Recent advances in CO₂ capture and reduction

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Given the continuous and excessive CO₂ emission into the atmosphere from anthropomorphic activities, there is now a growing demand for negative carbon emission technologies, which requires efficient capture and conversion of CO₂ to value-added chemicals. This review highlights recent advances in CO₂ capture and conversion chemistry and processes. It first summarizes various adsorbent materials that have been developed for CO₂ capture, including hydroxide-, amine-, and metal organic framework-based adsorbents. It then reviews recent efforts devoted to two types of CO₂ conversion reaction: thermochemical CO₂ hydrogenation and electrochemical CO₂ reduction. While thermal hydrogenation reactions are often accomplished in the presence of H₂, electrochemical reactions are realized by direct use of electricity that can be renewably generated from solar and wind power. The key to the success of these reactions is to develop efficient catalysts and to rationally engineer the catalyst–electrolyte interfaces. The review further covers recent studies in integrating CO₂ capture and conversion processes so that energy efficiency for the overall CO₂ capture and conversion can be optimized. Lastly, the review briefly some new approaches and future directions of coupling direct air capture and CO₂ conversion technologies as solutions to negative carbon emission and energy sustainability.

1. Carbon cycle and CO₂ emission

Carbon is the chemical backbone of life on Earth. Carbon compounds regulate the Earth’s temperature, make up the food that sustains us, and provide the energy that drives the global economy. The carbon cycle in nature is the global flow of carbon through the atmosphere, oceans, terrestrial biosphere, and lithosphere in various forms, such as carbon dioxide, organisms, limestone, coal and oil, as shown in Fig. 1A. Two main cycles are the land–atmosphere cycle and the ocean–atmosphere cycle. The land–atmosphere cycle occurs through two main drivers: photosynthesis and respiration. In the photosynthesis process, CO₂ is absorbed from the atmosphere and converted into fuels by plants or microbes, while in the respiration process CO₂ is produced as the final product from biological activities. In comparison with the land–atmosphere cycle, the ocean–atmosphere cycle plays a vital role in carbon storage because the ocean contains 50 times more carbon than the atmosphere. The driving mechanism of the ocean–atmosphere cycle is the difference in the partial pressure of CO₂ between the ocean and the atmosphere. This pressure varies with ocean temperature and local marine photosynthesis. The lower the ocean temperature, the smaller the carbon emissions. In all, nature balances these cycles well in equilibrium, maintaining the healthy evolution of life. Over the past century, however, fossil fuels have been massively consumed for energy uses (Fig. 1B). This has resulted in a dramatic increase in atmospheric CO₂, and as a result, caused a series of environmental issues, including global warming, acid rain, ocean acidification and rising sea levels (Fig. 1C).

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2. CO₂ capture

To combat anthropogenic CO₂ emission and to make our lifestyles sustainable, we must develop neutral or even negative carbon emission technologies. One such technology is CO₂ capture and storage.11,12 Recent studies have shown that the key barrier that limits the broad use of this process is the high energy penalty associated with CO₂ capture,12 which is aggravated by the fact that about half of the annual CO₂ emission is generated from widespread industrial sites. In 1999, Lackner introduced the concept of direct air capture of CO₂ to mitigate climate change, and it is now broadly defined as direct extraction of CO₂ from ambient air.13–16

A key step to successful CO₂ capture is to develop efficient adsorbents to bind CO₂ from air. An ideal CO₂ adsorbent should have high selectivity and adsorption capacity for CO₂, low heat of adsorption ($Q_{st}$), high recyclability, good thermal and chemical stability, fast kinetics and high cost-effectiveness (Fig. 2).17 The energetics of the CO₂ capture process is about the chemical bonding nature between CO₂ and an adsorbent, which can involve both weak physisorption and strong chemisorption. Such binding strength is defined by the isosteric heat of adsorption $Q_{st}$ (kJ mol⁻¹). For a given adsorbent, a high $Q_{st}$ value indicates an energy-intensive CO₂ regeneration process once it is captured, whereas a low $Q_{st}$ value may compromise the CO₂ adsorption capacity. Furthermore, a good adsorbent should have high selectivity for adsorbing CO₂ from a mixture of gases, especially from air, and have high thermal, chemical, and water stability to achieve high CO₂ capture efficiency under different operational conditions. The rate of CO₂ uptake should also be kinetically fast, the capture process should be easily engineered to large scale, and the overall cost for the capture process should be economically practical. Here we summarize some representative adsorbents that have been studied extensively for CO₂ capture, including aqueous hydroxide, solid alkali carbonates, organic amines, and porous materials.18,19

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Fig. 1  (A) The schematic highlights carbon fluxes through inland waters and includes pre-industrial and anthropogenic fluxes. Values are net fluxes between pools (black) or rates of change within pools (red); units are Pg C per year; negative signs indicate a sink from the atmosphere. Gross fluxes from the atmosphere to land and oceans, and the natural (Nat) and anthropogenic (Ant) components of net primary production—the net uptake of carbon by photosynthetic organisms—are shown for land and oceans. Gross primary production (GPP) and ecosystem respiration (R). (B) Energy source in the past and forecast from 1970 to 2050, and (C) CO₂ concentration in atmosphere, global temperature, sea level. Adapted from ref. 1 and 9 with permission. Copyright 2009 Nature Publishing Group and 2012 Chelsea Green Publishing.
2.1. Hydroxide-based adsorbents

Due to the relatively low concentration of CO\textsubscript{2} (412 ppm) in the atmosphere, CO\textsubscript{2} capture is usually carried out using chemical adsorbents with a strong CO\textsubscript{2} binding affinity. A common adsorbent is calcium hydroxide solution, which can react with CO\textsubscript{2} and form calcium carbonate as precipitate. The calcium carbonate can then be separated and dried for storage. The captured CO\textsubscript{2} can be accessed through a process known as calcination – the decomposition of calcium carbonate to form calcium oxide with CO\textsubscript{2} being released as a concentrated stream. Calcium hydroxide is then regenerated in a slaking process via hydration of calcium oxide, forming a recyclable loop. Many different types of adsorption devices, from traditional stagnant pools, packed towers to modern spray towers, have been designed and developed. Alternatively, solid inorganic bases are used for ultra-dilute CO\textsubscript{2} removal. Fig. 3 plots the equilibrium partial pressure of CO\textsubscript{2}, \(p_{CO_2,eq}\), as a function of temperature \((T)\), for various single-metal oxide–carbonate systems. Horizontal gray lines indicate \(p_{CO_2}\) of 0.05, 0.15, and 1 bar, respectively. Reprinted from ref. 21 with permission. Copyright 2008 and 2021 American Chemical Society.

2.2. Amine-based adsorbents

Amines are another common adsorbent employed for CO\textsubscript{2} capture. Using aqueous solutions of amines to capture CO\textsubscript{2} has been extended to commercial uses to remove CO\textsubscript{2} from CO\textsubscript{2}-rich natural gas streams. To date, amine adsorbents employed for direct air capture have been supported on solids to improve amine stability and recyclability. The strength of chemisorption between an amine and CO\textsubscript{2} ensures selective CO\textsubscript{2} uptake even at low CO\textsubscript{2} partial pressures, which makes the solid-supported amine adsorbents highly suitable for the direct air capture of CO\textsubscript{2}.

In a dry condition, CO\textsubscript{2} reacts with either a primary amine (eqn (1)) or secondary amine (eqn (2)) to produce an ammonium carbamate. When moisture is present, the reaction yields ammonium carbonate or bicarbonate (depending on the pH) (eqn (3) and (4)). Amine-containing sorbents have been divided into three classes: class 1 amine adsorbents are prepared by impregnating amines into the pores of a support; class 2 amine adsorbents are formed by covalently bonding amines to the walls of porous materials via silane linkage; and class 3 amine adsorbents are derived from polymerization of amines in situ to form polyamine structures tethered to the inner walls of the porous support. Fig. 4 shows some representative examples of these amine adsorbents.

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adsorption, CO₂ can be released from the adsorbent by an inert gas flow to drive the reaction equilibrium towards gaseous CO₂. An advantage of the amine adsorbent over the metal oxide one is its selective adsorption of CO₂ over H₂O, making it useful in the humid environment.

