An overview of CO₂ electroreduction into hydrocarbons and liquid fuels on nanostructured copper catalysts

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ABSTRACT

The increasing atmospheric levels of carbon dioxide (CO₂) must be controlled or better reverted to avoid undesirable climate changes. The electrochemical reduction of CO₂ into hydrocarbons is the best approach to solve this problem because it will recycle the ‘spent’ CO₂, known as carbon neutral cycle, and will probably be able to remit the energy crises. Nanostructured copper is a novel material known for the efficient and selective reduction of CO₂ into hydrocarbons. This review attempts to summarize the recent development of enlarged surface area nanostructured copper for the efficient reduction of CO₂ into hydrocarbons using renewable energy resources at low overpotentials. The effects of different reaction conditions (e.g. applied potential, CO₂ concentration and electrode surface) on the products and some relationships between these conditions and products are discussed here. Latest achievements in the CO₂ electroreduction technology, remaining challenges and perspective research directions for practical applications are also presented.

1. Introduction

Carbon dioxide (CO₂) is the most notorious greenhouse gas and its emissions into the atmosphere need to be drastically reduced to overcome the unpleasant effects of climate change and global warming (1–3). Two major approaches to overcome this issue are: (1) to switch from fossil fuel products to renewable energy resources such as water, wind and solar; however, the fraction of energy that can be obtained from these renewable energy resources is limited to 30% due to their intermittent nature; (2) to convert the captured CO₂ from fossil fuel power plants into useful economic chemicals and liquid fuels (4–9). Work has been done to look for synthesizing specialty chemicals such as formate and urea (10–12). However, the decrease in the level of atmospheric CO₂ on a large scale might be obtained by synthesizing fuels. In this world of decreasing fossil fuel resources and increasing energy demands, CO₂ conversion into low carbon liquid fuels seems to be the most attractive and promising solution.

The efficient, sustainable, low-toxic and large scale production of liquid fuels and higher hydrocarbons from renewable sources is one of the major challenges of advanced modern chemistry (13). In these carbon-based energy cycles, energy from renewable or nuclear power would be used to synthesize fuels from captured CO₂, which, when used, would not release additional CO₂ to the atmosphere (i.e. CO₂ neutral cycles). As such, these
systems such as catalysis and energy conversion/storage and promising potential for various typical applications, over the last decade due to their intriguing properties nanostructured materials, have attracted huge attention one possible tool to deal with global warming.

vehicles as enlarged speci- good yields) (densation of water to shift the equilibrium and achieve reduction of CO2 to hydrocarbons would be more efficient, simpler and time saving. An excellent finding along this road was the synthesis of hydrocarbons from direct reduction of CO2 with good current efficiency (up to 69% at 0°C and current density (5–10 mA cm−2) at a copper foil electrode, reported by Hori's group (18,19). Although this study could not lead to the production of a pure hydrocarbon product, a surprising range of hydrocarbons is formed. If the selectivity can be improved, the gaseous products blend (methane, hydrogen, ethylene and CO) would be very close to ‘hythane’, a clean burning hydrogen/natural gas mix that has been proposed as an alternative fuel for existing vehicles (20). Thus these reactions are of great interest as one possible tool to deal with global warming.

Nanostructured metals, a representative class of nanostructured materials, have attracted huge attention over the last decade due to their intriguing properties and promising potential for various typical applications such as catalysis and energy conversion/storage systems (21–29). Due to their unique properties, such as enlarged specific surface area and 2- and 3-dimensional interpenetrating structures, nanostructured metals can provide easy diffusion pathways to the substrate to access the electrolyte ions and a large number of active sites for the catalyst, leading to a faster reaction with high efficiency (20–22). Recently, a very promising nanostructured material, namely, copper foam with hierarchical porosity, was reported for the reduction of CO2 with high rate and selectivity for hydrocarbons (33). An outstanding discovery along this way, reported by Kanam’s group (34), was the use of oxide-derived nanos- tructured copper for the reduction of carbon monoxide (CO) into hydrocarbons and liquid fuels at low overpo- tentials with high Faraday efficiencies. They reported the production of oxygenates from the CO reduction with high Faraday efficiency. A Faraday efficiency of up to 57% was obtained for multi-carbon oxygenates on oxide-derived Cu electrode, with ethanol as the major product (42.9%), at −0.3 V vs. RHE (reversible hydrogen electrode) (34). Main products formed during the electro- reduction of CO2 at various nanostructured copper electrodes include formic acid, methane, CO, ethylene, ethanol, acetate, propylene and propanol.

