Reduction of CO_2 to Chemicals and Fuels: Thermocatalysis versus Electrocatalysis

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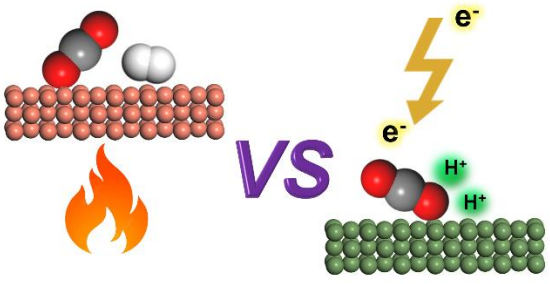
Abstract

Reducing carbon dioxide to valuable chemicals and fuels such as formic acid, carbon monoxide, methanol, methane, ethylene, ethanol, and higher alcohol products by renewable hydrogen via thermocatalysis or by renewable electricity via electrocatalysis provides an attractive and sustainable way for achieving carbon abatement and addressing the climate change challenge. The thermocatalytic pathway is easy to scale up and realize industrial-scale applications, but some of the reactions are limited by kinetics, and / or thermodynamics equilibrium. In contrast, the electrocatalytic approach is less mature but has advantages, including low temperature and low pressure, using water as a hydrogen source, and no limitation from thermodynamic equilibrium. However, the electrocatalysis process requires the development of more effective and stable electrocatalysts. In this review, the latest progress in converting CO_2 to various chemicals or fuels via thermocatalysis and electrocatalysis is summarized and compared with an emphasis on catalysts and reaction mechanisms. The similarity and differences between thermocatalysts and electrocatalysts as well as the thermocatalytic process and electrocatalytic process are discussed in detail. The combination of strength between thermocatalysis and electrocatalysis is also introduced and discussed. Future research directions of the CO_2 conversion process are outlooked.



TOC

1. Introduction

The amount of carbon dioxide (CO_2) in the atmosphere has increased along with human emissions since the industrial revolution in the 1750s.[1] Emissions rose slowly to about 10 billion tons a year in the mid-20th century before skyrocketing to more than 35 billion tons per year in recent years.[2] It is estimated that about 86% of the carbon emissions come from fossil fuel (coal, oil, and natural gas) utilization, and the remaining mainly come from land utilization.[3] Among the CO_2 emissions, about 46% goes to the atmosphere, 23% is dissolved in the ocean and 31% is absorbed by the land.[3]

CO_2 emission in the atmosphere is predicted to be closely related to climate change and global temperature increase.[4, 5] CO_2 dissolved in the ocean will cause acidification, posing threats to the earth's ecosystems.[6] To address the climate change issue, both efforts in CO_2 emission source control and recycling and utilization of emitted CO_2 are necessary. CO_2 emissions from the utilization of fossil fuels can be captured and further reduced to chemicals and fuels using renewable and clean energy. Utilization of CO_2 includes conversion of CO_2 to chemicals and fuels, mineralization of CO_2 for concrete building materials, etc.[3, 7, 8] Among these processes, catalysis is an effective, economic, and sustainable approach for converting CO_2 to chemicals and fuels.[9, 10] This technology is very attractive since it can reduce the usage of fossil fuels and provide an economic incentive to utilize CO_2. Currently, there are mainly three categories of catalytic approaches, namely, thermocatalytic, electrocatalytic, and photocatalytic ways. Thermocatalysis is typically conducted by flowing CO_2 and other gases (e.g., renewable H_2) over thermocatalysts at an increased temperatures and pressures. In contrast, the electrocatalytic process is reacting dissolved or gaseous CO_2 at the interface between electrolytes and electrodes (electrocatalysts), typically at ambient or near ambient conditions. The photocatalytic process is conducted under photo irradiation in the presence of a photocatalyst. The progress of

photocatalytic CO_2 reduction is well summarized in recent reviews,[11-13] so it is not discussed in this review.

So far, thermocatalytic hydrogenation of CO_2 can produce formic acid (HCOOH)/formate,[14] methane (CH_4),[15, 16] carbon monoxide (CO),[17] methanol (CH_3OH),[18] hydrocarbons,[19] olefins[20], and even aromatics[21, 22] on selected thermocatalysts, temperature, and pressure. In contrast, electrocatalytic reduction of CO_2 can also produce similar products such as HCOOH,[23] CO,[24] CH_4,[25] CH_3OH,[26] ethylene (C_2H_4),[27-29] ethanol (C_2H_5OH),[30, 31] and even higher products such as C3 to C6 hydrocarbons[32] on chosen electrocatalysts, potential range, and electrolyte.

Although there are many reviews regarding CO_2 reduction via thermocatalysis[19, 20, 33, 34] or electrocatalysis,[35-40] there are very few reviews that summarize and compare the commonalities, similarities, and differences between these two processes together.[41, 42] In principle, any heterogeneous reaction that involves redox or changes in oxidation states, adsorption of charged intermediates, or even heterolysis of small molecules should have parallels with electrochemical reactions occurring at electrified interfaces.[43] There are some catalysts that have been found both active in electrocatalysis and thermocatalysis for CO_2 reduction. For example, graphitic carbon nitride can work as a thermocatalyst, electrocatalyst, and even photocatalyst for CO_2 conversion.[44] Molybdenum sulfide, which has been widely investigated as hydrodesulfurization catalysts in thermocatalysis[45], also catalyzing the electrochemical hydrogen evolution reaction (HER)[46]. In both cases, the adsorption of hydrogen atom is a crucial factor affecting the catalytic performance, while the edge sites of molybdenum sulfide are considered as the main active sites for both hydrodesulfurization reaction[47] and electrochemical HER[48]. Moreover, metal nanoparticles that catalyze hydrogen peroxide (H_2O_2) synthesis by the electrochemical oxygen reduction reaction (ORR) can also work as thermocatalysts

for direct H_2O_2 synthesis via H_2 and O_2.[49] These studies suggest that there are some commonalities between the two processes.

In this review, the conversion of CO_2 to chemicals and fuels via thermocatalysis and electrocatalysis are summarized and compared with the emphasis of catalysts and reaction mechanisms. The similarities and differences between thermocatalyst and electrocatalysts as well as the thermocatalytic and electrocatalytic processes are discussed in detail. The combination of strength between thermocatalysis and electrocatalysis, as well as future reaction directions, are also elaborated and discussed. Through this review, it is hoped that researchers in different fields can learn from each other to develop more effective catalysts and catalytic process.

2. Thermocatalysis versus Electrocatalysis

Under ordinary conditions, the occurrence of a chemical reaction is accompanied by the liberation or absorption of heat. The temperature dependence of the reaction rate constant for an elementary reaction step can be described well by the Arrhenius equation, as shown in Figure 1a. In an electrochemical reaction, the electrons and ions are also considered as reactants or products, and their potential energy can be controlled by the potential applied to the electrode (electrocatalyst). The reaction rate of an electrochemical reaction can be adjusted by temperature and overpotential applied as described by the modified Arrhenius equation shown in Figure 1b.[50] A catalyst can bind or interact with the reaction intermediates so that the intermediates can be stabilized, and the activation energy can be greatly reduced.[51] From this perspective, the thermocatalysis process (Figure 1c) is similar to the electrocatalysis process (Figure 1d). In electrocatalysis, an electrolyte is needed to transfer the ions involved in the reaction process, and the reaction is typically occurred on the interface between the

electrocatalyst (electrode) and electrolyte. Therefore, electrocatalysis can be regarded as a special kind of heterogeneous catalysis. In thermocatalysis, the reaction proceeds via multiple elementary steps with various reaction intermediates. Similarly, in electrocatalysis, a series of elementary steps also happen to complete the reaction. Only one electron can be transferred in an elementary step according to the Mucus theory. In addition, pure chemical elementary steps (non-electron transfer steps) can also be involved in electrochemical reactions. The rate-determining steps in electrochemical reactions can be electron transfer steps or non-electron transfer steps (pure chemical steps, like the case in the thermocatalysis process).

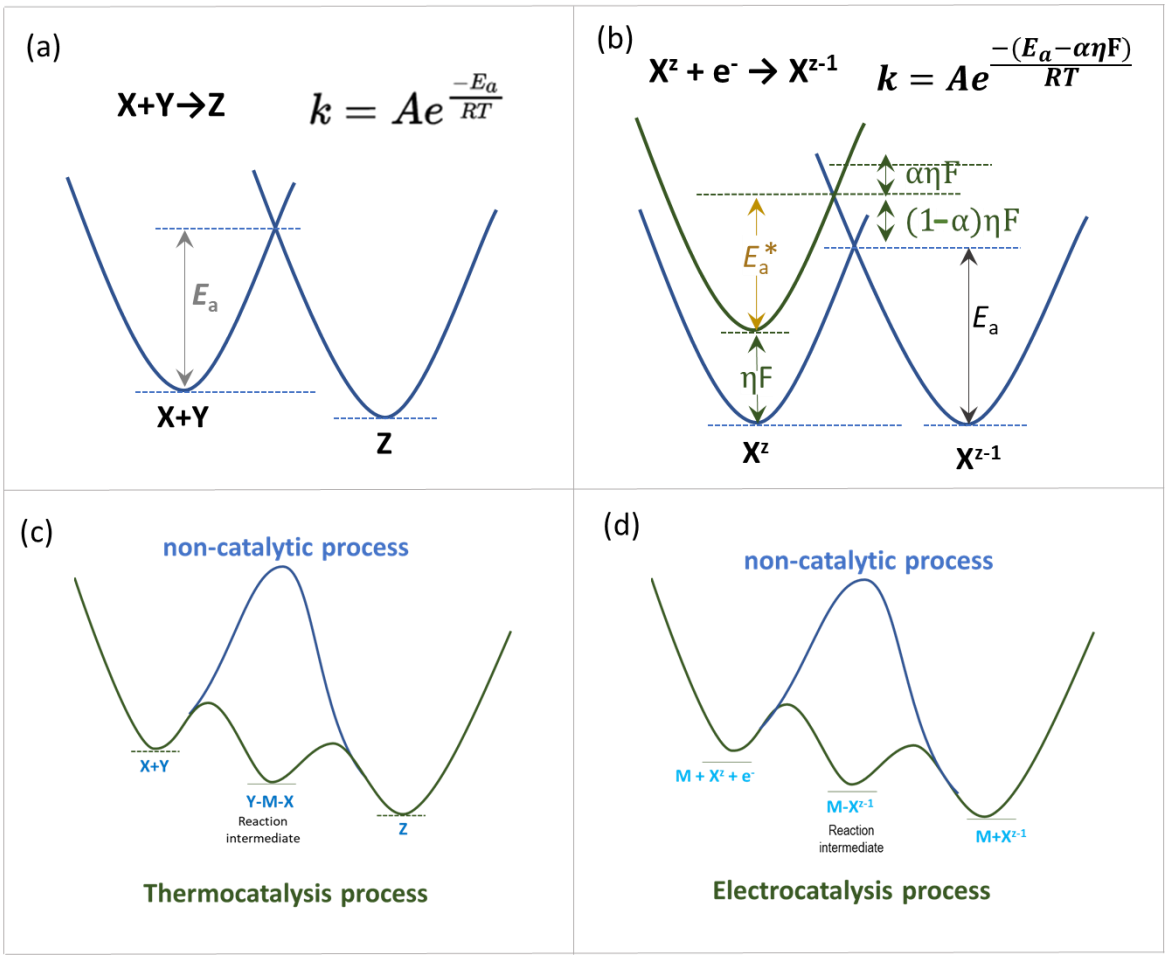


Figure 1. (a) conventional chemical reaction, (b) electrochemical reaction, (c) thermocatalysis process, and (d) electrocatalysis processes.

2.1 CO_2 reduction via thermocatalysis

In the thermocatalytic CO_2 hydrogenation/reduction process, temperature and pressure are the typical driving force to overcome the activation barrier and accelerate the reaction rate. Since nearly all the reactants are in contact with a thermocatalyst, the energy needed or released needs to be conducted through the reactants and thermocatalysts. The molar enthalpy change (Δ_rH^{Θ}) and Gibbs energy change (Δ_rG^{Θ}) of the typical CO_2 hydrogenation reactions are listed in Table 1. The conversion of some reactions in Table 1 is limited by the thermodynamic equilibrium, and a comprehensive thermodynamics analysis of these reaction can be found in Ref.[52] From the viewpoint of carbon abatement, the H_2 used in CO_2 reduction must come from renewable sources such as solar powered water electrolysis other than carbon sources such as coal and natural gas. The thermocatalysts for CO_2 hydrogenation require simultaneous activation of CO_2 molecules and H_2 molecules, and many transition metals and metal oxides show good activity and selectivity.

Table 1. The molar enthalpy change (Δ_rH^{Θ}) and Gibbs energy change (Δ_rG^{Θ}) of typical CO_2 hydrogenation reactions (all components are in the gas state).

No.	Reaction equation	Δ_rH^{Θ} kJ/mol	Δ_rG^{Θ} kJ/mol
1	$CO_2 + H_2 \rightarrow HCOOH$	14.9	43.5
2	$CO_2 + H_2 \rightarrow CO + H_2O$	41.2	28.6
3	$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$	−49.3	3.5
4	$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	−165.0	−113.5
5	$CO_2 + 3H_2 \rightarrow 1/2C_2H_4 + 2H_2O$	−64.0	−28.7
6	$CO_2 + 3H_2 \rightarrow 1/3C_3H_6 + 2H_2O$	−83.6	−42.1
7	$CO_2 + 3H_2 \rightarrow 1/4C_4H_8 + 2H_2O$	−90.3	−45.2

8	$CO_2 + 3H_2 \rightarrow 1/2C_2H_5OH + 3/2H_2O$	−86.7	−32.4
9	$CO_2 + H_2 \rightarrow C_xH_yO_z$ (higher products) + H_2O	N.A.	N.A.

