping points that would substantially change Earth system components with severe negative impacts on the planet's biomes and human welfare [2]. At odds with this imperative is the enormous and growing demand for energy, 80% of which is supplied by fossil fuels. Eliminating GHG emissions from the global energy system requires massive shifts, foremost being a transition from coal and natural gas power plants to renewable electricity. With a renewable grid, it is possible to decarbonize many energy services including light-duty transportation, heating, and cooling through direct electrification [3]. However, eliminating carbon-based products from other energy services is infeasible for the foreseeable future. Liquid fuels are indispensable for heavy-duty transport, aviation,

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and marine shipping, which comprise >60% of the ~100 million barrels consumed daily [4]. Demand for these services will increase with global economic growth. Carbon-based chemicals and materials are essential for every industry. Plastics alone account for 8% of oil and gas use and 4% of GHG emissions, with these numbers projected to double by 2050 [5]. The emissions problem cannot be solved without CO<sub>2</sub> utilization — the production of fuels and chemicals from CO<sub>2</sub>, H<sub>2</sub>O, and renewable energy. Decoupling carbon-based products from fossil resources also provides opportunities to improve global energy security. While these considerations have motivated researchers for many years, the unrivalled scale and time sensitivity of the problem pose an urgent need for actionable advances.

Non-fossil fuels and chemicals are currently made from biomass, thereby letting natural photosynthesis perform CO<sub>2</sub> conversion. With few exceptions, the feedstocks used for bio-based products are glucose or vegetable oils derived from agriculture. This practice competes with food production, which in a global market ultimately leads to the destruction of natural carbon sinks and biodiversity harbours (e.g., rainforests) to create more agricultural land [6]. To avoid this calamitous pitfall, it is critical to utilize inedible biomass (lignocellulose) that is obtained without land use change, ideally residuals from existing processes [7]. Judicious lignocellulose utilization could provide carbon-neutral replacements for petrochemical products. While much attention has focused on fuels, chemicals and materials are better matched to the scale of truly sustainable feedstocks. The research challenge is transforming recalcitrant and heterogeneous lignocellulosic feedstocks into useful products without using large quantities of non-renewable inputs.

Bio-based products are limited by the low solar-to-biomass efficiency of natural photosynthesis, which is typically <1% in plants [8]. Collecting and converting biomass to a useful product takes the overall sunlight-to-product efficiency even lower. Synthetic approaches are therefore essential to producing sustainable carbon-based products on the gigaton scale. Using renewable electricity to power the conversion of CO<sub>2</sub> and H<sub>2</sub>O into fuels and chemicals could achieve far greater efficiency than natural photosynthesis. As a simple example, a 10% sunlight-to-product efficiency could be achieved by combining a 20% efficient photovoltaic with a 50% efficient power-to-product process.

Renewable electricity can be used to power CO<sub>2</sub> conversion directly via CO<sub>2</sub> electrolysis. Building on seminal early studies [9], research in this area has grown exponentially in the past decade. Electrolysers that convert CO<sub>2</sub> into CO and O<sub>2</sub> have reached nascent commercialization [10]. Since CO is a common intermediate in chemical and fuel production, these systems could in principle provide renewable routes to high-volume products. Reaching an impactful scale hinges on improving their energy efficiency and manufacturability, which will likely require breakthroughs in materials (e.g., catalysts and separators) and better control of the transport phenomena that govern performance under process-relevant conditions [11]. Beyond CO, electrochemical CO<sub>2</sub> conversion using Cu catalysts produces more valuable products like ethylene, an emissions intensive super-commodity. While laboratory cells have shown promising ethylene selectivity and production rates, their development is currently far behind CO<sub>2</sub>-to-CO electrolysis.

An alternative to CO<sub>2</sub> electrolysis is to make H<sub>2</sub> via water electrolysis and then perform CO<sub>2</sub> hydrogenation. Water electrolysis is an established industrial technology, with >80% efficiency for the electrolyser and >65% for the full system (electricity to H<sub>2</sub> lower heating value) [12]. CO<sub>2</sub> can be hydrogenated to produce CH<sub>4</sub>, CO, or CH<sub>3</sub>OH selectively depending on the catalyst and process conditions. There are commercial processes to transform syngas (CO and H<sub>2</sub>) or CH<sub>3</sub>OH into multi-carbon fuels and chemicals. Combining CO<sub>2</sub> hydrogenation with these technologies would provide a renewable route to many high-volume products while leveraging existing infrastructure. Innovations in catalysts and process design are needed to improve CO<sub>2</sub> hydrogenation efficiency and its integration with downstream conversions to make these systems competitive with fossil fuels. Another approach is to hydrogenate CO<sub>2</sub> to multi-carbon fuels in a single step, thereby eliminating the need for a separate reactor to make CH<sub>3</sub>OH or CO [13]. This approach could be advantageous if the rates and product distributions can be greatly improved.