The aim of this review is to focus on nanostructured copper-based catalysts for the electrochemical reduction of CO2 into hydrocarbons and liquid fuels, along with the effect of different parameters on the synthesis of products which would help to better understand the reaction mechanism. It also presents the current status, remaining challenges and future opportunities for reduction of CO2 into useful products using renewable energy.

2. Review

2.1. Background

The production of hydrocarbons and liquid fuels from electrochemical reduction of CO2 has been the subject of various investigations because CO2 is the huge and sustainable carbon feedstock and its conversion into hydrocarbons and liquid fuels could provide an incentive for the CO2 capture (35,36). However, efficient and durable electrocatalysts for the electoreduction of CO2 and its derivatives into desirable fuels are not available at the present (37–39). Many catalysts can reduce the CO2 to carbon monoxide (CO) (33, 40–43) but the synthesis of liquid fuels requires that CO should be further reduced by using H2O as H+ ion source. CO is a derivative of CO2 which acts as an intermediate during the production of hydrocarbons. Although the conversion mechanism of CO2 to liquid fuels is not very clear at present but it is widely accepted that CO2 is first reduced to CO and then it is further converted to alcohols and other hydrocarbons through multistep electron transfer pathways. Earlier studies have found that CO reduction on Cu results in similar products as obtained from CO2 reduction, proposing that CO was an inter- mediate in the reduction of CO2 (44–46).

Since the discovery of Hori et al. in 1985, copper has been known as a good catalyst for the electrochemical conversion of CO2/CO to hydrocarbons (18). But in bulk form its efficiency and selectivity for higher hydrocar- bons and liquid fuels are far too low to fulfill commercial applications requirements. A mixture of compounds is produced on the polycrystalline Cu foil in CO saturated aqueous solutions, which at low overpotentials are dominated by H2 and at high overpotentials by the CO and HCO2, and by multi-carbon oxygenates and hydrocarbons at very extreme potentials (47,48). Particularly, H2O reduction to H2 outcompetes CO reduction on the copper electrodes unless extreme overpotentials are applied, at which gaseous hydrocarbons are the major products of CO2 reduction (42,43). Efficient catalysts,
therefore, for reducing CO₂ and its derivatives into a desirable fuel are highly required.

2.2. CO₂ reduction on nanostructured copper

Nanostructured copper has been reported as an exclusive novel material for the electrochemical reduction of CO₂ into hydrocarbons with high Faraday efficiency and selectivity (33,34,42,49–53). The onset potential for the reduction of CO₂ at porous copper foam was −1.0 V vs. Ag/AgCl with the formation of formic acid (HCOOH) initially (Figure 1). The Faraday efficiency of HCOOH rises from 4% to 26% at −1.1 V on nanostructured copper, which is appreciably higher than that on smooth copper (i.e. <1% at −1.1 V). This value increases to 37% at −1.5 V, which is the highest value of Faraday efficiency reported to date for HCOOH at a copper electrode (33). Furthermore, the production of propylene has been observed for the first time on a high surface area nanostructured copper foam electrode from CO₂ reduction (Figure 1).

The main primary reactions occurring during the electroreduction of CO₂ at a copper electrode are given below. A series of steps (1–6) are predicted for the electroreduction of CO₂ at the copper electrode (33). The asterisk (*) in any reaction indicates either a surface bound specie or a vacant active site.

\[
\begin{align*}
\text{CO}_2 + H^+ + e^- & \rightarrow HCOO^-(F\text{-intermediate pathway}), \\
\text{CO}_2 + H^+ + e^- & \rightarrow COOH^-(C\text{-intermediate pathway}), \\
HCOO^-/HCOOH^+ + H^+ + e^- & \rightarrow HCOOH^*, \\
HCOOH^+ & \rightarrow HCOOH + *, \\
COOH^+ + H^+ + e^- & \rightarrow C^0^+ + H_2O, \\
C^0^+ + H^+ + e^- & \rightarrow CHO^*, \\
& \rightarrow H^*, \\
H^+ + H^+ + e^- & \rightarrow H_2 + 2*, \\
2H^+ + 2e^- & \rightarrow H_2.
\end{align*}
\]

From the above reaction steps we can conclude the complete reactions for the formation of hydrocarbons and liquid fuels.