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\begin{align*}
\text{CO}_2 + 2\text{RNH}_2 & \rightleftharpoons \text{RNH}_3^+ + \text{RNHCOO}^- \\
\text{CO}_2 + 2\text{R}_1\text{R}_2\text{NH} & \rightleftharpoons \text{R}_1\text{R}_2\text{NH}_2^+ + \text{R}_1\text{R}_2\text{NCOO}^- \\
\text{CO}_2 + \text{R}_1\text{R}_2\text{NH} + \text{H}_2\text{O} & \rightleftharpoons \text{R}_1\text{R}_2\text{NH}_2^- + \text{HCO}_3^- + \text{H}^+ \\
\text{CO}_2 + \text{R}_1\text{R}_2\text{N} + \text{H}_2\text{O} & \rightleftharpoons \text{R}_1\text{R}_2\text{N}^- + \text{HCO}_3^- + \text{R}_1\text{R}_2\text{NH}^+ + \text{H}_2\text{O} \\
\end{align*}
\]

2.3. Adsorbents based on metal organic frameworks (MOFs)
The cleavage of adsorbed CO₂ in the formation of carbonate and carbamate is endothermic; and it requires a large energy input to regenerate in case of a strong adsorbent. Weak physisorption of CO₂ by porous materials has been explored extensively as an alternative to chemisorption to improve the energy efficiency of the capture process. Significant research progress has been made in CO₂ capture by micro and mesoporous materials, including metal–organic frameworks (MOFs), zeolites, zeolitic imidazole frameworks (ZIF), and porous polymers. MOFs consist of three-dimensional coordination polymer networks, constructed by the combination of metal ions/clusters with organic linkers/ligands. Fig. 5 shows crystalline structures of some well-known MOFs. Their CO₂ adsorption power can be tuned more conveniently by specific surface areas, pore volumes, pore sizes, metal centres, and surface functional groups, which make them especially attractive for selective CO₂ capture from a stream of gas mixture.

2.3.1. CO₂ adsorption via metal-binding in MOFs. As the pore structures of MOFs are sensitive to the adsorption of CO₂, functionalization of the inner and outer surface of the MOFs can tune their adsorption power. A typical approach is to make MOFs with unsaturated open metal sites (UOMSSs), which can be prepared by heating or vacuuming of the solvent-coordinated metal cations in MOFs. These exposed metal-coordination sites can build an electric field around them, providing the desired driving force for CO₂ adsorption. M–CO₂ binding is realized by direct interaction between the antibond-
ing d^2 orbital and the lone electron pairs on the oxygen in the CO_2 molecule. For an early transition metal cation with d electrons less than 4, its antibonding d-orbitals tend to bind to CO_2 more strongly. But for a late transition metal cation, its antibonding orbitals can be filled up, weakening its binding with CO_2.\footnote{For example, Mg_2(dobdc) (H_4dobdc = 2,5-dihydroxyterephthalic acid), Mg-MOF-74, and CPO-27-Mg structures with open metal sites bind to CO_2 at a fixed angle in an uniaxial fashion, as shown in Fig. 6A.\cite{33} Their CO_2 binding energies are around 67.2 kJ mol\(^{-1}\) (Fig. 6B).\cite{34} In the presence of the early transition metal (Ti or V) cation, their binding energies increase to 73.2–80.2 kJ mol\(^{-1}\), while in the presence of the late transition metal (Cr or Zn) cation, their binding energies drop to 32.2–50.8 kJ mol\(^{-1}\) (Fig. 6B).}

### 2.3.2. Enhancing CO_2 adsorption via functionalization of MOFs

MOFs modified with functional groups can change their surface properties and CO_2 adsorption power. A common strategy to modify MOFs is to add polar or amine-based moieties to the structure to enhance their interactions with CO_2, especially under low-pressure conditions. However, this enhancement needs to be regulated very carefully as the strong interaction with CO_2 also makes it difficult to regenerate the MOF adsorbent. Therefore, this functionalization should enable MOFs to show high CO_2 adsorption affinity, capacity, and selectivity, but low Q_0.

As an example, isoreticular MOF (IRMOFs)-74-III was functionalized with a series of organic linkers –CH_3, –NH_3, –CH_2NHBOc (Boc: tert-butoxycarbonyl), –CH_2NMeBoc, –CH_2NH_2, and –CH_2NHMe via the Suzuki–Miyaura coupling reaction (Fig. 7A).\cite{35,36} All the modified MOFs, except the ones containing the protective Boc groups, showed high and similar CO_2 adsorption behaviours at 25 °C/800 Torr, as shown in Fig. 7B.\cite{16} However, at low pressure, primary amine- and secondary amine-functionalized MOFs (IRMOF-74-III-CH_2NH_2 and IRMOF-74-III-CH_2NHMe, respectively) outperformed the other modified MOFs (Fig. 7C).\cite{16} A second CO_2 isotherm after evacuation of the sample at room temperature for 2 h and a third cycle with a heat treatment at 120 °C under vacuum (10 mTorr) for 1 h was recorded (Fig. 7D and E).\cite{16} The decrease in CO_2 uptake on the second cycle and recovery upon heat treatment indicated the presence of strongly bound CO_2. Further exploration of IRMOF-74-III-CH_2NH_2 using dynamic CO_2 adsorption under dry (16% CO_2; 84% dry N_2) and wet (16% CO_2; 84% wet N_2) conditions showed a negligible difference in the uptake rates for the CO_2 adsorption, suggesting the unique structural selectivity towards CO_2.\cite{13} NMR studies showed that the capture was realized by chemisorption between CO_2 and the functionalized organic linkers, forming carbamate ions and carbamic acids for IRMOF-74-III-CH_2NH_2 and IRMOF-74-III-CH_2NHMe, respectively. Incorporation of diamine groups into the same MOF to form IRMOF-74-III-(CH_2NH_2)_2 could provide an even higher CO_2 adsorption power at 25 °C/800 Torr (75 cm\(^3\) g\(^{-1}\)) than that of IRMOF-74-III-CH_2NH_2 (67 cm\(^3\) g\(^{-1}\)).\cite{37}

### 2.3.3. MOF pore size-dependent CO_2 adsorption

The pore size is a third common parameter that can be applied to control MOF’s CO_2 adsorption capability and selectivity. It is possible to synthesize MOFs with microporosity, mesopores or macropores, which can be controlled by the nature of metal precursors and organic linkers used during synthesis.\cite{38,39} For example, MOFs with pore size of 2.6, 2.4, and 2.2 nm could be synthesized using cobalt-organic linkers with slightly different configurations (IR-MOF-74-III).\cite{40} The benzene rings were termed as pore size tuners and the CO_2 adsorption of the three MOFs was enhanced as the pore size decreased from 2.6 to 2.2 nm. The competing adsorption of water could be suppressed by narrowing down the pore size as suggested by computational calculations and experimental demonstration on MOF-74 by inserting 2,4,6-tri[4-pyridyl]-1,3,5-triazine (tpt) into its hexagonal channels.\cite{41}

### 3. CO_2 reduction

Despite the fact that CO_2 capture is important to solve CO_2 emission problems, to realize energy sustainability, CO_2 must be converted back into chemical fuels, which requires the controlled reduction and protonation of CO_2. This process is unfortunately energetically uphill due to the high activation energy needed to break the stable O=C bonds and the apparent difference in free energy between CO_2 and the final products. For this reaction to be economically viable, suitable catalysts with high catalytic activity, selectivity and stability must be developed to achieve energy-efficient reduction of CO_2. Many chemistry processes, including thermochemistry, electrochemistry, photochemistry, and biochemistry processes, have been studied for CO_2 reduction. In this section we highlight the recent advances in thermo- and electro-catalytic reduction of CO_2.