2.2 CO_2 reduction via electrocatalysis

In the electrochemical reaction, an overpotential (the potential difference between the thermodynamically determined equilibrium potential and the applied potential to make the reaction proceed) is applied to overcome the activation barrier. A good electrocatalyst can maximally reduce the overpotential required for driving a specific electrochemical reaction, thereby improving the utilization efficiency of electric energy. The electrocatalysis process can also be done by different catalytic mechanisms, as shown in Figure 2. In this review, we mainly discuss the case of the heterogeneous way in an electrocatalytic film (Figure 2c). Typically, a proton-electron couple is used as reactant to reduce CO_2 ($CO_2 + nH^+ + ne^-$) by electrocatalysis, among which the chemical potential of electrons can be adjusted by the applied electrode potential. This is different from the thermocatalysis process, where the chemical potential of H_2 is adjusted by pressure and temperature.

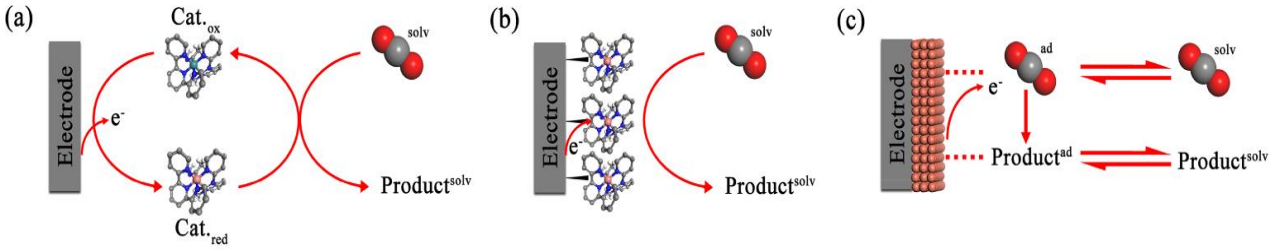


Figure 2. Schemes for CO_2 reduction by different catalytic mechanisms: (a) homogeneous, (b) immobilized, and (c) heterogeneous way in an electrocatalytic film. Reprinted with permission from ref.[53] Copyright American Chemical Society 2020.

Table 2 lists the basic information of the typical CO_2 electroreduction reaction. Since the electrochemical CO_2 reduction process involve the proton-electron couple and the equilibrium potentials of these reactions are close to 0 V vs. reversible hydrogen electrode (RHE), the hydrogen evolution reaction (HER) ($2H^+ + 2e^- \rightarrow H_2$, $E^0 = 0$ V vs. RHE) will compete with CO_2 reduction reactions. How to suppress HER is an essential topic in CO_2 electrochemical reduction. Figure 3 shows the schematic diagram of CO_2 reduction steps via electrochemical methods. Various intermediates and paths are proposed. In the electroreduction of CO_2, key reaction intermediates such as *CO, *OH, COOH*/CHO* and OCHO* would determine the final products.

Table 2. Basic information of CO_2 electrochemical reduction half-reactions.[54]

No.	Reaction equation	Equilibrium potential E^o (V vs. RHE)
1	$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	−0.20 (for pH < 4); −0.20 + 0.059[pH−4] (for pH > 4)
2	$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	−0.10
3	$CO_2+4H^+ + 4e^- \rightarrow HCHO + H_2O$	−0.07
4	$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH+H_2O$	0.02
5	$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	0.17
6	$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O$	0.08
7	$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_5OH+3H_2O$	0.09
8	$CO_2 + nH^+ + ne^- \rightarrow C_xH_yO_z$ (higher products) + mH_2O	NA

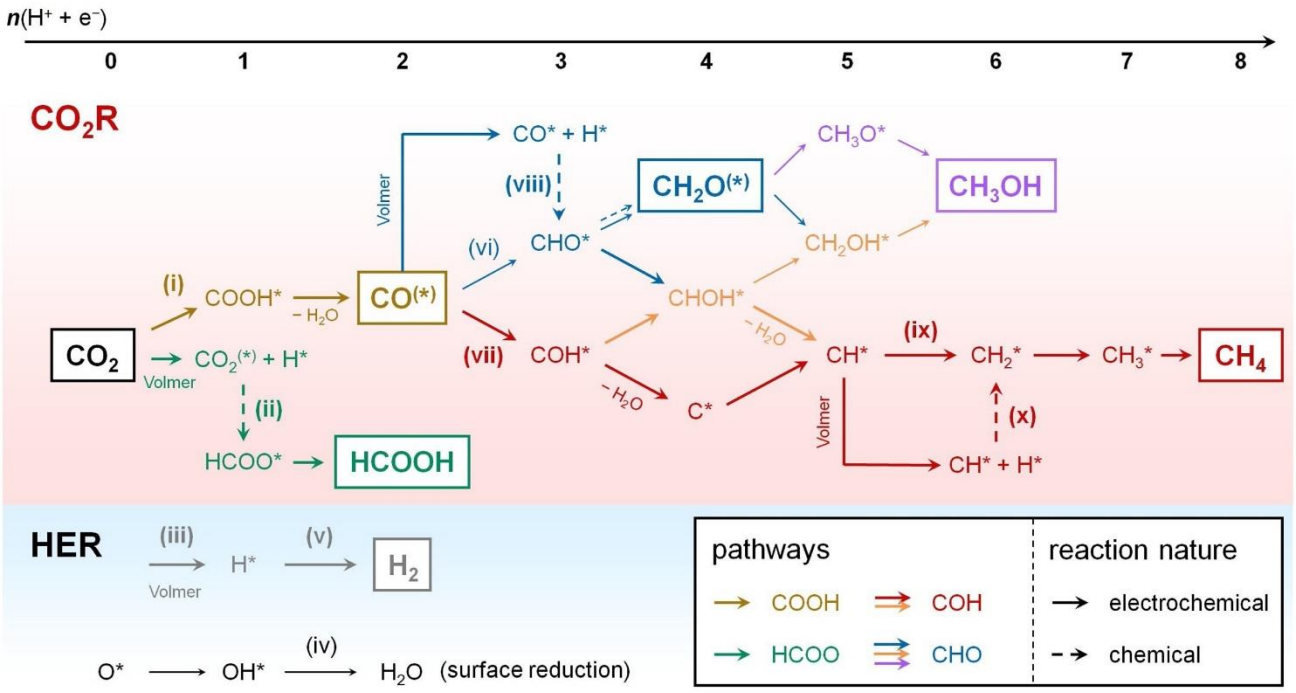


Figure 3. Schematic diagram of electrochemical CO_2 reduction reaction steps. Reprinted with permission from Ref.[55] Copyright Elsevier 2020.

Regarding the electrocatalysts for CO_2 reduction, Hori et al.[56] did a systematical investigation of CO_2 reduction on various metals, and they can be divided into four groups of materials according to the main products: (1) Pd, Ni, and Mo et al. as carbophilic metals primarily produce H_2 doing HER side reaction; (2) Au, Ag, and Zn as nonoxophilic and noncarbophilic metals primarily produce CO; (3) Pb, Sn, In, Bi, and Sn as oxophilic and noncarbophilic metals primarily produce formate; (4) Copper is unique for producing higher products beyond CO and formate.[57] (Figure 4a) The decorating metal on Cu in Figure 4b shows the relative binding strengths of CO* and OH* to those of Cu (Figure 4b) also determines the selectivity of electrochemical CO_2 reduction.

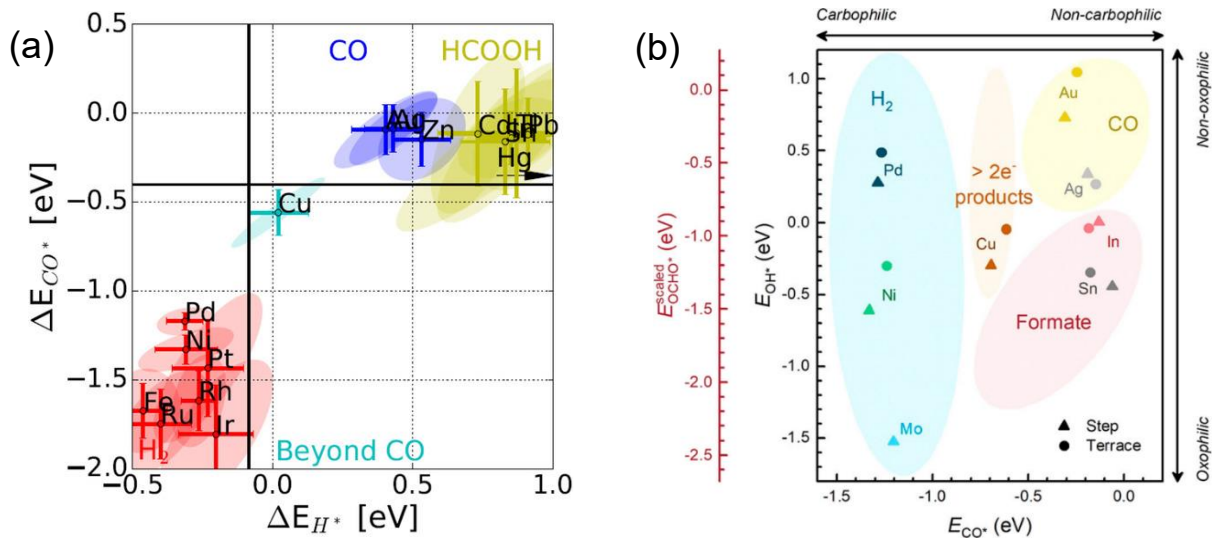


Figure 4. (a) Relationship between the binding energies of the intermediates *CO and *H of various metals with primary products in electrochemical CO_2 reduction. Reprinted with permission from Ref.[57] Copyright Wiley-VCH 2017. (b) Relationship between CO* binding energy and OH* binding energy with primary products in CO_2 reduction. Reprinted with permission from Ref.[58] Copyright American Chemical Society 2020.

3. Reduction of CO_2 to chemicals and fuels

In this section, the conversion of CO_2 to various chemicals and fuels via thermocatalysis and electrocatalysis will be summarized and compared according to their products. The typical thermodynamics, thermocatalysts and electrocatalysts, as well as reaction mechanisms, are summarized and discussed.

3.1 CO_2 to formic acid or formate

Formic acid is considered a promising hydrogen energy carrier.[59] Reduction of CO_2 by hydrogen to formic acid ($CO_2(g) + H_2(g) \leftrightarrow HCOOH(g)$, $\Delta G(298K) = 43.5$ kJ/mol, $\Delta H(298K) = 14.9$ kJ/mol) is a thermodynamically unfavorable reaction.[52] The standard equilibrium constant of the reaction is only

2.4×10^{-8} at 298 K. Therefore, nearly all thermocatalytic CO_2 hydrogenation to formic acid is conducted by adding organic or inorganic bases to shift the reaction equilibrium to formate. To recover formic acid from formate, acidification or separation is required. Supported metal catalysts are the typical heterogenous thermocatalysts used for this reaction, among which metal sites can activate hydrogen while the support can adsorb and activate CO_2.[60] For example, CeO_2 and ZnO supported palladium,[61] heterogeneous gold metal,[62, 63] and silica-tethered iridium,[64] are widely investigated for CO_2 hydrogenation to formate. Iridium[65] and ruthenium [66] molecular catalysts also demonstrated highly active for formate production. Theoretical calculation of CO_2 hydrogenation to formic acid on Ni(111) and Ni(110) [67, 68] shows that CO_2 hydrogenation to formate intermediate is more favorable than to carboxyl intermediate, as shown in Figure 5. However, further hydrogenation of formate to formic acid by surface H is hindered by a larger activation energy barrier. In contrast, for the carboxyl-mediated route to HCOOH, the first H addition to CO_2 presents a barrier much larger than the second hydrogen addition. Additionally, *COOH can decompose to *CO and *OH. Understanding the mechanism of formic acid formation can provide an important reference for explaining the formation of higher-order products, so research in this area still needs to be strengthened.

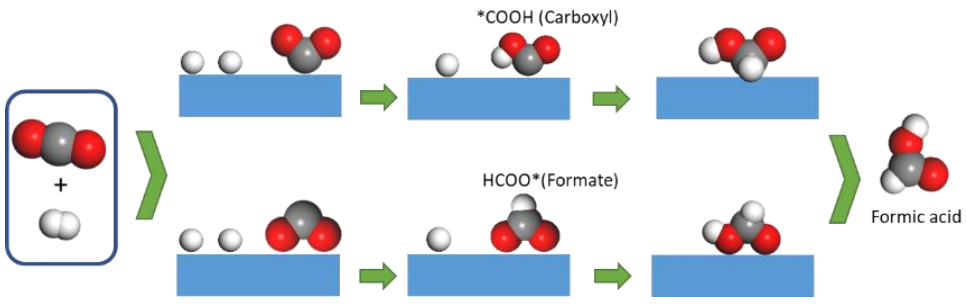


Figure 5. two pathways of thermocatalytic CO_2 hydrogenation to formic acid via *COOH (carboxyl) and HCOO*(formate) intermediates.

In contrast, the electroreduction of CO_2 to formic acid will not be limited by thermodynamics due to the introduction of external force (electricity). The equilibrium potential of this reaction is −0.20 V versus RHE for formic acid (pH < 4), or the equilibrium potential is −0.20 + 0.059[pH−4] (for pH > 4). Various molecular catalysts were investigated for electrocatalytic CO_2 reduction to formic acid, including Rh, In and Sn metalloprotoporphyrins[69], Ir[70, 71], and Ru[72] based molecular complex. In addition, tin[73], bismuth[74], indium[75], and lead[76] based metal electrocatalysts[77] are reported to be effective for formic acid / formate production. Recently, a Cu_2O nanoparticle film synthesized by square-wave electrochemical redox cycling of Cu foils afforded up to 98% Faradaic efficiency for electroreduction of CO_2 to nearly pure formate under ≥45 atm CO_2 in bicarbonate catholytes.[78] It should be noted that in most cases, the obtained formic acid is dissolved in the electrolyte, so all-solid-state reactors are designed to produce pure formic acid.[79, 80]

In electrocatalysis CO_2 reaction, a CO_2^- anion bound to the catalyst surface is firstly generated by the first electron transfer to CO_2. This anion can be further reduced to formate through a following electron couple proton transfer step as shown in Figure 6. The former is similar to the formate-intermediate mechanism in the thermocatalysis process. CO_2 can also be electrochemically reduced via *COOH intermediate through an electron-coupled proton transfer step, which can be further separated into two elementary steps, i.e. the electron transfer and proton transfer steps. Further reduction of *COOH can obtain *CO or HCOOH. In addition, protons can also be firstly electro reduced on catalyst surface to a bonded hydrogen atoms, then CO_2 is adsorbed to form carboxyl or formate, which is quite similar with the process in the thermocatalysis process (Figure 5). The reaction pathways of CO_2 reduction will depend on catalyst [54]. The thermodynamic theory of multiple proton-electron transfer predicts that for all reactions in which only 2 electrons (that is n = 2, such as producing formic acid or CO) are

transferred, ideal catalysts will exist that are able to catalyze the corresponding redox reactions in both directions, namely, both reduction and oxidation, with negligible overpotentials.[81] Therefore, the process of electroreduction of CO_2 to formic acid is expected to achieve high electricity utilization on high performance catalysts.