\[
\begin{align*}
\text{CO}_2 + 2H^+ + 2e^- & \rightleftharpoons CO + H_2O, \\
\text{CO}_2 + 2H^+ + 2e^- & \rightleftharpoons HCOOH, \\
\text{CO}_2 + 6H^+ + 6e^- & \rightleftharpoons CH_3OH + H_2O, \\
\text{CO}_2 + 8H^+ + 8e^- & \rightleftharpoons H_4 + 2H_2O, \\
2\text{CO}_2 + 12H^+ + 12e^- & \rightleftharpoons C_2H_5OH + 3H_2O, \\
2\text{CO}_2 + 12H^+ + 12e^- & \rightleftharpoons C_2H_4 + 4H_2O, \\
3\text{CO}_2 + 18H^+ + 12e^- & \rightleftharpoons C_3H_6 + 6H_2O, \\
2H^+ + 2e^- & \rightleftharpoons H_2.
\end{align*}
\]

The formation of HCOOH, CO and alcohols during the electroreduction of CO₂ has been reported for various Cu file electrodes; however, the porous copper nanofoam was the only catalyst that could generate propylene in detectable quantities. Although propylene has been measured at very low yields on copper nanofoam, it has not been observed on any other copper electrodes reported to date (33). The production of ethylene and propylene suggested that the porous copper foam could provide both the nanostructured surfaces and cavities that promote the reaction between CO₂ and hydrogen to produce the higher hydrocarbons (ethylene
of CO₂ electroreduction on copper nanofoam might be enlarged Faraday efficiency based on the observation of the following points:

1. Enlarged Faraday efficiency of formate at all potentials.
2. Reduced Faraday efficiency of CO and methane (CH₄).
3. Formation of saturated hydrocarbons, for example, C₂H₆.
4. Generation of novel C₃ hydrocarbons, such as C₃H₆.

Insight into the importance of points (1)–(3) was provided by Norskov et al. (56,57) in detail. They reported the detailed description of chemical processes occurring during the CO₂ electroreduction at the copper–water interface. Finally, point (4), the generation of novel C₃-hydrocarbons, namely propylene, might be caused by the hierarchical porous structure of copper nanofoam (33). The production of saturated hydrocarbons such as ethane and C₃ products such as propylene on hierarchical porous copper foams suggested that the mechanism of CO₂ electroreduction on copper nanofoam might be changed, as these products were not observed on a smooth copper surface by previous studies. The generation of the saturated hydrocarbons and C₃-products may be caused by the hierarchical porous structure of the copper foam because the residence time of the various intermediates within these confined spaces of pores may increase, allowing for the generation of products that were not observed on smooth copper electrodes. The idea that nanoporous electrodes favor the reaction pathways that are different from those observed at smooth electrodes via a confinement mechanism has been studied in detail in the electroreduction of O₂ at nanoporous Pt electrodes (27,58).

Nanostructured cuprous oxide (Cu₂O) has been reported as one of the promising nanostructured electrode materials for the efficient and selective production of ethylene from CO₂ electroreduction. Koper et al. (32) reported on monitoring the catalytic selectivity of the hydrocarbons produced from the CO₂ electroreduction on the cuprous oxide (Cu₂O)-derived Cu nanoparticles (NPs). Cu₂O films orientated in the [100] direction produced ethylene with good selectivity as compared to the [111] and [100] orientated films. However, after the start of the electrochemical process the selectivity was found to be highly dependent on initial Cu₂O film thickness. A good ethylene to methane ratio of ~8–12 was observed for thick Cu₂O films and a very high Faraday efficiency of up to 40% was noticed for ethylene production at thicker Cu₂O films. Yeo et al. (59) described the selective and tunable production of ethylene and ethanol from CO₂ reduction at the Cu₂O electrode. They demonstrated that by tuning the Cu₂O film thickness, Faraday efficiencies of 34–39% for ethylene and 9–16% for ethanol, and ethylene to methane ratio of up to ~100 can be achieved. The electroreduction of CO₂ into desired hydrocarbons was found to be highly dependent on the population of edges and steps on the catalyst. Lee et al. (60) described the selective production of ethylene from CO₂ electroreduction at Cu₂O electrodeposited on a carbon electrode. They demonstrated a very stable Cu₂O catalyst which remained intact upon prolonged electroreduction of CO₂ at low overpotentials, exhibiting a high Faraday efficiency of over 20% for the ethylene formation. These studies illustrate that electroreduction of CO₂ on the Cu₂O electrode produces ethylene primarily and its Faraday efficiency depends on the thickness and nanostructure of the Cu₂O electrode. In addition, selectivity of the hydrocarbons produced from electroreduction of CO₂ can be adjusted by optimizing the nanostructure of the electrode material.

