Frontiers of CO₂ Capture and Utilization (CCU) towards Carbon Neutrality

Lingyun ZHANG¹,², Yanfang SONG¹, Jialin SHI¹, Qun SHEN¹, Deng HU¹, Qiang GAO¹, Wei CHEN¹, Kien-Woh KOW², Chengheng PANG³,⁴, Nannan SUN¹, and Wei WEI¹,⁵

¹CAS Key Laboratory of Low-Carbon Conversion Science & Engineering, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, China
²Department of Chemical and Environmental Engineering, Faculty of Science and Engineering, University of Nottingham Ningbo China, Ningbo 315100, China
³Key Laboratory for Carbonaceous Wastes Processing and Process Intensification Research of Zhejiang Province, University of Nottingham Ningbo China, Ningbo 315100, China
⁴New Materials Institute, the University of Nottingham Ningbo China, Ningbo 315100, China
⁵School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China

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ABSTRACT

CO₂ capture, utilization, and storage (CCUS) technology is a rare option for the large-scale use of fossil fuels in a low-carbon way, which will definitely play a part in the journey towards carbon neutrality. Within the CCUS nexus, CCU is especially interesting because these processes will establish a new “atmosphere-to-atmosphere” carbon cycle and thus indirectly offer huge potential in carbon reduction. This study focuses on the new positioning of CCUS in the carbon neutrality scenario and aims to identify potential cutting-edge/disruptive CCU technologies that may find important application opportunities during the decarbonization of the energy and industrial system. To this end, direct air capture (DAC), flexible metal-framework materials (MOFs) for CO₂ capture, integrated CO₂ capture and conversion (ICCC), and electrocatalytic CO₂ reduction (ECR) were selected, and their general introduction, the importance to carbon neutrality, and most up-to-date research progress are summarized.

Key words: carbon neutrality, carbon reduction, decarbonization, CO₂, CCU

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Article Highlights:

• CCU will play an important role for carbon neutrality by establishing a new “atmosphere-to-atmosphere” carbon cycle.
• Under the carbon neutrality scenario, several cutting-edge/disruptive CCU technologies will gain extended application opportunities.
• Progresses and future perspectives for four cutting-edge/disruptive CCU technologies are summarized.

1. Introduction

1.1. Carbon neutrality

The history of human civilization is accompanied by the exploration and utilization of fossil energies. Their extensive use has been an important supporting factor for the continuous progress of human society, but it also has resulted in a huge amount of CO₂ emissions, which has led to serious problems such as the greenhouse effect and climate change (IPCC, 2014). Mitigating climate change has become one of the most important themes in the world today, and CO₂ reduction is at the central part of this issue. In this context, many countries and regions have put forward “carbon neutrality” commitments, and carbon neutrality is becoming a new benchmark for evaluating countries’ ambitions and actions to reduce carbon emissions (Energy & Climate Intelligence Unit, 2021).

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* Corresponding authors: Nannan SUN, Wei WEI
Emails: sunnn@sari.ac.cn, weiwei@sari.ac.cn

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Carbon peaking and neutrality correspond to major changes in production and lifestyles, and revolutionary adjustments must be made to the existing energy structure and industrial system. In this process, a new energy system characterized by a high proportion of renewables will undoubtedly make decisive societal and economic contributions through decarbonization (IEA, 2020a). However, the reliability of renewables needs further verification due to their intermittency and high dependency on large-scale energy storage technology. Therefore, fossil energy will inevitably exist in the energy system in a certain proportion (5%–10%) for a long time (IEA, 2020a; Qu et al., 2020). On one hand, fossil energy can act as a “stabilizer” by balancing the volatility of renewable energy. At the same time, fossil energy is very important to ensure a continuous supply of high-quality energy. On the other hand, high-carbon industries such as steel, chemicals, and cement are important pillars of the modern economy, but the technological processes in these industrial sectors are relatively mature, with high technological inertia and high replacement costs. Low-carbon transformation and structural upgrading need to be carried out in an orderly manner, and the high-carbon characteristics of these industries will not change in the short term. Therefore, the use of a certain proportion of fossil energy and fossil resources will play an irreplaceable role in ensuring energy security and maintaining the integrity of the industrial chain. However, their use will inevitably lead to a certain amount of carbon emissions, which cannot be fully absorbed through the natural carbon sinks. As a result, artificial carbon sink technology, namely CO2 capture, utilization, and storage (CCUS), will act as a safeguard towards carbon neutrality (IEA, 2020b).