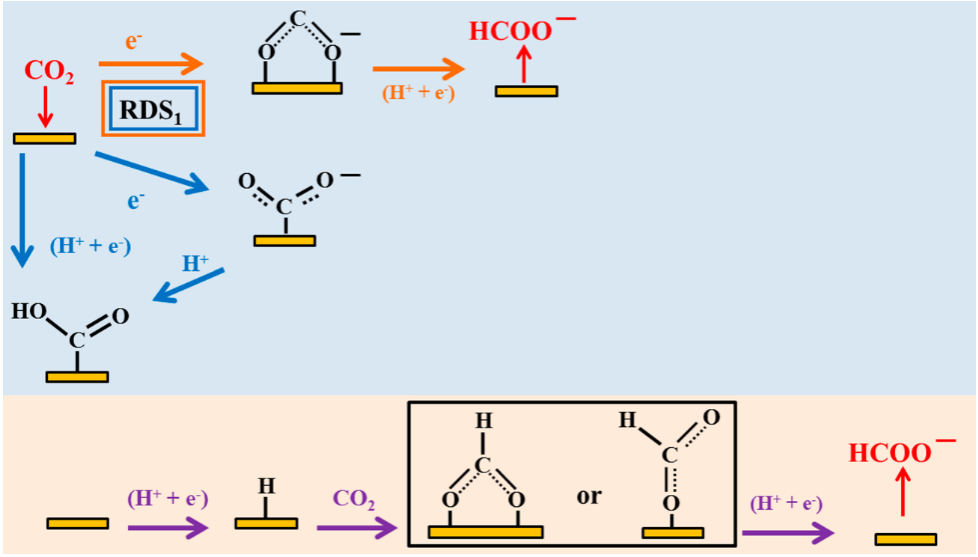


Figure 6. Reaction elementary steps of electrocatalytic CO_2 to formate (formic acid). Reprinted with permission from Ref. [54] Copyright 2015 American Chemical Society.

3.2 CO_2 to carbon monoxide

Reduction of CO_2 to carbon monoxide (CO) via thermocatalysis is also known as the reverse water-gas shift reaction ($CO_2 + H_2 \leftrightarrow CO + H_2O$, ΔG (298 K) = 28.6 kJ/mol, ΔH (298 K) = 41.2 kJ/mol). This reaction is a thermodynamically less favorable, endothermic reaction. Pressure has little effect since the number of molecules does not change after the reaction. A CO_2 equilibrium conversion of only ~5% can be reached at 100 °C and of ~80% can be obtained at 800 °C with H_2/CO_2 molar ratio of 4.[52] Oxides supported precious metals Pt[82], Pd[83], Rh[84], and Au[85] and nonprecious metals Cu[86], Fe[87, 88], and Ni[89] were reported to be active and selective toward the production of CO. Typically, the

dispersion or particle size and surface morphology of metals will affect the activity and selectivity for CO.[90] In addition, the reaction temperature can also tune the selectivity of CO_2 hydrogenation to CO. For example, a Ni supported on CeO_2, which is highly selective for CH_4 (> 99 %) below 300 °C, can shift to 90% CO at 700 °C.[52] The elementary reaction steps of CO production are suggested via carboxyl intermediate, as shown in Figure 5. Decomposition of carboxyl generates *CO and *OH, then CO desorbs while *OH is further reduced to H_2O. Another possible route is via a direct C-O bond cleavage pathway.[90]

The electrochemical reduction of CO_2 to CO has an equilibrium potential of −0.10V versus RHE. It is a two-electron and two-protons transfer process. Thermodynamically, it can proceed via two proton-coupled electron transfer (PCET) process[91] as follows:

$$CO_2(g) + * + H^+(aq) + e^- \leftrightarrow COOH* \quad (1)$$

$$COOH* + H^+(aq) + e^- \leftrightarrow CO* + H_2O(l) \quad (2)$$

$$CO* \leftrightarrow CO(g) + * \quad (3)$$

Nørskov et al. [91] calculated the trends in the electrocatalytic activity of metals and enzymes for CO_2 reduction to CO. Figure 7 shows the free energy diagrams for CO_2 electroreduction to CO on Au(211) and Pt(211) surface. For Au surface with weak adsorption, the first PCET step is the rate-determining step, while for Pt surface with strong adsorption, the reaction rate is limited by the desorption of CO. Experimental results show that gold and silver-based catalysts are highly selective for CO_2 electrochemical reduction to CO.[92, 93] Kinetic studies of CO_2 reduction to CO on planar silver and gold electrodes in aqueous electrolytes are conducted by mathematical modeling method and the results show that gold is more selective for CO compared with silver [94]. A recent study indicate that CO_2 electroreduction cannot occur on copper, gold and silver electrodes without metal cations in solution.[95]

The partially dissolved metal cations are necessary to stabilize the CO_2^- intermediate via a short-range electrostatic interaction. In addition, earth-abundant metal (Ni, Fe, and Co) and nitrogen-doped carbon electrocatalysts also showed high selectivity for CO_2 reduction to CO[96-98]. Pyrrolic nitrogen ligands selectively bind Ni atoms in a distorted square-planar geometry that strongly resembles the active sites of molecular metal–porphyrin catalysts is considered as the active sites for the reaction.[99] In addition, syngas (mixture of H_2 and CO) can be obtained on some catalysts with lower selectivity for CO, for example, palladium-based electrocatalysts[100]. In CO_2 reduction to CO process, the side reaction (hydrogenation evolution reaction) will cause a pH increase near the electrode surface. Thus, CO_2 will be consumed and its surface concentration on electrocatalysts decrease, leading a lower Faraday efficiency and carbon efficiency.

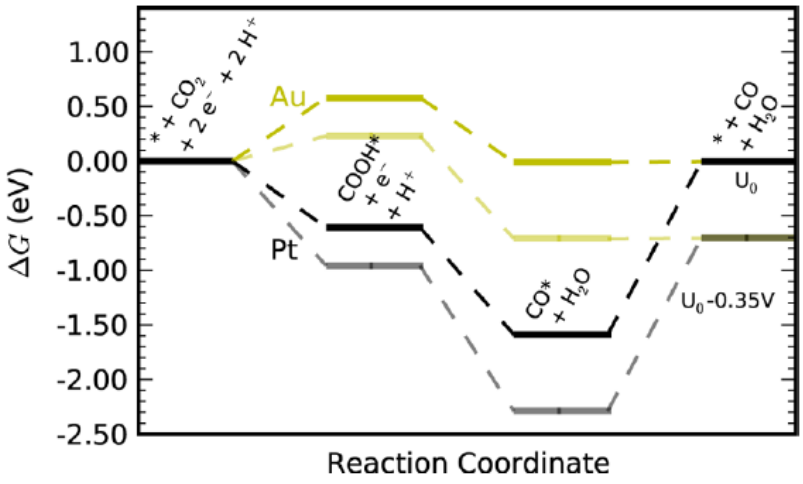


Figure 7. Free energy diagrams for CO_2 electroreduction to CO on Au(211) and Pt(211) at the reversible potential, U_0, for CO evolution and at a 0.35 V overpotential. Reprinted with permission from ref [91]. Copyright 2013 American Chemical Society.

Recently, Jaramillo and co-workers[101] investigated Ni, N-doped carbon catalyst which works both as

an electrocatalyst for the reduction of CO_2 to CO and a thermal catalyst for CO_2 to CO via the reverse water gas shift (RWGS) reaction as shown in Figure 8a. Advanced characterization techniques reveal that this catalyst facilitates RWGS on dispersed Ni sites in agreement with CO_2 electroreduction active site studies. A generalized reaction driving force that includes temperature and potential is constructed to facilitate faster kinetics in electrochemical CO_2 reduction relative to RWGS due to lower intrinsic barriers (Figure 8b and 8c).

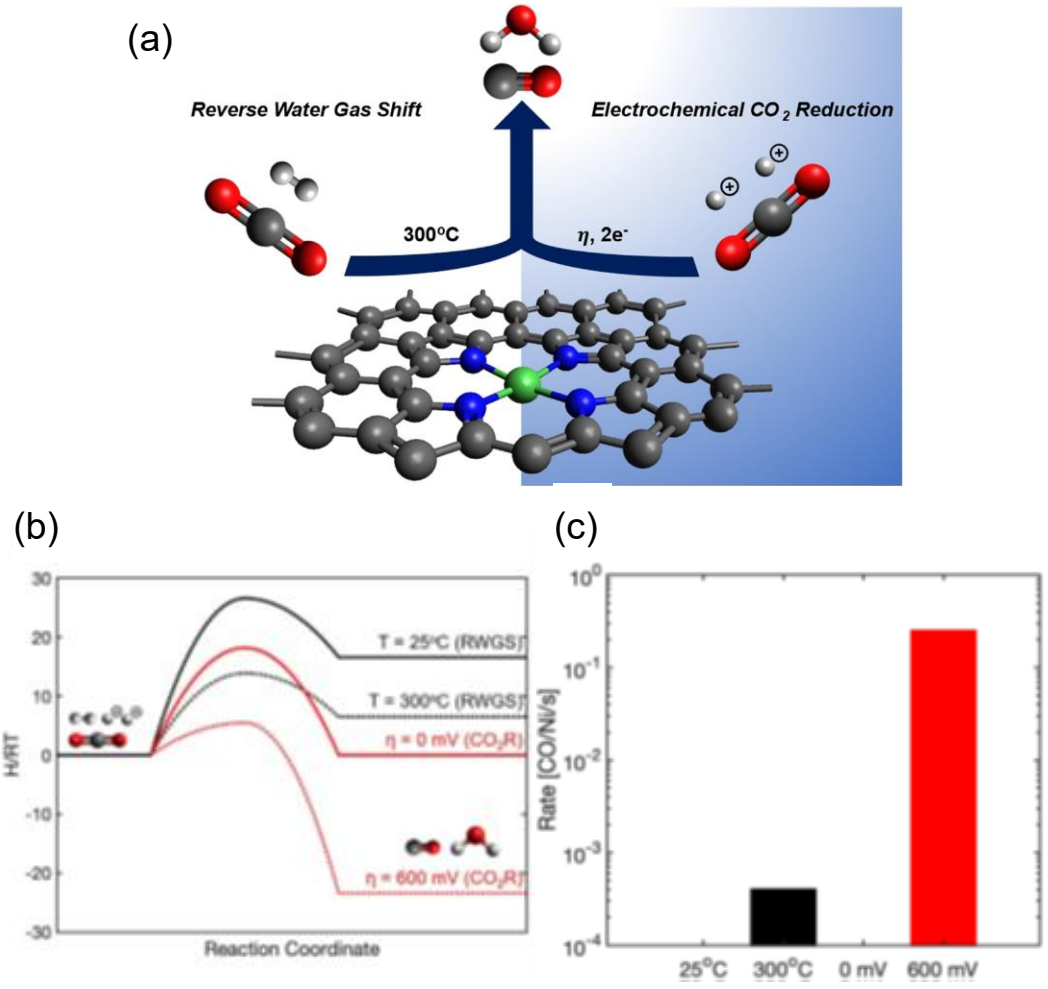


Figure 8. A Ni, N-doped carbon catalyst works both as an electrocatalyst and thermocatalyst for CO_2 reduction to CO. Reprinted with permission from ref[101]. Copyright 2021 Wiley.

3.3 CO_2 to methanol

Methanol, an important platform molecule, is considered as a promising energy carrier or alternative fuel as well. Research progress on heterogeneous catalysts for methanol synthesis from carbon dioxide hydrogenation has been well reviewed.[18, 102, 103] Various thermocatalysts including Pd/ZnO catalysts [104], In_2O_3 based catalysts[105, 106], ZnO-ZrO_2 solid solution catalyst [107], $MZrO_x$ (M = Cd, Ga) solid-solution catalysts[108] for direct CO_2 hydrogenation to methanol have been investigated. The active sites for CO_2 hydrogenation to methanol on Cu/ZnO catalysts are intensively studied [109] but still in debate[110]. The binding energies of key intermediates for CO_2 hydrogenation to methanol over oxide-supported copper are the key to the selectivity[86]. In addition, both Pd and oxygen vacancy are found to affect the performance of CO_2 hydrogenation to methanol over Pd/In_2O_3 [111]. A special Ni-Ga catalyst was discovered to be highly active and selective for carbon dioxide reduction to methanol.[112] Similar nickel–gallium catalysts were also investigated for catalyzing the electrochemical reduction of CO_2 but the main products are methane, ethylene, and ethane.[113] In addition, copper-zinc alloy catalysts, which is selective for methanol in thermocatalyst, exhibited Faradaic efficiency values as high as 33.3% for C_2H_4 in CO_2 electroreduction.[29]

In the electrocatalytic conversion of carbon dioxide to methanol on transition metal surfaces, Jaramillo et al. [114] found that all metals studied (Au, Ag, Zn, Cu, Ni, Pt, and Fe) can produce methane or methanol, although the selectivity is very low. The metal surface's binding energy for CO is regarded as the key factor for their activity and selectivity towards methanol and methane. Other metals, such as molybdenum–bismuth bimetallic chalcogenide, is reported to be efficient for the electrocatalytic reduction of carbon dioxide to methanol.[115] Different from metal catalysts, molecular catalysts such as iron tetradentate phosphine complex are found to be selective (Faraday efficiency of 68.5 %) for electrocatalytic reduction of CO_2 to methanol.[116] Moreover, a molecular cobalt phthalocyanine catalyst

immobilized on carbon nanotubes catalyzes the six-electron reduction of CO_2 to methanol with appreciable activity and selectivity.[117] In addition, the pyridinium ion is found to be a novel homogeneous catalyst for reducing CO_2 to methanol with faradaic yields of up to 30% at hydrogenated Pd electrodes.[118] Although some progress has been made, metallomacrocyclic catalysts are still far from meeting the practical requirement for direct electrochemical CO_2-to-methanol conversion.[119] Hernandez et al. compared the technical, environmental, and economic feasibility of CO_2 conversion to methanol via thermocatalytic and electrocatalytic technology[120]. It is suggested that the CO_2 electroreduction process must be optimized (improving catalysts performance and mass transfer) to achieve industrial production rates and the same maturity level of the thermocatalytic approach.