Recently, Alivisatos et al. (49) explained well the effect of structural morphology of nanostructured copper on the selectivity of the products obtained from CO₂ electroreduction. They described that copper NPs supported on a glassy carbon electrode (n-Cu/C) could achieve up to four times greater current densities for methane production as compared to copper foil electrodes. The n-Cu/C electrode exhibited the highest Faraday efficiency for methanation reported to date (80%). Alivisatos further suggested that there were many morphological, structural and chemical differences between the mentioned copper NPs and copper foil electrodes, which could be responsible for the enlarged Faraday efficiency of methanation. The thickness of initially evaporated films had a dramatic effect on the Faraday efficiency for methanation. The relatively thin films (Figure 2(a)) produced isolated nanoscale aggregates upon polarization on the electrodes (Figure 2(b)) and these electrodes had high yield of methanation (Figure 2(e)). On the other hand,
highly connected networks of fused NPs (Figure 2(d)), which resemble a polycrystalline foil, were produced by the polarization of thicker films (Figure 2(c)) and these electrodes exhibited low Faraday efficiencies for methanation (Figure 2(e)) (49). This suggests that more isolated NPs expose catalytic sites that are more effective for methanation, which were lost as they fused to form dense aggregates. This investigation explained the reason behind the lack of enlarged methanation yields from dense films of copper NPs studied by previous researchers (50, 61). These results demonstrated a continuum of catalytic behavior that exists between electrodes which exhibit nanoparticle-like and foil-like behavior. Thus, this behavior can be systematically tuned by adjusting the mass loading of copper on glassy carbon (Figure 2(e)). A previous systematic study of CO₂ reduction at single crystal electrodes also demonstrated similar concepts that the introduction of a particular step-edge present on a (210) single crystal can enhance methanation yield (52).

Strasser et al. (51) studied the effect of particle size during the catalytic electroreduction of CO₂ at size-controlled copper NPs. With decrease in the particle size (particularly below 5 nm) the catalytic activity and selectivity for H₂ and CO increased dramatically. The selectivity for hydrocarbons was highly decreased. Changes in the number of low-coordinated surface sites and their stronger chemisorption were related to surging H₂ and CO selectivities, higher catalytic activity and smaller hydrocarbon selectivity. Their presented activity-selectivity-size relationships could provide novel insights into the CO₂ electroreduction reactions on nanoscale surfaces.

Figure 3 describes the dependence of overall catalytic activity of CO₂ reduction on particle size at two different electrode potentials, \( E = -1.1 \) V/RHE and \( E = -1.0 \) V/RHE (1). The graphs compare the overall activity of bulk Cu and Cu NPs down to about 5 nm, after which a dramatic trend toward higher catalytic activity with smaller Cu NPs becomes evident. The smallest Cu NP catalyst (~2 nm) displayed a 100% enlargement in Faradaic current density (~48 mA/cm²), while the 2.3 nm NP catalyst showed 50% increment in activity compared to the Cu foil.

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**Figure 2.** Continuum of catalytic behavior between nanoparticle-like and foil-like electrodes: 3 nm evaporated copper film (a) prior to and (b) following polarization at \(-1.25 \) V/RHE for 10 min, and 15 nm evaporated copper film (c) prior to and (d) following polarization at \(-1.25 \) V for 10 min. (e) Methanation Faradaic efficiency and gravimetric methanation current as a function of evaporated copper film thickness from which it is evident that thin evaporated films behave like thin-Cu/C electrodes while thick evaporated films behave like copper foils. Reprinted with permission from ref. 49. Copyright © 2014 American Chemical Society.

**Figure 3.** Particle size effect during catalytic CO₂ electroreduction. The Faradaic current densities at \(-1.1 \) and \(-1.0 \) V/RHE are plotted against the size of the Cu NP catalysts. The current densities have been normalized by the Cu particle surface area after subtraction of the glassy carbon background signal. Error bars indicate scatter in particle size distributions. Lines are guides to the eye. Data of a Cu foil electrode (‘foil’) are inserted as reference. Conditions: 0.1 M KHCO₃, pH = 6.8, 25°C. Reprinted with permission from ref. 51. Copyright © 2014 American Chemical Society.
foil electrode. The observed trend illustrates a dramatic activity-enhancing size effect of nanoscale spherical Cu surface during CO₂ reduction.

It is well known that NP size effects basically originate from size-dependent surface metal atomic coordination number and its corresponding surface electronic structure (51). That is why a 3-D particle model and its corresponding coordination structure (Figure 4) are well suited to help understand particle size effects. It is explained as follows.

The smallest Cu NPs within the size range of about 2 nm showed a dramatic increase in overall catalytic activity, which is attributed to the high ratio of low-coordinated surface atoms (CN < 8), starting as low as CN = 5 for NP diameters below 4 nm (Figure 4(b)). In this size regime, particle size effects are often referred to as ‘catalytic finite size effects’, and small variations in size induce drastic changes in the NP’s electronic structure, while quantum effects may become non-negligible (62,63). Following the arguments on stepped surfaces, step and kink atoms of Cu NPs with such low CNs are expected to exhibit stronger chemisorption of CO₂, CO, atomic H and COₓHᵧ as compared to larger particles or bulk Cu surfaces.

