The reduction of carbon dioxide into useful products such as fuels and chemicals is a topic of intense research activity at present, driven by the need to reduce atmospheric CO\textsubscript{2} levels and avoid catastrophic temperature rises across the world. In this review, we consider a range of different technological approaches to CO\textsubscript{2} conversion, their current status and the molecules which each approach is best suited to making. In Part I, the biological, catalytic and electrocatalytic routes are presented.

1. Introduction

Anthropogenic CO\textsubscript{2} emissions from fossil fuels use and industry amounted to around 33 billion tonnes in 2019 (1, 2), mainly arising from the power generation sector. The use of carbon capture and storage (CCS) is considered a key contributor in the portfolio of options for achieving the CO\textsubscript{2} emission reduction targets agreed by the international community in 2015 during the 21st Conference of Parties on Climate Change (COP21). With the premise of keeping the Earth’s temperature rise below 2°C (and more ideally below 1.5°C) above the pre-industrial average (the ‘two degree scenario’), this will require that at least 94 billion tonnes of CO\textsubscript{2} are captured and stored until 2050 (3, 4). The extent of deployment will naturally depend on the economics together with government support and political will, but nevertheless a consequence is that CO\textsubscript{2} capture implementation will make large quantities of ‘pure’ CO\textsubscript{2} available within the next 10 years. Although the focus on CO\textsubscript{2} is being its contribution to climate change, value can be obtained from its use as a feedstock for a range of products and services. It can either be used directly (unconverted) such as for enhanced oil recovery (EOR) and for the food and beverage industry or indirectly through being converted to fuels, chemicals and building materials (Figure 1). At present, the annual consumption of CO\textsubscript{2} is approximately 230 million tonnes, with fertiliser production, namely urea, being the largest consumer (~130 million tonnes CO\textsubscript{2}), followed by its use for EOR (~70–80 million tonnes CO\textsubscript{2}) (5). With the growing interest for further development and investment in some of the newer (less technically mature) conversion routes then in the future these indirect CO\textsubscript{2} users could start contributing more towards the CO\textsubscript{2} consumption figures.

The use of CO\textsubscript{2} as a raw material is viewed in the literature as becoming much more widespread than it is currently, possibly generating a ‘CO\textsubscript{2} economy’
Carbon dioxide capture and utilisation (CCU) has even been proposed as an alternative to CCS as a climate change mitigation strategy, notably where CCS opportunities are limited, but the present scale of applications is too small to have a large impact in emission reductions, as pointed out by others (7). In the context of potential mitigation options this view is also relevant if considering a widespread electrochemical-based solution to CO₂ emissions (viz. CO₂ electroreduction) due to the seemingly inconceivable electricity demands and scale of marketplace that would be required for it to be considered a prime choice for addressing the climate change targets (8). However, directionally some benefit in emissions is obtained from using the waste CO₂ for the synthesis of fuels, powered by renewable electricity such as solar, wind, hydroelectric and geothermal (9). This approach comes under the umbrella of power-to-X schemes and has been reviewed in the literature (10–12). Many of the processes rely on water electrolysis to produce hydrogen, itself a gaseous fuel, followed by thermocatalytic reduction of captured CO₂ to produce synthesis gas (syngas), formic acid, methanol, methane (synthetic natural gas (SNG)) or higher hydrocarbons. Power-to-X schemes could produce carbon-based fuels as storage vectors at times when electricity production outweighs demand, which is a significant problem of the intermittent wind or solar power generation. One challenge in these schemes is the inevitable loss of efficiency when multiple processes are coupled together. From an electricity perspective it is more efficient to use electricity directly than to make chemicals; however, market demand for sustainable fuels and chemicals means that these concerns can be overcome, especially when electricity prices are low. It should be noted that compared with some of the more niche CO₂ uses, the market sector for fuels is vast and while this makes the opportunity for deriving them from CO₂ appealing it also brings about its own challenges. The potential scale of deployment is very large, with a choice of distributed or centralised production, which also needs to be supported by electrolyser manufacturing scale-up if water electrolysis is required. The processes are often energy intensive leading to high production costs to compete with their fossil fuel based equivalents. Regulatory requirements and technical specifications for some of the products (including whether product blends are acceptable rather than pure products), would also need to be met. Nevertheless, with process improvements gained from further development and project investment from governments with industrial support, it’s seen as an important area to target for CO₂ utilisation.

In addition to electrochemical and thermocatalytic routes other options include biological-based conversions that use CO₂ as the carbon source, and a co-reagent such as hydrogen for energy supply, with some technologies already reaching
commercial status. Examples are LanzaTech’s gas fermentation technology platform for producing fuels and chemicals such as ethanol and 2,3-butanediol (13) and Electrochaea’s methanation process (14). Both the direct use of CO₂, or CO₂ conversion, should not be viewed as a mitigation strategy per se for reasons already mentioned, but instead as an enabler for increasing the value of a CO₂ capture project and helping the ‘business case’. By displacing the use of fossil fuels and promoting a more sustainable circular economy, CO₂ reuse can also help improve a country’s energy security. Furthermore, there is also the positive social-economic impact through creation of jobs around the construction and operation of such a facility.

