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Cu-Based Electrocatalysts for Carbon Dioxide Conversion to Value-Added Chemicals

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Cu-Based Electrocatalysts for Carbon Dioxide Conversion to Value-Added Chemicals

Qingyang Li

**Problem Report submitted to
the Statler College of Engineering and Mineral Resources
at West Virginia University
in partial fulfillment of the requirements for the degree of
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in
Chemical Engineering**

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Efficiency and Selectivity; Pathway and Mechanism**

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ABSTRACT

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Qingyang Li

Massive usage of fossil fuel has been causing considerable emission of CO₂, which increases the temperature of the planet and greatly threatens human living environment, such as soil degradation, lower agricultural productivity, desertification, less biodiversity, fresh-water reduction, ocean acidification, ozone sphere destruction, etc. A number of technologies are being developed to reduce the CO₂ amount, however, all existing technologies except utilizing CO₂ as a feedstock, are hardly to essentially close the anthropogenic carbon loop. Currently, considering the economy and operability, electroreduction of CO₂ seems to be the most promising strategy to convert CO₂ to high value chemicals.

During the process of CO₂ electroreduction, Cu-based catalysts become the most popular because they meet the requirements of activating CO₂ and intermediates, suppression of hydrogen formation, and electron transportation. Herein, the factors that affect the Cu-based catalysts' performance, including morphology, particle sizes, presence of atomic-scale defects, surface roughness, residual oxygen atoms, and so on, have been surveyed and discussed. In addition, the most probable reaction pathways to synthesize the desirable C₂ products under different situations have been identified, which follow $*CO + *CO \rightarrow *COCO$, $*CO + *COH \rightarrow C_2$, $*CO + *CHO \rightarrow C_2$ and $*COH \rightarrow *CH_2 \rightarrow C_2$. This report will benefit the design and optimization of Cu-based catalysts for the conversion of CO₂ to high value chemicals with high efficiency and selectivity.

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List of abbreviations (Alphabetical):

Abbreviation	Full Name
ADF	Annular dark-field
DAT	3,5-diamino-1,2,4-triazole
DFT	Density functional theory
EDS/ EDX	Energy dispersive X-ray spectroscopy
EEL	Electron energy loss
FE	Faradaic efficiency
FT	Fischer-Tropsch
GCP	Global Carbon Project
HER	Hydrogen evolution reaction
Hupd	Hydrogen underpotential deposition
NA	Nanoalloys
NC	Nanocubes
NP	Nanoparticles
NPS	National Park Service
NS	Nanosheets
NW	Nanowires
OLEMS	Online electrochemical mass spectrometry
PorCu	Copper-porphyrin
RDS	Rate-determining steps
RHE	Reversible hydrogen electrode
SEM	Scanning electron microscope
SHE	Standard hydrogen electrode
STEM	Scanning transmission electron microscope
TEM	Transmission electron microscope
TPD-MS	Temperature Programmed Desorption Mass Spectrometry
TPR	Temperature programmed reduction
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

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Chapter 1. Introduction

Greenhouse gases are mainly composed of carbon dioxide (CO_2), carbon monoxide (CO), nitrogen oxides (NO_x), methane (CH_4) and fluorinated gases, making much contribution to sustain the earth's temperature for the reason that greenhouse gases can absorb thermal radiation from the earth's surface and then re-emits the radiation back to the earth (Figure 1.1). However, continuously increasing greenhouse gases have been dramatically increasing the temperature of our planet due to massive usage of fossil fuel and other industrial activities in which produced considerable emission of CO_2 , NO_x , hydrocarbons, CO , and so on (Figure 1.2). Rising temperature may cause soil degradation, lower agricultural productivity, desertification, less biodiversity, fresh-water reduction, ozone sphere destruction, etc. Excessive greenhouse gases also have a directly negative effect on human living environment, such as natural disasters, malnutrition, and increased mortality induced by heat wave [1-3].

Figure.1.1 Greater concentrations of greenhouse gases mean more solar radiation is trapped within the Earth's atmosphere, making temperatures rise. Source: W. Elder, NPS

Figure.1.2 Global average land-sea temperature anomaly relative to the 1961-1990 average temperature in degrees celsius (°C). Source: Hadley Center (Had CRUT4).

Notably, CO₂, accounting for nearly 77% of greenhouse gases, has extremely increased after industrial revolution and should be principally responsible for global warming [4,5]. Before industrial revolution, new-produced CO₂ can be consumed by plants to keep the concentration of CO₂ balanced. In recent years, it is clearly realized that the human-generated CO₂ greatly exceeds the threshold of nature's capability (Table1.1). It is reported by Global Carbon Project (GCP) that global CO₂ emission from burning fossil fuels, the culprit of CO₂ emission, increased by 2.7 percent in 2018, after a 1.6 percent increase in 2017.

Table 1.1. Increase of carbon dioxide in the atmosphere for the last 1000 years [2,3].

Year	Period (year)	Concentration (ppm)	Increase (ppm)	Increase rate (ppm/year)
1000-1800	800	270-280	10	0.01
1800-1950	150	280-310	30	0.2
1958-1975	17	315-330	15	0.9
1975-2002	27	330-370	40	1.5 (8 billion tons)
2002-2010	8	370-388	18	2.25 (12 billion tons)
2010-2018	8	388-407	19	2.38

In the past decades, people gradually realized the significance and urgency of controlling CO₂ concentration to prevent the Earth's temperature from continuously increasing. Though relative methods and research are conducted to solve those problems, the effect is limited and the CO₂ concentration continues to grow [6,7]. Therefore, many nations, especially those main emission countries, have issued more strict laws and taken more actions to reverse the situation. For example, in 2011, the US Department of Energy (DOE) invested \$106 million in various CO₂-utilization projects, and in 2018, DOE invested \$17.6 millions and \$44 millions in Technologies Capable of Reducing CO₂ Capture Cost and Energy Penalties, and Advanced Carbon Capture Technologies Projects, respectively. In addition, the European Union has set up a prize worths €1.5 million for a technology demonstrating viable CO₂ utilization in 2020. China is expected to invest \$4-5 billion in CO₂ recycling from main emission sources, such as coal, steel, cement and paper industries [8-10].

Based on the previous and current supports from society and governments, technologies are being developed and applied to further solve the problems. In the following chapters, these technologies will be discussed in detail.

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Chapter 2. Current technologies and on-going research for CO₂ treatment

Introduction

CO₂ is generated from both nature and human activities. Natural sources are composed of decomposition, ocean release and respiration, while human activities include cements and papers production, deforestation, and burning of fossil fuel, etc. Basically, there are two ways to control and even reduce the CO₂ concentration: 1) replacing the traditional fossil fuel, which accounts for 87 percent of all human-produced CO₂ emissions, with renewable clean energy, such as solar, wind and bioenergy; 2) capturing, sequestration and utilization of CO₂ [1-3]. Here, we will focus on the second method. Although the concentration of CO₂ has dramatically increased in past decades, its absolute concentration in the air is still low at about 0.04% [4-6]. Therefore, the first challenge is to capture diluted CO₂ in the air. After CO₂ is captured, it can be sequestered or utilized as a feedstock to produce chemicals or fuels.

2.1 Carbon dioxide capture

In order to utilize carbon dioxide, the first step is to capture it efficiently. In theory, CO₂ even at low concentration can be transported and injected underground, however, energy cost and other associated costs make this approach impractical [7-9]. Therefore, pure CO₂ needs to be produced for the purpose of transportation and storage. CO₂ capture requires the separation of CO₂ from other species contained in industrial gases, such as flue gas, synthetic gas, air, or raw natural gas [10,11]. These separation steps can be accomplished by physical or chemical solvents, filtration membranes, solid adsorbents, or cryogenic separation. There are two approaches to

collect CO₂ with high concentration: 1) capture it from the large emission factories, utility plant, steel and cement plants; 2) and collect it directly in the atmosphere [12,13].