Carbon dioxide utilization depends on the provision of a concentrated CO<sub>2</sub> supply. Several tens of millions of tons of relatively high purity (95–99%) CO<sub>2</sub> is emitted from ethanol fermentation and ammonia synthesis plants [14]. As of 2022, operational carbon capture and

sequestration (CCS) facilities have the capacity to capture >40 Mton/yr and >200 Mton/yr additional capacity is under development [15]. With amine scrubbing technology, capturing CO<sub>2</sub> from coal flue gas requires <250 kWh of equivalent work per ton [16], or ~3% the energy required to convert CO<sub>2</sub> to fuel at 50% energy efficiency. To supply gigaton-scale utilization, CO<sub>2</sub> will eventually need to be captured directly from air. Leading direct air capture (DAC) technologies require ~2 MWh of electricity per ton if a heat pump is used and 0.7 MWh if waste heat is used [17], which could be provided by integrating DAC with CO<sub>2</sub> utilization.

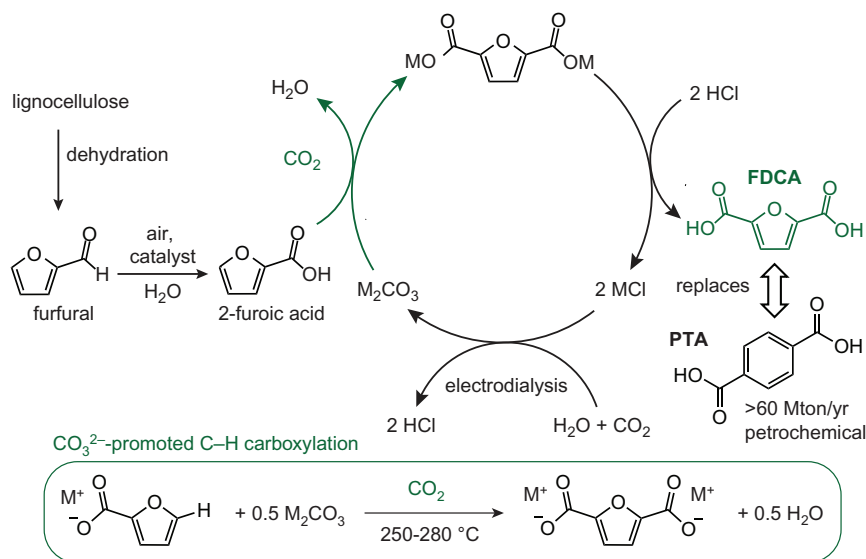
## My recent research contributions to CO<sub>2</sub> utilization

Over the past several years, my group has developed carbonate-promoted and carbonate-catalysed reactions to unlock new ways of utilizing CO<sub>2</sub> for chemical and fuel synthesis. Our approach was originally inspired by the Calvin cycle, which fixes CO<sub>2</sub> using the enzyme RuBisCO to perform C–H carboxylation — the conversion of a C–H bond and CO<sub>2</sub> into a carboxylate (C–CO<sub>2</sub><sup>−</sup>) using a base to remove the proton. RuBisCO only carboxylates ribulose-1,5-bisphosphate, which has an activated C–H bond. Attracted by its conceptual simplicity, we began investigating ways to generalize C–H carboxylation for the synthesis of carboxylic acids with high-volume applications.

The challenge with C–H carboxylation is that most C–H bonds have very high pK<sub>a</sub>s (>30). Deprotonating such bonds typically requires very strong bases (e.g., organolithiums) that have emissions footprints far outweighing the CO<sub>2</sub> that is consumed in a C–H carboxylation reaction. To avoid indirectly releasing more CO<sub>2</sub> than is consumed, one needs a base that can be regenerated with minimal energy and resource use. We concluded that carbonate (CO<sub>3</sub><sup>2−</sup>) is the only viable option [18]. In conventional solution-phase chemistry, CO<sub>3</sub><sup>2−</sup> is a weak base that cannot deprotonate high-pK<sub>a</sub> C–H bonds. We therefore began exploring solvent-free systems to see if it is possible to increase CO<sub>3</sub><sup>2−</sup> basicity in these unusual media. Salts composed of alkali cations and carboxylate anions proved fruitful. Depending on the cation and the carboxylate structure, these salts can form molten phases at temperatures below the onset of

decomposition. We discovered that when CO<sub>3</sub><sup>2-</sup> is dissolved in an alkali carboxylate melt, it can reversibly deprotonate high-pK<sub>a</sub> C–H bonds in the presence of CO<sub>2</sub>, which leads to C–H carboxylation [18, 19]. Using the alkali carboxylate itself as the substrate, simply heating a mixture of alkali carboxylate and alkali carbonate under CO<sub>2</sub> beyond a melting transition results in CO<sub>3</sub><sup>2-</sup>-promoted C–H carboxylation.