From the outset, the conversion of CO₂ into fuels and chemicals by chemical reduction presents a thermodynamically uphill challenge, as is suggested firstly by its large C=O double-bond energy (750 kJ mol⁻¹) and the higher, i.e. less negative, Gibbs free energies for some of the main carbon-based reduction products listed in Table I. The conversion chemistry is driven by the free energy differences between the reactants and products indicating their relative stabilities (16). With CO₂ being the most highly oxidised product in many carbon-based processes, including chemical and biological pathways, it exhibits the lowest energy state of all carbon-containing binary neutral species. The large energy required to reduce it is a significant obstacle and would be reflected in the energy consumption costs of any economic evaluation. This energy can either be supplied as physical energy, for example thermal or electrical, or indirectly via the use of reactive chemical species as reagents, such as hydrogen that exhibit a higher Gibbs free energy to promote the conversion of CO₂ from a thermodynamics perspective. One result of the energetic challenges inherent in the CO₂ conversion chemistry is there being an exciting opportunity for catalyst development in this area, to generate the reaction rates and product selectivities required for an economic process (17).

A question that often arises is which fuels or chemicals should industry target for scale-up and production and which conversion technology should be used, with a realisation that some technologies are still in early-stage development such as direct low temperature CO₂ electroreduction exhibiting performance challenges with respect to product selectivity and energy conversion efficiency. The answer to this will often be dictated by the process economics and market demand for the product and a technoeconomic assessment (TEA) comparing technologies and target products will be an important decision-making exercise. The economics depend on not only the capital cost of the technology equipment items (including reactant purification, product separation duties and ancillary equipment) but also on the availability, intermittency and costs of energy such as renewable electricity and heat, which vary depending on location and can greatly influence the operating costs. Furthermore, this might be supplemented by any government incentives that might exist, for example the latest Renewable Energy Directive (RED II) for transport fuels in the European Union (EU) (18), which itself could be revised as a result of the European Green Deal initiative (19). As a result, a credible business case for justifying deployment of a particular technology to produce a target fuel or chemical product would be dependent on the policies within the host country (or shared policies between countries as in the EU) and also site-specific providing accessibility to the CO₂ feedstock and a suitable energy supply. Such a lined-up scenario is highlighted by the commercial renewable methanol facility that is owned and operated by Carbon Recycling International (CRI). The George Olah plant is located in Iceland’s Svartsengi geothermal field near Grindavík on the Reykjanes peninsula and exploits captured CO₂ from the nearby Svartsengi geothermal power station and renewable electricity.

Table I. Properties of Target Products That can be Made from Carbon Dioxide (15)

<table>
<thead>
<tr>
<th>Carbon-containing target product</th>
<th>Chemical formula</th>
<th>Oxidation state of carbon</th>
<th>Gibbs free energy of formation (∆G°f), kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide (reactant)</td>
<td>CO₂ (g)</td>
<td>+4</td>
<td>-394.4</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>CO (g)</td>
<td>+2</td>
<td>-137.2</td>
</tr>
<tr>
<td>Formic acid</td>
<td>HCOOH (l)</td>
<td>+2</td>
<td>-361.4</td>
</tr>
<tr>
<td>Methanol</td>
<td>CH₃OH (l)</td>
<td>-2</td>
<td>-166.6</td>
</tr>
<tr>
<td>Methane</td>
<td>CH₄ (g)</td>
<td>-4</td>
<td>-50.5</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C₂H₅OH (l)</td>
<td>-2</td>
<td>-174.8</td>
</tr>
<tr>
<td>Ethylene</td>
<td>C₂H₄ (g)</td>
<td>-2</td>
<td>+68.4</td>
</tr>
<tr>
<td>n-Propanol</td>
<td>C₃H₇OH (l)</td>
<td>-2</td>
<td>-166.7</td>
</tr>
</tbody>
</table>
from the Icelandic grid to produce electrolytic hydrogen for use in methanol synthesis via the direct hydrogenation of CO₂. The methanol is used in gasoline blends with the George Olah plant effectively recycling 5500 tonnes of CO₂ a year. The renewable methanol product from this facility is sold under the brand name of Vulcanol™ and is displacing a small amount of fossil fuels in the transport sector (20, 21).

Greenhouse gas (GHG) emission reduction often plays an integral part in the justification of a CO₂ utilisation plant and a full and robust life cycle assessment (LCA) is required to confirm CO₂ mitigation benefits compared to the conventional (often fossil fuel) route, taking into account the whole value chain from CO₂ origin to the final use of the product: a ‘cradle-to-grave’ analysis. Any climate change benefits will depend on the source of the CO₂ feedstock (fossil fuel, biomass or directly from air), the carbon footprint of the conventional product or process route that is being displaced, the nature of the energy used for the conversion, the scale of the CO₂-utilising process and the lifetime of the CO₂ in the final product. The analysis would reflect that the CO₂ avoided is not the same as CO₂ used.