2.1.1 Capture CO₂ from industrial sources

Basically, there are three different technologies that can be used to capture CO₂ from the large industrial sources as shown in Figure 2.1, including post-combustion, pre-combustion, and oxyfuel. Post-combustion approach separates CO₂ from the flue gas produced by the primary fuel combustion in the air [14-16]. In pre-combustion approach, fuel reacts with steam and air or oxygen first to produce syngas (CO and H₂). Then, CO is converted to CO₂ by further reaction with steam via water-gas-shift reaction, and H₂ is separated as fuel. In this process, a lot of work needs to be done in the early stage, but the separation is relatively easier in the later stage, and hydrogen can be utilized in many industrial processes. Oxy-fuel system uses oxygen to substitute air for primary combustion, producing flue gases dominated by water vapor and CO₂. This process requires the separation of oxygen from the air first. The flue gas produced by this method has a very high concentration of CO₂ [17-20]. It is economically feasible to capture CO₂ in power plants with post-combustion system under certain conditions. CO₂ separation from natural gas is a matured technology. The technology of pre-combustion has been widely used in the fertilizer manufacturing and hydrogen production industries.

Figure 2.1. Summary of CO₂ capture technologies [18].

Organic solvent and membrane are usually used to separate and capture CO₂. Normally, organic solvents, such as monoethanolamine (MEA) and ammonia, are considered as the most available and widely used technology. However, it is not reasonable to consider it as a sustainable technology for its high cost and difficulty in regeneration. Membrane technology will be one of the most promising technologies, because it is compact, modular, mobile, low cost and environment-friendly [21-25].

2.1.2 Capture CO₂ from atmosphere

Chemically scrubbing CO₂ directly from the ambient air is another technology for CO₂ capture [26]. Though it is costly and energy-intensive, it is still an attractive technology because its potential scale of deployment is enormous [27-29].

2. 2 CO₂ storage and sequestration

CO₂ sequestration is considered as a potential technology for large-scale reduction of CO₂ concentration in the air. The idea is to inject compressed CO₂ into the ground or ocean to store it there for a long period of time [30-32]. For oceanic fixation, liquid carbon dioxide is injected into the ocean at different depths via ocean pipelines or marine transportation vessels, allowing it to dissolve in water or form stable carbon dioxide lakes. On land, liquid carbon dioxide is injected into the underground formation where it is locked by water dissolution, physical adsorption or chemical reactions (Figure 2.2).

In 2013, the United States Geological Survey (USGS) released the first comprehensive, geologically-based probabilistic assessment for CO₂, showing a range of 2,400 to 3,700 metric gigatons of potential CO₂ storage in USA. In addition, assessment also proved that carbon dioxide can be successfully injected using today's engineering practices and technologies [33,34]. However, Geological and oceanic sequestration have significant disadvantages. For example, when CO₂ is injected into the ocean, it may lead to the acidification of seawater, endangering the ecosystem. In addition, there is a risk of leakage that could contaminate groundwater or endanger organisms after it is buried underground. In the past, sequestration of CO₂ in the underground was practiced for its convenience and low cost. However, in recent years, the social acceptance becomes lower and lower for the uncertainty and controversy [35,36].

Figure 2.2. CO₂ sequestration underground and in sea. Source: Reagan Smith Energy Solutions, INC.

2.3 CO₂ utilization

According to the report from Energy Information Administration (EIA), in the coming decades, energy consumption will increase continuously and fossil fuel still dominates the energy market, which means CO₂ emission will further threaten our lives (Figure 2.3). Closing material cycle is a fundamental principle of industrial ecology. Hence, the best way to avoid sustained CO₂ increase in the atmosphere is to keep the carbon balanced in biosphere [37-40]. Obviously, CO₂ utilization is more consistent with this principle than CO₂ sequestration. Basically, there are two ways to utilize CO₂: 1) use it “as is”; 2) used it as feedstock to synthesize fuels and chemicals.

Figure 2.3. World energy consumption tendency. Source: U.S. Energy Information Administration, International Energy Outlook 2017.

2.3.1 Use CO₂ “as is”

Every year, about 20 million tonnes of CO₂ are widely utilized in industries “as is” [41]. For example, it is used as shield gas in manufacturing and construction industries at a large scale. In food industry, people use it to prevent fungal and bacterial growth, carbonate soft drinks, beers and wine, de-cafeinate coffee, keep food fresh, etc [42,43]. In oilfield, engineers use CO₂ foam to enhance oil recovery. Interestingly, CO₂ can be captured to enhance the growth of plants as some studies have shown that increasing the concentration of CO₂ appropriately is beneficial to photosynthesis [44]. In addition, it is also used for neutralizing alkaline water, and producing fire extinguishers.

2.3.2 CO₂ is used as feedstock for chemical synthesis

Statistically, over 90% of commercially available organic chemicals are produced from crude oil. CO₂ conversion to organic chemicals will help reduce the emitted CO₂ in air and the consumption of petroleum. In reality, industry has made some progress in utilizing CO₂ as raw

materials to produce chemicals (Table 2.1). Two notable examples are salicylic acid and urea produced from CO₂ which account for approximately 60% of the total worldwide consumption.

Table 2.1. Major commodity chemicals currently synthesized from CO₂ on an industrial scale globally. First three groups data are cited from reference [45] and the other data are cited from reference [46].

Chemical	Production (ton)
Cyclic carbonates	80,000 in 2010
Salicylic acid	89,800 in 2013
Urea	164,000,000 in 2015
Polycarbonate (Asahi Kasei process)	605,000
Polypropylene carbonate	76,000
Acetylsalicylic acid	90,000
Methanol	4000

Thanks to the advances in technology, more and more methods for CO₂ utilization have been developed in recent decades. For example, since 2013, Calera has been using CO₂ to produce pure calcium carbonate, which is turned into fiber cement boards [47,48]. More research has being conducted to convert CO₂ to cyclic carbonates due to its rapid growth in the area of electrolytes for lithium ion batteries [49,50]. Another promising area is the production of polyols, which are used as the raw material for polymers to further produce adhesives, coatings, mattresses, insulation refrigerator, and so on.

2.3.3 CO₂ conversion to fuel

People have been debating the unmeaning topic for several decades when fossil energy will run out. First, it is hard to predict the amount of fossil fuel because it is subjected to many uncertain factors, such as the development of exploration and exploitation technology, and the

consumption rate. Second, the environment cannot enduringly tolerate the use of fossil as the main energy source and the energy configuration must be changed because fossil energy will inevitably cause global warming, acid rain, haze, and so on. Therefore, establishing a renewable carbon system will not only reduce CO₂ emissions, but also alleviate other pollution caused by fossil processing and transportation. Though tremendous work has been done to convert CO₂ to high-value products, it is impossible to essentially close the anthropogenic carbon loop. Because about 70% fossil fuel is combusted to generate energy while only 7% is used as chemical products according to the data from EIA (Figure 2.4). Therefore, to prevent continuous carbon accumulation in ecosphere, fossil fuel must be replaced by other energy without carbon emission, such as solar, wind and water.

Figure 2.4. Usage pattern of US fossil fuel. Source: U.S. Energy Information Administration, Monthly Energy Review.

Reduction of CO₂ to fuel has become the most promising strategy because it helps reduce the amount of CO₂ in air and CO₂ can work as an energy storage matrix where other energy can be stored and transported. At least six potential CO₂ conversion technologies are current topics to

realize 3E (efficiency, effect and economy) and implement on industrial scale. Some of them are close to commercialization, some are at the benchtop scale, and some have yet to be scientifically proven (Figure 2.5).

Figure 2.5. Proposed timeline of CO₂ utilization methods [54]. Note: the specific time ranges are based on extrapolation of timeline development of other disruptive technologies such as the advent of 3D printing, solar energy adoption, and electric vehicle development.