3.4 CO_2 to methane

Methane (CH_4), as the main component of natural gas, is also a greenhouse gas. Methane is emitted during the production and transportation of fossil fuels and from livestock and other agricultural practices, land use, and by the decay of organic waste in municipal solid waste landfills. Hydrogenation of CO_2 to CH_4, also known as methanation, can make synthetic natural gas and replace part of natural gas by using the existing gas distribution system. If renewable hydrogen is considered, the carbon emission can be reduced. CO_2 methanation is a thermodynamically more favorable reaction compared with CO_2 reduction to CO. However, a catalyst facilitating high CO_2 conversion and selectivity to CH_4 needs to be developed due to kinetic limitations. Figure 9 lists the possible reaction mechanism for CO_2 methanation. Ni-based catalysts are mostly studied for CO_2 methanation because of their high activity and low cost. However, conventional alumina-supported Ni catalysts are easily deactivated because of coke deposition and the sintering of Ni particles during the strongly exothermic process.

Therefore, other materials, such as hydrotalcite-derived materials and bimetallic catalysts (such as Ni-Fe) for CO_2 methanation, are investigated.[121] Other noble metals such as rhodium, ruthenium, and palladium dispersed on various supports were also investigated for CO_2 methanation, but Ni-based ones are still the most promising for industrial applications considering its activity and cost[15]. Thermodynamically, a lower temperature is more beneficial for higher CH_4 selectivity and equilibrium conversion of CO_2. Thus, efforts are also made to conduct CO_2 methanation at low temperatures, which can also reduce the sintering of catalysts.[122] Three possible reaction mechanisms of CO_2 methanation on Ni(111) surface were proposed[123]. The first one is via formate intermediate, while the second is the direct dissociation of $*CO_2$ to *CO and *O. The last mechanism contains a reaction intermediate of $C(OH)_2*$. Among these three paths, the direction dissociation is suggested as the optimal path. A recent mechanistic study of CO_2 methanation over Rh/TiO_2 catalysts[124] shows that the methane production rate per surface Rh atoms increases as metal particle size increases up to ca. 7 nm. Smaller Rh particles tend to bind *CO intermediate stronger than larger ones, and *CO dissociation is aided by the presence of H species and that a likely surface intermediate is Rh carbonyl hydrides. Apart from the active nickel sites, the support also plays an essential role in CO_2 methanation.[123] The support can affect CO_2 adsorption, CO_2 activation, methanation mechanism, and deactivation process.[90]

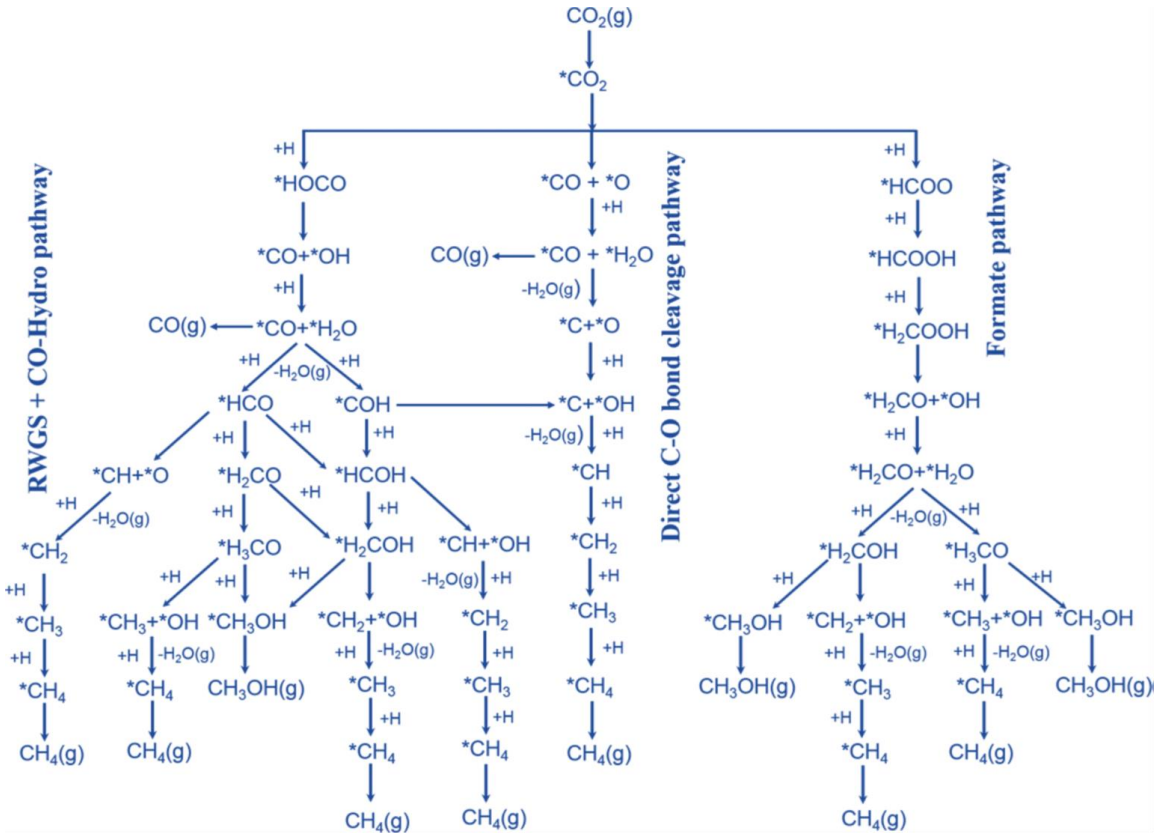


Figure 9. Possible reaction pathways of CO_2 hydrogenation to CO, CH_3OH, and CH_4. *(X) indicates adsorbed species. Reprinted with permission from Ref.[90] Copyright 2015 American Chemical Society.

In the electrocatalytic conversion of carbon dioxide to methane, eight electrons and eight protons need to be transferred. The selectivity to methane (Faraday efficiency) via CO_2 electroreduction is generally low compared with formate and CO, but CH_4 as a product has been observed on various transition metal surfaces, including Au, Ag, Zn, Cu, Ni, Pt, and Fe.[114] The activity descriptors for CO_2 electroreduction to methane on transition-metal catalysts were theoretically analyzed by Norskov and co-workers[125], as shown in Figure 10. For weak adsorption metal surfaces such as Au and Ag, the reaction is limited by the protonation of CO_2 to COOH. For other metals such as Cu, Ni, Pt, Rh, and Pd, it is found that the protonation of adsorbed CO is singled out as the most important step dictating the overpotential. Cu is predicted to be the best of all the seven metals investigated, but a larger

overpotential is needed to overcome the kinetics barrier. In the multi-electron transfer reduction of CO_2, a similar universal energetic scaling between *CO and *HCO intermediates leads to an overpotential for the eight-electron reduction of CO_2 to methane.[125] The binding energy *CHO must be strengthened relatively to *CO to make the catalyst more effective as reducing CO_2 to CH_4.

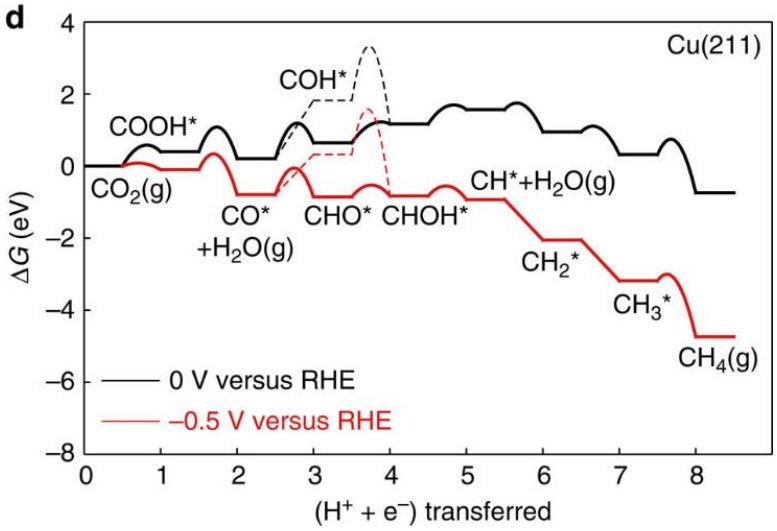


Figure 10. (d) free energy diagram for the reduction of CO_2 to CH_4 on Cu(211) at 0 V and −0.5 V versus RHE.[126] Copyright the authors by Creative Commons Attribution 4.0 International License.

3.5 CO_2 to ethylene

Ethylene is widely used in the chemical industry, and it is one of the most globally produced organic compounds. Although the hydrogenation of CO_2 to ethylene is a thermodynamically favorable reaction, there are rare reports about the thermocatalytic hydrogenation of CO_2 to ethylene with high selectivity. With methanol as an intermediate, it is reported that CO_2 can be hydrogenated to ethylene and propene via bifunctional catalysts.[20] However, a significant amount of CO as a byproduct is observed. Controllable C-C coupling to selectively forming ethylene is quite challenging in thermocatalysis approach.

In contrast, CO_2 can be reduced to ethylene at high selectivity on copper based electrocatalysts in the electroreduction process. Various methods, including tuning surface oxygen[28], fluorine modification[30], surface modification[127], as well as structural control[27] of Cu catalysts and laser-prepared CuZn alloy catalyst[29], are used to enhance the selectivity to ethylene. In the electrocatalysis route, CO dimer is considered as the primary intermediate during the reaction process.[128] It is also found that C2 products are favored in CO_2 electrochemical reduction under alkaline conditions. The mechanistic insights of a recent work[129] elucidate how reaction conditions can stabilize critical intermediates and lead to significant enhancements in selectivity and activity towards higher value added C2 products.

3.6 CO_2 to ethanol

Ethanol is another important industrial chemical and alternative fuel. Various catalysts, such as Cu@Na-Beta catalysts[130], ordered Pd–Cu Nanoparticles[131], supported Co_2C[132] or Co[133] catalysts, and promoted Rh/SiO_2 catalysts[134] are reported to be highly active and selective for thermocatalytic CO_2 hydrogenation to ethanol. However, the ethanol yield is far below methanol under similar reaction condition, further suggesting the selective C-C coupling is quite challenge in thermocatalysis.

In the electrocatalysis process, copper-based electrocatalysts dominated in the CO_2 electroreduction to ethanol process. The oxygen content controlled by selective oxidation/reduction in bimetallic AgCu foam electrocatalysts plays an important role in ethanol formation from CO_2.[135] Oxide-derived Cu_xZn catalysts were reported to selectivity reduction of CO_2 to ethanol via electrocatalysis way.[136] It is demonstrated that the selectivity of CO_2 reduction toward ethanol could be tuned by introducing a cocatalyst (Zn sites) to generate an in-situ source of mobile CO reactant, which can promote the ethanol production over ethylene.[136] In the electrocatalytic process, the atomically dispersed copper can even

form metallic clusters and act as active sites for selective electrocatalytic CO_2 reduction to ethanol[31]. Abild-Pedersen et al. [137] suggested that the carbon and hydroxide binding strengths will determine the trends in C2 oxygenate/hydrocarbon selectivity during CO_2 electrochemical reduction process. In short, the selectivity of ethanol in both thermocatalysis and electrocatalysis processes remains low, and more effective catalysts are needed. Understanding the oxygenate/hydrocarbon formation mechanism will facilitate the design of more efficient catalysts.

3.7 CO_2 to other higher carbon (C2+) products

In the electrocatalysis approach, copper catalysts show the highest potential for producing higher carbon products. A total of 16 different CO_2 reduction products were observed on copper.[138] A scheme forming multi-carbon products is proposed, as shown in Figure 11. Enol-like surface intermediates are proposed to account for the observed eleven distinct C2+ oxygenated products including aldehydes, ketones, alcohols, and carboxylic acids. Recently, electrochemical reduction of carbon dioxide to 1-butanol on oxide-derived copper, although the Faradaic efficiency is only 0.056 %, with a 1-butanol partial current density of −0.080 mA cm^{-2} at −0.48 V vs. RHE). [139] In contrast, Cu typically produces only single carbon atom products (e.g., CO, CH_4, and methanol) in gas-phase thermocatalysis. Theoretical study of C-C coupling in CO_2 electroreduction on copper electrodes[140] suggests that the control of hydrogen (proton and electron pairs) chemical potential by the applied potential at room temperature is unique to the electrochemical environment. In addition to Cu, some other catalysts show obvious selectivity to produce higher carbon products. For example, the electrocatalytic reduction of CO_2 to acetic acid can be achieved by a molecular manganese corrole complex immobilized on a carbon paper electrode [141] with a faradaic efficiency of 63 % and a turnover frequency of 8.25 h^{-1}.

Long-chain hydrocarbons by CO_2 electroreduction using polarized nickel catalysts are also achieved although the Faradaic efficiencies is only up to 6.5% .[32] How to improve the selectivity of advanced carbon products will be an important research direction for electrochemical CO_2 reduction in the future.