In terms of the origin of the CO₂ feedstock then in the first instance it would invariably be from point sources, for example power stations or industrial cement or steel works, with CO₂ clean-up and concentration being required for the majority of utilisation processes. However, there has been much interest lately in direct air capture (DAC) of CO₂ with differing capture technologies being developed and showcased (22, 23). Although from a fundamental analysis (24) the separation energy would conceivably be significantly higher than that from an industrial point-source (0.04 vol% CO₂ in atmospheric air vs. for example a power station flue-gas containing 8–15% CO₂ depending on the fossil fuel) and hence also the separation cost, several companies are working on this and have already attained both demonstration and commercial operating levels. There have been projections made for the CO₂ capture cost from DAC to come down to approximately US$100 tonne⁻¹ within a decade (22, 23), which although encouraging is still high compared to cost targets for the demonstrated and in some cases commercialised liquid amine-based capture systems. However, as well as delivering a high-purity CO₂ stream and reducing the costs and emissions associated with any transport of the CO₂ feedstock, an obvious advantage of DAC is that it is not limited to locating the conversion or direct utilisation plant close to a CO₂ point-source. This attribute lends itself towards smaller-scale distributed production rather than necessarily building a large centralised facility that takes advantage of the economies of scale. The use of DAC CO₂ would close the carbon loop and likely provide improved carbon mitigation benefits from either carbon neutral or carbon negative emissions (depending on final product), to be quantified by an LCA. Furthermore, a DAC-based source of the CO₂ feedstock could qualify for government incentives for fuels and chemicals in the future. Currently the EU’s RED II allows for DAC-derived CO₂ for producing synthetic fuels (renewable fuels of non-biological origin (RFNBO)), but also accommodates the use of lower cost CO₂ from point-sources such as power station flue-gas, so not exclusively incentivising the deployment of DAC (23). Like for many developing technologies within the CCU space, government support through grants and tax credits and robust CO₂ accounting frameworks will ultimately be needed to help drive the technology through the metaphorical ‘valley of death’ and into commercialisation with an investable package.

This paper provides a perspective on some of the different CO₂ conversion technologies and their applicability to target products that are being developed by both academia and industry. It covers a range of approaches, which are mainly catalytic in nature including homogeneous and heterogeneous (thermo)catalytic, electrocatalytic and biological methods, each of which are at different technology readiness levels (TRL) and exhibiting different strengths and research challenges.

### 2. Biological Routes from Carbon Dioxide to Products

In nature, the bulk of CO₂ reduction is carried out by plants and autotrophic microorganisms, that are capable of converting CO₂ and an external energy source into biomass and side products. Central to autotrophic metabolism are carboxylase enzymes, that incorporate CO₂ (or in some cases, HCO₃⁻) to specific organic molecules. Autotrophs also possess energy harvesting systems, that take reducing potential from light or inorganic electron donors for CO₂ reduction.

Recent advances in genetic engineering have led to the use of these biological tools (autotrophic microorganisms, a variety of carboxylases, autotrophic energy-harvesting systems) and others as modular units to create synthetic biological routes from CO₂ to virtually any product of interest.
This review discusses three such synthetic biology approaches for CO₂ reduction.

The first approach is to use autotrophic microorganisms with genetic engineering and process optimisation to maximise yield and purity of their natural products (C1 to C4) or to add heterologous enzymatic pathways that lead to new products (Table II). A commercial example is LanzaTech’s acetogenic strain Clostridium autoethanogenenum, that naturally converts CO, CO₂ and hydrogen to ethanol, acetate, 2,3-butanediol and other products. Strain selection and evolution combined with the development of the gas fermentation process have led to improved ethanol production. LanzaTech’s first commercial plant was established in China in 2018 and is located at a steel mill, using industrial waste gas as feedstock. Biomass and other organic waste can also be gasified, giving Clostridia and other acetogenic bacteria versatility in feedstock. The enzymatic pathway acetogens use, Wood-Ljungdahl, is the most energy-efficient natural autotrophic pathway. Depending on the species, acetate is either the main product or precursor and hydrogen is used as the source of reducing energy (25). Other species of Clostridia have been used to produce butanol (26).

Photoautotrophic microorganisms such as microalgae and cyanobacteria are another example, using light to split water to generate oxygen, as well as hydrogen and H⁺ gradient for energy. This is used for the Calvin cycle (also known as the Calvin-Benson-Bassham cycle or the reductive pentose pathway), an enzymatic pathway that requires a lot of energy to fix CO₂. Microalgae, typically grown in large scale in ponds and can use wastewater, convert CO₂ to biomass for animal feed and a range of lipids for biodiesel (27). Chemical production from CO₂ has seen recent advances due to the expansion of available genetic tools for cyanobacteria. Combined with improved photobioreactor design, this has enabled production of 1-butanol at 4.8 g l⁻¹ (302 mg day⁻¹) from Synechocystis, the highest production rate of 1-butanol from CO₂ (28). Phytonix Corporation is a producer of biobutanol and biooctanol using cyanobacteria (29).