Electrocatalytic conversion of CO₂ is closest to commercialization [51-53]. Many startup and established companies, such as Opus-12, Mitsui Chemicals, Carbon Recycling International, and Carbon Electrocatalytic Recycling Toronto, are currently at the forefront to monetize the technology [54,55]. With the cost decrease of renewable energy, electrocatalysis will become more and more attractive [56].

However, CO₂ is extremely stable due to the strong C=O double bond with bonding energy of 750 kJ mol⁻¹ which is considerably larger than that of C-C (336 kJ mol⁻¹), C-O (327 kJ mol⁻¹), and C-H (411 kJ mol⁻¹) [57]. Significant energy is required to break the C=O bond. Meanwhile, it is very difficult to control the reaction paths and lots of products may be produced during the reduction process, increasing the difficulty in products separation (Table 2.3).

Table 2.3. Standard electrochemical potentials for CO₂ reduction [58].

Reduction potentials of CO ₂	E° [V] vs SHE at pH 7
$\text{CO}_2 + \text{e}^- \rightarrow \text{CO}_2^-$	-1.9
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}$	-0.61
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$	-0.52
$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_4 + 4\text{H}_2\text{O}$	-0.34
$\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{HCHO} + \text{H}_2\text{O}$	-0.51
$\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	-0.38
$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	-0.24
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	-0.42

The foreground of CO₂ reduction for commercial use is dependent on the development of highly efficient and selective catalysts with relatively low energy cost. In recent years, much progress have been made on catalyst to reduce the energy barrier and control reaction pathway [59,60]. In the coming chapter, we will focus on the most popular catalysts, Cu-based catalysts, and summarize the factors influencing their performance.

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Chapter 3. Recent advances in CO₂ reduction on copper-based electrocatalysts

Introduction

Electrocatalysis is one of the most promising approaches for its renewable and environmental friendly properties as well as it has the potential to sustain solar-fuel-based economy. Many valuable products, such as CO, formate, methanol, methane, ethanol and ethylene, can be produced via electrocatalysis, which can be directly or indirectly used in industrial processes. For example, ethanol can be blended in gasoline for auto-engines, and CO can be converted to many chemicals via Fischer-Tropsch synthesis. Although it possesses great potential, the application is seriously held back by its high overpotential, poor selectivity and low faradaic efficiency. Therefore, it is urgent to study the reaction mechanism and develop tailor-made electrocatalysts.

The design of electrocatalytic reactor is critical in CO₂ reduction. Though many kinds of reactor configurations have been developed to enhance CO₂ conversion, the working principle is similar (Scheme 3.1). Typically, there are four main components in a reactor, including anode, cathode, membrane and electrolyte. Specifically, H₂O is oxidized to O₂ spilling at the anode, while CO₂ is electrochemically reduced to produce CO and low carbon organic compounds on the cathode, such as CH₃OH, CH₃CH₂OH, C₂H₄ and CH₄. According to the statistical data, platinum is commonly used as anode, and KHCO₃ dominates electrolyte field [3]. Many studies have reported improvement on the performance of membrane. Currently, Nafion produced by Dupont is the most popular one [4,5]. Multitudinous metals and their derivatives, such as Cu, Zn,

Ag, Au, Co, Pd, Bi, etc., are used as cathode. Scheme 3.2 details the structure and components of an electrochemical reactor [2].

In this chapter, we will discuss the progress in Cu-based catalysts because Cu is the most researched catalyst having the potential to be commercialized.

Scheme 3.1. Schematic illustration of electrochemical reduction of CO_2 [1].

Scheme 3.2. A schematic drawing of the full electrochemical cell including a buffer layer with circulating liquid electrolyte [2].

The binding energies of CO^* and H^* ($*$ denotes a surface adsorption site) are used as the descriptors for the correlation between the electrocatalytic performance and the surface property of different metals. It seems weak binding strength of CO^* may cause massive CO formation because it is hard to absorb CO after it is formed on those metals, such as Au, Ag and Zn. While weak binding strength of H^* may cause high proportion of H_2 because it is hard to absorb H^* after it is formed on those metals, such as Ni and Pt. Among those metal catalysts, Cu possesses the intermediate binding strength to CO^* and does not have hydrogen underpotential deposition (H_{upd}). Those are the reason why copper is the only metal producing various hydrocarbons with relative high efficiency (Figure 3.1 and Table 3.1). Currently, Cu is the most commonly studied and may be the most suitable for large-scale application due to its cheap price and excellent catalytic property [3,4].

Figure 3.1. The binding energies of the intermediates, ΔE_{CO^*} and ΔE_{H^*} , ($\text{CO}^* = \text{CO}^*$, $\text{H}^* = \text{H}^*$) [3].

Table 3.1. Reported faradaic efficiencies of various products measured for the electroreduction of CO₂ in 0.1M KHCO₃ [4].

Electrode	Potential (V vs. SHE)	Current density (mA cm ⁻²)	Faradaic efficiency (%)							
			CH ₄	C ₂ H ₄	C ₂ H ₆ O ^b	C ₃ H ₈ O ^c	CO	HCOO ⁻	H ₂	Total
Pb	-1.63	5.0	0.0	0.0	0.0	0.0	0.0	97.4	5.0	102.4
Hg	-1.51	0.5	0.0	0.0	0.0	0.0	0.0	99.5	0.0	99.5
Tl	-1.60	5.0	0.0	0.0	0.0	0.0	0.0	95.1	6.2	101.3
In	-1.55	5.0	0.0	0.0	0.0	0.0	2.1	94.9	3.3	100.3
Sn	-1.48	5.0	0.0	0.0	0.0	0.0	7.1	88.4	4.6	100.1
Cd	-1.63	5.0	1.3	0.0	0.0	0.0	13.9	78.4	9.4	103.0
Bi	-1.56	1.2	-	-	-	-	-	77	-	-
Au	-1.14	5.0	0.0	0.0	0.0	0.0	87.1	0.7	10.2	98.0
Ag	-1.37	5.0	0.0	0.0	0.0	0.0	81.5	0.8	12.4	94.6
Zn	-1.54	5.0	0.0	0.0	0.0	0.0	79.4	6.1	9.9	95.4
Pd	-1.2	5.0	2.9	0.0	0.0	0.0	28.3	2.8	26.2	60.2
Ga	-1.24	5.0	0	0.0	0.0	0.0	23.2	0.0	79.0	102.0
Cu	-1.44	5.0	33.3	25.5	5.7	3.0	1.3	9.4	20.5	103.5
Ni	-1.48	5.0	1.8	0.1	0.0	0.0	0.0	1.4	88.9	92.4
Fe	-0.91	5.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	94.8
Pt	-1.07	5.0	0.0	0.0	0.0	0.0	0.0	0.1	95.7	95.8
Ti	-1.60	5.0	0.0	0.0	0.0	0.0	tr.	0.0	99.7	99.7

Though Cu looks like the best metal catalyst for electrocatalytic CO₂ reduction, its performance needs to be improved to achieve high efficiency and selectivity. As shown in Figure 3.2, under relative low potential of -0.75 V vs. RHE (Reversible Hydrogen Electrode), only H₂, CO and formate are produced [5]. According to previous research, the underlying reasons for high selectivity of Cu were related to local pH near electrode, morphology, particle sizes, the presence of atomic-scale defects, surface roughness, strains, and/or residual oxygen atoms in the catalysts, etc [6-9]. Experimental and computational results suggested that the active sites, chemical kinetics and transport effects greatly contributed to high efficiency and selectivity. Here, we summarize the factors influencing the performance of Cu-based catalysts.

Figure 3.2. Current efficiency for each product as a function of potential (left) and Tafel plot of the partial current going to each product (right), respectively [5].