### 3.1. CO_2 activation

CO_2 is a very stable molecule, with a bond dissociation energy of 525.9 kJ mol\(^{-1}\) and ionization potential of 13.777 eV, making CO_2 activation difficult and costly.\cite{42} One-electron reduction of CO_2 is believed to be the first step to initiate the reduction and other reaction processes that convert CO_2 to re-
sable forms of carbon. The electronic structure of CO$_2$ in different charge states can be summarized in its Walsh diagram (Fig. 8A).$^{43}$ In the ground state of neutral CO$_2$, the highest occupied molecular orbital (HOMO) is the fully occupied $1\pi_g$ orbital. An excess electron will be accommodated in the $2\pi_u$ orbital, which is stabilized by bending the molecule, leading to a deviation of the molecular symmetry from $D_{\infty h}$ to $C_{2v}$. The singly occupied molecular orbital (SOMO) in this radical anion is of $a_1$ symmetry, with an OCO angle calculated to be 138°, and it can be described as pseudo-antibonding. At the same time, the bonding $1\pi_g$ orbital transforms into $a_2$ and $b_2$ orbitals that have been characterized as largely nonbonding.$^{44}$ Consistent with the pseudo antibonding nature of the HOMO of CO$_2^-$, its C-O bond length (124 pm) is greater than that of the neutral CO$_2$ (117 pm).

The free CO$_2^-$ radical anion is metastable and has been observed in mass spectrometry with measured lifetime up to milliseconds.$^{44}$ The radical anion can be stabilized by interaction with a matrix or by solvation. The solvated CO$_2^-$ radical anion has been observed in bulk solutions as well as in (CO$_2$)$_n$$^{-}$ ($n = 6$–13) cluster ions.$^{44}$ While the first electronic excited state of neutral CO$_2$ is in the deep ultraviolet (UV), the radical anion has its lowest excited state in the near UV range. The electronic absorption band of CO$_2^-$ is at about 235 nm and CO$_2^-$ can dissociate upon excitation and lose its excess electron by charge transfer, making it challenging to fully characterize CO$_2^-$.

Understanding the binding between CO$_2$ and a metal surface is of great importance for developing a metal catalyst to catalyse CO$_2$ reduction reaction. CO$_2$ can bind to metal atoms via different binding motifs, as summarized in Fig. 8B.$^{44}$ These modes are abbreviated as $\eta^1$-C, $\eta^1$-O, $\eta^2$(C,O)$_1$, and $\eta^2$(O,O)$_2$, where superscripts denote the number of bonds.

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**Fig. 7** (A) Synthetic pathway for the functionalized organic linkers used in the synthesis of IRMOF-74-III, in the preparation of –CH$_3$ (5a), –NH$_2$ (5b), –CH$_2$NHBOc (5c), and –CH$_2$NMeBOc (5d) functionalized linkers. On the right is shown a schematic representation of the IRMOF-74-III pore as functionalized with the organic linkers 5a–5d and post-synthetic deprotection of Boc groups. Color code: C in gray, O in red, functional groups in purple, Mg as blue polyhedra. (B) Comparison of CO$_2$ uptake at 25 °C for IRMOF-74-III-CH$_3$ (gray), –NH$_2$ (green), CH$_2$NH$_2$ (red), –CH$_2$NHMe (blue), –CH$_2$NHBOc (purple), and –CH$_2$NMeBOc (cyan). (C) Expansion of the low-pressure range (>1 Torr). Carbon dioxide isotherms at 25 °C for IRMOF-74-III-CH$_2$NH$_2$ (D) and –CH$_2$NHMe (E). Uptakes for samples after activation (first cycle), after first CO$_2$ uptake (second cycle), and after 120 °C heating for 1 h for regeneration (third cycle) are shown in circles, triangles, and squares, respectively. Reprinted from ref. 36 with permission. Copyright 2014 American Chemical Society.

**Fig. 8** (A) Walsh diagram of CO$_2$, with illustrations of the highest occupied molecular orbitals of the anion (top) and the neutral (bottom). (B) Structural motifs of metal–CO$_2$ interactions. Reprinted from ref. 43 and 44 with permission. Copyright 2014 Abingdon: Taylor & Francis and 2018 Annual Reviews.
between the metal atoms and bound CO$_2$, and the chemical element symbols describe the atoms directly interacting with the metal. Electron reduction of metal–CO$_2$ leads to the formation of metal–CO$_2$ cluster anions, $[\text{M(CO}_2\text{n)}]$ that can serve as simplified models for studying CO$_2$ binding to metal atoms present on catalyst surfaces.\textsuperscript{45–47}

3.2. Thermal reduction of CO$_2$

The reduction of CO$_2$ in a thermo-catalytic process has attracted much attention as it not only reduces CO$_2$ emission, but also directly produces value-added chemicals and fuels.\textsuperscript{48} To transform CO$_2$ to downstream products, its thermodynamic reaction barrier must be overcome.\textsuperscript{49} Using H$_2$ as a high-energy reactant to reduce CO$_2$ has been a common approach, as H$_2$ can be generated from water electrolysis by renewable (solar or wind) electricity.\textsuperscript{48} Therefore, this conversion of CO$_2$ by catalytic thermo-hydrogenation is one of the most attractive approaches to sustainable energy and a carbon-neutral cycle (Fig. 9A).\textsuperscript{50}

3.2.1. Reversible water-gas shift (RWGS) reaction to CO.

CO is considered as the most crucial intermediate in CO$_2$ conversion as it can be coupled in methanol synthesis and Fischer–Tropsch (FT) synthesis of various chemicals and fuels (Fig. 9B).\textsuperscript{51} CO is generally produced by the reversible water-gas shift (RWGS) reaction, in which CO$_2$ is hydrogenated under a high-temperature and high-pressure condition. However, this reaction quickly reaches its equilibrium, and as a result, the reaction has a low conversion yield (23%) at 300 °C and 1 MPa.\textsuperscript{52} Two mechanisms have been reported to explain the CO$_2$ hydrogenation to CO. The first one is a redox mechanism, which is usually observed on the surface of Cu-based catalysts. CO$_2$ is reduced by Cu$^+$ to form CO*, which is desorbed from the surface to form CO product, and Cu$^+$ is then reduced back to Cu$^0$ by H$_2$ with water being formed as a byproduct.\textsuperscript{53} This is further supported by density functional theory (DFT) calculations and Fourier-transform infrared spectroscopy (FTIR) spectroscopy studies over a Cu/ZnO catalyst.\textsuperscript{54} The CO$_2$ hydrogenation may also follow the formate pathway, in which CO$_2$ is first converted to formate that is further dehydrated to form CO.\textsuperscript{55}

Metals on oxide supports are considered as promising catalysts as the metal centres could easily dissociate H$_2$, which is followed by transfer of H$^+$ to CO$_2$ adsorbed on the oxide support.\textsuperscript{56} Various catalysts based on transition metals on different oxide supports have been studied for the RWGS reaction. Among them, Cu or Pt-based catalysts supported on CeO$_2$ are the most extensively studied.\textsuperscript{57} In studying monometallic and bimetallic Pt-based catalysts on different oxide supports for selective CO$_2$ conversion to CO, it was found that active metal controlled the product selectivity, while the support effect dominated the activity of CO$_2$ conversion.\textsuperscript{58} For the monometallic Pt catalysts, a reducible support (CeO$_2$) showed higher activity than an irreducible support ($\gamma$-Al$_2$O$_3$) because of the increased oxygen vacancies found in the CeO$_2$ structure, which are beneficial for oxygen exchange with CO$_2$. Among the bimetallic Pt-based catalysts supported on CeO$_2$, PtCo showed the highest CO selectivity with little CH$_4$ production due to the weak binding of CO on the metal surface (Fig. 10A).\textsuperscript{58} Based on the d band theory, the CO/CH$_4$ ratio selectivity increases when the values of the d-band centre move towards more negative values for the Pt, Co, and Ni-based catalysts on either CeO$_2$ or $\gamma$-Al$_2$O$_3$ supports (Fig. 10B).\textsuperscript{58} Such correlation between CO selectivity and metal d-band centre is potentially helpful for predicting selective CO$_2$ reduction catalysts.