The ‘Knallgas’ bacterium Cupriavidus necator also utilises the Calvin cycle, but takes reducing energy from hydrogen or formate. This bacterium naturally accumulates polyhydroxybutyrate, a bioplastic precursor. With genetic engineering, it has been exemplified to produce branched-chain alcohols and alkanes from CO₂ (25). C. necator has been used in microbial electrosynthesis (MES, discussed later) where formate or hydrogen is produced from the cathode.

The second approach is to take model heterotrophic (not able to grow on CO₂) microorganisms and introduce carboxylases or autotrophic pathways that enable CO₂ utilisation. These organisms, with well-established use in industrial fermentations, are capable of high growth rates (specific growth rates of 0.5 h⁻¹ to >3 h⁻¹) and high productivities when grown on sugars or other carbon sources. In addition, their well-characterised metabolism and a wide range of available genetic tools make them ideal hosts for genetic engineering. Genetic modifications and the introduction of the Calvin cycle including ribulose-1,5-bisphosphate carboxylase/oxygenase (RuBisCO) into bacterium Escherichia coli enabled the phospho-sugar synthesis from CO₂ (30). In yeast Saccharomyces cerevisiae, the same approach led to 10% increased ethanol production from glucose and galactose, at the expense of side product glycerol (31). More recently, the introduction of Calvin cycle components and the modification of a native metabolic pathway of the

<table>
<thead>
<tr>
<th>Class</th>
<th>Specific examples</th>
<th>Energy source</th>
<th>Natural products</th>
<th>Engineered products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetogens</td>
<td>Clostridia</td>
<td>Hydrogen</td>
<td>C2 to C4: acetate, ethanol, 2,3-butanediol</td>
<td>Butanol, butyrate, acetone</td>
</tr>
<tr>
<td>Cyanobacteria</td>
<td>Synechocystis spp., Synechococcus spp.</td>
<td>Light</td>
<td>&gt;C10, biomass</td>
<td>Propionate isobutyraldehyde, L-lactic acid, 2,3-butanediol, 1-butanol, acetone</td>
</tr>
<tr>
<td>Microalgae</td>
<td>Chlamydomonas</td>
<td>Light</td>
<td>&gt;C10, biomass high in fatty acid for biodiesel, animal feeds</td>
<td>–</td>
</tr>
<tr>
<td>Knallgas</td>
<td>Cupriavidus necator</td>
<td>Hydrogen, formate</td>
<td>&gt;C10, polyhydroxybutyrate</td>
<td>Branched alcohols, alkanes</td>
</tr>
</tbody>
</table>
methylotropic yeast *Pichia pastoris* has enabled growth on CO$_2$ as a sole carbon source (specific growth rate of 0.018 h$^{-1}$). This is a significant demonstration of conversion of an industrial heterotroph to a synthetic autotroph. *Pichia* is widely used for the production of commercial enzymes and pharmaceutical chemicals and can use methanol as a carbon source. This work facilitates the use of *Pichia* for CO$_2$ conversion into commodity or specialty chemicals using methanol as an energy source (32).

The third approach is to integrate the first two: a simultaneous or sequential fermentation of autotroph (to reduce CO$_2$ to a C1 or C2 product, such as formate, ethanol or acetate) and heterotroph (to utilise the first product as a substrate for >C2). This combines the beneficial characteristics of both types of organisms. An example is the two-stage process using the acetogen *Moorella thermoacetica* to convert CO$_2$, CO and H$_2$ to acetate, which was then used in a separate bioreactor by the oleaginous yeast *Yarrowia lipolytica* to make triglycerides (33).

As genetic engineering and bioreactor designs continue to improve, certain bottlenecks become apparent. Limited energy and CO$_2$ uptake occurs due to inefficient microbial photosystems (in photosynthesis, only 1% of light energy is utilised for biomass and product conversion) and the low solubility of both CO$_2$ and hydrogen in aqueous solutions. CO$_2$ conversion is also rate-limited by the carboxylase enzymes in CO$_2$-fixation pathways, which evolved in environments where fast kinetics was not a requirement. These bottlenecks are being addressed through further engineering and targeted evolution of biological energy-harvesting systems and individual carboxylases and through studies of natural CO$_2$-concentrating mechanisms such as carboxysomes (subcellular compartments where RuBisCO is localised). Aided by advances in bioinformatics and high-throughput enzyme production, more efficient synthetic carboxylation pathways (featuring faster carboxylases and less energy-demanding steps) are also being designed, constructed and tested in either cell-free systems or microbial organisms.

### 3. Catalytic Conversion of Carbon Dioxide to Products

#### 3.1 C1 Molecules

Some key transformations of CO$_2$ into relevant C1 molecules are well known – reduction to carbon monoxide, methanol and methane. The reduction of CO$_2$ to methane is the largest change of carbon’s oxidation state possible, from +4 to –4, requiring four molecules of hydrogen or eight electrons to achieve. This makes it a very energy intensive transformation, –165 kJ mol$^{-1}$, but the consequence is that methane is an energetic fuel, with 800 kJ mol$^{-1}$ released on combustion.