3.1 Fabricated Cu as the only metal for CO₂ conversion

3.1.1 The effects of current and potential

In 2018, Dan Ren et al[10] conducted a survey of the current and potential for CO₂ conversion, which showed the selectivity of HCOO⁻/CO, C₂H₄, and CH₄ was greatly affected by current and potential as long as under the mass transport limitation of CO₂. Four Cu catalysts (metallic and oxide-derived) with different surface roughness were prepared via electrodeposition, termed as Cu-10, CuO-1, CuO-10, and CuO-60 with post-reduced roughness to be 1.4, 5, 48, and 186, respectively. The result showed that total current was positively related to the surface roughness and applied potential, while the maximum current for CO₂ reduction

was around -20 mA cm^{-2} when the total currents were around -40 mA cm^{-2} (Figure 3a). When the total current exceeded a particular value, the current density decreased and more H_2 was produced due to the low CO_2 concentration and buildup of OH^- near electrode (Figure 3b). It was proved that different energy barriers were the reason causing CO , HCOO^- , C_2H_4 , $\text{C}_2\text{H}_5\text{OH}$, and CH_4 at different potential windows (Figures 3.3d-e). The morphology of Cu catalysts affected not only catalytic active sites, but also roughness for limiting current density in the suitable potential window for different products [11,12].

Figure 3.3. a) Total geometric current density; b) current density for CO_2 reduction; c) faradaic efficiency of methane on Cu-10 and CuO-1; d) faradaic efficiency of ethylene and ethanol on CuO-1, CuO-10, and CuO-60 catalysts; and e) faradaic efficiency of carbon monoxide and formate on CuO-60 catalyst [10].

3.1.2 The effects of catalyst structure

According to literature reports, noble metals and ionic liquids were competent to selectively reduce CO_2 to CO with high selectivity at low current density [13]. Unfortunately, they were restricted for bulk application due to high cost. Inspired by solid oxide fuel cell and hollow fiber from nickel and stainless steel, Recep Kas et al [14] prepared Cu hollow fibers used for CO production. The Cu hollow fibers could be employed as both gas diffuser and cathode attributed to a defect-rich porous structure as well as extraordinary improvement in mass transport (Figure 3.4). The hydrogen evolution was suppressed while the current density was unprecedentedly high at low potentials. Hence, CO_2 was converted with total faradaic efficiencies up to 85% at overpotentials between 200 and 400 mV, and 75% CO faradaic efficiency was achieved at a potential of -0.4 V versus RHE [15], which showed excellent performance compared with other catalysts (Figure 3.5).

Figure 3.4. SEM images of Cu hollow fibers: a) outer surface, 50 mm; b) outer surface, 2 mm; c) cross-sectional of a perpendicularly broken, 100 mm; d) outer surface and cross-section in the parallel direction to the length, 50 mm, e) cross-sectional image of the Cu hollow fiber, 500 μm ; and f) Cu hollow fiber employed as an electrode at 20 mL min^{-1} gas flow [14].

Figure 3.5. Comparison of the performance of different electrodes on the basis of the partial current density with CO at variable potentials [14].

3.1.3 The effects of pH value

The pH value at the electrode/electrolyte interface is proved to greatly influence the selectivity of final products. High pH is prone to CO coupling which further produces C_2H_4 [16]. In order to further improve the selectivity of hydrocarbon products affected by pH, Cu nanowire was synthesized with different length and density (longer length was corresponding with higher density). Longer Cu nanowire electrode was always surrounded with higher pH electrolyte, because the HCO_3^- in electrolyte was hard to diffuse into the Cu NW arrays and the OH^- generated by CO_2 reduction was hard to diffuse out the Cu NW arrays (Figure 3.6). C_2H_4 accompanied with other products (e.g C_2H_6 and ethanol) were generated on relatively longer Cu nanowires [17]. The result was supported by previous conclusion that CO coupling step was favored at a high local pH near the catalyst surface [18]. It could be an efficient approach to systematically control products on Cu nanowire by varying Cu nanowire length and even pH of electrolyte.

Figure 3.6. a) Schematic illustration of the diffusion of electrolytes into Cu nanowire arrays; b and c) faradaic efficiency of various products at 8.1-μm-length Cu NW arrays and 3-μm-length Cu NW arrays, respectively [17].

3.1.4 The effects of particle size

It is well known that varying the size of the catalytically active species is another strategy to tune surface chemisorption and enhance catalytic activities and selectivity in many reactions, such as ammonia synthesis, hydrogenation, electrocatalytic CO oxidation [19,20]. In 2014, Rulle Reske et al [21] investigated the size effects of Cu nanoparticles (NP) on the CO_2 reduction activity and, in particular, on product selectivity. The results showed the particles from 2 to 15 nm caused unexpected selectivity and activity variation. Generally, Cu NP exhibited higher current densities as the size decreased, which meant smaller size may cause higher activity, especially when the size was smaller than 5 nm (Fig 3.7). However, high activity was not

equivalent to high selectivity. If CO and H₂ were the preferred products to serve as feedstock for gas-to-liquid reaction technologies, the smaller size of Cu nanoparticles may be the better choice, while size smaller than 5 nm should be avoided for hydrocarbon products. Here, it was deduced that small Cu size may cause strong bonding between intermediate reaction species (*CO and *H) and catalyst, inhibiting the mobility of CO and H to form hydrocarbon.

Figure 3.7. a) Linear sweep voltammetry and; b) composition of gaseous products of CO₂ reduction on Cu NP with different size [21].

3.1.5 The effects of subsurface oxygen

It has been reported by many groups that oxide-derived copper showed higher CO binding energy which changed the products of CO₂ reduction [22,23]. However, the mechanism of this phenomenon was not clear until Andre Eilert et al [24] proved the presence of oxygen and absence of oxide copper based on Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) and quasi in situ Electron Energy Loss Spectroscopy (EELS). In 2016, Andre Eilert et al exposed a polycrystalline copper to electrochemical oxidation-reduction cycles to prepare the catalyst. Results showed the new catalyst improved overall CO₂ reduction activity and product yield towards more ethylene versus methane (Fig3.8). It was proposed that residual subsurface oxygen

formed by oxidation-reduction cycles changed the electronic structure of the catalyst and created sites with higher carbon monoxide binding energy by reducing the σ -repulsion. Therefore, C-C bond formation was kinetically favored due to higher CO coverage on the catalyst [25,26].

Figure 3.8. a) Cyclic voltammogram of an oxidation-reduction cycle of Cu in 0.1 M KHCO_3 and 4 mM KCl; b and c) online electrochemical mass spectrometry results of CO_2 reduction with polycrystalline Cu (b) and Cu after an oxidation-reduction cycle (c) [24].

3.1.6 The effects of sulfur and surface defect

Atomic vacancy defects influence electrocatalytic performance by adjusting the electronic structure of neighboring atoms and consequently influence the energy barriers of the rate-limiting reaction intermediates [27,28]. A core-shell nanoparticles structure catalyst designated as $\text{Cu}_2\text{S-Cu-V}$ (where V denotes vacancy) was synthesized based on the theory that copper sulfide could provide a means to form stable surface defects and control the density of surface vacancies by introducing sulfur into the Cu structure (Figure 3.9). Due to the synergetic effect of Cu_2S core and the surface copper vacancies, the $\text{Cu}_2\text{S-Cu-V}$ played an excellent role in suppressing unwanted C_2 products and shifted product distribution towards alcohols [29].

Figure 3.9. Catalyst design and structural characterization. a) Schematic illustration of Cu₂S-Cu-V electrocatalyst design; b) TEM and c) EDS mapping of the original V-Cu₂S nanoparticles; d) EDS mapping; e) high-resolution TEM; f) EDS line scan and g) the ratio of Cu/S concentration of the reduced Cu₂S-Cu-V nanocatalysts after electrochemical reduction. V-Cu indicates Cu with surface vacancies [29].