In addition to Pt, other precious metals, such as Ir, Ru, Rh and Pd, are reported to be highly active hydrogenation catalysts.\textsuperscript{59} Alternatively, Cu, Fe and Ni-based catalysts are also being explored for large-scale RWGS.\textsuperscript{60} Cu/Co$_2$O$_3$ was found to be especially active as a RWGS catalyst at low temperature (300 °C) and ambient pressure, reaching 100% CO selectivity.\textsuperscript{61} The enhanced activity was attributed to synergies of Cu nano-
particle (NP) and CeO₂ support in their redox behaviours and oxygen vacancies (Fig. 11A). In situ Ce L₂-edge XANES measurement for CeO₂ and Cu–CeO₂ supported on mesoporous silica SBA-15 (denoted as SCe and SCuCe, respectively) was performed during sample reduction at 300 °C in H₂ (Fig. 11B and C). No change was observed in SCe after reduction, while there was partial reduction of Ce⁴⁺ to Ce³⁺ for SCuCe. Similarly, Cu structure change upon CO₂ treatment at 120 °C was detected by in situ X-ray absorption spectroscopy (XAS) measurement (Fig. 11D and E). The spectra corresponded well with the Cu₂O standard, suggesting that Cu⁰ species in SCuCe-re are oxidized to Cu⁺ species via CO₂ treatment at 120 °C. The rapid desorption of CO from Cu⁺—CO intermediate at the reaction temperature led to product formation, which was followed by facile reduction of Cu and Ce by hydrogen spillover. The results suggest that the synergistic effect between oxygen vacancies and Cu redox property is essential for the oxide-supported Cu catalyst to show high RWGS activity and selectivity.

3.2.2. Thermal reduction of CO₂ to methanol. Methanol is an important chemical feedstock for uses in combustion engines, fuel cells, and in the synthesis of downstream value-added products, such as dimethyl ether and hydrocarbons. Conventional Cu catalysts are popular choices for methanol synthesis from CO₂. In the Cu/ZnO catalyst system, the high catalytic activity is attributed to the special Cu/ZnO interfacial and Cu/ZnO surface alloy effects, as confirmed by studying CuZn(111) and ZnO/Cu(111) catalysis. In this study, CuZn was found to undergo surface oxidation under reaction conditions and the surface Zn was transformed into ZnO. The catalysis showed a volcano-plot trend between methanol production and ZnO coverage on Cu(111) (Fig. 12A and B). Similarly, CuZn(211) catalysis was further enhanced once the CuZn surface was partially covered with ZnO. The catalysis enhancement was attributed to the strong metal-support interaction, which strengthens the surface binding to intermediates and increases the catalytic activity.

Since CO₂ conversion to methanol is sensitive to catalyst structure, it is important to maintain the catalyst dispersion and prevent the catalyst from sintering and deactivation under the reaction conditions. Various strategies have been proposed to solve the deactivation issues, including the use of reducible supports and encapsulation of Cu in metal organic frameworks (MOFs). For example, a Cu-MOF-based composite catalyst was prepared by encapsulating Cu within the Zr-based UiO-66 porous structure. The stabilized Cu showed much higher activity toward methanol formation (Fig. 12C). Additionally, the SiO₂-supported Ni–Ga intermetallic catalyst was found to be more active than the conventional Cu/ZnO/Al₂O₃ catalyst for the CO₂ reduction to methanol at ambient pressure. A specific stoichiometric ratio (Ni₉Ga₃) was required in the catalyst formulation, which was stabilized by SiO₂, to achieve high selectivity. Interestingly, redox-active In₂O₃ was also found to be a promising catalyst component with high methanol selectivity and remarkable stability due to its ability to form oxygen vacancies and metallic In in the reaction process. Once the In₂O₃ catalyst was supported on ZrO₂, its catalytic activity was further improved and the methanol conversion rate increased significantly.

Fig. 11 (A) Schematic illustration of synergy of Cu/CeO₂ for CO₂ hydrogenation. (B–E) XAS spectra of Cu and Ce oxidation state change during reaction (note that SCe = SBA-supported CeO₂ and SCuCe = SBA-supported Cu–CeO₂). Adapted from ref. 61 with permission. Copyright 2018 American Chemical Society.

Fig. 12 (A, B) CO₂ conversion to methanol. (C) Initial TOFs of methanol formation over Cu-catalysts and Cu on UiO-66. The reaction rates were measured after 1 h. Reaction conditions: 7 sccm of CO₂, 21 sccm of H₂, 10 bar, and 175 °C. Adapted from ref. 66 and 70 with permission. Copyright 2017 American Association for the Advancement of Science and 2016 American Chemical Society.
selectivity reached 99.8% with a CO2 conversion of 5.2% and long-term stability of 1000 h under the industrially relevant reaction conditions.

3.2.3. Fischer–Tropsch reaction. The C2+ hydrocarbons, such as alkanes, olefins and liquid fuels, are important for today's chemical and energy industries. For example, olefins are currently produced on the order of 200 million tons per year and widely used in synthetic rubbers, plastics and cosmetics. However, these hydrocarbons are traditionally generated from non-renewable fossil fuels, which results in large amounts of CO2 emission. Ideally, CO2 can be used as a precursor for the synthesis of these hydrocarbons.

The FT reaction is a common route for the transformation of syngas (CO + H2) to C2+ hydrocarbons. To achieve the direct hydrogenation of CO2, two successive reaction steps need to be incorporated into one reaction system: the reduction of CO2 to CO via RWGS reaction and hydrogenation of CO to hydrocarbons via FT reaction. In the two-step reaction process, the CO conversion (up to 87%) is much higher than the CO2 conversion (up to 45%). Therefore, improving the catalytic efficiency of the CO2 conversion has been an important target. Fe-based catalysts have been widely used in CO2 hydrogenation because of their high activity for both RWGS and FT synthesis. Fe catalysts with alkali metal promoters are reported to significantly enhance the selectivity towards long-chain hydrocarbons. These alkali metals, especially K, promote Fe catalysis by weakening the affinity with H2 and enhancing the adsorption of CO2 and CO intermediate.

Different promotional effects were observed by combining a Fe-based MOF catalyst with various elements (Fig. 13A). K was found to enhance the olefin selectivity drastically from 0.7% to 36% (Fig. 13B). CO2 and H2 chemisorption measurement showed that CO2 uptake was enhanced while H2 adsorption was weakened upon K addition, leading to stronger Fe–C interaction and higher selectivity toward olefins. The obtained C2–C4 olefin space time yield (STY) of the Fe/C + K (0.75) catalyst was among the best catalysts published (Fig. 13C).

In addition to alkali metals, transition metal components, such as Cu and Co components, were also found to promote Fe-catalysed CO2 hydrogenation to hydrocarbons. Cu is known to be a highly active catalyst for methanol synthesis from CO2, but when it combines with Fe, it enhances Fe catalysis for both RWGS and CO hydrogenation by suppressing CH4 formation and promoting C2–C7 production. The catalyst support is also an important factor to increase the selectivity for light olefins. For example, the ZrO2-supported K–Fe (K–Fe/ZrO2) catalyst exhibited much higher selectivity to lower olefins than the SiO2-supported one; the carbon-coated Fe-catalyst was much better dispersed and stabilized, and was highly active for the CO2 conversion at atmospheric pressure with higher selectivity to C2–C4 olefins. In addition, methanol has also been studied as a starting precursor for synthesis of olefins. It too requires two reaction steps: CO2 hydrogenation to methanol and methanol conversion to hydrocarbons as described in recent reviews.

Despite the great promise demonstrated from thermal reduction of CO2 to value-added chemicals, these thermal reactions require the use of high temperature and high pressure, which makes it challenging to stabilize the catalysts in the reaction conditions and to lower energy consumption.

3.3. Electrochemical reduction of CO2

Electrochemical CO2 reduction reaction (CO2RR) is an appealing alternative to thermal reduction for converting CO2 to value-added chemicals as the reaction can be promoted by renewable electricity under ambient conditions, and be catalysed more selectively by catalyst engineering, as illustrated in Fig. 14A. The electrochemical CO2RR on the surface of a metal catalyst is generally divided into three steps: CO2 adsorption, charge transfer, and product dissociation. Each of these three steps plays an important role in controlling catalyst selectivity and final product distribution. The CO2RR pathways have been studied extensively to understand various products detected from CO2RR. Fig. 14B is just an example to show these complicated pathways leading to the formation of C1 and C2 products. The commonly accepted key reaction steps are CO2 binding, protonation and reduction to *COOH, which can be further hydrogenated to form formate, or dehydrated to form CO that can either be released from the catalyst surface or function as a key intermediate for the next steps of hydrogenation and C–C coupling to C1 and C2, products.