1.2. CO2 capture, utilization, and storage (CCUS)

CCUS is a major technological option for the end treatment of CO2 and includes three technical steps of CO2 capture, CO2 utilization, and CO2 storage. CO2 capture is mainly used to separate and enrich CO2 from various emission sources and even the air, and it is the beginning of the entire CCUS chain. CO2 utilization uses CO2 as a raw material or working medium by chemical, biological, or geological methods, and completes carbon emission reduction at the same time. CO2 storage injects CO2 into a certain geological environment and isolates the CO2 from the atmosphere for a very long period during which the CO2 may be fixed by carbonation reaction with underground minerals.

CCUS is a recognized technology that can achieve large-scale emission reductions. The International Energy Agency (IEA) predicted that to achieve global carbon neutrality by 2070, CCUS technology will not only contribute 15% of emission reductions but also provide inevitable solutions to cement, steel, chemical, and long-distance transport industries (IEA, 2020b). The IPCC special report “Global warming of 1.5°C” pointed out that by 2030 and 2050, global CCUS capacity will reach 100–400 million tons yr\(^{-1}\) and 3–6.8 billion tons yr\(^{-1}\), respectively (IPCC, 2018).

Under the new target of carbon neutrality, the positioning of CCUS has changed significantly. CCUS technology is the only option for the low carbon utilization of fossil energies on a large scale, which is of great significance to energy security. Meanwhile, CCUS technology is a necessary solution for the decarbonization of industries that have difficulty reducing their emissions, and it is the major option to solve the problem of unavoidable “process emissions” in industries such as steel, chemical, cement, and non-ferrous metals. CCUS technology is also the main source for the necessary carbon element under the carbon neutralization scenario, which avoids the massive exploitation and utilization of fossil resources. Last but not least, the negative emission effect achieved by the coupling of CCUS and renewables is a guarantee for achieving the carbon neutrality target; which is impossible to achieve by source reduction or energy-saving approaches alone.

CCUS can be further divided into CCS and CCU according to their different approaches of CO\(_2\) abatement. In general, CCS can provide huge capacity for direct CO\(_2\) reduction as suitable reservoir volumes for CO\(_2\) storage are more than enough to accommodate all the potential emissions. The CCU pathway, on the other hand, is significantly less efficient for direct reduction. This is because for most CCU technologies, any consumed CO\(_2\) by the process will be re-released at the end of the product life-cycle (Stevenson, 2019). In fact, the importance of CCU is its great potential for indirect reduction of CO\(_2\) emissions by avoiding the use of fossil carbon. As such, a new “atmosphere-to-atmosphere” carbon cycle can be established, while the traditional “lithosphere-to-atmosphere” mode can be largely replaced (Hepburn et al., 2019). As such, the overall CO\(_2\) reduction capacity of CCU is high enough to apply considerable impact on carbon neutrality, and it is likely to create economic benefits as well.

Nevertheless, under the carbon-neutral scenario, routes for future CCU R&D may vary significantly, but one of the key features is that the necessity and application potential of some cutting-edge/disruptive CCUS technologies will greatly increase. In response to the above trends, this paper summarizes several cutting-edge/disruptive CCU technologies that are expected to play important roles in the carbon neutralization process from different dimensions. The latest progress and possible future trends are discussed to provide a reference for the research layout in the CCU field.

2. Direct air capture (DAC) and its indispensable carbon-negative feature for carbon neutrality

Direct air capture (DAC), as indicated by its name, is a process that captures CO\(_2\) from the ambient air. This technology is appealing because, to some extent, it de-couples the emission source and carbon sink (i.e., the relative locations of the emission source and downstream CO\(_2\) utilization/storage sites will not be a necessary concern). Therefore, infrastructure and expenditures for long-distance transportation of
CO₂ can be avoided, resulting in the great potential to reduce the cost of CO₂ abatement. Additionally, DAC directly uses air as the upstream source, which is a preferred technology to address mobile emission sources (such as vehicles) and micro emission sources (such as buildings) (Sanz-Pérez et al., 2016).