3.2 Cu alloy catalysts

Previous work has demonstrated that electrochemical CO₂ reduction with a planar Cu foil as the catalyst will produce at least 16 different products in varying quantities, which require high energy consumption in product separation. Cu-based bimetallic catalysts have been recognized as another class catalysts for CO₂ electroreduction at lower overpotential. It possesses the ability to produce specific products by modulating the adsorption and desorption of key intermediates on the catalyst surface. In the past years, many published research reported to focus on developing bimetallic Cu-based catalysts. Recent research indicated that different pattern and distribution of the bimetallic catalyst impacted not only product distribution, but also the yield [30].

3.2.1 The selectivity to CH₄

Copper based catalysts are well known for the conversion of CO₂ to CO and other deep reduction products with relatively favorable efficiencies at room temperature. In 2018, 4% Cu-doped CeO₂ nanorods electrocatalyst was used for CH₄ production with a faradaic efficiency as high as 58% at -1.8V [31]. In this type of catalyst, copper was well dispersedly loaded on the CeO₂ at the single atomic/ionic level preventing the copper being oxidized and aggregating. There were up to three oxygen vacancies around each Cu site because of the substitution action of Cu (Figure 3.10). The synergetic effect of Cu, CeO and oxygen vacancy resulted in a highly effective catalytic site for electroreduction. The result also mentioned that the C-C banding was substantially prohibited on the catalyst due to atomic dispersion of the electrocatalytic Cu sites, dramatically enhancing CH₄ formation [32,33].

Figure 3.10. Theoretical calculations of the most stable structures of Cu-doped CeO_2 (110) and their effects on CO_2 activation [31].

3.2.2 The selectivity for syngas

Though Cu-based catalysts have excellent performance for CO_2 reduction, there are still two problems need to be solved, poor resistance to oxidation and selectivity. To solve the problems, an ultrathin $\text{Cu}/\text{Ni}(\text{OH})_2$ nanosheets catalyst was engineered using sodium formate as protector to prevent Cu being oxidized and $\text{Ni}(\text{OH})_2$ as supporter for preventing Cu nanosheets from being sintered during electrocatalysis (Figure 3.11A-E). Because the redox potential of HCOO^- was lower than Cu, HCOO^- suppressed oxidation of Cu similar to the cathodic protection in galvanized iron pipes. $\text{Cu}/\text{Ni}(\text{OH})_2$ exhibited both excellent CO_2 adsorption ability and superior charge transport kinetics. It was cost-effective, and the nanosheets provided a current density of 4.3 mA cm^{-2} with a CO Faradaic efficiency of 92% at a low overpotential of -0.39 V. Interestingly, syngas was the only products and the ratio of CO and H_2 was tunable by applying different potentials [34,35]. The high selectivity may be attributed to the following reasons: 1) $\text{Cu}/\text{Ni}(\text{OH})_2$ had excellent ability to absorb CO_2 while poor ability to absorb CO; 2) $\text{Cu}/\text{Ni}(\text{OH})_2$

exhibited a superior charge transport kinetics; 3) the existence of HCOO^- prevented the Cu from being oxidized; 4) the Cu was well dispersed (Figures 3.11 F, G).

Figure 3.11. A) TEM image of the Cu/Ni(OH)₂ nanosheets after being stored in air at room temperature for 90 days; B) XRD patterns of the nanosheets after storing in air at room temperature for 7 to 90 days; c) TPD-MS profiles of the Cu/Ni(OH)₂ nanosheets heated in vacuum, whereas the bottom shows relative ionization intensities of the main decomposition products at different temperatures, the top displays the accumulative ionization intensity (m/z, mass/charge ratio); D) FTIR spectrum of the nanosheets and E) adsorption model of formate on Cu (color codes: cyan, Cu; red, O; gray, C; white, H). F) STEM and G) EDX mapping images of the Cu/Ni(OH)₂ nanosheets [34].

When particle size was between 5 and 15 nm, Cu exhibited similar catalytic selectivity in hydrocarbon formation, while the catalytic performance and selectivity unexpectedly increased with decreasing Cu particle size when its size was below 5 nm. Meanwhile, previous work proved that finely controlled size of Pd displayed high Faradaic efficiency and current density for CO production. Here, Zhen Yin et al [36] synthesized the Cu-Pd bimetallic alloy with different ratio supported on carbon to produce CO. Pd₈₅Cu₁₅/C catalyst showed good activity and

selectivity (Figure 3.12) because the rate-determining steps of CO₂ absorption and CO desorption were improved while the H⁺ combination was inhibited due to synergistic effect of electronic effect and geometric effect.

Figure 3.12. CO₂ reduction activity over PdCu/C and Pd/C catalysts in CO₂-saturated 0.1 M KHCO₃ solution [36].

3.2.3 The selectivity for multiple-carbon products

Recently, many alloying catalysts have been synthesized to convert CO₂ to multiple-carbon products, especially oxygenated species such as alcohols, because these products are generally more valuable than their hydrocarbon counterparts and they are in liquid form under ambient conditions which simplify the subsequent processing, storage, and distribution [37].

CuPd nanoalloys

It was another challenge to evaluate the relationship between the atomic arrangements/ratios (Figure 3.13) and the performance of CO₂ reduction. Related studies [38] were conducted to elucidate the mechanism, showing the phase-separated bimetallic catalysts produced C₂

chemicals while the well-ordered catalysts favored the conversion of CO_2 to CH_4 . For the phase-separated catalysts, the Cu atoms structure may allow for favorable molecular distance and small steric hindrance for dimerizing $^*\text{CO}$ and $^*\text{COH}$ which were further converted to C_2 products. While for the ordered structure, Pd stabilized surface $^*\text{CHO}$ which were further converted to CH_4 . It was shown that electronic effect played less important role than geometric/structural effect which determined catalytic selectivity and activity, because Cu had much higher d-band position than PdCu. It was further proved that Cu had much better performance to produce C_2 than that of Pd (Figure 3.14). Based on a literature report, the orientation of intermediate toward the active sites influenced the reaction, similarly, different ratios of component in the bimetallic catalysts caused various orientations of the intermediate on the surface, therefore led to different selectivity [39].

Figure 3.13. a) Illustration of the prepared CuPd nanoalloys with different structures; b) XRD patterns of CuPd nanoalloys, Cu, Pd and CuPd alloys; c-e) high-resolution TEM images of Cu (red) and Pd (green) [38].

Figure 3.14. Faradaic efficiencies for a) CO; b) CH₄; c) C₂H₄; d) C₂H₅OH for catalysts with different Cu:Pd ratios: Cu, Cu₃Pd, CuPd, CuPd₃, and Pd [38].

CuZn nanoalloys

Among all products from the reduction of CO₂, ethanol is an attractive liquid fuel. However, due to the barrier of higher energy needed for C-C coupling, previously mentioned Cu nanostructure only produced ethanol with faradaic efficiency generally < 20 % while ethylene as the primary C₂ product [40]. Though heteroatoms have been added to Cu to improve selectivity between ethanol and ethylene, it is hard to realize both high partial current and high selectivity [41]. In order to overcome the shortcoming, ZnO was used to modify the CuO nanowires surface using atomic layer deposition (ALD) to improve selectivity. Compared to commonly used methods, such as electrodeposition, annealing or solution processing, ALD was flexible to adjust various bimetallic structures and/or the ratio between different metallic components. As a result, 48.6 % faradaic efficiency and 97 mA cm⁻² partial current density for C₂ liquids was achieved at -0.68 V. 32 % faradaic efficiency of ethanol was formed at -1.15 V and the partial current density increased from 7.5 mA cm⁻² on Cu to 10.5 mA cm⁻² on CuZn. According to the

systematic analysis of the electrocatalytic behavior, it was believed that the presence of Zn modified the binding energy of CO on Cu, which was combined with $\ast\text{CH}_3$ to form $\ast\text{COCH}_3$, a precursor of ethanol [42].