3.3.1. Metal nanoparticle catalysis. Metal nanoparticles with large surface areas and controlled surface structures have been studied extensively as catalysts for CO2RR.
summarizes some representative nanoparticle catalysts that are selective for CO$_2$RR to CO.$^{[93]}$ Ultrathin Au nanowires of about 2 nm in width and hundreds of nm in length were found to be among the most active and selective catalyst for the CO$_2$ reduction to CO.$^{[93]}$ The CO selectivity is sensitively dependent on the length of the nanowires. The 500 nm Au nanowires showed the onset potential of CO$_2$ reduction to CO at $-0.2$ V (with 37% FE) but reached 94% FE and mass activity (1.84 A g$_{Au}^{-1}$) at $-0.35$ V. DFT calculation revealed that both COOH and CO preferentially bind to the edge site on the Au nanowires, with COOH binding marginally (0.04 eV) stronger than that on the Au(211) edge but CO binding 0.23 eV weaker than that on the Au$_{13}$ corner, suggesting that nanowire surface with maximal edge sites facilitates CO$_2$ reduction to COOH and further to CO.$^{[93]}$ In addition to Au, Ag, Pd, SnO$_2$-coated Cu, and Ni-N were also found to be selective in catalysing CO$_2$RR to CO, as summarized in Fig. 15.$^{[100-103]}$ When Pd, In, Sn, and Bi nanoparticles were employed as catalysts for the CO$_2$RR, formate (HCOO$^-$) was the main product.$^{[104-107]}$

Compared with the formation of CO and formate, selective reduction of CO$_2$ to C$_2$ products has been challenging, and Cu has been the major component that is required to catalyze the C$\cdots$C formation.$^{[92,95]}$ Recent studies have suggested that the key active components are Cu–Cu$_2$O mixtures, as observed in the CO$_2$RR studies on partially oxidized Cu electrode.$^{[108-111]}$ Cu(0) and residual subsurface oxygen species are considered to play important roles towards enhanced performance. The oxidation state of Cu can be reversibly transformed between Cu(0) and Cu(i) under the electrochemical reaction conditions. The presence of Cu(i) and Cu(0) significantly improves the kinetic and thermodynamic processes of CO$_2$ activation and *CO dimerization. In situ spectroscopy studies, such as electrochemical liquid transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and XAS studies, have shown that the catalyst surface undergoes dynamic structural changes under CO$_2$RR conditions. For example, over the electroreduction time period, CuO nanosheets were seen fragmenting into smaller species and floating in the liquid layer (Fig. 16A).$^{[112]}$ In situ grazing incidence X-ray absorption spectroscopy (GIXAS) and X-ray diffraction (GIXRD) were also used to study thin Cu electrode (50 nm thick) and to characterize the near-surface structure of the electrode under the CO$_2$RR conditions (Fig. 16B and C).$^{[88,113]}$ It was found that during the catalytic reaction, the surface of the polycrystalline Cu electrode was partially oxidized to Cu$_2$O. The co-existence of Cu(0) and Cu(i) on the catalyst surface during the CO$_2$RR was further proved by *operando* time resolved XAS.$^{[114]}$ It is now commonly believed that there is a synergistic effect between Cu(0) and Cu(i), which promotes the C$\cdots$C coupling of intermediates in the reaction process, favouring the formation of C$_2$+ products. The role played by the Cu(i) effect in enhancing CO$_2$RR to hydrocarbons was further supported by the Cu$_3$N nanocube-catalysed CO$_2$RR for the formation of C$_2$H$_4$ as a major product.$^{[115]}$ This high selectivity to C$_2$H$_4$ was attributed to the Cu(i) stabilization by N and Lewis basicity of N on the Cu(100) facet, facilitating C$\cdots$C coupling and C$\equiv$O/C=O hydrogenation.

### 3.3.2. Single-atom catalysis

Single-atom catalysts, with isolated metal atoms dispersed on conductive carriers, have
demonstrated excellent catalytic performance in many chemical reactions. These catalysts integrate the benefits of both homogeneous and heterogeneous catalysts, and provide an ideal platform for optimizing chemical reactions via their easily controllable coordination sites and electronic structures, strong metal-support interactions, as well as their maximal atom utilization. The electrochemical reduction of CO2 over single metal atom sites can be traced back to the 1970s when cobalt and nickel phthalocyanines were first found to be active for CO2 reduction. Since then, metal–organic complexes with well-defined M–N sites have been extensively studied for CO2RR with high catalytic performance and durability. In these M–N structures, both C and N coordinated to M also show important synergy effects (via electronic polarization) on the M catalysis to facilitate CO2 activation and further reactions. For example, C–Zn,Ni ZIF-8 catalysts with undercoordinated Ni–N sites (x < 3) showed much enhanced CO2-to-CO activity and selectivity compared with the Ni–phthalocyanine one with well-defined Ni–N4 sites. DFT calculations revealed that the free energy for *COOH formation was lower on the Ni–N sites than on the Ni–N4 sites. This low coordination effect on catalysis enhancement was also observed from the Co–N catalysts. When the Co–N coordination number was decreased from 4 to 2 (Fig. 17A and B), the Co–N2 sites showed the best CO2RR performance with both high activity and selectivity towards the formation of CO (Fig. 17C and D). More and more single-atom catalysts are emerging to show promising catalysis for the CO2 reduction to C-products beyond CO. These results have been nicely summarized in several recent reviews.

Fig. 16 (A) Schematic overview (timeline) of the experimentally observed evolution of the CuO nanosheet morphology probed by the in situ TEM E-chip flow cell, H-cell, and flow cell electrolyser. (B) XANES at the Cu K-edge of the CuO nanosheet catalyst after CO2 reduction for different minutes. (C) Grazing incidence X-ray diffraction of Cu(pc) at a probe depth of 2.6 nm before and after releasing the applied potential. Adapted from ref. 112 and 113 with permission. Copyright 2020 American Chemical Society and 2021 Nature Publishing Group.

Fig. 17 (A) XAS spectra confirm the atomic dispersion of Co atoms in Co–N2, Co–N3, and Co–N4, and suggest the lowest N coordination number in Co–N2. (B) XPS of all four samples. (C) (a) Linear sweep voltammetry (LSV) of Co–N2, Co–N3, Co–N4, and Co NPs and pure carbon paper as background. (D) CO faradaic efficiencies at different applied potentials. Adapted from ref. 119 with permission. Copyright 2018 Wiley-VCH.
Up to now, various catalysts have been demonstrated to show promising catalysis for CO₂RR to value-added chemicals under ambient conditions. Their catalysis performance is better understood at the atomic scale, and many factors, including atomic composition, atom oxidation states and coordination environment, have been identified as important to improving catalysis activity and selectivity. Despite these advances, controlling catalytic CO₂RR to a C₂ product is still a challenging task due to the strong competition from the reaction pathways that lead to the formation of C₁ products. Key factors to maximize C₂+/C₁ ratios need to be identified, and catalyst structures developed for such catalysis should also stay stable in the CO₂RR condition.

3.4. Catalyst–electrolyte interface engineering for CO₂ reduction

As electrochemical reactions occur at interfaces of catalysts and electrolytes, and as the CO₂RR needs the presence of protons to form hydrocarbons, interface engineering to control proton concentration and hydrophobicity is equally important for fast binding and reduction of CO₂. Recent advances in surface chemistry and spectroscopy also offer new opportunities to probe reaction mechanisms of CO₂RR at the interfaces and, in turn, guide the design of such interfaces for catalysis enhancement.¹²²–¹²⁵ Electrochemical systems that can be used to optimize gas transport,¹²⁶–¹²⁹ electrolyte functions,¹³⁰–¹³³ intermediate detection,¹³⁴–¹³⁹ and reaction pathway engineering,¹⁴⁰–¹⁴² have been rapidly developed to improve the overall catalytic performance. In this section, we highlight how interfacial engineering can be applied to optimize electrolyte and catalyst surface ligand effects to enhance CO₂RR catalysis.