DAC delivers its carbon reduction capacity by coupling with either CO₂ conversion or CO₂ storage. Firstly, CO₂ obtained from DAC can be used as a raw material to replace fossil resources to produce carbon-based chemicals. In this context, the resulting products will be carbon neutral throughout their life cycles. Practically, this reshapes the existing chemical industry, leading to a disruptive impact on the entire industry and supply chain. Secondly, coupling of DAC with CO₂ storage has a significant carbon-negative effect, and its capacity is huge if large-scale deployment and application can be carried out. This offers a solution to the historical emissions and meets the demand of “reducing atmospheric CO₂ concentration” in response to climate change. Furthermore, such a carbon-negative effect may also have beneficial impacts on the energy and industrial system, promoting DAC to become an important part in the new model of carbon-neutral social and economic infrastructure (Goglio et al., 2020).

Compared with industrial emission sources, the concentration of CO₂ in the air is extremely low, only slightly higher than 400 ppm. This means that the DAC process is very unfavourable in terms of thermodynamics. Therefore, it faces great technological challenges in aspects of absorbents/adsorbents, efficiency, and energy costs. These adverse factors often cause the consumption of a large amount of materials and energy, even achieving a level that may offset the CO₂ reduction capacity of the DAC process (Deutz and Bardow, 2021). Overall, the technological maturity of DAC is still low, and its application is still in early infancy. In recent years, related studies have mainly focused on high-performance absorbents/adsorbents, prototype demonstrations, and life cycle assessments.

2.1. Absorbents/adsorbents for DAC

Absorbents and adsorbents are the most important components of a DAC technology system, and their performance directly dictates the overall cost and efficiency of the process. At present, most DAC studies and demonstrations have focused on solid adsorbents, and only a few experiments have used liquid absorbents with alkali metal hydroxide solution as the main component. The reason is because those solid adsorbents possess obvious advantages in terms of kinetics, stability, and environmental footprints (Shi et al., 2020).

Physical adsorbents (such as activated carbons, molecular sieves, etc.) are rarely used for DAC, mainly due to their weak interaction with the CO₂ molecules, which leads to extremely low adsorption capacity and selectivity in low CO₂ concentration environments (i.e., air). For example, Kumar et al. compared the CO₂ adsorption performance of four physical adsorbents and an immobilized organic amine sample, which is a typical chemical adsorbent. They found that although the performances of these samples only showed slight differences in 15 vol.% CO₂, the CO₂ adsorption capacities of physical adsorbents are more than one order of magnitude lower than those of chemical adsorbents in DAC conditions (Kumar et al., 2015).

Compared with physical adsorbents, chemical adsorbents are more widely used for DAC. Among them, immobilized organic amines are a kind of important CO₂ chemical adsorbent. The earliest prototype of these adsorbents comes from the “molecular basket” material proposed by Song’s group (Fig. 1) (Xu et al., 2002; Ma et al., 2009). Then, Sayari’s group (Franchi et al., 2005; Sayari and Belmabkhout, 2010) and Jones’ group (Hicks et al., 2008; Didas et al., 2015) systematically developed the preparation method of immobilized organic amines, and in-depth studies on their adsorption behaviours and structure-performance relationship for CO₂ capture were performed. Due to the strong interaction between these adsorbents and the CO₂ molecules, their application in the DAC process has attracted extensive attention. For example, Goeppert et al. reported that fumed silica supported poly (ethyleneimine) (PEI) can effectively adsorb CO₂ from the air (Goeppert et al., 2011). In 2011, Choi et al. (2011) used 3-aminopropyl trimethoxysilane and tetraethylorthotitanate modified PEI as the adsorption components, which were loaded on porous SiO₂, and they found that this type of material exhibited great DAC performance (adsorption capacity > 2 mmol g⁻¹) and the use of modifiers can significantly improve the stability of PEI, rendering the material with excellent stability (Choi et al., 2011). Keller et
al. used carbon nanotubes as a carrier for PEI to prepare a hollow fibre adsorbent. The adsorption capacity of CO$_2$ reached 1.07 mmol g$^{-1}$ under DAC conditions (Keller et al., 2018). In addition to the commonly used impregnation method, immobilization of amines can also be achieved by surface grafting. Although adsorbents prepared in this way have slightly lower CO$_2$ uptakes under DAC conditions, their overall stability can be significantly improved (Potter et al., 2017; Sabatino et al., 2021).