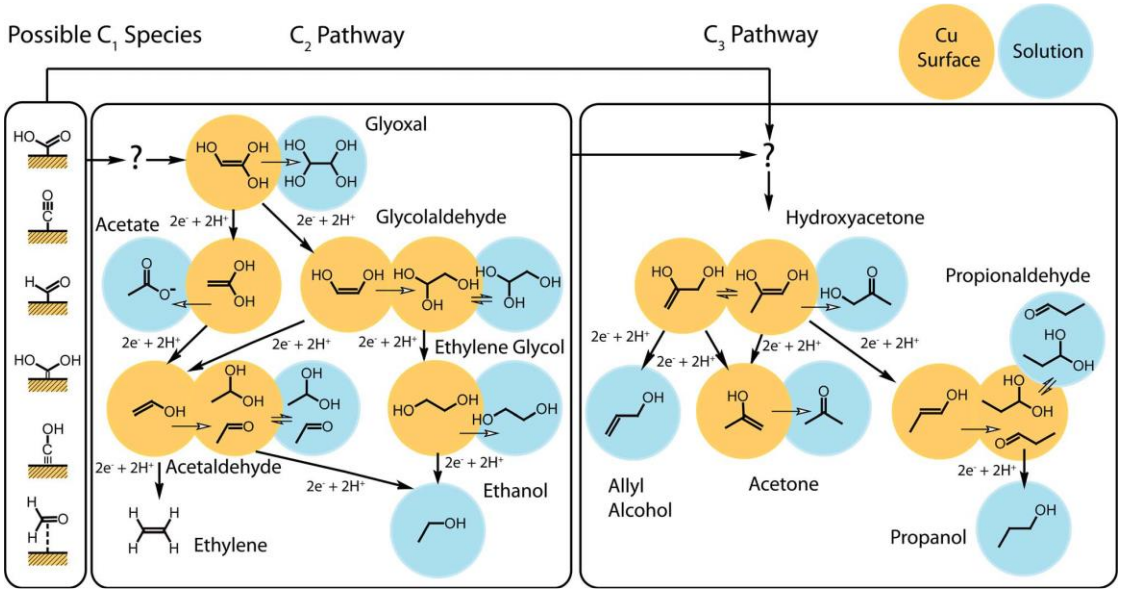


Figure 11. Proposed reaction pathway for C2 and C3 products with enol-like surface intermediates on Cu surface. Adopted with permission from Ref [138], Copyright 2012 The Royal Society of Chemistry.

Regarding the progress of CO_2 reduction to higher carbon products, the thermocatalysis approach made progress far beyond electrocatalytic processes. In the thermocatalytic CO_2 hydrogenation approach, complex products such as light olefins[20], aromatics[22, 142], gasoline[143], and liquid fuels[144, 145] with decent yield have been reported. Typically, in these process, bifunctional catalysts are used with the first catalyst to generate methanol from CO_2 hydrogenation, then convert methanol to high-value products on another catalyst. In contrast, Fischer–Tropsch synthesis (FTS)-based CO_2 hydrogenation is another different process, which combines the reduction of CO_2 to CO via the reverse water gas shift

reaction and hydrogenation of CO to hydrocarbons via FTS. These FTS based CO_2 hydrogenation processes can produce lighter olefins[146], C5+ products such as gasoline and diesel liquid fuels and other value-added chemicals such as aromatics and isoparaffins[147]. For instance, Fe- and FeCo-based catalysts can achieve ≥ 54.6% CO_2 conversion and ≥ 47.0% C5+ selectivity. CO_2 FTS can also produce higher alcohols (C2+OH)[148, 149]. In both thermocatalytic and electrocatalytic CO_2 conversion process, the surface science of the catalyst regulates C–C coupling process.[150] Understanding surface science under reaction conditions will play an important role in the design and development of catalysts.

4. Thermocatalysis and electrocatalysis coupled system

There are usually two ways to combine the advantages of thermocatalysis and electrocatalysis. One is to conduct the electrocatalytic CO_2 reduction at high temperature and pressure[151-153] (to introduce thermocatalysis), the other is to apply the electric field in the thermocatalytic CO_2 reduction process [154-157]. Both methods have been studied, and some progress has been made. For example, compared with the CO_2 electrochemical reduction at room temperature, electrolysis of CO_2 ($2CO_2 \rightarrow 2CO + O_2$) at high temperatures (600 -1000 ^oC) exhibits higher current density and energy efficiency.[151] In the high-temperature solid oxide electrolysis cells (SOECs), CO_2 and H_2O are fed in the cathode and typically reduced to CO (and H_2). Meanwhile, the O^{2-} ions are transferred to the anode and oxidized to O_2 through an O^{2-} ions membrane / conducting electrolyte. Ni and perovskite are the typical cathode materials. However, the cell degradation is the major challenge for the practical application of SOECs. The main degradation reasons for electrodes are agglomeration, depletion, carbon formation, poisoning, and decomposition. To address these problems, low temperature SOFC as a self-promoted reactor for CO_2 catalytic hydrogenation was proposed.[158]

Coupled thermal–electrochemical catalysis could offer an attractive approach to upgrading CO_2 into value-added products if selective electrocatalysts and integrated devices were developed. There are some signs of progress have been reported. For example, CO_2 electrolyzer that operates at low overpotential and ambient pressure can selectively produce either CO or CH_4 with high selectivity (>95%) using Ir–ceria-based catalysts in an intermediate temperature (400 °C).[159] Moreover, coupling electrocatalytic CO_2 reduction with thermocatalysis enables the formation of a lactone monomer[160], which is not a typical product in single electrocatalytic or thermocatalytic processes. At last, in the catalyst development aspect, carbon-based materials[101] and core–shell structured catalysts[161] are proposed to bridge thermocatalysis and electrocatalysis and even photocatalytic process.

5. Conclusion and Outlook

Reducing CO_2 to valuable chemicals and fuels such as formic acid, carbon monoxide, methanol, methane, ethylene, ethanol, etc. by renewable hydrogen via thermocatalysis or by renewable electricity via electrocatalysis provides an attractive and sustainable way to addressing the climate change challenge. The thermocatalytic pathway can easily scale up and realize industrial-scale applications, but some of the reactions are limited by slow kinetic or thermodynamic equilibrium. In contrast, the electrocatalytic approach for CO_2 reduction is much less mature but has some advantages, such as low temperature and low pressure, using water as a hydrogen source, and is not restricted by thermodynamic equilibrium. In general, the thermocatalytic approaches have made more significant progress than electrocatalytic approaches in generating multi-carbon products via CO_2 reduction. Future research directions for CO_2 conversion process may consider the following two aspects.

(1) Electrochemical promoted thermocatalysis route

There is still much room for research to introduce an external field, such as an applying electronic field to facilitate the CO_2 reduction reaction.[10] In addition, the synergies between electrocatalytic and thermocatalytic routes for CO_2 conversion to alcohols over Cu/ZnO catalysts has already proposed.[162] Solid electrolyte CO_2 reduction cell operates at a relative high temperature (200-250 ºC) can be considered. In that kind of reactor, CO_2 can be directly reduced by proton and electron on the electrocatalyst surface via electrocatalytic way ($xCO_2 + nH^+ + ne^- \rightarrow$ product + yH_2O). Meanwhile, part of proton and electron will recombine to H_2 molecule or hydrogen atom on the catalyst surface and react with CO_2 via the thermocatalytic way ($CO_2 + H_2 \rightarrow$ product + H_2O). It is worth to emphasize that, in traditional thermocatalytic reactor, the chemical potential of H_2 and CO_2 gas can only be adjusted by temperature and pressure. Here, the total chemical potential of hydrogen species and CO_2 can be further tuned by electric potential (for $H^+ + e^-$ part). At the same time, the electrical potential may affect or influence the electronic structure of the catalysts, which again promote the thermocatalytic process. To achieve this concept, development of high temperature (e.g. 200-250 ºC) proton transfer membrane is necessary. Recent research shows that phosphoric acid-doped intrinsically ultramicroporous membranes can operate at 200 ºC for fuel cells[163], which is very promising for this application.

(2) Tandem system / catalysts for CO_2 reduction

The tandem system includes electrocatalytic–thermocatalytic reaction scheme for CO_2 reduction to higher carbon products. For example, CO_2 can be reduced to syngas (CO and H_2, H_2 is generated via side reaction) via electrocatalytic approach and then the syngas can be converted to higher products such as C3 oxygenates via thermocatalytic approach[164]. The tandem system can also be a thermocatalytic process followed by electrocatalytic process, however, no such process has been

demonstrated and intensive research is necessary. The tandem thermocatalysts like the methanol synthesis via CO_2 hydrogenation catalysts as an intermediate, then the methanol can be further converted to higher products. Similar concept is applied in thermocatalytic process, for example, Jaramillo and coworkers developed a tandem gold-on-copper electrocatalyst which offers gold for CO generation and copper for further CO reduction to alcohols.[165] The rational design of bifunctional catalysts based on surface science and theoretical calculations has great potential to make breakthrough in both CO_2 thermocatalytic and electrocatalytic. The recent rise of machine learning and artificial intelligence promises to speed up the development process.

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Author contributions

J. Gao drafted manuscript; Y. Liu revised the manuscript.

Competing interests

The authors declare no competing financial interests.

Reference

(1) Wang, R.; Assenova, V. A.; Hertwich, E. G. Energy system decarbonization and productivity gains reduced the coupling of CO2 emissions and economic growth in 73 countries between 1970 and 2016. *One Earth* **2021**, *4*, 1614-1624.

(2) Mac Dowell, N.; Fennell, P. S.; Shah, N.; Maitland, G. C. The role of CO2 capture and utilization in mitigating climate change. *Nature Climate Change* **2017**, *7*, 243-249.

(3) Hepburn, C.; Adlen, E.; Beddington, J.; Carter, E. A.; Fuss, S.; Mac Dowell, N.; Minx, J. C.; Smith, P.; Williams, C. K. The technological and economic prospects for CO(2) utilization and removal. *Nature* **2019**, *575*, 87-97.

(4) Matthews, H. D.; Gillett, N. P.; Stott, P. A.; Zickfeld, K. The proportionality of global warming to cumulative carbon emissions. *Nature* **2009**, *459*, 829-832.

(5) Davis, S. J.; Caldeira, K.; Matthews, H. D. Future CO2 emissions and climate change from existing energy infrastructure. *Science* **2010**, *329*, 1330-1333.

(6) Siegenthaler, U.; Sarmiento, J. L. Atmospheric carbon dioxide and the ocean. *Nature* **1993**, *365*, 119-125.

(7) Song, C. Global challenges and strategies for control, conversion and utilization of CO2 for sustainable development involving energy, catalysis, adsorption and chemical processing. *Catalysis Today* **2006**, *115*, 2-32.

(8) Geerlings, H.; Zevenhoven, R. CO2 mineralization-bridge between storage and utilization of CO2. *Annu Rev Chem Biomol Eng* **2013**, *4*, 103-117.

(9) Nørskov, J. K.; Studt, F.; Abild-Pedersen, F.; Bligaard, T. Heterogeneous Catalysis and a Sustainable Future. In *Fundamental Concepts in Heterogeneous Catalysis*, Nørskov, J. K., Studt, F., Abild-Pedersen, F., Bligaard, T. Eds.; Wiley, 2014; pp 1-5.

(10) Xu, Y.; Zhou, Z.; Zou, M.; Liu, Y.; Zheng, Y.; Yang, Y.; Lan, S.; Lan, J.; Nan, C.-W.; Lin, Y.-H. Multi-field driven hybrid catalysts for CO2 reduction: Progress, mechanism and perspective. *Materials Today* **2022**, *54*, 225-246.

(11) Wagner, A.; Sahm, C. D.; Reisner, E. Towards molecular understanding of local chemical environment effects in electro- and photocatalytic CO2 reduction. *Nature Catalysis* **2020**, *3*, 775-786.

(12) Nahar, S.; Zain, M. F. M.; Kadhum, A. A. H.; Hasan, H. A.; Hasan, M. R. Advances in

Photocatalytic CO(2) Reduction with Water: A Review. *Materials (Basel)* **2017**, *10*, 629.

(13) Ran, J.; Jaroniec, M.; Qiao, S. Z. Cocatalysts in Semiconductor-based Photocatalytic CO(2) Reduction: Achievements, Challenges, and Opportunities. *Adv Mater* **2018**, *30*, 1704649.

(14) Sun, R.; Liao, Y.; Bai, S.-T.; Zheng, M.; Zhou, C.; Zhang, T.; Sels, B. F. Heterogeneous catalysts for CO2 hydrogenation to formic acid/formate: from nanoscale to single atom. *Energy & Environmental Science* **2021**, *14*, 1247-1285.

(15) Frontera, P.; Macario, A.; Ferraro, M.; Antonucci, P. Supported Catalysts for CO2 Methanation: A Review. *Catalysts* **2017**, *7*,

(16) Ashok, J.; Pati, S.; Hongmanorom, P.; Tianxi, Z.; Junmei, C.; Kawi, S. A review of recent catalyst advances in CO2 methanation processes. *Catalysis Today* **2020**, *356*, 471-489.

(17) Chen, X.; Chen, Y.; Song, C.; Ji, P.; Wang, N.; Wang, W.; Cui, L. Recent Advances in Supported Metal Catalysts and Oxide Catalysts for the Reverse Water-Gas Shift Reaction. *Front Chem* **2020**, *8*, 709.

(18) Jiang, X.; Nie, X.; Guo, X.; Song, C.; Chen, J. G. Recent Advances in Carbon Dioxide Hydrogenation to Methanol via Heterogeneous Catalysis. *Chem Rev* **2020**, *120*, 7984-8034.

(19) Yang, H.; Zhang, C.; Gao, P.; Wang, H.; Li, X.; Zhong, L.; Wei, W.; Sun, Y. A review of the catalytic hydrogenation of carbon dioxide into value-added hydrocarbons. *Catalysis Science & Technology* **2017**, *7*, 4580-4598.

(20) Gao, J.; Jia, C.; Liu, B. Direct and selective hydrogenation of CO2 to ethylene and propene by bifunctional catalysts. *Catalysis Science & Technology* **2017**, *7*, 5602-5607.

(21) Li, Z.; Qu, Y.; Wang, J.; Liu, H.; Li, M.; Miao, S.; Li, C. Highly Selective Conversion of Carbon Dioxide to Aromatics over Tandem Catalysts. *Joule* **2019**, *3*, 570-583.

(22) Ni, Y.; Chen, Z.; Fu, Y.; Liu, Y.; Zhu, W.; Liu, Z. Selective conversion of CO(2) and H(2) into aromatics. *Nat Commun* **2018**, *9*, 3457.

(23) Duarah, P.; Haldar, D.; Yadav, V. S. K.; Purkait, M. K. Progress in the electrochemical reduction of CO2 to formic acid: A review on current trends and future prospects. *Journal of Environmental Chemical Engineering* **2021**, *9*, 106394.