3.4.1. pH gradient, cation, and anion effects. Most electrocatalytic CO₂RRs are operated in an electrochemical reaction system with aqueous electrolyte. The electric double layer formed between the electrolyte and the electrode contains key intermediate species that can dominate the mass transport and catalytic evolution process of CO₂.¹⁴³ A number of parameters can be chosen to optimize the electric double layer structure and to control the local environment on the catalyst surfaces, including electrolyte buffer capacity,¹⁴⁴ anion/cation types and concentrations,¹⁴⁵ localized pH,¹⁴⁶ and proton/CO₂ accessibility.¹⁴⁷,¹⁴⁸ Therefore, the selection of an appropriate electrolyte is of critical importance to tune the CO₂RR activity and selectivity. For example, when operating in an aqueous electrolyte, the reduction of protons, commonly known as the hydrogen evolution reaction (HER), competes with CO₂RR; and it, in turn, lowers the overall electrocatalytic efficiency towards CO₂RR.¹⁴⁹ However, because of the continuous consumption of protons through proton-coupled CO₂RR and HER, the accumulation of OH⁻ near the surface of a catalyst results in a higher local pH, creating a pH gradient between the interfacial area of the catalyst and electrolyte.¹⁵⁰ The presence of this pH gradient can affect mass transport of different reaction species, such as OH⁻, CO₂, HCO₃⁻ and CO₃²⁻, and as a result, dominate the reactions pathways.¹⁴⁴,¹⁴⁶,¹⁵¹

The CO₂RR selectivity can be improved by increasing the CO₂ concentrations and by inhibiting the HER near the electrode–electrolyte interfaces. Due to the relative low solubility of CO₂ in aqueous electrolyte, a high local pH is required to increase the local CO₂ concentration and to suppress HER.¹⁵² This was better demonstrated when a mesoporous Au-inverse opal (Au–IO) structure served as the catalyst for CO₂RR. In the CO₂RR condition, the partial current density related to CO₂RR was increased with reduction potentials regardless of the thickness of the Au–IO film (Fig. 18A), while that related to HER was decreased initially before increase only slightly at more negative potentials, and, more importantly, the thicker the Au–IO film, the smaller the partial current density (Fig. 18B).¹⁵³ Here a beneficial pH gradient was created in the pores of the Au–IO film, which enhanced CO₂ adsorption and conversion to C₂O, but limited proton diffusion and HER (Fig. 18C).¹⁵³ This was further confirmed by in situ electrochemical analysis, showing the pH changes near the electrode surfaces.¹⁵⁰,¹⁵⁴ Another way of promoting CO₂RR is to increase the CO₂ pressure, and therefore the CO₂ concentration, as demonstrated in the Cu-catalysed CO₂RR to ethylene (FE 44%) when the CO₂ pressure was set at 9 atm during the electrolysis.¹⁵⁵ This improved selectivity to ethylene was attributed to the increase in *CO concentration in the initial catalysis steps, promoting *CO→CO coupling and hydrogenation.

Metal cations would accumulate near the surface of electrodes under reductive potentials, forming an electric double layer, which could affect the mass transport of CO₂. As shown in Fig. 19A, the constructed electrode–electrolyte interface is assigned to the inner Helmholtz plane (IHP) within which intermediate species are populated, and outer Helmholtz...
plane (OHP) beyond which the hydrated cations are present.\textsuperscript{143} Under a reductive potential, the hydrated cations are attracted to the electrode surface due to the Coulomb attraction, participating in the chemical reactions, modifying the catalyst surface electronic structure, and even blocking active sites on the catalyst surface. Therefore, the catalytic performance of a catalyst on CO\textsubscript{2}RR can be highly dependent on the electrolyte. For example, when a Ag electrode was studied for CO\textsubscript{2}RR to CO, it was found that CO FE\textsubscript{s} were only around 40\% when the Li\textsuperscript{+}- and Na\textsuperscript{+}-based electrolyte was used as the reaction medium, but the FE\textsubscript{s} reached 85–90\% when the electrolyte contained a larger cation, such as K\textsuperscript{+}, Rb\textsuperscript{+} or Cs\textsuperscript{+} (Fig. 19B).\textsuperscript{156} Compared with smaller cations, which are strongly hydrated, the larger cations are weakly hydrated and more accessible to the surface of the electrode, leading to the decrease in their pK\textsubscript{a} and increase in the localized CO\textsubscript{2} concentration. A similar cation size effect was also observed when a Cu electrode was studied for CO\textsubscript{2}RR in 0.1 M MHCO\textsubscript{3} electrolyte. Increasing the cation size from Li\textsuperscript{+} to Cs\textsuperscript{−} in the electrolyte, the FE for H\textsubscript{2} was decreased, but the FE for C\textsubscript{2}H\textsubscript{4} and C\textsubscript{3}H\textsubscript{6} was increased (Fig. 19C).\textsuperscript{157} It was believed that the larger cations helped to stabilize the polar species, such as *CO\textsubscript{2}, *CO, and *OCCO, more efficiently in the reduction condition, favouring their further coupling and hydrogenation (Fig. 19D). As a comparison, CH\textsubscript{4} FE was rarely affected by the cation sizes due to the negligible cation interaction with the nonpolar *H and *CHO intermediate species.

Similarly, anions in electrolytes can also affect the CO\textsubscript{2}RR performance of metal catalysts. These anions, for example halides, can function as soft bases to bind to Au and Cu strongly to modify the catalyst surface structure or morphology during the CO\textsubscript{2}RR, as demonstrated in the CO\textsubscript{2}RR catalysis of plasma-activated Cu foil.\textsuperscript{158} It was found that I\textsuperscript{−} ions enhanced the reactivity dramatically (lowered the onset potential) as compared with Br\textsuperscript{−} and Cl\textsuperscript{−} ions, and the total FE for C\textsubscript{2}–C\textsubscript{3} products (ethylene, ethanol, and propanol) reached 65\% at −1.0 V (vs. RHE). I\textsuperscript{−} ions were thought to be strongly adsorbed on the electrode surface, enhancing the CO\textsubscript{2} binding through the formation of I\textsuperscript{−}C bonds. Anions can also regulate the pH change near the catalyst surface, affecting the catalyst’s CO\textsubscript{2}RR performance.\textsuperscript{159}

3.4.2. Surface ligand effects. Adding ligands on the surface of catalysts offers a powerful way to control the interface of catalyst–electrolyte.\textsuperscript{160} The inspiration is from nature where the catalytic efficiency of metalloenzymes heavily relies on the coordination environment of metal sites, e.g., protein frameworks in both first and second coordination spheres. Protein frameworks, despite not being catalytically active by themselves, are an essential component in tuning the activity and selectivity of metal sites. Modifying metal catalysts with surface ligands, therefore, can also enhance electrocatalytic performance toward CO\textsubscript{2}RR. Such modification is usually achieved by covalent or non-covalent binding of organic surfactants to metal surfaces.\textsuperscript{161−164} Surface ligands can boost the intrinsic catalytic activity of metal catalysts by reducing CO\textsubscript{2} activation barriers,\textsuperscript{163−167} by changing mass transport during CO\textsubscript{2}RR,\textsuperscript{168−170} and/or by defining the local environment to suppress byproduct formation (e.g., HER).\textsuperscript{171}

The common organic ligand used for metal surface modification is thiol in the form of R–SH, where R represents an organic substituent. –SH has strong bonding affinity with all catalytically active metal surfaces. –S\textsuperscript{−} is a softer base than –O\textsuperscript{−} and can bind to a Group 10 or 11 metal even more strongly to impact its catalysis for CO\textsubscript{2}RR.\textsuperscript{172} There have been numerous studies in modifying catalyst surfaces with thiols to improve the CO\textsubscript{2}RR selectivity.\textsuperscript{168,173,174} One example is to modify a polycrystalline Au film electrode with three different thiols, 2-mercapto-propanionic acid (MPA), 4-pyridylethylmercaptop (4-PEM), and cysteine (CYS), and to study the thiol effects on the Au catalysis for CO\textsubscript{2}RR.\textsuperscript{175} Such modifications did not improve Au catalysis for CO\textsubscript{2}RR to CO (the surface coverage generally reduced the Au catalysis selectivity to CO), but they changed other parts of the Au catalysis: the 4-PEM-modified Au showed improved selectivity to formate (from 10\% FE on Au to 22\% on PEM-Au), while the MPA-modified Au showed nearly 100\% FE towards H\textsubscript{2} and the CYS-modified Au was more active (not more selective) for generating CO and H\textsubscript{2}. These Au catalysis changes upon the surface modifications were attributed to the proton-induced desorption mechanism associated with pK\textsubscript{a} of the thiol ligands, as illustrated in the 4-PEM-modified Au catalysis for the improved selectivity to formate (Fig. 20A), in which 1e\textsuperscript{−} reduction of pyridine to pyridinium also helped to bind and reduce CO\textsubscript{2} to facilitate the second proton binding to CO\textsubscript{2} and its conversion to formate.\textsuperscript{176} Not surprisingly, MPA with the smallest pK\textsubscript{a} promotes HER.