Much of the existing technology in methanation is focussed on the conversion of CO/CO$_2$ mixtures to methane, conversion of syngas derived from coal or biomass to SNG or the removal of low levels of CO and CO$_2$ from gas streams as a purification process. More recently, the focus has shifted towards storing and transporting renewable energy and creating more sustainable fuels through power-to-X type processes (34). The technology is typically based on heterogeneous nickel catalysts which are efficient at the conversion. **Scheme I** shows chemistries based on CO or CO$_2$ hydrogenation.

Methanol synthesis (35), by way of contrast, is performed to make methanol directly. The feedstock is typically a mixture of CO$_2$, CO and

![Scheme I. Chemistries based on CO or CO$_2$ hydrogenation](https://doi.org/10.1595/205651321X16081175586719)
hydrogen and catalysts are mainly based on copper or copper/zinc oxide. The precise detail of the reaction mechanism is still contested in the literature, but the presence of both CO and CO$_2$ is generally required (36).

Both methanation and methanol synthesis are mature technologies, but work is underway to tune them towards the different requirements of CO$_2$ conversion driven by the requirements of climate change. From the process point of view, hydrogen should be supplied in a sustainable form. In principle, this could be blue hydrogen (from steam reforming with CCS) or green hydrogen (from water electrolysis). Practically, it seems unlikely to couple blue hydrogen to a CO$_2$ hydrogenation process, since the amount of CO$_2$ generated by the steam reforming reaction could easily dwarf the amount converted into methane or methanol. There are challenges today with the availability of electrolysis at the scale needed to supply hydrogen to industrial methanol plants, but significant efforts are being made to scale up electrolysers.

One important difference between working with CO and CO$_2$ is that more water is produced from the CO$_2$-based chemistries (Scheme I) as more oxygen needs to be removed to access reduced products. This leads to impacts on the process, for example changing the separation required, but also on the catalyst which will need a greater level of water tolerance. Catalysts and catalyst supports can be damaged hydrothermally by steam or water so some level of reformulation is likely to be required to counter this. Catalysts are developed specifically for CO$_2$ hydrogenation applications (37). Much of this work is based on modification to the existing copper or copper/zinc-based catalysts, but other metals such as palladium (38) and indium (39) are promising alternatives.

Homogeneous systems have been developed for methanol synthesis directly from CO$_2$ and hydrogen. These are usually catalysed by Ru(II) phosphine complexes (40), although iron complexes (41) have also been shown to be active. An amine additive is used in these systems to capture the CO$_2$ and is eliminated in the final hydrogenation – an interesting feature where the carbon capture is built into the catalyst system.

One interesting consequence of an increasing conversion of CO$_2$ to methanol could be the further growth of methanol as a key intermediate. A number of methanol conversion technologies are already in commercial practice or at advanced stages of development (Scheme II) and others could be developed. As these are already mature pathways they present methods of converting CO$_2$ into a range of fuels and chemicals.

The reverse water-gas shift reaction (49) is receiving increased attention as a method for converting CO$_2$ into syngas using renewable hydrogen. This is attractive as it allows existing, high-TRL processes to be run in two steps from CO$_2$. However, unlike the forward water-gas shift reaction, the reverse water-gas shift reaction is not well commercialised at present. This is due to issues with equilibria, selectivity to methane, carbon laydown and the high temperatures needed to drive the reaction forward. A range of catalysts are being evaluated at laboratory scale for the reverse water-gas shift reaction. Many of these are based on copper (50), especially copper-ceria (51), but iron (52), nickel (53), platinum (54) and molybdenum carbide (55) catalysts are also under investigation. In light of the challenges to develop a commercialised process, other methods for activation of CO$_2$ to CO such as electrochemistry or photochemistry are interesting.

### 3.2 Larger Molecules

The direct reduction of CO$_2$ to ethanol has not been widely studied. Most catalysts proposed for this transformation are either based on modification of existing methanol synthesis catalysts such as copper-zinc-alumina, or on Fischer-Tropsch (FT) type mechanisms, and both give rise to challenges in selectivity: to methanol in the former case and to other carbon chain length products in the latter.

One interesting approach is the use of cobalt aluminium oxides prepared from a precipitated hydrotalcite precursor which gave over 90% selectivity to ethanol (56), albeit at laboratory scale. The main byproducts were other short chain alcohols, such as methanol and propanol, along with smaller amounts of CO. A second study (57) used PdCu/TiO$_2$ catalysts to hydrogenate CO$_2$ to ethanol with similar selectivity, finding that the optimal catalyst composition was based on Pd$_3$Cu nanoparticles.

Homogeneous catalysis approaches have been applied to use CO$_2$, in particular for the synthesis of fine chemicals. The interest stems from the non-toxic nature of CO$_2$ compared with other potential C1 reagents such as formaldehyde or CO. Strong reducing agents such as silanes or boranes are typically used to reduce CO$_2$, although some reactions have been reported where CO$_2$ and hydrogen are reacted together using a ruthenium
hydride system to convert C–H and N–H bonds into C–CH$_3$ and N–CH$_3$ respectively (58). In other systems, CO$_2$ is converted to carbonates (59) by reaction with simple alcohols such as methanol or with epoxides (60) to give cyclic carbonates with significant complexity. A different application of this technology is in the synthesis of polyurethanes. The German company Covestro have developed a process for utilising waste CO$_2$ in polymers used in mattresses and other applications (61). The polyurethane synthesis process uses cobalt and zinc catalysts.