For Cu NPs in the intermediate size range (5–18 nm), the populations of surface atoms with CN = 8 and 9 amount to about 12% and 20%, respectively (Figure 4(b)), and remain surprisingly constant over the entire intermediate size range. These population numbers are significantly smaller compared to those found on low-index smooth extended surfaces, such as the (100), (111) or (211) surfaces. With methane and ethylene forming preferentially on the (111) (CN = 9) and (100) (CN = 8) sites, respectively, changes in the relative populations of the (111) and (100) facets provide a plausible explanation for both the sudden steep drop in faradaic selectivities between Cu bulk surfaces and Cu NPs, as well as the selectivity plateau between 2 and 15 nm discernible in Figure 4 (51).

Very recently, Verdaguer-Casadevall et al. (64) reported an interesting CO reduction on another oxide-derived Cu electrode. CO electroreduction activity on oxide-derived Cu (OD-Cu) was found to be correlated with metastable surface features that bind CO strongly. OD-Cu electrodes prepared by H₂ reduction of Cu₂O precursors reduce CO to acetate and ethanol with nearly 50% Faraday efficiency at moderate overpotentials. They proposed that the active sites for CO reduction on OD-Cu surfaces were strong CO-binding sites supported by grain boundaries.

The type of products formed during CO₂ electroreduction is significantly impacted by the electrolytes used, potentials applied and the morphology and surface geometry of the copper surfaces. Table 1 gives an overview of Faraday efficiencies (%) of products obtained from CO₂ reduction on various copper catalysts.

### 2.3. Reaction pathways and intermediates

CO and formate are formed initially before the production of hydrocarbons at higher cathodic potentials. Copper NPs prepared by traditional vapor condensation produce about 96% CO from the reduction of CO₂ (53). The reason might be that CO is produced before the production of alcohols. Although the conversion mechanism of CO₂ to liquid fuels is not very clear at present, it is widely accepted that CO₂ is first reduced to CO and then further converted to alcohols and other hydrocarbons through multistep electron transfer pathways. Earlier studies have found that CO reduction on Cu results in similar products as obtained from CO₂ reduction, proposing that CO was an intermediate in the reduction of CO₂ (45,46). Further reactions of formate do not produce any measurable products (65).
Two voltage-dependent pathways were predicted for the electrochemical reduction of CO₂ at a copper electrode (56,57,66).

1. The formate (OCHO) or F-intermediate pathway
2. The carboxyl (COOH) or C-intermediate pathway

The F-intermediate pathway leads exclusively to formic acid and the C-intermediate pathway yields formic acid and high-order hydrocarbons. Calculations of the products obtained from both pathways have been performed on the (111), (100) and (211) surfaces of copper. The F-intermediate pathway dominates on the (111) and (100) surfaces, because it incurs the lowest change in free energy of the two pathways (56). It was proposed that if the (100) and (200) surfaces of copper are assumed to be equivalent in density functional theory calculations, production of HCOOH via the F-intermediate pathway would be enhanced at copper nanofoam as 22% more of the (200) surface was observed comparatively (33).

These studies clearly show that during CO₂ reduction the electrode surface is dominated by adsorbed CO which acts as an intermediate during the production of hydrocarbons. The second point was well presented in the work of Smith et al. (67), where saturated solutions of both CO₂ and CO showed similar spectra. Due to high coverage of CO during CO₂ reduction, it was proposed that adsorbed CO reduction was the rate-determining step for the overall reaction to hydrocarbons’ formation. Therefore, many studies have been carried out on the reduction of CO as this has an advantage of only a few reaction steps to be considered (34,64,66,68–70).

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Table 1. An overview of Faraday efficiencies (%) of products obtained from CO₂ electroreduction on various copper catalysts.