Another example is to use the thiol-terminated imidazolium to improve Au catalysis for the formation of ethylene glycol
Ag catalysis for CO2RR once a Ag electrode was modified separately with ligand dendrites at the total current density of 30 mA cm⁻². 

When the Au electrode was modified with different imidazolium–SH ligands (Fig. 20B), the Au catalysis showed the ligand length-dependent CO2RR catalysis selectivity with 1-(2-mercaptoethyl)-3-methylimidazolium bromide (IL-2)-modified Au exhibiting highest FE (87%) towards ethylene glycol. Such enhancement in selectivity to ethylene glycol was attributed to more efficient coupling of imidazolium aldehyde intermediates in the reaction condition. In the presence of a longer ligand chain on the Au surface, the interaction between imidazolium and Au gets weaker, limiting the charge transfer for the formation of imidazolium aldehyde intermediates.

Surface ligand modification can also be used to control the microenvironment of catalytic sites and to impact catalysis efficiency. When modifying the catalyst surface with a hydrophobic ligand, the surface area becomes hydrophobic, which allows CO2 to accumulate, creating a triphasic interface of gas–electrode–electrolyte. For example, when modified with 1-octadecanethiol (ODT), the Cu dendritic surface became superhydrophobic with a water contact angle of 153°. Such a molecule ligands can vary the surface properties, polymer

Fig. 20 Comparison of partial current density and FE for thiolate ligands on polycrystalline Au: (A) proposed reaction mechanism of the formate production at 4-PEM and Au interfaces. (B) Schematic of Au electrodes with 1-methylimidazolium-terminated SAMs (IL-2, IL-6, IL-8, and IL-12). (C) FE of C2 products on both wettable and hydrophobic Cu dendrites at the total current density of 30 mA cm⁻². Adapted from ref. 175, 171 and 168 with permission. Copyright 2015 Royal Society of Chemistry and 2019 Nature Publishing Group.

When the Au electrode was modified with 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (Cb) (Fig. 22A) showed a much higher FE of CO2 (83%) and current density (7.6-fold) than the plain Au NPs (FE of CO2 = 5%) at the potential of −0.57 V. The tridentate NHC ligand timtmbMe (Fig. 22B)-modified Pd electrode showed not only high selectivity for CO2RR but also stability. In the presence of timtmbMe, the Pd catalyst exhibited a larger total current density and positively shifted onset potentials relative to the parent palladium foil (Fig. 22C). The onset potential for CO2RR appeared at −0.12 V, which is about 265 mV, positively shifted relative to that of the unmodified Pd. The FE of C1 products increased from the initial 23% to 86% (with timtmbMe, the Pd catalyst exhibited a larger total current density and positively shifted onset potentials relative to the parent palladium foil (Fig. 22C). The onset potential for CO2RR appeared at −0.12 V, which is about 265 mV, positively shifted relative to that of the unmodified Pd. The FE of C1 products increased from the initial 23% to 86% (with timtmbMe, the Pd catalyst exhibited a larger total current density and positively shifted onset potentials relative to the parent palladium foil (Fig. 22C). The onset potential for CO2RR appeared at −0.12 V, which is about 265 mV, positively shifted relative to that of the unmodified Pd. The FE of C1 products increased from the initial 23% to 86% (with timtmbMe, the Pd catalyst exhibited a larger total current density and positively shifted onset potentials relative to the parent palladium foil (Fig. 22C). The onset potential for CO2RR appeared at −0.12 V, which is about 265 mV, positively shifted relative to that of the unmodified Pd. 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ligands form a protective coating layer of 10–50 nm that could “gate” the accessibility of catalytic metal NPs. Monodentate and multidentate polymer NHC ligands were first studied to stabilize metal catalysts under reductive potentials and to improve the CO2RR selectivity.162 The multidentate polymer NHC ligand poly(vinylbenzyl N-methylbenzyl N-heterocyclic carbene) (PVBMB-NHC57, P1) was synthesized using quaternization of N-methyl benzimidazole with poly(vinylbenzyl chloroide) (PVBC). The monodentate NHC-terminated polystyrene (PS65-NHC, P2) was prepared from the end-group functionalization of the halogen-terminated one through atom transfer radical polymerization (ATRP). After counterion exchange with KHCO3, the two imidazolium-ended polymers could graft to Au NPs (∼14 nm) at relative high grafting density, 1.3 and 0.9 chains per nm² for P1 and P2, respectively (Fig. 23A).162 When catalysing the CO2RR, the Au-P1/C and Au-P2/C showed both higher activity and selectivity than the Au/C due to their more efficient role in suppressing HER (Fig. 23B).162 The polymer-modified Au NPs had ~75% ECSA retention. Even after 11 h electrolysis, the Au-P1/C still had a FE of 86% while the unmodified Au NPs only had <10% FE left. The polymeric NHC-binding strategy could be applied to Pd/C (Fig. 23D), which showed the desired enhancement in both selectivity (FE of CO was increased from 45% to 60%) and stability (ECSA retention was improved from 10% to 91% after 2 h electrolysis).162 As a control, Pd/C modified with thiol-terminated PS ligands and other ligands (Fig. 23D and E)162 were all less stable than the Pd/C modified with polymer NHC.

Very recently, a nanoparticle/ordered-ligand interlayer (NOLI) was proposed and applied to enhance CO2RR efficiency.169 The NOLI structure was created by the collective dissociation of bound ligands (alkylphosphonate) from a dense assembly of metal (Au, Ag or Cu) NPs. Under the reductive potentials, covalently bonded ligands detached but were maintained on the surface through the non-covalent interactions between ligands in the densely packed assembly, as illustrated in Fig. 24A.169 Consequently, this allows K⁺ to transport onto the catalyst surface to balance the overall charge, creating a pseudocapacitive pocket interlayer. Specifically, the ligand chains form a hydrophobic domain around the pocket that facilitates the diffusion of CO₂, while inhibiting the diffusion of water/protons, into the NOLI structure, favouring CO₂ conversion over the HER.192 The Ag–NOLI improved the activity and selectivity towards CO formation dramatically in CO₂RR, whereas the turnover and selectivity drop to a level similar to Ag foil when the ligand layer was removed (Fig. 24B and C), supporting the importance of the NOLI structure in stabilizing the catalytic metal.
the selective CO₂-to-CO transformation. This NOLI structure was demonstrated to be highly active and selective across several metals with up to 99% CO selectivity and onset over-potentials as low as 27 mV. Interestingly, even without strong chemical binding, the ligand density (with respect to the NP surface area) remains relatively stable throughout electrolysis (Fig. 24D). DFT calculations reveal that the specific configuration for the NOLI facilitates the bending of the adsorbed CO₂ molecule, thus promotes the rate-limiting step of the polarization of non-polar CO₂ with an electron transfer to form the intermediate \( \text{CO}_2^- \).