Scientists also propose to alloy Ag with Cu to bring their superiority into full play, because Ag is a highly selective catalyst for CO production while Cu possesses the capability to further reduce CO to more valued products [43,44]. CuAg nanoporous structure catalyst was synthesized using 3,5-diamino-1,2,4-triazole (DAT) as an inhibitor (Figure 3.15). Because of the existence of DAT, the nucleation of Cu or Ag was inhibited, and Cu and Ag were homogeneously mixed via electrodeposition. The catalyst exhibited excellent efficiency with about 60% C_2H_4 and 25% $\text{C}_2\text{H}_5\text{OH}$ at a relatively low applied potential (-0.7 V vs. RHE) and a high current density (300 mA cm^{-2}) [45]. According to previous research results [46], Cu_2O was mainly responsible for high yield of CH_3OH . It was deduced here that high selectivity towards C_2H_4 and $\text{C}_2\text{H}_5\text{OH}$ was because the incorporation of Ag into the alloy. In one aspect, Ag oxide could be reduced by Cu due to the formation enthalpies of Cu_2O (-169 kJ mol^{-1}) and Ag_2O (-31.1 kJ mol^{-1}); In another aspect, Cu was more likely to be oxygenated to Cu_2O because Cu atoms in the CuAg samples tended to carry a slightly positive charge. In 2018, Drew Higgins [47] prepared CuAg thin films with nonequilibrium Cu/Ag alloying for CO_2 reduction, further explaining why Ag could improve the selectivity to C_2 products. The results indicated that though the overall reduction activity decreased for CuAg versus Cu, Ag miscibility into Cu increased the activity and selectivity toward liquid carbonyl products likely due to the decreased surface binding energies of oxygen-containing intermediate species. Meanwhile, it was observed that the competing products of hydrocarbons and H_2 were significantly suppressed. Density functional theory (DFT) simulation suggested that Ag doped in Cu weakened the binding energy of $\ast\text{H}$ species, causing

the steadily decrease in activity and selectivity toward hydrocarbons and the H_2 when the ratio of Ag/Cu increased. The better understanding of the underlying mechanisms may further improve selectivity toward liquid carbonyl products.

Figure 3.15. a) XRD and b) XPS patterns of CuAg-poly (6% Ag) electrodeposited without DAT, Cu-wire (0% Ag) electrodeposited with DAT, and CuAg-wire (6% Ag) electrodeposited with DAT [45].

3.3 Organic Cu

It was reported that the hydrophobicity of electrode was regarded as a determinant on the selectivity of CO_2 reduction, because its submerged hydrophobic surfaces trapped appreciable amounts of gas at the nanoscale which facilitates CO_2 accumulation at the Cu-solution interface [48,49]. Inspired by the plastrons of diving bell spider composed of hydrophobic hairs that trapped air and thereby allowed the spider to respire under water, a hierarchically structured Cu dendrites electrode was synthesized with super hydrophobic surface generated by 1-octadecanethiol treatment (Figure 3.16). As a result, H_2 evolution was substantially suppressed from 71% faradaic efficiency to 10%, while CO_2 reduction was increased from 24% to 86%, of which C_2 products comprised 74% FE [50].

Figure 3.16. The illustration of a-b) wettable dendrite electrode and c-d) hydrophobic dendrite electrode for electroreduction [50].

Zhe Weng et al [51] synthesized a Cu centered organic catalyst in 2016, copper-porphyrin complex (copper(II)-5,10,15,20-tetrakis-(2,6-dihydroxyphenyl) porphyrin), called PorCu (Figure 3.17). It was used as a heterogeneous electrocatalyst for reducing CO_2 to hydrocarbons in aqueous media. At the point of -0.976 V , the partial current densities of CH_4 and C_2H_4 were 13.2 and 8.4 mA cm^{-2} , while the corresponding turnover frequencies were 4.3 and $1.8\text{ molecules site}^{-1}\text{ s}^{-1}$, respectively. The catalytic reaction rates for hydrocarbon products were higher than other reported molecular metal complex catalyst and most Cu based electrocatalysts at around $\sim -1\text{ V}$. It was considered the Cu center and OH groups in the porphyrin structure played indispensable role for the high conversion [52,53]. Especially, the PorCu molecular structure with the Cu center in the +1 oxidation state worked as the active catalyst for electrochemically converting CO_2 to CH_4 and C_2H_4 , and the OH groups may help bind certain reaction intermediates or provide an intra molecular source of protons.

Figure 3.17. Synthetic routes for copper-porphyrin molecular catalysts [51].

3.4 Conclusion

In this chapter, we discuss why Cu is the most popular metal and briefly introduce the electrochemical cell used for CO₂ electroreduction. Furthermore, referring to recent representative Cu-based catalysts, we illustrate factors influencing the performance of catalysts and primarily explain how those factors impact the activity and selectivity of CO₂ conversion. Those factors are pH value, morphology, particle sizes, the presence of atomic-scale defects, surface roughness, and/or residual oxygen atoms, and so on. In summary, these factors can benefit selectivity and yield by optimizing binding capability of CO₂ and intermediates, suppressing hydrogen formation and improving electron transportation. There are many methods that are introduced to optimize the performance of Cu-based catalyst. For example, doping Cu with other metal proves to be an effective and feasible option. Doping may help change both the inner structure and outer structure simultaneously, further optimizing the binding energy, improving electron transportation and suppressing hydrogen formation. This chapter can guide us to produce more ideal catalysts, in addition, the information presented in this chapter can be a foundation to summarize the property and mechanism in next chapter.

Nevertheless, it is very difficult to fairly and objectively compare current results used for analyzing the catalytic performance of different catalysts due to a lack of standardized methods for measuring and reporting activity data [54]. The conversion rate of CO₂ is influenced by catalyst type, electrolyte, hydrodynamics of the electrochemical cell, etc. Hence, the recommended measurements should evaluate the data in the absence of a convolution of intrinsic kinetics and mass transport effects and will not introduce artifacts from impurities, either from the electrolyte or counter electrode. In addition, electrochemical reactions rates should be

normalized to both the geometric electrode area and the electrochemically active surface area to facilitate the comparison of reported catalysts [55,56].

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Chapter 4 Performance and mechanism of Cu-based catalysts

Introduction

Electrochemistry has been becoming more and more important because of renewable energy consumption and storage. Progresses in controllable synthesis approaches and characterization of catalyst have significant benefit in understanding fundamental mechanism and developing highly efficient catalysts. Meanwhile, numerical models have being supplemented the experimental results to simulate the reaction path and calculate the energy cost. In this chapter, we will summarize and discuss the catalytic property and mechanism.

4.1 Catalytic performance

Cu-based catalysts are the most promising to realize commercial utilization for valued chemicals production, such as methane, ethanol and ethylene. Various types of Cu-based catalysts (pure Cu, Cu bimetallic, organic Cu, etc.) have been developed to achieve this goal [1]. Table 4.1 summarizes the cu-based catalysts and their performance for different chemical products in recent years.

Table 4.1. Summary of electrocatalytic reduction toward carbon products performance on different catalysts [1].