(24) Küngas, R. Review—Electrochemical CO2 Reduction for CO Production: Comparison of Low- and High-Temperature Electrolysis Technologies. *Journal of The Electrochemical Society* **2020**, *167*,

044508.

(25) Pan, H.; Barile, C. J. Electrochemical CO2 reduction to methane with remarkably high Faradaic efficiency in the presence of a proton permeable membrane. *Energy & Environmental Science* **2020**, *13*, 3567-3578.

(26) Yang, D.; Zhu, Q.; Chen, C.; Liu, H.; Liu, Z.; Zhao, Z.; Zhang, X.; Liu, S.; Han, B. Selective electroreduction of carbon dioxide to methanol on copper selenide nanocatalysts. *Nat Commun* **2019**, *10*, 677.

(27) Zhang, B.; Zhang, J.; Hua, M.; Wan, Q.; Su, Z.; Tan, X.; Liu, L.; Zhang, F.; Chen, G.; Tan, D.; et al. Highly Electrocatalytic Ethylene Production from CO(2) on Nanodefective Cu Nanosheets. *J Am Chem Soc* **2020**, *142*, 13606-13613.

(28) Zhang, W.; Huang, C.; Xiao, Q.; Yu, L.; Shuai, L.; An, P.; Zhang, J.; Qiu, M.; Ren, Z.; Yu, Y. Atypical Oxygen-Bearing Copper Boosts Ethylene Selectivity toward Electrocatalytic CO(2) Reduction. *J Am Chem Soc* **2020**, *142*, 11417-11427.

(29) Feng, Y.; Li, Z.; Liu, H.; Dong, C.; Wang, J.; Kulinich, S. A.; Du, X. Laser-Prepared CuZn Alloy Catalyst for Selective Electrochemical Reduction of CO(2) to Ethylene. *Langmuir* **2018**, *34*, 13544-13549.

(30) Ma, W.; Xie, S.; Liu, T.; Fan, Q.; Ye, J.; Sun, F.; Jiang, Z.; Zhang, Q.; Cheng, J.; Wang, Y. Electrocatalytic reduction of CO2 to ethylene and ethanol through hydrogen-assisted C–C coupling over fluorine-modified copper. *Nature Catalysis* **2020**, *3*, 478-487.

(31) Xu, H.; Rebollar, D.; He, H.; Chong, L.; Liu, Y.; Liu, C.; Sun, C.-J.; Li, T.; Muntean, J. V.; Winans, R. E.; et al. Highly selective electrocatalytic CO2 reduction to ethanol by metallic clusters dynamically formed from atomically dispersed copper. *Nature Energy* **2020**, *5*, 623-632.

(32) Zhou, Y.; Martín, A. J.; Dattila, F.; Xi, S.; López, N.; Pérez-Ramírez, J.; Yeo, B. S. Long-chain hydrocarbons by CO2 electroreduction using polarized nickel catalysts. *Nature Catalysis* **2022**, *5*, 545-554.

(33) Sancho-Sanz, I.; Korili, S. A.; Gil, A. Catalytic valorization of CO2 by hydrogenation: current status and future trends. *Catalysis Reviews* **2021**, 1-75.

(34) Ye, R. P.; Ding, J.; Gong, W.; Argyle, M. D.; Zhong, Q.; Wang, Y.; Russell, C. K.; Xu, Z.; Russell, A. G.; Li, Q.; et al. CO(2) hydrogenation to high-value products via heterogeneous catalysis. *Nat*

Commun **2019**, *10*, 5698.

(35) Lim, R. J.; Xie, M.; Sk, M. A.; Lee, J.-M.; Fisher, A.; Wang, X.; Lim, K. H. A review on the electrochemical reduction of CO2 in fuel cells, metal electrodes and molecular catalysts. *Catalysis Today* **2014**, *233*, 169-180.

(36) Costentin, C.; Robert, M.; Saveant, J. M. Catalysis of the electrochemical reduction of carbon dioxide. *Chem Soc Rev* **2013**, *42*, 2423-2436.

(37) Long, C.; Li, X.; Guo, J.; Shi, Y.; Liu, S.; Tang, Z. Electrochemical Reduction of CO2over Heterogeneous Catalysts in Aqueous Solution: Recent Progress and Perspectives. *Small Methods* **2018**, *3*, 1800369.

(38) Ma, W.; He, X.; Wang, W.; Xie, S.; Zhang, Q.; Wang, Y. Electrocatalytic reduction of CO(2) and CO to multi-carbon compounds over Cu-based catalysts. *Chem Soc Rev* **2021**, *50*, 12897-12914.

(39) Nitopi, S.; Bertheussen, E.; Scott, S. B.; Liu, X.; Engstfeld, A. K.; Horch, S.; Seger, B.; Stephens, I. E. L.; Chan, K.; Hahn, C.; et al. Progress and Perspectives of Electrochemical CO(2) Reduction on Copper in Aqueous Electrolyte. *Chem Rev* **2019**, *119*, 7610-7672.

(40) Lei, Y.; Wang, Z.; Bao, A.; Tang, X.; Huang, X.; Yi, H.; Zhao, S.; Sun, T.; Wang, J.; Gao, F. Recent advances on electrocatalytic CO2 reduction to resources: Target products, reaction pathways and typical catalysts. *Chemical Engineering Journal* **2023**, *453*, 139663.

(41) Xu, L.; Xiu, Y.; Liu, F.; Liang, Y.; Wang, S. Research Progress in Conversion of CO(2) to Valuable Fuels. *Molecules* **2020**, *25*,

(42) Tackett, B. M.; Gomez, E.; Chen, J. G. Net reduction of CO_2 via its thermocatalytic and electrocatalytic transformation reactions in standard and hybrid processes. *Nature Catalysis* **2019**, *2*, 381-386.

(43) Fortunato, G. V.; Pizzutilo, E.; Katsounaros, I.; Gohl, D.; Lewis, R. J.; Mayrhofer, K. J. J.; Hutchings, G. J.; Freakley, S. J.; Ledendecker, M. Analysing the relationship between the fields of thermo- and electrocatalysis taking hydrogen peroxide as a case study. *Nat Commun* **2022**, *13*, 1973.

(44) Samanta, S.; Srivastava, R. Catalytic conversion of CO2 to chemicals and fuels: the collective thermocatalytic/photocatalytic/electrocatalytic approach with graphitic carbon nitride. *Materials Advances* **2020**, *1*, 1506-1545.

(45) Prins, R.; De Beer, V. H. J.; Somorjai, G. A. Structure and Function of the Catalyst and the

Promoter in Co—Mo Hydrodesulfurization Catalysts. *Catalysis Reviews* **1989**, *31*, 1-41.

(46) Benck, J. D.; Hellstern, T. R.; Kibsgaard, J.; Chakthranont, P.; Jaramillo, T. F. Catalyzing the Hydrogen Evolution Reaction (HER) with Molybdenum Sulfide Nanomaterials. *ACS Catalysis* **2014**, *4*, 3957-3971.

(47) Lauritsen, J. V.; Nyberg, M.; Nørskov, J. K.; Clausen, B. S.; Topsøe, H.; Lægsgaard, E.; Besenbacher, F. Hydrodesulfurization reaction pathways on MoS2 nanoclusters revealed by scanning tunneling microscopy. *Journal of Catalysis* **2004**, *224*, 94-106.

(48) Jaramillo, T. F.; Jorgensen, K. P.; Bonde, J.; Nielsen, J. H.; Horch, S.; Chorkendorff, I. Identification of active edge sites for electrochemical H2 evolution from MoS2 nanocatalysts. *Science* **2007**, *317*, 100-102.

(49) Adams, J. S.; Kromer, M. L.; Rodriguez-Lopez, J.; Flaherty, D. W. Unifying Concepts in Electro- and Thermocatalysis toward Hydrogen Peroxide Production. *J Am Chem Soc* **2021**, *143*, 7940-7957.

(50) O'Hayre, R.; Cha, S.-W.; Colella, W.; Prinz, F. B. Chapter 3 - Fuel Cell Reaction Kinetics. In *Fuel Cell Fundamentals*, 3rd ed.; O'Hayre, R., Cha, S.-W., Colella, W., Prinz, F. B. Eds.; Wiley, 2016.

(51) Bligaard, T.; Nørskov, J. K.; Dahl, S.; Matthiesen, J.; Christensen, C. H.; Sehested, J. **The Brønsted–Evans–Polanyi relation and the volcano curve in heterogeneous catalysis**. *Journal of Catalysis* **2004**, *224*, 206-217.

(52) Jia, C.; Gao, J.; Dai, Y.; Zhang, J.; Yang, Y. The thermodynamics analysis and experimental validation for complicated systems in CO 2 hydrogenation process. *Journal of Energy Chemistry* **2016**, *25*, 1027-1037.

(53) Zhang, S.; Fan, Q.; Xia, R.; Meyer, T. J. CO(2) Reduction: From Homogeneous to Heterogeneous Electrocatalysis. *Acc Chem Res* **2020**, *53*, 255-264.

(54) Kortlever, R.; Shen, J.; Schouten, K. J.; Calle-Vallejo, F.; Koper, M. T. Catalysts and Reaction Pathways for the Electrochemical Reduction of Carbon Dioxide. *J Phys Chem Lett* **2015**, *6*, 4073-4082.

(55) Tang, M. T.; Peng, H.; Lamoureux, P. S.; Bajdich, M.; Abild-Pedersen, F. From electricity to fuels: Descriptors for C1 selectivity in electrochemical CO2 reduction. *Applied Catalysis B: Environmental* **2020**, *279*,

(56) Hori, Y.; Wakebe, H.; Tsukamoto, T.; Koga, O. Electrocatalytic process of CO selectivity in electrochemical reduction of CO2 at metal electrodes in aqueous media. *Electrochimica Acta* **1994**, *39*,

1833-1839.

(57) Bagger, A.; Ju, W.; Varela, A. S.; Strasser, P.; Rossmeisl, J. Electrochemical CO(2) Reduction: A Classification Problem. *ChemPhysChem* **2017**, *18*, 3266-3273.

(58) Nishimura, Y. F.; Peng, H. J.; Nitopi, S.; Bajdich, M.; Wang, L.; Morales-Guio, C. G.; Abild-Pedersen, F.; Jaramillo, T. F.; Hahn, C. Guiding the Catalytic Properties of Copper for Electrochemical CO(2) Reduction by Metal Atom Decoration. *ACS Appl Mater Interfaces* **2021**,

(59) Eppinger, J.; Huang, K.-W. Formic Acid as a Hydrogen Energy Carrier. *ACS Energy Letters* **2016**, *2*, 188-195.

(60) Bulushev, D. A.; Ross, J. R. H. Heterogeneous catalysts for hydrogenation of CO2 and bicarbonates to formic acid and formates. *Catalysis Reviews* **2018**, *60*, 566-593.

(61) Zhang, Z.; Zhang, L.; Yao, S.; Song, X.; Huang, W.; Hülsey, M. J.; Yan, N. Support-dependent rate-determining step of CO2 hydrogenation to formic acid on metal oxide supported Pd catalysts. *Journal of Catalysis* **2019**, *376*, 57-67.

(62) Preti, D.; Resta, C.; Squarcialupi, S.; Fachinetti, G. Carbon dioxide hydrogenation to formic acid by using a heterogeneous gold catalyst. *Angew Chem Int Ed Engl* **2011**, *50*, 12551-12554.

(63) Lv, X.; Lu, G.; Wang, Z.-Q.; Xu, Z.-N.; Guo, G.-C. Computational Evidence for Lewis Base-Promoted CO2 Hydrogenation to Formic Acid on Gold Surfaces. *ACS Catalysis* **2017**, *7*, 4519-4526.

(64) Xu, Z.; McNamara, N. D.; Neumann, G. T.; Schneider, W. F.; Hicks, J. C. Catalytic Hydrogenation of CO2to Formic Acid with Silica-Tethered Iridium Catalysts. *ChemCatChem* **2013**, *5*, 1769-1771.

(65) Kanega, R.; Ertem, M. Z.; Onishi, N.; Szalda, D. J.; Fujita, E.; Himeda, Y. CO2 Hydrogenation and Formic Acid Dehydrogenation Using Ir Catalysts with Amide-Based Ligands. *Organometallics* **2020**, *39*, 1519-1531.

(66) Weilhard, A.; Qadir, M. I.; Sans, V.; Dupont, J. Selective CO2 Hydrogenation to Formic Acid with Multifunctional Ionic Liquids. *ACS Catalysis* **2018**, *8*, 1628-1634.

(67) Peng, G.; Sibener, S. J.; Schatz, G. C.; Ceyer, S. T.; Mavrikakis, M. CO2 Hydrogenation to Formic Acid on Ni(111). *The Journal of Physical Chemistry C* **2012**, *116*, 3001-3006.

(68) Peng, G.; Sibener, S. J.; Schatz, G. C.; Mavrikakis, M. CO2 hydrogenation to formic acid on Ni(110). *Surface Science* **2012**, *606*, 1050-1055.

(69) Birdja, Y. Y.; Shen, J.; Koper, M. T. M. Influence of the metal center of metalloprotoporphyrins

on the electrocatalytic CO2 reduction to formic acid. *Catalysis Today* **2017**, *288*, 37-47.

(70) Kang, P.; Zhang, S.; Meyer, T. J.; Brookhart, M. Rapid selective electrocatalytic reduction of carbon dioxide to formate by an iridium pincer catalyst immobilized on carbon nanotube electrodes. *Angew Chem Int Ed Engl* **2014**, *53*, 8709-8713.

(71) Kanega, R.; Onishi, N.; Wang, L.; Himeda, Y. Electroreduction of Carbon Dioxide to Formate by Homogeneous Ir Catalysts in Water. *ACS Catalysis* **2018**, *8*, 11296-11301.

(72) Machan, C. W.; Sampson, M. D.; Kubiak, C. P. A Molecular Ruthenium Electrocatalyst for the Reduction of Carbon Dioxide to CO and Formate. *J Am Chem Soc* **2015**, *137*, 8564-8571.

(73) Chen, Y.; Kanan, M. W. Tin oxide dependence of the CO2 reduction efficiency on tin electrodes and enhanced activity for tin/tin oxide thin-film catalysts. *J Am Chem Soc* **2012**, *134*, 1986-1989.