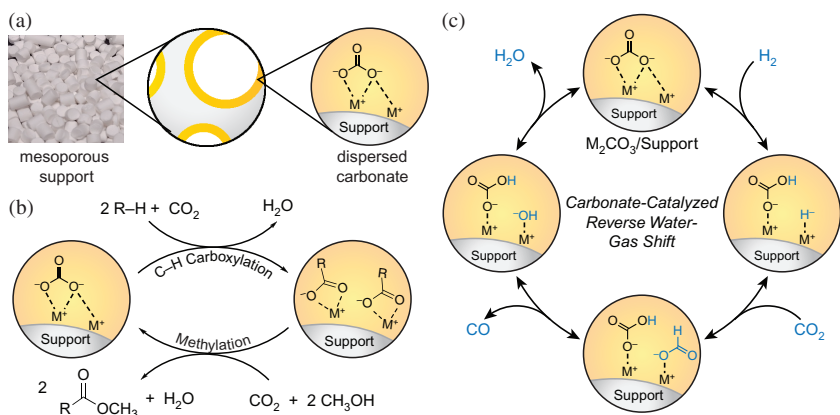
We have used CO<sub>3</sub><sup>2-</sup>-promoted C–H carboxylation to develop a new route to furan-2,5-dicarboxylic acid (FDCA) (Fig. 1) [18, 20]. FDCA is a substitute for purified terephthalic acid (PTA), a petrochemical used to make polyethylene terephthalate (PET), which is the world's second largest commodity plastic [21]. In our route, CO<sub>3</sub><sup>2-</sup>-promoted C–H carboxylation converts alkali furan-2-carboxylate into the dicarboxylate, from which FDCA is isolated by protonation. The salt by-product is converted back to alkali carbonate and acid at a low energy input using electro dialysis technology. Furan-2-carboxylic acid can be made by aerobic oxidation of furfural, which is the only chemical currently produced on large scale from lignocellulose. Thus, CO<sub>3</sub><sup>2-</sup>-promoted C–H carboxylation enables



**Fig. 1.** Carbonate-promoted C–H carboxylation of furan-2-carboxylate and its use to synthesize FDCA from lignocellulose, air, and CO<sub>2</sub>. FDCA is a PTA replacement.

the conversion of lignocellulose, air, and  $\text{CO}_2$  into a building block for commodity polymers. More recently, we have extended this C–H carboxylation chemistry to make lignocellulose-derived furanic polyamides with favourable thermal properties [22–24].

To expand the generality of this approach, a new strategy was needed to enable  $\text{CO}_3^{2-}$  to promote C–H carboxylation of gas-phase reactants. We found that dispersing  $\text{M}_2\text{CO}_3$  into mesoporous supports (oxide or carbon materials) disrupts the  $\text{M}_2\text{CO}_3$  crystallinity, generating an amorphous, high surface area  $\text{M}_2\text{CO}_3$  with undercoordinated  $\text{CO}_3^{2-}$  ions that behave as superbases at elevated temperatures (Fig. 2(a)). We have used these materials (“dispersed carbonates”) to perform C–H carboxylation of arenes (e.g., benzene) and heteroarenes (e.g., 1-methyl indole) by simply heating the dispersed carbonates under elevated pressure of  $\text{CO}_2$  and substrate at 280–400°C [25, 26]. The carboxylate products can be converted into isolable methyl esters with concomitant regeneration of the dispersed carbonates by treating the product with methanol and  $\text{CO}_2$  or with dimethyl carbonate at 160–280°C. Thus, two-step cycles of C–H carboxylation and methylation can be used to convert (hetero)arenes into aromatic esters (Fig. 2(b)).



**Fig. 2.** (a) Schematic depiction of alkali carbonate ( $\text{M}_2\text{CO}_3$ ) dispersed in a mesoporous support. (b) Synthesis of (hetero)arene esters from (hetero)arenes using C–H carboxylation and methylation. (c) Carbonate-catalysed reverse water–gas shift catalysis.