Porous framework materials are a type of functional materials developed rapidly in recent years. The structure of these materials is highly ordered and can be finely characterized by various spectroscopic methods, thereby providing new dimensions for studying DAC mechanisms and performance tuning (Custelcean, 2021). For example, by the engineering of ligand for metal-organic frameworks (MOFs), Kumar et al. replaced the SiF$_6^{2-}$ pillar in SIFSIX-3-Ni material with TiF$_6^{2-}$, which led to enhanced interaction between the framework and CO$_2$, and thus the DAC performance of the material was effectively improved (Kumar et al., 2017). Bhatt et al. further explored possible strategies by adjusting the pore size, pore shape, and surface functional groups of MOFs, and a CO$_2$ adsorption capacity of 1.30 mmol g$^{-1}$ could be achieved at the condition of 400 ppm and 25°C, which is on a similar level to immobilized amine-based adsorbents (Bhatt et al., 2016). It should be noted that although the low-pressure CO$_2$ adsorption performance can be significantly improved through the optimization of MOFs structure, in general, its adsorption mechanism still relies on physical interactions, so it is easily affected by competitive adsorption of moisture. In fact, MOFs can also be used as carriers to prepare amine-based DAC adsorbents (Lu et al., 2013; Lee et al., 2014; Liao et al., 2016; Sen et al., 2019), and under the synergistic effect of multiple functional sites, the resulting materials may exhibit excellent DAC performance through several types of new adsorption mechanisms. For example, McDonald et al. used N, N’-dimethylethylenedi-amine (mmen) to functionalize Mg$_2$(dobpdc) (dobpdc$^{4-}$=4,4’-dioxidobiphenyl-3,3’-dicarboxylate). It was found that during the adsorption of CO$_2$, there is a process of CO$_2$ insertion into the metal-amine bond, so the obtained CO$_2$ adsorption isotherm has step-shaped characteristics. This unique behaviour makes the material possess a higher working capacity than other chemical adsorbents (McDonald et al., 2015). Through the tunability of MOFs structure and the optimization of external amines, CO$_2$ adsorption capacity, kinetics, and regeneration performance under DAC, conditions can be further improved (Lee et al., 2014; Liao et al., 2016; Kim et al., 2020b; Martell et al., 2020).

In recent years, some new adsorption strategies have also been used for DAC processes. Based on the affinity difference between materials to CO$_2$ and water, researchers have proposed the concept of moisture-swing adsorption. In this process, the material captures CO$_2$ from air in a dry environment, while the competitive adsorption of moisture in a wet environment will liberate CO$_2$ molecules from the adsorbent surface (Shi et al., 2016; Yang et al., 2018). Inagaki et al. found that the aqueous solution of m-xylene diamine (MXDA) can absorb CO$_2$ in the air and generate water-insoluble MXDA·CO$_2$ crystals. After simple filtration and separation, heating of MXDA·CO$_2$ can release CO$_2$ and complete the regeneration of MXDA. This process avoids the large amount of energy consumption required for the evaporation of solvent water in the traditional liquid absorption method (Inagaki et al., 2017). Based on a similar strategy, Brethomé et al. used a cheap and easily available amino acid aqueous solution to absorb CO$_2$, and then the CO$_2$ loaded solution further reacted with guanidine compounds to form insoluble carbonates, which regenerated the amino acids simultaneously, and then the separated carbonate can be decomposed under relatively mild conditions to release CO$_2$ (Brethomé et al., 2018).

Table 1 summarizes recent research results on DAC sorbents. Overall, the research and development of DAC sorbents/adsorbents still face great challenges. In this study, a model was designed to estimate the cost of DAC