An alternative approach to making larger molecules is through a FT type mechanism. Of particular interest are iron catalysts, which possess reverse water gas shift (RWGS) activity and so are able to convert CO$_2$ to CO. As the CO is further reacted, equilibrium does not constrain the conversion which can be reached. The catalyst structure is important in determining the products made. Iron oxide sites are responsible for reduction of CO$_2$ into CO, which is then converted on iron carbide sites into a range of hydrocarbon products. The precise structure is a complex function of the catalyst precursor and the activation and reaction conditions (temperature, pressure, conversion level, gas feed mixture and other factors) as this determines the distribution of active sites. A typical iron FT catalyst promoted with zinc and potassium was tested at 220°C and 30 bar pressure with H$_2$:CO$_2$ = 1 and a space velocity of 6 l g$_{cat}$⁻¹ h⁻¹ (62). The products were CO and light hydrocarbons with a significant proportion of alkenes at a CO$_2$ conversion just below 10%. A cobalt catalyst run under similar conditions was more active but had a much higher selectivity to methane.

Modified catalysts can be tailored to produce alkenes. For example, a potassium-promoted iron oxide catalyst activated in H$_2$/CO at 350°C then used in 3:1 H$_2$:CO$_2$ at 5 bar gave 35% selectivity to C2–C4 alkenes and 25% selectivity to C3–C9 alkenes (63) with the other major products being methane and CO. Modifying the catalyst by addition of a zeolite has been shown to make a gasoline-range product. This intriguing catalyst contains three separate types of active sites: iron oxide to reduce CO$_2$, iron carbide to catalyse the FT reaction and the acid sites of the zeolite which form aromatic molecules from the primary products of the FT reaction (Figure 2).

The process gave 78% selectivity to gasoline-range hydrocarbons (64), although much of this is aromatics which may not be appropriate in all fuel applications. The concept can be taken further to make aromatics from CO$_2$. A similar catalyst was used (65) to make around 30% of aromatics at 30–40% CO$_2$ conversion. A mixture of aromatics was produced, with the main components being C9 and C10 products.

Catalysis offers viable routes into many molecules, characterised by adapting well-known syngas-based processes for C1 molecules such as methane and methanol, making use of methanol conversions to access other molecules and building on processes such as FT to make fuels.

4. Electrocatalytic Conversion of Carbon Dioxide to Products

Synthetic fuels from renewable energy sources (known as ‘e-fuels’) have become increasingly attractive to achieve GHG emission targets as discussed in the introduction. Increasingly abundant low-cost renewable electricity combined with site specific advantages and policies, has enabled electrochemical processes to compete
with traditional thermocatalysis methods, for example the George Olah plant outlined in the introduction coupling hydrogen through electrolysis with thermocatalysis to produce methanol. Water electrolysis is a well-established technology with many reviews (66, 67), hence this section focuses on going beyond hydrogen to the direct electrochemical reduction of CO\(_2\). This area, while much more embryonic, is pushing towards pilot scale with companies like Siemens and Evonik Industries (68), Avantium (69), Opus 12 (70), CERT Systems (71) and Skyre (72) developing commercial systems. High temperature electrolysis to produce CO and syngas (73, 74) using solid oxide electrolyser cell (SOEC) systems could be advantageous if coupled with thermochemical processes to reduce heating cycles. SOECs are not able to reduce CO\(_2\) directly to other hydrocarbons and oxygenates, unlike low temperature electrolysis.

### 4.1 What are the Possible Products of Carbon Dioxide?

Pioneering work carried out by Hori and coworkers (75) in the 1980s marked the birth of CO\(_2\) reduction as a new branch of electrochemical research, showing that the choice of metal catalyst can give control over the mechanism and therefore the product. Figure 3 succinctly plots these metals based on their hydrogen and CO adsorption energies (76), realising four groups yielding different CO\(_2\) reduction products. Note the correlation between the binding of the two intermediates (CO and hydrogen), deemed the scaling relation (76, 77).

Here we shall examine the CO\(_2\) reduction mechanism at a catalyst surface and explore how hydrocarbon products may be generated. The mechanism may be explained in two steps: 2e\(^-\) reduction to CO or formate and further reduction from the CO intermediate (78).

The rate determining step of CO\(_2\) reduction to CO is the adsorption of CO\(_2\) onto the surface of the catalyst (78, 79). This area, while much more embryonic, is pushing towards pilot scale with companies like Siemens and Evonik Industries (68), Avantium (69), Opus 12 (70), CERT Systems (71) and Skyre (72) developing commercial systems. High temperature electrolysis to produce CO and syngas (73, 74) using solid oxide electrolyser cell (SOEC) systems could be advantageous if coupled with thermochemical processes to reduce heating cycles. SOECs are not able to reduce CO\(_2\) directly to other hydrocarbons and oxygenates, unlike low temperature electrolysis.