Carboxylation in the gas phase provided an entry point to CO<sub>2</sub> hydrogenation catalysis. Interestingly, benzene and H<sub>2</sub> have the same heterolytic bond dissociation enthalpy (400 kcal/mol). Given their ability to promote C–H carboxylation of benzene, we envisioned that dispersed carbonates would catalyse the reverse water–gas shift (RWGS) reaction (CO<sub>2</sub> hydrogenation to CO) via a cycle shown schematically in Fig. 2(c). Analogous to C–H carboxylation, deprotonation of H<sub>2</sub> by CO<sub>3</sub><sup>2-</sup> forms a hydride (H<sup>-</sup>) that attacks CO<sub>2</sub> to form formate (HCO<sub>2</sub><sup>-</sup>). Unlike C–CO<sub>2</sub><sup>-</sup>, however, HCO<sub>2</sub><sup>-</sup> is not a terminal product. Proton transfer from C to O promotes dissociation to CO and OH<sup>-</sup>, which deprotonates HCO<sub>3</sub><sup>-</sup> to form H<sub>2</sub>O and regenerate CO<sub>3</sub><sup>2-</sup>, thereby closing the catalytic cycle.

RWGS is endothermic ( $\Delta H^\circ = 41$  kJ/mol). One of the biggest challenges for RWGS catalysis is suppressing CO<sub>2</sub> hydrogenation to CH<sub>4</sub>, which is very exothermic ( $\Delta H^\circ = -165$  kJ/mol). Current RWGS technologies utilize Ni steam reforming catalysts that are unselective. To suppress methane, these catalysts must be operated at very high temperatures (typically >900°C) where the endothermic RWGS reaction becomes thermodynamically favoured [27]. By contrast, we envisioned that CO<sub>3</sub><sup>2-</sup>-catalysed CO<sub>2</sub> hydrogenation would be highly selective for RWGS because alkali carbonates have very little affinity for CO and therefore no way to reduce CO further to CH<sub>4</sub>.

Gratifyingly, dispersed carbonates have proven to be highly active, robust, and extremely selective RWGS catalysts in a temperature regime where CH<sub>4</sub> is strongly thermodynamically favoured [28]. High-performing catalysts can be prepared from very low-cost materials — e.g., K<sub>2</sub>CO<sub>3</sub> and mesoporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> — using procedures commonly employed for high-volume catalyst manufacturing. Because they do not contain transition metals, dispersed carbonates are tolerant to impurities found in CO<sub>2</sub> streams, such as H<sub>2</sub>S.

By producing the CO component of syngas, RWGS catalysis provides a link between established water electrolysis and syngas-to-liquids technologies to enable integrated power-to-liquid (PtL) systems for producing sustainable liquid fuels. Water electrolysis is projected to reach >200 GW operational capacity in the next decade [29]. Syngas conversion using Fischer–Tropsch technology is proven on scale in plants that produce >100,000 barrels per day of liquid hydrocarbon fuels and chemicals [30],



while recently commercialized gas fermentation technology converts syngas into ethanol [31]. The efficiency and cost of PtL systems that utilize water electrolysis and syngas-to-liquid processes depend critically on the performance of the RWGS unit that links them together. The very high-temperature regime required for conventional Ni catalysts necessitates expensive materials of construction and complicates heat integration with the rest of a PtL process. Ni is also a liability for high-volume catalyst applications given the surge in demand from batteries. Carbonate-catalysed RWGS provides opportunities to build new PtL process designs that lower the barrier to scaling.

## **Outlook to future developments of research on CO<sub>2</sub> utilization**

The next 10 years are critical for demonstrating that CO<sub>2</sub> utilization can be a significant source of carbon-based products and contributor to emissions drawdown. A healthy competition between electrochemical and chemical (e.g., hydrogenation) approaches will increase the likelihood that CO<sub>2</sub> utilization technologies compete with fossil incumbents. Successful technologies will not only optimize efficiency but also creatively integrate with existing infrastructure and industrial emission streams. There are abundant opportunities for the research community to accelerate the trajectory of established pathways or unveil new ones. Dividing effort between fundamental and applied research is counterproductive. Integrating science with device engineering and process design has the greatest likelihood of creating advances that will translate to real technologies. Given the urgency and enormity of the carbon problem, the only meaningful measure of the impact of a research development in CO<sub>2</sub> utilization will be the scale at which it is ultimately utilized and the emissions reductions that result. The “impact factor” for CO<sub>2</sub> utilization research will eventually be measured only in tons.



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