| Catalyst                  | Electrolyte | Experimental conditions | C₂H₄ | C₂H₅OH | C₂H₆ | CO | CH₄ | Formic acid | Other | C₂H₄/CH₄ |
|---------------------------|-------------|-------------------------|------|--------|------|----|-----|-------------|-------|----------|
| Polycrystalline Cu (47)   | 0.1 M KHCO₃ | −5 mA/cm²               | 30.1 | 6.9    | NR   | 2.0 | 29.4 | 9.7         | 3.0   | 1.0      |
| Polycrystalline Cu (48)   | 0.1 M KHCO₃ | −1.05 V vs. RHE         | 26.0 | 9.8    | NR   | 1.1 | 24.4 | 2.1         | 4.8   | 1.1      |
| Cu(100) (53)              | 0.1 M KHCO₃ | −5 mA/cm²               | 40.4 | 9.7    | NR   | 0.9 | 30.4 | 3.0         | 7.7   | 1.3      |
| Cu(Si-4f)100 × (111) (55) | 0.1 M KHCO₃ | −5 mA/cm²               | 50.0 | 7.4    | NR   | 1.1 | 5.0  | 4.6         | 14.1  | 10       |
| Cu mesocrystals (78)      | 0.1 M KHCO₃ | −0.99 V vs. RHE         | 27.2 | NR    | NR   | 0.55| 1.47 | 4.3         | NR    | 18       |
| Cu-halide confined mesh (79) | 3.0 M KX | −2.4 V vs. Ag/AgCl       | 60.5–79.5 | 1.6–1.9 | 0.8–1.8 | 2.8 | 4.3–6.6 | 0.1–0.7 | 0.1–0.6 | 9–17     |
| Electrodeposited Cu$_{2}$O (32) | 0.1 M KHCO₃ | −1.1 V vs. RHE         | 12–33 | NR | 0–9 | 1–3 | 0–4 | 22          | NR    | 8–12     |
| Electrodeposited Cu$_{2}$O (60) | 0.5 M KHCO₃ | −1.82 V vs. Ag/AgCl     | 26   | NR   | NR  | 6   | 1    | 8           | NR    | 26       |
| Cu NPs (50)               | 0.1 M KCO₃  | −1.1 V vs. RHE           | 36   | NR   | 34  | 1 | NR  | 36          |       |
| Oxide-derived Cu-1 (34)   | 0.1 M KOH   | −0.30 V vs. RHE          | 0.6  | 42.9  | 0   | NR  | NR  | 13.6        | NR    |          |
| Oxide-derived Cu-2 (34)   | 0.1 M KOH   | −0.30 V vs. RHE          | 0.6  | 42.9  | 0   | NR  | NR  | 13.6        | NR    |          |
| Cu nanofoam (33)          | 0.5 M KHCO₃ | −1.5 V vs. RHE           | 1.4  | NR   | 1.2 | 8–10| 0.2  | 37          | 0.2   | 7        |
| Cu/C (49)                 | 0.1 M NaHCO₃ | −1.25 V vs. RHE         | 4–6  | NR   | 0.1–1 | 80 | NR  | 0.06        |       |
| Cu NPs (57)               | 0.1 M KHCO₃ | −1.1 V vs. RHE           | 0–10 | NR | 20–25 | NR | NR  | 1.66        |       |
| Cu-O-derived Cu (80)      | 0.1 M KHCO₃ | −1.0 V vs. RHE           | 3.4–32.1 | 16.4 | 30.1 | 0–20 | NR | 20–28        | 0–5 | N.R      |
| Cu-O (59)                 | 0.1 M KHCO₃ | 0.99 V vs. RHE           | 34–39 | 9–16 | 0.04–0.4 | 2 | 37 | 1.0          | 0–100 |         |

Note: NR, not reported.
The activity of CO electroreduction was measured by using steady-state conditions through constant potential electrolysis in CO-saturated (1 atm) 0.1 M KOH solution at ambient temperature. Polycrystalline Cu foil had shown lower current densities and H2 was the only detectable product under these similar conditions. Another study has shown 22% total Faraday efficiency for CO reduction at very negative potentials (around −0.7 V vs. RHE) and its Faraday efficiency for oxygenates was only 7% (45). A maximum of 65% Faraday efficiency from CO reduction have been reported for polycrystalline copper foil at −0.9 V vs. RHE but Faraday efficiency of oxygenates was only 10% (70).

Higher geometric current densities were achieved with oxide-derived Cu than Cu NPs because of their roughness factor, which assisted the product quantification and comparison of their selectivities (Figure 5). Faraday efficiency was ≥94% for H2 at all potentials for the Cu NPs' electrode and small remaining current was related to ethanol, acetate and ethylene formation. On the other hand, a much higher tendency of CO reduction was shown by oxide-derived Cu electrodes. The oxide-derived Cu-1 electrode had shown a total CO reduction efficiency of 57% at −0.3 V vs. RHE, while oxide-derived Cu-2 had shown 48% Faraday efficiency at −0.4 V vs. RHE. These values decreased at more negative potentials because of catalyst reaching mass-transport-current density for reduction of CO. Oxide-derived Cu electrodes represented higher intrinsic CO reduction activity due to its higher Faraday efficiency as compared to Cu NPs (54). The detailed mechanism can be observed vividly in Figure 6. It is suggested that CO2 is first converted to CO (ads) active species at copper or possibly at another electrode and binds to the catalyst. This CO (ads) may dimerize in the presence of an alkaline media and form C2O2 (ads). The hydrogenation process of these species would produce CH2CHO (ads). Two pathways originate from this intermediate toward the formation of ethylene and ethanol. (1) The hydrogenation of CH2 group leads to the formation of acetaldehyde, which is ultimately reduced to ethanol. (2) The hydrogenation of C in the carbonyl group leads to the formation of ethylene and O (ads) which quickly forms water.