Catalyst	E/V	Faradaic efficiency/%						$J_{C_{2+}}$ (mA cm ⁻²)
		CO	CH ₄	C ₂ H ₄	C ₂ H ₅ OH	propanol	C ₂₊	
Phase-separated CuPd ^{a)}	-0.74			48	15			
Cu NCs/Cu foils ^{a)}	-0.96			32			60.5	41
Ag-Cu core-shell ^{b)}	-1.06		18	25				
Cu ₂ O derived Cu NP ^{b)}	-1.1			19				
Cu mesocrystal ^{b)}	-0.99		1.47	27.2				
Cu nanowire array ^{b)}	-1.1			17.4		8		
Prism Cu ^{b)}	-1.1						35	10
Cu NPs covered Cu foil ^{b)}	-1.1		1				36	N.A.
Electropolished Cu foil ^{b)}	-1.05						40.6	2.8
44-nm Cu cubic NPs ^{b)}	-1.1			41			46.4	1.4
Cu NPs ensembles ^{b)}	-0.75						~50	
3.6-um Cu ₂ O film ^{b)}	-0.99			34.26	16.37		50.8	17.8
OD-Cu ₄ Zn ^{b)}	-1.05						51	15
Cu ₂₈ Ag ₇₂ ^{b)}	Pulse			12.8	17.3		54.2	
Cu(100) single electrode ^{b)}	-1		30.4	40.4	9.7	1.5	57.8	2.9
18-nm Cu ^{b)}	-1.03			42.6	11.8	5.4	59.8	18.7
Cu(100) ^{b)}	-0.97						60	2
Pd ₈₅ Cu ₁₅ /C ^{b)}	-0.89	86						
Plasma Oxidized Cu ^{b)}	-0.9			60			60	12
CuOx-Vo ^{b)}	-1.4			63			63	
Ag-Cu ₂ O PS ^{c)}	-1.2		1.7	7.8	20.1			

Mesoporous Cu film ^{d)}	-0.8						57	7
N-doped graphene dots ^{d)}	-0.75			31			67	40
Cu DAT wire ^{d)}	-0.69						68.9	124
Au ₃ Cu ^{d)}	-0.38	90.2						
Ultrathin Cu/Ni(OH) ₂ NS ^{d)}	-0.39	92						
Nanoporous Cu ^{e)}	-0.67			38.6	16.6	4.5	62	411
ZnO/CuO ^{e)}	-0.68			18.1	41.4	5.5	66.7	
CuAg wire ^{e)}	-0.68			60	25		85	265
Surface Reconstructed Cu ^{f)}	-2.6			56		5	73	17
Abrupt Cu interface ^{g)}	-0.67						81	608
3D porous hollow fibre copper ^{h)}	-0.4	72						

As can be seen in the Table 4.1, there are many factors influencing the selectivity and productivity, such as type of metal, surface structure, shape. Basically, to make products with high value, high energy will be required. For example, CO can be produced at a current of ~-0.4V with high production, while approximately -0.7V will be required to produce more valuable carbon chemicals. Though it is very hard to do quantitative analysis due to too many uncertain/various factors, qualitative analysis can be done to further guide experimental or computational study to design and synthesize more reliable Cu-based catalysts. According to the basic knowledge of electrochemistry and the published catalysts in Table 4.1, we may obtain the following summarization.

First, currently, Cu is the most important metal for CO₂ conversion. Scientists studied the shape and the particle size of Cu-based catalysts to produce more efficient catalysts. From the

macro scene, catalysts with high specific surface area are more efficient because they provide more adsorption sites for CO₂ and intermediates, which have been partially proved by the evidences listed in the above table that the abrupt Cu interface has very high current for CO₂ conversion at low potential and most Cu are produced to nanoscale size. At the micro level, it cannot be guaranteed that higher productivity of target product will be achieved when the particle size because smaller. Because too small particle size may result in the shortage of multi-sites to produce products with more than one carbon. This deduction may be supported by Rulle Reske's experiment, showing that the main product will be CO and H₂ when the particle size of the catalyst is smaller than 2 nm.

Second, the doped metal in Cu is significant to determine the final product. Different metal doped in Cu may cause different product preference and the ratio of metals doped in the Cu also influence the product distribution. For one thing, specific metal may increase the current. For another thing, it can improve the adsorption site to avoid the steric hindrance. Basically, Au, Pd, Zn and Ag catalysts favor the formation of CO, which means it is hard to produce products with more value when they are used alone. However, when Au and Ag is doped in Cu, they can reduce the energy cost to produce more valuable products. For example, CuAg wire and ZnO/CuO are excellent catalysts to produce C₂₊ products with high efficiency at relatively low potential, and faradaic efficiency are 85 and 66.7 at -6.8 V, respectively. However, when Pd and Au are doped in Cu, the effect to increase organic carbon chemicals is limited or even counterproductive. The possible reason is that there is competition in the alloy which means Cu may be stronger to absorb CO₂ than Zn and Au, while it is weaker to absorb CO₂ than Pd and Au. Another possible reason is that the atomic radius of doped atom (Pd:169 pm, Au:174 pm,

Ag:165 pm, Zn:142 pm, Cu:145 pm) may not match the bond length of C-C, resulting in blocking C-C formation.

4.2 Mechanism and pathways for CO₂ conversion to C₂ products

Understanding electrocatalytic mechanism and the relationship between catalyst's structure and performance on molecular level will further provide sights and thoughts to design and improve catalysts to enhance CO₂ reduction ability and produce more high-value products. However, proposing a conclusive mechanism for the reduction of CO₂ is challenging, as more than ten chemicals are produced from CO₂. Besides, these chemicals include a broad mix of aldehydes, ketones, carboxylic acids, and alcohols, out of which 12 are C₂ or C₃ species, showing the complexity of this reaction. Therefore, a lot of work have been done to improve the efficiency and selectivity. Though the relationships between catalytic performances and various factors (pH, defect, size, shape, chemical bond, etc.) have been experimentally investigated, most publications have not systematically discussed the reaction pathway and mechanism. As we know, the electron transfer to adsorbate is thought to have low kinetic barrier. The step for achieving C-C coupling determines the rate and selectivity of C₂ products, because it needs to overcome the barrier of C-C bond formation which consumes much energy.

There is nearly no debate that CO₂ will be converted to HCOOH and CO first. HCOOH can not be converted to other chemicals further. Normally, CO is ideal product because it is the intermediate to electrocatalytically produce organic carbon chemicals, such as CH₄, C₂H₄, and CH₃CH₂OH. Experiments also reveal that the product distribution of CO reduction is as same as that of CO₂ reduction. Those are why many researches focus on CO conversion when they study the mechanism of CO₂ conversion.

To obtain more valuable organic carbon chemicals, the first step is to prohibit the formation of HCOOH and the desorption of CO. Since CO and formate products involve very different reaction mechanism, formate formation can be suppressed by controlling pH, designing new nanoscale catalysts and modifying the properties of the electrolyte, to obtain high concentration of CO. Meanwhile, it is found that Cu(100) only leads to CO formation without HCOO^- . Ruud Kortlever et al [2] proposed the reaction pathways in Figure 4.1. They pointed out that when the applied potential was -0.8V, the reaction occurred on the Cu(111) facet and the products tended to be C_1 and CH_4 was dominant when $^*\text{CHO}$ and $^*\text{COH}$ were the intermediates. When the applied potential was low, reaction occurred on Cu(100) and $^*\text{CO}$ dimerization occurred on Cu(100) facet to produce C_2 products which was dominated by C_2H_4 . Ming Ma et al [3] proposed that there were two pathways to produce C_2 products (Figure 4.2) and C_2H_4 could be produced from both $^*\text{CO} \rightarrow ^*\text{COH} \rightarrow \text{C}_2\text{H}_4$ and $^*\text{CO} + ^*\text{CO} \rightarrow ^*\text{COCO}$ paths. However, both research only focused on thermodynamic level, ignoring the influence of reaction barriers. For example, though direct dimerization of $^*\text{CO}$ is thermally available under low potential, it is obvious that the barrier of dimerization of adsorbed $^*\text{CO}$ is still very high under an electric field and it is unfavorable from kinetic perspective [4].

Figure 4.2. Proposed reaction paths for electrocatalytic reduction of CO₂ on Cu nanowire arrays [3].

In 2013, electron-ion transfer reactions were taken into account to study reaction kinetics of elementary steps. The results indicated that the reduction of CO was the key selectivity-determining step on Cu(111) and *COH played a critical role in forming methane/ethylene. C₂H₄ was produced through nonelectrochemical *CH₂ dimerization as shown in Figure 4.3. Moreover, it was further proved that reaction environment and potential were essential for determining intermediates content and the formation of methane/ethylene [5].