(74) Wu, D.; Liu, J.; Liang, Y.; Xiang, K.; Fu, X. Z.; Luo, J. L. Electrochemical Transformation of Facet-Controlled BiOI into Mesoporous Bismuth Nanosheets for Selective Electrocatalytic Reduction of CO(2) to Formic Acid. *ChemSusChem* **2019**, *12*, 4700-4707.

(75) Ma, W.; Xie, S.; Zhang, X. G.; Sun, F.; Kang, J.; Jiang, Z.; Zhang, Q.; Wu, D. Y.; Wang, Y. Promoting electrocatalytic CO(2) reduction to formate via sulfur-boosting water activation on indium surfaces. *Nat Commun* **2019**, *10*, 892.

(76) Lee, C. H.; Kanan, M. W. Controlling H+ vs CO2 Reduction Selectivity on Pb Electrodes. *ACS Catalysis* **2014**, *5*, 465-469.

(77) Ding, P.; Zhao, H.; Li, T.; Luo, Y.; Fan, G.; Chen, G.; Gao, S.; Shi, X.; Lu, S.; Sun, X. Metal-based electrocatalytic conversion of CO2 to formic acid/formate. *Journal of Materials Chemistry A* **2020**, *8*, 21947-21960.

(78) Li, J.; Kuang, Y.; Meng, Y.; Tian, X.; Hung, W. H.; Zhang, X.; Li, A.; Xu, M.; Zhou, W.; Ku, C. S.; et al. Electroreduction of CO(2) to Formate on a Copper-Based Electrocatalyst at High Pressures with High Energy Conversion Efficiency. *J Am Chem Soc* **2020**, *142*, 7276-7282.

(79) Zheng, T.; Liu, C.; Guo, C.; Zhang, M.; Li, X.; Jiang, Q.; Xue, W.; Li, H.; Li, A.; Pao, C. W.; et al. Copper-catalysed exclusive CO(2) to pure formic acid conversion via single-atom alloying. *Nat Nanotechnol* **2021**, *16*, 1386-1393.

(80) Fan, L.; Xia, C.; Zhu, P.; Lu, Y.; Wang, H. Electrochemical CO(2) reduction to high-concentration pure formic acid solutions in an all-solid-state reactor. *Nat Commun* **2020**, *11*, 3633.

(81) Koper, M. T. M. Thermodynamic theory of multi-electron transfer reactions: Implications for electrocatalysis. *Journal of Electroanalytical Chemistry* **2011**, *660*, 254-260.

(82) Goguet, A.; Shekhtman, S.; Burch, R.; Hardacre, C.; Meunier, F.; Yablonsky, G. Pulse-response TAP studies of the reverse water–gas shift reaction over a Pt/CeO2 catalyst. *Journal of Catalysis* **2006**, *237*, 102-110.

(83) Pettigrew, D. J.; Trimm, D. L.; Cant, N. W. The effects of rare earth oxides on the reverse water-gas shift reaction on palladium/alumina. *Catalysis Letters* **1994**, *28*, 313-319.

(84) Erdőhelyi, A. Hydrogenation of Carbon Dioxide on Supported Rh Catalysts. *Catalysts* **2020**, *10*,

(85) Wang, L. C.; Tahvildar Khazaneh, M.; Widmann, D.; Behm, R. J. TAP reactor studies of the oxidizing capability of CO2 on a Au/CeO2 catalyst – A first step toward identifying a redox mechanism in the Reverse Water–Gas Shift reaction. *Journal of Catalysis* **2013**, *302*, 20-30.

(86) Kattel, S.; Yan, B.; Yang, Y.; Chen, J. G.; Liu, P. Optimizing Binding Energies of Key Intermediates for CO2 Hydrogenation to Methanol over Oxide-Supported Copper. *J Am Chem Soc* **2016**, *138*, 12440-12450.

(87) Gu, M.; Dai, S.; Qiu, R.; Ford, M. E.; Cao, C.; Wachs, I. E.; Zhu, M. Structure–Activity Relationships of Copper- and Potassium-Modified Iron Oxide Catalysts during Reverse Water–Gas Shift Reaction. *ACS Catalysis* **2021**, *11*, 12609-12619.

(88) Loiland, J. A.; Wulfers, M. J.; Marinkovic, N. S.; Lobo, R. F. Fe/γ-Al2O3 and Fe–K/γ-Al2O3 as reverse water-gas shift catalysts. *Catalysis Science & Technology* **2016**, *6*, 5267-5279.

(89) Sun, F.-m.; Yan, C.-f.; Wang, Z.-d.; Guo, C.-q.; Huang, S.-l. Ni/Ce–Zr–O catalyst for high CO2 conversion during reverse water gas shift reaction (RWGS). *International Journal of Hydrogen Energy* **2015**, *40*, 15985-15993.

(90) Kattel, S.; Liu, P.; Chen, J. G. Tuning Selectivity of CO(2) Hydrogenation Reactions at the Metal/Oxide Interface. *J Am Chem Soc* **2017**, *139*, 9739-9754.

(91) Hansen, H. A.; Varley, J. B.; Peterson, A. A.; Norskov, J. K. Understanding Trends in the Electrocatalytic Activity of Metals and Enzymes for CO2 Reduction to CO. *J Phys Chem Lett* **2013**, *4*, 388-392.

(92) Zhao, S.; Jin, R.; Jin, R. Opportunities and Challenges in CO2 Reduction by Gold- and Silver-Based Electrocatalysts: From Bulk Metals to Nanoparticles and Atomically Precise Nanoclusters. *ACS*

Energy Letters **2018**, *3*, 452-462.

(93) Monteiro, M. C. O.; Philips, M. F.; Schouten, K. J. P.; Koper, M. T. M. Efficiency and selectivity of CO(2) reduction to CO on gold gas diffusion electrodes in acidic media. *Nat Commun* **2021**, *12*, 4943.

(94) Delacourt, C.; Ridgway, P. L.; Newman, J. Mathematical Modeling of CO[sub 2] Reduction to CO in Aqueous Electrolytes. *Journal of The Electrochemical Society* **2010**, *157*, B1902.

(95) Monteiro, M. C. O.; Dattila, F.; Hagedoorn, B.; García-Muelas, R.; López, N.; Koper, M. T. M. Absence of CO2 electroreduction on copper, gold and silver electrodes without metal cations in solution. *Nature Catalysis* **2021**, *4*, 654-662.

(96) Hu, X.-M.; Hval, H. H.; Bjerglund, E. T.; Dalgaard, K. J.; Madsen, M. R.; Pohl, M.-M.; Welter, E.; Lamagni, P.; Buhl, K. B.; Bremholm, M.; et al. Selective CO2 Reduction to CO in Water using Earth-Abundant Metal and Nitrogen-Doped Carbon Electrocatalysts. *ACS Catalysis* **2018**, *8*, 6255-6264.

(97) Yang, H. B.; Hung, S.-F.; Liu, S.; Yuan, K.; Miao, S.; Zhang, L.; Huang, X.; Wang, H.-Y.; Cai, W.; Chen, R.; et al. Atomically dispersed Ni(i) as the active site for electrochemical CO2 reduction. *Nature Energy* **2018**, *3*, 140-147.

(98) Ju, W.; Bagger, A.; Hao, G. P.; Varela, A. S.; Sinev, I.; Bon, V.; Roldan Cuenya, B.; Kaskel, S.; Rossmeisl, J.; Strasser, P. Understanding activity and selectivity of metal-nitrogen-doped carbon catalysts for electrochemical reduction of CO(2). *Nat Commun* **2017**, *8*, 944.

(99) Koshy, D. M.; Chen, S.; Lee, D. U.; Stevens, M. B.; Abdellah, A. M.; Dull, S. M.; Chen, G.; Nordlund, D.; Gallo, A.; Hahn, C.; et al. Understanding the Origin of Highly Selective CO(2) Electroreduction to CO on Ni,N-doped Carbon Catalysts. *Angew Chem Int Ed Engl* **2020**, *59*, 4043-4050.

(100) Tackett, B. M.; Lee, J. H.; Chen, J. G. Electrochemical Conversion of CO(2) to Syngas with Palladium-Based Electrocatalysts. *Acc Chem Res* **2020**, *53*, 1535-1544.

(101) Koshy, D. M.; Nathan, S. S.; Asundi, A. S.; Abdellah, A. M.; Dull, S. M.; Cullen, D. A.; Higgins, D.; Bao, Z.; Bent, S. F.; Jaramillo, T. F. Bridging Thermal Catalysis and Electrocatalysis: Catalyzing CO(2) Conversion with Carbon-Based Materials. *Angew Chem Int Ed Engl* **2021**, *60*, 17472-17480.

(102) Dang, S.; Yang, H.; Gao, P.; Wang, H.; Li, X.; Wei, W.; Sun, Y. A review of research progress on

heterogeneous catalysts for methanol synthesis from carbon dioxide hydrogenation. *Catalysis Today* **2019**, *330*, 61-75.

(103) Zhong, J.; Yang, X.; Wu, Z.; Liang, B.; Huang, Y.; Zhang, T. State of the art and perspectives in heterogeneous catalysis of CO(2) hydrogenation to methanol. *Chem Soc Rev* **2020**, *49*, 1385-1413.

(104) Bahruji, H.; Bowker, M.; Hutchings, G.; Dimitratos, N.; Wells, P.; Gibson, E.; Jones, W.; Brookes, C.; Morgan, D.; Lalev, G. Pd/ZnO catalysts for direct CO2 hydrogenation to methanol. *Journal of Catalysis* **2016**, *343*, 133-146.

(105) Wang, J.; Zhang, G.; Zhu, J.; Zhang, X.; Ding, F.; Zhang, A.; Guo, X.; Song, C. CO2 Hydrogenation to Methanol over In2O3-Based Catalysts: From Mechanism to Catalyst Development. *ACS Catalysis* **2021**, *11*, 1406-1423.

(106) Dang, S.; Qin, B.; Yang, Y.; Wang, H.; Cai, J.; Han, Y.; Li, S.; Gao, P.; Sun, Y. Rationally designed indium oxide catalysts for CO(2) hydrogenation to methanol with high activity and selectivity. *Sci Adv* **2020**, *6*, eaaz2060.

(107) Wang, J.; Li, G.; Li, Z.; Tang, C.; Feng, Z.; An, H.; Liu, H.; Liu, T.; Li, C. A highly selective and stable ZnO-ZrO(2) solid solution catalyst for CO(2) hydrogenation to methanol. *Sci Adv* **2017**, *3*, e1701290.

(108) Wang, J.; Tang, C.; Li, G.; Han, Z.; Li, Z.; Liu, H.; Cheng, F.; Li, C. High-Performance MaZrOx (Ma = Cd, Ga) Solid-Solution Catalysts for CO2 Hydrogenation to Methanol. *ACS Catalysis* **2019**, *9*, 10253-10259.

(109) Kattel, S.; Ramirez, P. J.; Chen, J. G.; Rodriguez, J. A.; Liu, P. Active sites for CO(2) hydrogenation to methanol on Cu/ZnO catalysts. *Science* **2017**, *355*, 1296-1299.

(110) Studt, F.; Behrens, M.; Kunkes, E. L.; Thomas, N.; Zander, S.; Tarasov, A.; Schumann, J.; Frei, E.; Varley, J. B.; Abild-Pedersen, F.; et al. The Mechanism of CO and CO2Hydrogenation to Methanol over Cu-Based Catalysts. *ChemCatChem* **2015**, *7*, 1105-1111.

(111) Rui, N.; Wang, Z.; Sun, K.; Ye, J.; Ge, Q.; Liu, C.-j. CO2 hydrogenation to methanol over Pd/In2O3: effects of Pd and oxygen vacancy. *Applied Catalysis B: Environmental* **2017**, *218*, 488-497.

(112) Studt, F.; Sharafutdinov, I.; Abild-Pedersen, F.; Elkjaer, C. F.; Hummelshoj, J. S.; Dahl, S.; Chorkendorff, I.; Norskov, J. K. Discovery of a Ni-Ga catalyst for carbon dioxide reduction to methanol. *Nat Chem* **2014**, *6*, 320-324.

(113) Torelli, D. A.; Francis, S. A.; Crompton, J. C.; Javier, A.; Thompson, J. R.; Brunschwig, B. S.; Soriaga, M. P.; Lewis, N. S. Nickel–Gallium-Catalyzed Electrochemical Reduction of CO2 to Highly Reduced Products at Low Overpotentials. *ACS Catalysis* **2016**, *6*, 2100-2104.

(114) Kuhl, K. P.; Hatsukade, T.; Cave, E. R.; Abram, D. N.; Kibsgaard, J.; Jaramillo, T. F. Electrocatalytic conversion of carbon dioxide to methane and methanol on transition metal surfaces. *J Am Chem Soc* **2014**, *136*, 14107-14113.

(115) Sun, X.; Zhu, Q.; Kang, X.; Liu, H.; Qian, Q.; Zhang, Z.; Han, B. Molybdenum-Bismuth Bimetallic Chalcogenide Nanosheets for Highly Efficient Electrocatalytic Reduction of Carbon Dioxide to Methanol. *Angew Chem Int Ed Engl* **2016**, *55*, 6771-6775.

(116) Bi, J.; Hou, P.; Liu, F. W.; Kang, P. Electrocatalytic Reduction of CO(2) to Methanol by Iron Tetradentate Phosphine Complex Through Amidation Strategy. *ChemSusChem* **2019**, *12*, 2195-2201.

(117) Wu, Y.; Jiang, Z.; Lu, X.; Liang, Y.; Wang, H. Domino electroreduction of CO(2) to methanol on a molecular catalyst. *Nature* **2019**, *575*, 639-642.

(118) Seshadri, G.; Lin, C.; Bocarsly, A. B. A new homogeneous electrocatalyst for the reduction of carbon dioxide to methanol at low overpotential. *Journal of Electroanalytical Chemistry* **1994**, *372*, 145-150.

(119) Liu, X.; Li, B.-Q.; Ni, B.; Wang, L.; Peng, H.-J. A perspective on the electrocatalytic conversion of carbon dioxide to methanol with metallomacrocyclic catalysts. *Journal of Energy Chemistry* **2022**, *64*, 263-275.