Electrolysis data (Figure 7) give some insights into the CO reduction mechanism on oxide-derived Cu. It is indicated by the absence of C1 products that C–C coupling is very rapid when the CO reduction starts (73) or maybe initial e− transfer is coupled to the C–C bond formation between a CO from solution and surface bound CO (69). It is estimated that acetate formation results from the attack of HO− on a surface-bound ketene or some other carbonyl-containing intermediate after the formation of the C–C bond. This argument is supported by the formation of increased acetate observation when electrolysis is performed in a 1 M KOH solution (Figure 7) (34).

2.4. Influence of electrolyte, temperature and pressure

The Gouy–Chapman theory (58) describes the relationship between the Debye length of electrical double layer (EDL) and electrolyte concentration, where the increase in electrolyte concentration results in a decrease
in EDL thickness. At a critical value of electrolyte concentration, the EDL becomes thin enough that the electric field of adjacent pores does not overlap anymore. Instead, the electric field maps the exact shape of the pore and, hence, provides the extra surface area to participate in electrochemical reactions.

Chronoamperometric measurements in Figure 8 show that at a smooth copper electrode the current density gradually increases from 7 to 31 mA/cm² (~4.5X) with the increase of electrolyte concentration from 0.1 to 1 M KHCO₃. On the other hand, at copper nanofoam (60 s) the current density increases sharply from 10 to 82 mA/cm² (~8X) above a critical concentration of 0.5 M KHCO₃ (33). Thus these data show that nanoscale pores present inside the copper foam are only accessible at a concentration above 0.5 M KHCO₃ (i.e. at this point the thickness of the double layer is minimum). These 3-dimensional small electroactive areas enable the production of C₂ and C₃ products, for example, propylene, due to increase in the residence time of surface intermediates (33).

The reaction temperature also influences the product distribution from CO₂ reduction. It was reported in galvanostatic measurements being carried out over the range of 0–40°C that lower temperature resulted in a change in current density for formate, ethylene and methane. Current efficiencies for ethylene formation and hydrogen evolution were decreased and efficiency of methane was increased, reaching a value of 65% at 0°C (33).

It was confirmed by Kanan’s group (34) that geometric current densities of CO reduction increases with the increase of CO pressure. At potentials between −0.3 and −0.5 V the geometric current density was 1.8–2.4-fold higher at 2.4 atm of CO as compared to 1 atm CO (Figure 9). The Faraday efficiency for CO reduction was also significantly improved at potential E < −0.3 V under these conditions. These results point out that the practical current densities may be possibly obtained by further increasing the CO transport to catalyst.

An important factor to be considered during these reactions is the local concentration of pH and CO₂ at the electrode surface. Generation of OH⁻ ions or consumption of H⁺ ions during various reactions causes the increase of pH value. The local pH increased at current exceeding a value of 2 mA/cm². Likely, this will limit the hydrogen evolution at higher overpotentials. A lower CO₂ concentration will decrease the formation of CO and formate along with a quick drop in product recovery of CO, likely due to its further high reaction rate for the formation of CH₄ and C₂H₄ (74).

Koper et al. (74) investigated the effect of local pH on the electroreduction of CO and CO₂ at Cu (111) and Cu (100) single-crystal electrodes. The electrochemical reduction of CO resulted in the formation of methane as a main product on Cu (111) and ethylene on Cu (100). Considerable variations were observed for the formation of ethylene at different pH values. At pH 1, only a small fraction of ethylene was observed on Cu (100) while at pH 7 and 12 ethylene was formed in significant quantities starting at about −0.4 V vs. RHE. The onset potential for the formation of ethylene on Cu (100) shifted with change in pH, from −0.8 V at pH 2 to −0.3 V at pH 13. The results suggested that formation of ethylene was highly dependent on local pH, and shifted to less negative potentials with increasing pH. The effect of local pH on the reduction products of CO₂ was studied at pH 1 and 7. At Cu (111) no CO₂ reduction
product was observed at pH 1, while at pH 7 ethylene and methane formation showed similar potential dependence. At Cu (100) methane was selectively formed at pH 1, starting at about −0.55 V and at pH 7 ethylene was formed at lower potentials than that of methane formation. Hence, the formation of ethylene through CO₂ electroreduction at Cu (100) was strongly dependent on the local pH, with no detectable quantities at pH 1 to considerable amounts at pH 7.