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Pioneering work carried out by Hori and coworkers (75) in the 1980s marked the birth of CO\(_2\) reduction as a new branch of electrochemical research, showing that the choice of metal catalyst can give control over the mechanism and therefore the product. Figure 3 succinctly plots these metals based on their hydrogen and CO adsorption energies (76), realising four groups yielding different CO\(_2\) reduction products. Note the correlation between the binding of the two intermediates (CO and hydrogen), deemed the scaling relation (76, 77).

Here we shall examine the CO\(_2\) reduction mechanism at a catalyst surface and explore how hydrocarbon products may be generated. The mechanism may be explained in two steps: 2e\(^-\) reduction to CO or formate and further reduction from the CO intermediate (78).

The rate determining step of CO\(_2\) reduction to CO is the adsorption of CO\(_2\) onto the surface of the catalyst (78, 79). The activation energy for CO\(_2\) adsorption is large because of the reorganisation
energy involved in forming a bent $\text{CO}_2^{-}\text{ads}$ intermediate (78). The particular catalyst surface dictates the metastability of different $\text{CO}_2^{-}\text{ads}$ coordination modes as the catalyst affects the overpotential, or activation energy, for $\text{CO}_2$ to $\text{CO}_2^{-}\text{ads}$ (80, 81).

A catalyst with a high $\text{CO}_2$ to $\text{CO}_2^{-}\text{ads}$ overpotential has weak $\text{CO}_2^{-}\text{ads}$ adsorption so coordinates $\text{CO}_2^{-}\text{ads}$ through oxygen and favours protonation to HCOOH shown in Figure 4(a) (78). These catalysts include mercury, cadmium, lead, thallium, indium and tin, with tin or SnO generally favoured (82–85). Due to weak $\text{H}^{-}\text{ads}$, competitive hydrogen production is not a major concern, generally giving this route high Faradaic efficiencies (FEs) $>90\%$.

At materials with a low overpotential for $\text{CO}_2$ to $\text{CO}_2^{-}\text{ads}$ such as platinum, nickel and iron, the radical anion intermediate coordinates through carbon (or mixed carbon/oxygen) and reacts to form CO$_2^{-}\text{ads}$. CO eventually coats the metal surface deactivating the $\text{CO}_2$ reduction pathway (75, 78, 81). As exemplified by Figure 3, these metals also bind hydrogen favourably, therefore generally turn to hydrogen production (i.e. low selectivity towards $\text{CO}_2$ reduction products). A few studies have shown carbonaceous species at very low overpotential before hydrogen formation dominates but this is economically impractical, discussed below.

Materials which reduce $\text{CO}_2$ at a medium overpotential bind $\text{CO}_2^{-}\text{ads}$ through the carbon or mixed carbon/oxygen, stabilising it for dissociation to CO on the surface (81). Gold, silver and zinc are good $\text{CO}_2$ to CO examples where CO is very weakly bound, leaving the catalyst before further reduction (75, 86), likewise $\text{H}^{-}\text{ads}$ remains weak enough to allow high FEs ($>90\%$) to be achieved. Silver is generally favoured (83, 85, 87, 88).

Copper also comes under this medium overpotential category but with a slightly stronger $\text{CO}_2^{-}\text{ads}$ energy, it allows the intermediate to remain loosely adsorbed meaning it is mobile and able to undergo C–C coupling reactions to form products like ethylene (see possible mechanism in Figure 4(b)), amongst other hydrocarbons and alcohols (75, 78). With increased $\text{CO}_2^{-}\text{ads}$ comes increased $\text{H}^{-}\text{ads}$ and with it hydrogen production as a byproduct, limiting the FEs achieved. Kuhl et al. (89) measured 16 $\text{CO}_2$ reduction products on a copper plate (Figure 5). Because $\text{CO}_2$ is a C1 carbon building block there are numerous mechanistic pathways to reach a plethora of products and even more intermediates (90) for the 12e$^{-}$ reduction to either ethylene or ethanol. In this case how does one control selectivity to a preferred product while limiting hydrogen production?

Many variations of copper catalysts have been studied (81, 85, 91), and these are evaluated using metrics based on FE (the proportion of electrons which are used to make the desired product), current density (which is a measure of the reaction rate per unit area of electrode) and overpotential (which is a measure of how energy efficient the system is and reflects both catalyst and cell design).

Generally, the most prevalent product is ethylene, examples go up to 65–75% FE at impressive partial current densities of 500–1100 mA cm$^{-2}$ at high pH (92, 93). By tuning the copper surface
with CeO$_x$ (94) or by addition of a CO forming cocatalyst such as gold (95) or an iron porphyrin (96), FE for ethanol can be achieved at up to 43% at 128 mA cm$^{-2}$.

Methanol at first appearance seems one of the easier products to form considering it is a C1 molecule with a 6e$^-$ reduction (fewer than for ethylene and ethanol), but has been particularly challenging to produce. Albo and Irabien (97) showed 42% FE at 10 mA cm$^{-2}$ in a gas diffusion electrode (GDE) setup, while other methods have used the combined effort of mixed copper catalysts (palladium-copper (98) and copper-selenium (99)) to tune electronic properties of the active site and ionic liquids to possibly increase the CO$_2$:H$_2$O ratio at the electrode electrolyte interface, to achieve ~80% FE at 30–40 mA cm$^{-2}$. Some claims on different catalysts such as RuO$_x$ have been disproven (100).