(120) Guzmán, H.; Salomone, F.; Batuecas, E.; Tommasi, T.; Russo, N.; Bensaid, S.; Hernández, S. How to make sustainable CO2 conversion to Methanol: Thermocatalytic versus electrocatalytic technology. *Chemical Engineering Journal* **2021**, *417*,

(121) Mebrahtu, C.; Krebs, F.; Abate, S.; Perathoner, S.; Centi, G.; Palkovits, R. CO2 Methanation: Principles and Challenges. In *Horizons in Sustainable Industrial Chemistry and Catalysis*, Albonetti, S., Perathoner, S., Quadrelli, E. A. Eds.; Studies in Surface Science and Catalysis, Vol. 178; Elsevier, 2019; pp 85-103.

(122) Lee, W. J.; Li, C.; Prajitno, H.; Yoo, J.; Patel, J.; Yang, Y.; Lim, S. Recent trend in thermal catalytic low temperature CO2 methanation: A critical review. *Catalysis Today* **2021**, *368*, 2-19.

(123) Ren, J.; Guo, H.; Yang, J.; Qin, Z.; Lin, J.; Li, Z. Insights into the mechanisms of CO2

methanation on Ni(111) surfaces by density functional theory. *Applied Surface Science* **2015**, *351*, 504-516.

(124) Karelovic, A.; Ruiz, P. Mechanistic study of low temperature CO2 methanation over Rh/TiO2 catalysts. *Journal of Catalysis* **2013**, *301*, 141-153.

(125) Peterson, A. A.; Nørskov, J. K. Activity Descriptors for CO2 Electroreduction to Methane on Transition-Metal Catalysts. *The Journal of Physical Chemistry Letters* **2012**, *3*, 251-258.

(126) Liu, X.; Xiao, J.; Peng, H.; Hong, X.; Chan, K.; Norskov, J. K. Understanding trends in electrochemical carbon dioxide reduction rates. *Nat Commun* **2017**, *8*, 15438.

(127) Li, F.; Thevenon, A.; Rosas-Hernandez, A.; Wang, Z.; Li, Y.; Gabardo, C. M.; Ozden, A.; Dinh, C. T.; Li, J.; Wang, Y.; et al. Molecular tuning of CO(2)-to-ethylene conversion. *Nature* **2020**, *577*, 509-513.

(128) Cheng, D.; Zhao, Z. J.; Zhang, G.; Yang, P.; Li, L.; Gao, H.; Liu, S.; Chang, X.; Chen, S.; Wang, T.; et al. The nature of active sites for carbon dioxide electroreduction over oxide-derived copper catalysts. *Nat Commun* **2021**, *12*, 395.

(129) Liu, X.; Schlexer, P.; Xiao, J.; Ji, Y.; Wang, L.; Sandberg, R. B.; Tang, M.; Brown, K. S.; Peng, H.; Ringe, S.; et al. pH effects on the electrochemical reduction of CO((2)) towards C(2) products on stepped copper. *Nat Commun* **2019**, *10*, 32.

(130) Ding, L.; Shi, T.; Gu, J.; Cui, Y.; Zhang, Z.; Yang, C.; Chen, T.; Lin, M.; Wang, P.; Xue, N.; et al. CO2 Hydrogenation to Ethanol over Cu@Na-Beta. *Chem* **2020**, *6*, 2673-2689.

(131) Bai, S.; Shao, Q.; Wang, P.; Dai, Q.; Wang, X.; Huang, X. Highly Active and Selective Hydrogenation of CO(2) to Ethanol by Ordered Pd-Cu Nanoparticles. *J Am Chem Soc* **2017**, *139*, 6827-6830.

(132) Zhang, S.; Liu, X.; Shao, Z.; Wang, H.; Sun, Y. Direct CO2 hydrogenation to ethanol over supported Co2C catalysts: Studies on support effects and mechanism. *Journal of Catalysis* **2020**, *382*, 86-96.

(133) Wang, L.; Wang, L.; Zhang, J.; Liu, X.; Wang, H.; Zhang, W.; Yang, Q.; Ma, J.; Dong, X.; Yoo, S. J.; et al. Selective Hydrogenation of CO(2) to Ethanol over Cobalt Catalysts. *Angew Chem Int Ed Engl* **2018**, *57*, 6104-6108.

(134) Kusama, H.; Okabe, K.; Sayama, K.; Arakawa, H. CO2 hydrogenation to ethanol over promoted

Rh/SiO2 catalysts. *Catalysis Today* **1996**, *28*, 261-266.

(135) Dutta, A.; Montiel, I. Z.; Erni, R.; Kiran, K.; Rahaman, M.; Drnec, J.; Broekmann, P. Activation of bimetallic AgCu foam electrocatalysts for ethanol formation from CO2 by selective Cu oxidation/reduction. *Nano Energy* **2020**, *68*, 104331.

(136) Ren, D.; Ang, B. S.-H.; Yeo, B. S. Tuning the Selectivity of Carbon Dioxide Electroreduction toward Ethanol on Oxide-Derived CuxZn Catalysts. *ACS Catalysis* **2016**, *6*, 8239-8247.

(137) Peng, H. J.; Tang, M. T.; Halldin Stenlid, J.; Liu, X.; Abild-Pedersen, F. Trends in oxygenate/hydrocarbon selectivity for electrochemical CO((2)) reduction to C(2) products. *Nat Commun* **2022**, *13*, 1399.

(138) Kuhl, K. P.; Cave, E. R.; Abram, D. N.; Jaramillo, T. F. New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces. *Energy & Environmental Science* **2012**, *5*, 7050-7059.

(139) Ting, L. R. L.; Garcia-Muelas, R.; Martin, A. J.; Veenstra, F. L. P.; Chen, S. T.; Peng, Y.; Per, E. Y. X.; Pablo-Garcia, S.; Lopez, N.; Perez-Ramirez, J.; et al. Electrochemical Reduction of Carbon Dioxide to 1-Butanol on Oxide-Derived Copper. *Angew Chem Int Ed Engl* **2020**, *59*, 21072-21079.

(140) Montoya, J. H.; Peterson, A. A.; Nørskov, J. K. Insights into C-C Coupling in CO_2 Electroreduction on Copper Electrodes. *ChemCatChem* **2013**, *5*, 737-742.

(141) De, R.; Gonglach, S.; Paul, S.; Haas, M.; Sreejith, S. S.; Gerschel, P.; Apfel, U. P.; Vuong, T. H.; Rabeah, J.; Roy, S.; et al. Electrocatalytic Reduction of CO(2) to Acetic Acid by a Molecular Manganese Corrole Complex. *Angew Chem Int Ed Engl* **2020**, *59*, 10527-10534.

(142) Cui, X.; Gao, P.; Li, S.; Yang, C.; Liu, Z.; Wang, H.; Zhong, L.; Sun, Y. Selective Production of Aromatics Directly from Carbon Dioxide Hydrogenation. *ACS Catalysis* **2019**, *9*, 3866-3876.

(143) Wei, J.; Ge, Q.; Yao, R.; Wen, Z.; Fang, C.; Guo, L.; Xu, H.; Sun, J. Directly converting CO(2) into a gasoline fuel. *Nat Commun* **2017**, *8*, 15174.

(144) Gao, P.; Li, S.; Bu, X.; Dang, S.; Liu, Z.; Wang, H.; Zhong, L.; Qiu, M.; Yang, C.; Cai, J.; et al. Direct conversion of CO(2) into liquid fuels with high selectivity over a bifunctional catalyst. *Nat Chem* **2017**, *9*, 1019-1024.

(145) Gao, P.; Zhang, L.; Li, S.; Zhou, Z.; Sun, Y. Novel Heterogeneous Catalysts for CO(2) Hydrogenation to Liquid Fuels. *ACS Cent Sci* **2020**, *6*, 1657-1670.

(146) Jiang, F.; Liu, B.; Geng, S.; Xu, Y.; Liu, X. Hydrogenation of CO2 into hydrocarbons: enhanced catalytic activity over Fe-based Fischer–Tropsch catalysts. *Catalysis Science & Technology* **2018**, *8*, 4097-4107.

(147) Wei, J.; Yao, R.; Ge, Q.; Wen, Z.; Ji, X.; Fang, C.; Zhang, J.; Xu, H.; Sun, J. Catalytic Hydrogenation of CO2 to Isoparaffins over Fe-Based Multifunctional Catalysts. *ACS Catalysis* **2018**, *8*, 9958-9967.

(148) He, Z.; Qian, Q.; Ma, J.; Meng, Q.; Zhou, H.; Song, J.; Liu, Z.; Han, B. Water-Enhanced Synthesis of Higher Alcohols from CO2 Hydrogenation over a Pt/Co3O4 Catalyst under Milder Conditions. *Angew Chem Int Ed Engl* **2016**, *55*, 737-741.

(149) Li, S.; Guo, H.; Luo, C.; Zhang, H.; Xiong, L.; Chen, X.; Ma, L. Effect of Iron Promoter on Structure and Performance of K/Cu–Zn Catalyst for Higher Alcohols Synthesis from CO2 Hydrogenation. *Catalysis Letters* **2013**, *143*, 345-355.

(150) Jiang, Y.; Long, R.; Xiong, Y. Regulating C-C coupling in thermocatalytic and electrocatalytic CO (x) conversion based on surface science. *Chem Sci* **2019**, *10*, 7310-7326.

(151) Song, Y.; Zhang, X.; Xie, K.; Wang, G.; Bao, X. High-Temperature CO(2) Electrolysis in Solid Oxide Electrolysis Cells: Developments, Challenges, and Prospects. *Adv Mater* **2019**, *31*, e1902033.

(152) Zhang, X.; Song, Y.; Wang, G.; Bao, X. Co-electrolysis of CO2 and H2O in high-temperature solid oxide electrolysis cells: Recent advance in cathodes. *Journal of Energy Chemistry* **2017**, *26*, 839-853.

(153) Zheng, Y.; Wang, J.; Yu, B.; Zhang, W.; Chen, J.; Qiao, J.; Zhang, J. A review of high temperature co-electrolysis of H(2)O and CO(2) to produce sustainable fuels using solid oxide electrolysis cells (SOECs): advanced materials and technology. *Chem Soc Rev* **2017**, *46*, 1427-1463.

(154) Chatzilias, C.; Martino, E.; Tsatsos, S.; Kyriakou, G.; Katsaounis, A.; Vayenas, C. G. Kinetic study of CO2 hydrogenation on Ru/ YSZ catalyst using a monolithic electropromoted reactor (MEPR). *Chemical Engineering Journal* **2022**, *430*, 132967.

(155) Chatzilias, C.; Martino, E.; Katsaounis, A.; Vayenas, C. G. Electrochemical promotion of CO2 hydrogenation in a monolithic electrochemically promoted reactor (MEPR). *Applied Catalysis B: Environmental* **2021**, *284*, 119695.

(156) Zagoraios, D.; Tsatsos, S.; Kennou, S.; Vayenas, C. G.; Kyriakou, G.; Katsaounis, A. Tuning the

RWGS Reaction via EPOC and In Situ Electro-oxidation of Cobalt Nanoparticles. *ACS Catalysis* **2020**, *10*, 14916-14927.

(157) Zagoraios, D.; Panaritis, C.; Krassakopoulou, A.; Baranova, E. A.; Katsaounis, A.; Vayenas, C. G. Electrochemical promotion of Ru nanoparticles deposited on a proton conductor electrolyte during CO2 hydrogenation. *Applied Catalysis B: Environmental* **2020**, *276*, 119148.

(158) Chatzilias, C.; Martino, E.; Vayenas, C. G.; Kyriakou, G.; Katsaounis, A. A low temperature SOFC as a self-promoted reactor for CO2 catalytic hydrogenation. *Applied Catalysis B: Environmental* **2022**, *317*, 121778.

(159) Li, M.; Hua, B.; Wang, L.-C.; Sugar, J. D.; Wu, W.; Ding, Y.; Li, J.; Ding, D. Switching of metal–oxygen hybridization for selective CO_2 electrohydrogenation under mild temperature and pressure. *Nature Catalysis* **2021**, *4*, 274-283.

(160) Ponsard, L.; Nicolas, E.; Tran, N. H.; Lamaison, S.; Wakerley, D.; Cantat, T.; Fontecave, M. Coupling Electrocatalytic CO(2) Reduction with Thermocatalysis Enables the Formation of a Lactone Monomer. *ChemSusChem* **2021**, *14*, 2198-2204.

(161) Das, S.; Perez-Ramirez, J.; Gong, J.; Dewangan, N.; Hidajat, K.; Gates, B. C.; Kawi, S. Core-shell structured catalysts for thermocatalytic, photocatalytic, and electrocatalytic conversion of CO(2). *Chem Soc Rev* **2020**, *49*, 2937-3004.

(162) Guzman, H.; Salomone, F.; Bensaid, S.; Castellino, M.; Russo, N.; Hernandez, S. CO(2) Conversion to Alcohols over Cu/ZnO Catalysts: Prospective Synergies between Electrocatalytic and Thermocatalytic Routes. *ACS Appl Mater Interfaces* **2022**, *14*, 517-530.

(163) Tang, H.; Geng, K.; Wu, L.; Liu, J.; Chen, Z.; You, W.; Yan, F.; Guiver, M. D.; Li, N. Fuel cells with an operational range of –20 °C to 200 °C enabled by phosphoric acid-doped intrinsically ultramicroporous membranes. *Nature Energy* **2022**, *7*, 153-162.

(164) Biswas, A. N.; Xie, Z.; Xia, R.; Overa, S.; Jiao, F.; Chen, J. G. Tandem Electrocatalytic–Thermocatalytic Reaction Scheme for CO2 Conversion to C3 Oxygenates. *ACS Energy Letters* **2022**, *7*, 2904-2910.

(165) Morales-Guio, C. G.; Cave, E. R.; Nitopi, S. A.; Feaster, J. T.; Wang, L.; Kuhl, K. P.; Jackson, A.; Johnson, N. C.; Abram, D. N.; Hatsukade, T.; et al. Improved CO2 reduction activity towards C2+ alcohols on a tandem gold on copper electrocatalyst. *Nature Catalysis* **2018**, *1*, 764-771.