4. Coupled CO₂ capture and conversion

Both CO₂ capture and CO₂ conversion processes are considered as promising strategies to reduce CO₂ emissions, therefore mitigating global warming and other associated environmental concerns. However, most of the present CO₂ reduction studies, either thermal or electrochemical conversion, are based on pure CO₂ as the feedstock, and there exist large gaps between the capture and conversion processes. In a conventional CO₂ capture and conversion process, CO₂ is first captured from either ambient air or flue gas by various capture technologies. Then CO₂ is desorbed, compressed and utilized in the preparation of value-added products by chemical reduction reactions. From the perspective of the whole system, however, the desorption and compression steps are energy-intensive, imposing a large energy penalty on the processes of CO₂ capture and conversion. Therefore the combination of CO₂ capture and conversion has been suggested in a single integrated CO₂ capture and utilization process. The energetics comparison between independent and coupled CO₂ capture and conversion processes is shown in Fig. 25. Dilute CO₂ can be captured through the formation of CO₂–X adduct for both processes; however, the independent one requires an additional regeneration step to produce pure CO₂ for electrocatalysis, causing an extra capture “overpotential” energy. If both pathways have the same energetic level for CO₂RR intermediates, integrated configurations could achieve lower overall energy requirements due to the energy saving through bypassing the capture media regeneration step. Therefore, integrating the capture and conversion processes is critical to decrease the cost and make the overall process energy efficient.

To date, coupling between CO₂ capture and conversion via thermo- and electro-catalysis has been studied only in a few reports. Therefore, this section summarizes the recent progress made in these two catalysis areas. The integrated capture and conversion were first demonstrated in 2013. In the report, polyamines and amidine bases were used for CO₂ capture in...
alcohol solvents, and the capture products were subsequently hydrogenated to obtain alkylammonium formate salts by a Ru-based homogeneous catalyst at 40 bar H2. The best conversion performance was achieved when CO2 was captured by 1,5-diaza bicycle [4.3.0] non-5-ene and glycol to form alkyl carbonate, which was then reduced to formate with 55% yield. It should be noted that the captured CO2 can facilitate hydrogenation and yield better performance in comparison with equivalent free gaseous CO2, indicating the CO2 activation upon capture with amines. CO2 could also be captured by amines in aqueous media and subsequently converted to alkylammonium formate salts (Fig. 26A).197 The major advancement of this capture/conversion system over the previously reported one is the use of a biphasic solvent, shown in Fig. 26B. CO2 can be captured as carbamate or bicarbonate in aqueous amine solution, while the catalyst is dissolved in an organic solvent. This allows easy separation of the catalyst and formate product, and higher reaction rate due to good solubility of the captured CO2 in water. The captured CO2 was selectively converted to formate (up to 95% yield) in the presence of homogeneous Ru- and Fe-based pincer complexes.

Recently, the coupled capture and conversion further led to the synthesis of methanol at a 79% yield.198 In this process, CO2 was captured by a short-chain polyamine, pentaethylhexamine (PEHA), to form ammonium carbamate and bicarbonate, which was further hydrogenated at 155 °C and 50 bar of H2 for 55 h in the presence of a pincer Ru-complex catalyst (Fig. 27A). It should be noted that formate and formamide are essential intermediates for amine-assisted hydrogenation of CO2 to CH3OH. Similarly, alcohol-assisted CO2 hydrogenation to methanol via formate ester has also been studied extensively, and was further extended to a new approach of CO2 capture and conversion to methanol via alkali-metal hydroxides in ethylene glycol (Fig. 27B).199 Different from amines, hydroxides do not suffer from volatility and oxidative degradation issues. More importantly, due to their high CO2 affinity, these hydroxides have high efficiency for direct air capture of CO2. In the one-pot system, CO2 from atmospheric air was efficiently captured by an ethylene glycol solution of KOH to form alkyl carbonate intermediate, which was hydrogenated at 140 °C and 70 bar of H2 for 72 h to form to methanol at a 100% yield. Such a high yield synthesis of methanol was attributed to the facile hydrogenation of the ester intermediate. Also in the process, hydroxide was partially re-generated and could be used for the next round of CO2 capture and conversion.

In the case of combining capture and electrocatalysis, CO2 can be captured by an aqueous solution of inorganic hydroxides to yield corresponding bicarbonates. Even though bicarbonate is commonly used as electrolyte for conventional CO2 electrolysis, it can also serve as the carbon precursor for electrochemical reduction. So far, direct electrolysis of bicarbonate has not been reported yet, but the indirect electrochemical reduction reaction of bicarbonate solution has been achieved using a bipolar membrane (BPM) as the ion-exchange membrane in a flow cell where bicarbonate could be converted to molecular CO2 due to local acidification.200 Electrolysis of the N2-saturated 3.0 M KHCO3 solution yielded CO with a FE of 81% at 25 mA cm−2, which is comparable to the conventional gaseous CO2 electrolysis in bicarbonate solution. Similarly, amines were used to capture CO2 to form carbamate adducts.201 Electrolysis of the CO2-saturated 30% (w/w) monoethanolamine (MEA) aqueous solution led to the formation of formate with FE reaching up to 60.8% in the presence of a porous Pb electrode and cetyltrimethylammonium bromide. One challenge associated with the direct electrolysis of carbamate is the electrostatic repulsion between carbamate ion and the cathode surface. To address this issue, an alkali cation...
could be added into the aqueous MEA solution to change the interfacial structure near the electrode, thereby improving the electron transfer from the electrode to the carbamate and the electrochemical performance, as shown in Fig. 28A and B.202 For example, adding 2 M KCl as supporting electrolyte and by using Ag as a catalyst, CO was formed at 72% FE and a current density of 50 mA cm$^{-2}$ (Fig. 28C). The amine electrolyte was recycled 10 times and could still be used for the capture and conversion reaction without obvious FE$_{CO}$ drop, demonstrating the promising stability of the electrolyte for continuous CO$_2$ capture and conversion (Fig. 28D).

5. Concluding remarks

A sustainable carbon cycle is essential for maintaining the healthy evolution of life globally. However, human activities, especially the ever-demanding energy consumption, have led to excessive depletion of fossil fuels, and severely affected the well-established equilibrium of the carbon cycle in nature. Given the threat of excessive CO$_2$ emission, there is now a growing demand for negative carbon technologies. Carbon capture and storage as well as direct air capture are promising technologies that could be utilized to minimize and/or reduce CO$_2$ emissions. Various adsorbent materials have been developed for CO$_2$ capture, including aqueous hydroxides, solid alkali carbonates, organic amines, and porous materials. To date, the investigations of direct air capture adsorbents have focused more on the use of solid-supported amine materials for improved stability and recyclability. The chemical reactions between CO$_2$ and amines ensure significant CO$_2$ uptake even at low CO$_2$ partial pressures with much higher selectivity. The physical adsorption strategy using porous materials is also considered as an attractive alternative to conventional chemical adsorption approaches. Moreover, the modification of metal centres and functional groups as well as pore sizes could incorporate both chemisorption and physisorption capability within one adsorbent structure, and in turn offer better CO$_2$ adsorption capability and selectivity. Looking into the future, practical CO$_2$ adsorbent materials that are highly active, selective, recyclable, and cost-effective are still in demand.

The reduction of CO$_2$ into value-added chemicals and fuels is equally important to carbon neutral and sustainable energy. Thermal catalysis of CO$_2$ hydrogenation has been attractive because H$_2$ can be generated from water electrolysis by renewable energy. However, this method does require high temperature and pressure for the conversion to complete. Electrochemical CO$_2$ reduction, in comparison, can be initiated by renewable electricity under ambient conditions. To lower the activation energy barrier of CO$_2$ and to convert CO$_2$ to value-added chemicals, active, selective, and stable catalysts need first to be developed. Catalyst–electrolyte interfaces should also be well-engineered to eliminate all interfacial and mass transport issues during the reaction. Despite the great advances made in these areas, the development of efficient catalysts still posts some serious challenges for practical applications.

Integrated CO$_2$ capture and conversion removes the cost of CO$_2$ release and compression and could potentially improve the overall energy efficiency of the system. Recently, the feasibility and potential benefits of integrated CO$_2$ capture and conversion systems have been demonstrated. But still, there is much to do in research and development to uncover the fundamental mechanisms that lead to efficient transformation of the captured CO$_2$ to the targeted carbon products. Once the new catalysts and the reduction processes are materialized, coupling CO$_2$ conversion with direct air capture will become a true integrated technology for realizing negative CO$_2$ emission and energy sustainability.

Conflicts of interest

There are no conflicts of interest to declare.

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References