A multitude of other species have been produced but still at relatively low current densities. Methane has been produced at 80% FE at a partial current density of 9 mA cm$^{-2}$ (101). Oxalic acid has been made at 29% FE using silver catalysts (102). C3+ molecules present a greater challenge due to the range of possible intermediates and products, but some progress has been made with propanol at 10% FE at low current densities on copper nanoparticles (NPs) (103). Remarkably, 2,3-furandiol has been made with 71% FE using nickel phosphide catalysts (104).

There is an increasing variety of alternative catalysts with reviews on homogeneous (105) and tethered (106) molecular catalysts and metal free (107) catalysts. It is interesting to note that metal free catalysts have been able to replicate C–C coupling. For example, a range of carbonaceous species including ethylene at up to 31% FE have been measured on nitrogen-doped quantum dots (108).

### 4.2 What are the State of the Art Systems?

While catalyst optimisation can improve activity and product selectivity, the catalyst environment and therefore the cell architecture plays a large role too (109).

To compare the cell performance, the cell efficiency is a very useful term which combines the energy efficiency to produce the molecules (overpotential in the electrochemical sense) and the current efficiency or selectivity (the focus of the discussion above) (110, 111). It is worth noting that in an electrochemical system the reaction of interest is the cathodic reduction of CO$_2$, and this needs balancing with an anodic reaction, generally the oxygen evolution reaction; the energy efficiency includes both these reactions. Rate of reaction, measured as a partial current density to the desired product, is also important for the electrolyser to operate with a reasonable plant footprint. Jouy et al. (111) gave an example target for alcohols of 3 V at 70% FE cell efficiency (for example, 28% for ethanol) at a rate >300 mA cm$^{-2}$.

Two other key components, durability and conversion efficiency, are reported to a lesser extent and are mentioned in the future perspectives section.

Table III lists a selection of the most recent achievements in CO$_2$ reduction to some of the key products, with cells on the road to commercialisation reported where possible, else laboratory experiments are reported to give a feel of the current TRL. Cell geometry is very important to achieving these goals (109, 114, 115), with examples of different cell geometries shown in Figure 6 from laboratory
scale H-cells to more commercially viable flow cells and membrane electrode assemblies (MEAs). Vennekaetter et al. (115) discuss the benefits and drawbacks of different cell geometries. The MEA (Figure 6(d)) allows the electrodes to be placed much closer together giving these systems comparatively higher energy efficiencies. While in their case a perfluorosulfonic acid (PFSA) based membrane with either a copper or silver catalyst gave no CO\(_2\) reduction products, others have shown a tin nanoparticulate catalyst on a PFSA half MEA can give 94% FE for formic acid at a 40% cell efficiency and a silver catalyst on an alkaline based MEA can give 94% FE CO at a 49% cell efficiency (83). Alkaline membrane technologies are still in their early days of development, leading others to develop flow cells which can achieve similar FEs for CO and formate with 15–40% cell efficiencies (84, 87, 88). In addition, flow cells allow control over the pH and cation which have all been shown to affect the product distribution (75, 92, 116), making it the preferred choice for more complex products (>2e\(^-\)) (a zero gap anode with a GDE cathode flow cell can achieve the next highest energy efficiencies, (Figure 6(c)). For example, ethylene formation at 65–75% FE achieved...
20% cell efficiency with a remarkable rate of up to 1100 mA cm\(^{-2}\) \citep{93}. However, this system was demonstrated at pH 15, raising the question of how mitigation of carbonate formation would affect the system economics. Alternatively, for longevity, would it be better to develop catalysts and electrodes capable of achieving high FEs at near neutral conditions?

4.3 Future Perspectives

Much emphasis has been put on catalyst development in this area and with new materials and structures coming through, this is still an important part of development, especially for the more obscure molecules (methanol, C3+). However, some target molecules such as CO, formate and ethylene have shown good FEs at close to industrially relevant current densities. In these systems the questions of focus need to be: how the electrodes or cells can be scaled up, what degradation routes can be mitigated for longer running times \citep{117}, how production costs can be driven lower by increasing cell efficiencies and how conversion efficiencies can be driven up to reduce additional separation steps afterwards.

Finally, the integration of these reactions needs to be considered in complete processes as to whether it is coupled with a CO\(_2\) source to create a fuel in one step (formate, methanol, ethanol or propanol) or whether it is integrated into a multistep process.

This could be multiple electrochemical steps (recent studies have shown ethanol may be formed from CO at a higher yield \citep{118}) or coupling electrochemical to thermochemical or biochemical, for example an electrochemical step to CO is further upscaled to longer chain hydrocarbons through FT \citep{119} or an electrochemical step to formate is then fed to a biocatalyst to form isobutanol and 3-methyl-1-butanol \citep{120}. These ideas and how processes may be integrated are expanded on in the discussion section in Part II \citep{121}.

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