3. Current status, remaining challenges and future opportunities

To make CO₂ reduction commercially applicable, it is highly required that highest Faraday efficiency, highest energetic efficiency and highest current density should be achieved for a single product. Currently, many reports have been presented for each of the CO₂ reduction products, exhibiting a high Faraday efficiency, high energetic efficiency or high current density, but combining all these figures of merit has been a challenge (45,47,48,70).

The catalysts for the selective production of various products from CO₂ reduction have been developed, but the catalysts that could exhibit low overpotentials (i.e. less than 0.2 V) combined with high current density (i.e. greater than 100 mA/cm²) required for commercial applications are still lacking. These catalysts can be developed by deep and fundamental studies focusing on the reaction mechanism occurring on the catalyst during CO₂ reduction, an area in which only a few reports are presented (75–77).

The low catalyst activity, selectivity and stability are major technological challenges behind the commercialization of CO₂ electroreduction into liquid fuels. To deal with these challenges, we propose some research directions for the future.

(1) Improvement in the catalytic activity and stability of electrocatalyst by exploring new materials. Almost all of the pure metals and their associated compounds have been studied as a catalyst material for CO₂ electroreduction; even some improvement has been achieved in catalytic activity, selectivity and stability but still these advances are not enough for commercial applications. Developing new materials, therefore, for required performance should be emphasized. We propose two important types of materials here: (i) composite materials and (ii) nanstructured materials. Composite materials, which are usually synthesized by the combination of different materials, should have different properties and catalytic performance than that of their individual parts because each of the individual parts in the composite experiences a synergistic effect on its properties. This effect comes from optimizing particle size, active sites, porosity, specific surface area, electron conductivity and protection from mechanical and chemical degradation. In this way, the obtained composites may have optimum catalytic activity, selectivity and stability in CO₂ electroreduction. Furthermore, nanostructured materials, such as nanoporous materials, nanoaerogels, nano-tubes/rods, nanoplates/sheets and so on, due to their unique properties – such as higher specific surface area, 2- and 3-dimensional structures – can offer easy pathways for electron/proton, leading to faster reaction kinetics, more efficient electrolyte ions contact and increased active sites for the catalytic process.

(2) Fundamental understanding of the mechanism and theoretical and experimental modeling. For designing, synthesizing and optimizing new catalysts to improve catalytic activity, selectivity and stability, a sufficient fundamental understanding of the mechanism by theoretical and experimental modeling is necessary. For example, the fundamental understanding of the CO₂ electroreduction mechanism and its relationship to the catalyst structure, composition and active sites, by using both theoretical calculations (calculations at the molecular/electronic level) and experimental techniques, is highly desired for developing new catalysts.

(3) Optimizing the electrode/reactor design for commercial applications. For the industrial-scale CO₂ electroreduction, important limitations are the catalyst degradation and slow transfer of CO₂ to the electrode surface, both of which might be related to the electrode/reactor design. It is widely accepted that catalyst degradation is related to the material itself but also related to the environment. Optimizing the electrode/reactor design, besides optimizing catalyst stability, to optimize the operating conditions is also highly important for better performance.

In summary, a significant key opportunity exists in the optimization of electrode structure and composition. Based on the study of different researchers, CO₂ electroreduction is very sensitive to the structure and composition of the materials. We believe that with further efforts focused on developing innovative composite materials and nanostructured materials to overcome the challenges of inadequate catalyst activity, selectivity and stability, CO₂ electroreduction will become commercially applicable in the near future.
4. Conclusion

Electroreduction of CO\textsubscript{2} to high-order hydrocarbons and low carbon fuels is a promising research and development subject for controlling the extortionate and environmentally unfavorable CO\textsubscript{2} emissions. It also presents the way to produce useful fuels to solve our decreasing energy issues. Nanostructured copper is a novel material for the production of liquid fuels from electroreduction of CO\textsubscript{2}. We believe that with continuous and substantial studies focused on developing innovative composites, nanostructured and nanoporous catalyst materials will overcome the challenges of catalytic activity, selectivity, stability and Faraday efficiency required for practical applications. We hope that with these successful studies CO\textsubscript{2} electroreduction technology will become commercially applicable in the near future.

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