Figure 4.3. Proposed reaction paths for CO₂ electroreduction on Cu(111) [5].

In 2016, Xiao et al [6] predicted the atomistic mechanisms for the pathways of products during CO reduction at different pH conditions on Cu(111) facet. Free energies for CO reduction (Figure 4.4) indicated that C₁ products were relatively easy to be produced at acidic atmosphere while C₂ chemicals preferred $\text{*CO} + \text{*COH}/\text{*CHO}$ pathway at neutral pH or $\text{*CO} + \text{*CO} \rightarrow \text{*COCO}$ pathway at alkaline atmosphere. At low pH = 1 with potential of -0.80 V, multi-carbon production was kinetically suppressed, C₁ products were mainly produced through *COH pathway. At neutral pH value with potential of -1.17 V, though both $\text{*CO} + \text{*CO} \rightarrow \text{*COCO}$ and $\text{*CO} + \text{*COH}/\text{*CHO}$ pathways might be accessible, *COH reduction was dominant and C₁ was the main product. At high pH = 12, C₁ pathway was kinetically blocked and $\text{*CO} + \text{*CO} \rightarrow \text{*COCO}$ pathway was predominant. However, we must point out that *COCO is highly unstable on the Cu(111) surface. Compared to *CHO , *COH was favored due to their activation barriers of *COH (0.21 eV) and *CHO (0.39 eV) calculated by DFT at -1.15 V on Cu(111) facet [2].

Figure 4.4. Free energy of CO electrochemical reduction on Cu(111) at pH = 1, 7 and 12, respectively [6].

Though Cu(111) facet can be utilized to produce C₁ products and C₂ products, C₁ is preferential. Dimerization of the intermediates *CHO or *COH toward ethylene is believed to be the pathway that produces ethylene once current density reaches 10 mA cm⁻² and takes place on both Cu(100) and Cu(111) facet. However, Cu(100) is a more active surface than Cu(111), leading to lower overpotentials for both C₁ and C₂ products. Earlier work showed C₁ was preferentially formed on Cu(111), while C₂H₄ was the main product on Cu(100) [9]. In addition, pH value was a significant factor for the product selectivity. At pH = 1 (acidic), CH₄ was observed without C₂H₄ or other C₂ products on both Cu(100) and Cu(111) [7]. In contrast, C₂H₄

production was comparable with CH₄ production in the presence of neutral and basic solutions. As C₂ products was more valuable, reaction on Cu(100) was desirable for its higher performance than Cu(111) to produce C₂ products. Meanwhile, recent experiments showed that under standard electrochemical conditions, Cu(100) may be more stable. In 2015, Tao Cheng et al [8] reported *CHO was the main intermediate for C₁ products on Cu(100), rather than *COH. In 2018, Alejandro Garza et al [10] proposed another reaction pathway for the reduction of CO to C₂ products at high potentials on Cu(100). It showed *CO + *CHO → *COCHO occurred first, and then *COCHO was converted to C₂H₄ or CH₃CH₂OH (Figure 4.5), meaning *CHO was the main intermediate when reaction occurred on Cu(100). Based on the previous research, we try to summarize the possible pathways for CO₂ conversion to C₂ products. Basically, there are four pathways for C₂ formation, which are *CO + *CO → *C₂, *CO + *COH → C₂, *CO + *CHO → C₂ and *COH → *CH₂ → C₂. When the potential is small (~-0.4V), though the reaction thermally follows *CO + *CO → *COCO pathway on Cu(100), it is hard to react due to kinetics barrier [9]. When the potential is high, the reaction mainly follows the path *CO + *COH → C₂H₄ or *COH → *CH₂ → C₂ on Cu(111). On Cu(100) surface at high potentials, *CO + *CHO → C₂ is supposed as the main way to produce C₂. Different reaction pathways for C₂ products are summarized in Figure 4.5.

Figure 4.5. Summarized mechanisms for the reduction of CO to C₂ products [1,10].

After we elucidate the reaction mechanism, we can design the effective catalyst to obtain the aimed product. For example, *C₂H₃O is the common reaction intermediate for both ethylene and ethanol formation (Figure 4.5. b, c), therefore, it is possible to modify the catalyst's structure to suppress ethylene production while promote the hydrogenation of the intermediate and finally enhance the selectivity towards alcohols [11,12].

4.3 Conclusion

High overpotential of the reaction and low activity of currently known catalysts still hamper this process from commercialization. Cu-based catalysts are known to electrochemically convert CO_2 to hydrocarbons and/or oxygenates at considerably high faradaic efficiency, however, other products such as CO, HCOO^- , and H_2 are also produced at fairly high faradaic efficiencies. The existing catalysts are hard to satisfy the industrial usage ($\text{FE} \gg 50\%$ for C_2 products, current density $\ll -200 \text{ mA cm}^{-2}$ while applied potentials $\gg -1.0 \text{ V vs. RHE}$ [8]. In addition, to satisfy the industrial requirements, the catalysts should be durable, however, few research results related to catalyst's lifetime have been reported.

CO_2 can be directly converted to valuable products in the presence of catalyst in one step or two steps which reduced CO_2 to CO first and then converted to fuels with higher energy. This technology can satisfy long-distance and heavy freight transportation requirements. Although CO_2 can be catalytically converted to fuels, it requires high energy. In particular, the reduction of H_2O to H_2 considerably compete with synthesis to fuel at low potential. There is a debate that two steps may be more attractive for lower energy cost and higher selectivity and controllability, because CO reduction activity may be obscured in the presence of a large excess of CO_2 [13]. According to our study, the two step reaction may have more advantages compared with one step reaction [14-17]. On one hand, CO is the intermediate to convert CO_2 to chemical products. Though Cu may be the best catalyst to directly convert CO_2 to organic products, it does not mean it is the best candidate to convert CO_2 to CO. Actually, there are many metals used to produce CO, such as Ag, Au, and Co, most of which achieve the FE more than 90% under relative low potential. On the other hand, the adsorption energy and mechanism of CO on the catalyst surface is significantly different with that of CO_2 . The adsorption atom is C for CO adsorption on the

catalyst while O become the adsorption atom for CO₂ adsorption. Compared to CO₂, CO can be easier adsorbed due to its structure. Hence, recently, more and more research are focused on CO conversion.

Current mechanism achievement of converting CO₂ to value-added products are not enough and the debates of reaction pathways are still existing. Because many factors influence the catalyst's performance and it is very hard to build the models to precisely reflect the real situation [18-20]. Though more computational and experimental work need to be done to further elucidate the mechanism of producing C₂ products, the following summaries may be universally accepted.

- i) The applied potential is a determining factor influencing the reaction. Though low potential is beneficial, it is impossible to fulfill our goals under certain value. For example, direct dimerization of *CO is thermally available under low potential, it is obvious that the barrier of dimerization of adsorbed *CO is still very high under an electric field and it is kinetically unfavorable. Theoretically, no matter what reaction situation we create, the kinetic barrier exist. At current situation, the range from -0.65 to -1.0 V may be reasonable and acceptable.
- ii) Facet is an important factor when we consider the selectivity of CO₂ conversion. Normally, Cu(111) facet prefers to produce C₁ products while Cu(100) facet prefers to convert CO₂ to C₂ products. That is why much research focus on Cu(100) now.
- iii) The reaction to produce C₂ products is pH sensitive. C₂ products can be produced with high yield under higher pH value. The situation is corresponding with our former finding that longer nanowire may lead to higher C₂ yield.

- iv) It is useful to dope suitable atoms into Cu-based catalysts to change its electrical structure or space structure to further improve the efficiency and selectivity of the catalysts.
- v) In reality, making a single proton-electron pair transfer to $\ast\text{CO}$ intermediates to form $\ast\text{CHO}/\ast\text{COH}$ could promote the occurrence probability of coupling to other $\ast\text{CO}$ derived intermediates.

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