| Reference          | Sorbents       | Mechanisms       | Adsorption capacity (mg-CO$_2$ g$^{-1}$) | Temperature (°C) | Pressure (bar) |
|-------------------|----------------|------------------|----------------------------------------|-----------------|---------------|
| (Kumar et al., 2015) | TEPA-SBA-15    | chemisorption    | 158                                    | 20              | 400 ppm       |
|                   | Zeolite 13X    | physisorption    | 5.8                                    | 20              | 400 ppm       |
|                   | HKUST-1        | physisorption    | 2.1                                    | 20              | 400 ppm       |
|                   | Mg-MOF-74     | physisorption    | 40                                     | 20              | 400 ppm       |
|                   | SIFSIX-3-Ni    | physisorption    | 58                                     | 20              | 400 ppm       |
| (Goepert et al., 2011) | FS-PEI-33     | chemisorption    | 75                                     | 25              | 400 ppm       |
| (Choi et al., 2011) | PEI-silica     | chemisorption    | 103                                    | 25              | 400 ppm       |
|                   | A-PEI/silica   | chemisorption    | 99                                     | 25              | 400 ppm       |
|                   | T-PEI/silica   | chemisorption    | 96                                     | 25              | 400 ppm       |
| (Keller et al., 2018) | CNT-PEI       | chemisorption    | 47                                     | 25              | 350 ppm       |
| (Bhatt et al., 2016) | NbOFFIVE-1-Ni  | chemisorption    | 57                                     | 25              | 400 ppm       |
| (McDonald et al., 2015) | mmen-Mg$_2$(dobpdc) | chemisorption | 154                                    | 25              | 1000 ppm     |
| (Kim et al., 2020b)  | Mg$_2$(dobpdc) (3-4-3) | chemisorption | 150                                    | 90              | 4000 ppm     |
adsorbents and the corresponding relationship between adsorbent performance and its highest allowable cost was studied (Fig. 2). Based on this model, it is found that if the service life of an adsorbent is 1000 cycles, its cost must be less than $1 kg\(^{-1}\). Currently, there are hardly any adsorbents so low in cost. Increasing adsorbent service life can reduce its highest allowable cost; with 100 000 cycles, the allowable cost of MOF (Diamine) materials is the highest, reaching $90 kg\(^{-1}\). However, the price of MOF material is generally higher than $10 000 kg\(^{-1}\), and its stability is far from the requirements (Shi et al., 2020). This work verifies the difficulty of developing DAC adsorbents from a cost perspective, but it should be mentioned that recently, several groups have reported several CO\(_2\) adsorbents with excellent comprehensive performance, which provides new opportunities for reducing the cost of DAC technology (Nandi et al., 2015; Yue et al., 2017; Cavalcanti et al., 2018; Mukherjee et al., 2019; Lin et al., 2021).

### 2.2. Prototype demonstrations of DAC

Devices and demonstrations are also major focuses in the DAC field. This is because the concentration of CO\(_2\) in the air is low, so the gas processing capacity of the DAC process is huge, and there is little experience in an engineering perspective to date. Over the past decade, developed countries in Europe and America have attached great importance to the development and application of DAC, and several small-scale prototypes and demonstrations have been reported, which has laid an important foundation for the future development of DAC technology.

Climeworks, a company based in Switzerland, is the first company in the world that provides customers with CO\(_2\) captured from the air. In 2017, the company built the world’s first commercial DAC device in Switzerland, which adopted modular design and used 18 adsorption units. An overall capture capacity of several hundred tons of CO\(_2\) per year was achieved. In 2021, Climeworks built its latest Orca plant in Iceland. The Orca plant has a capture capacity of 4000 t yr\(^{-1}\) (Fig. 3) and is the largest DAC demonstration in the world to date. The captured CO\(_2\) is injected 700 m underground for mineralization and storage (Climeworks, 2021).

DAC technology from Global Thermostat uses temperature-swing adsorption and adopts immobilized organic amine adsorbents. Global Thermostat established the first pilot plant in 2010 and the first commercial DAC plant in Alabama in 2018. It is reported that the energy consumption can be reduced to less than 6 GJ (t CO\(_2\))\(^{-1}\), which is around the minimum for existing DAC demonstrations (Zhu et al., 2020).

Carbon Engineering established its first DAC pilot plant by using KOH and Ca(OH)\(_2\) solutions as absorbents in 2015, and in 2017, the company succeeded in the conversion of air-captured CO\(_2\) to liquid fuels. In 2019, the company began to design and build a million-ton DAC demonstration project. Its carbon capture cost is estimated to be $94–$232 (t CO\(_2\))\(^{-1}\), with an energy consumption intensity of about 8.81 GJ (t CO\(_2\))\(^{-1}\) (Keith et al., 2018; Engineering, 2021).

### 2.3. Life-cycle assessment (LCA) of DAC

At present, there are still some controversies around the economic and environmental benefits of DAC. Therefore, its full life cycle assessment is also a research hotspot. By applying LCA to the actual operation data, Deutz et al. found that the DAC demonstration currently carried out by Climeworks has already achieved a carbon-negative effect. The carbon capture efficiencies of its two DAC plants reached 85.4% and 93.1%, respectively. However, the environmental benefits of the DAC process are closely related to energy sources. In an energy structure dominated by renewables, it is expected that the large-scale deployment of DAC technology (reaching 1% of global carbon emissions) will not be limited by materials and energy, and related environmental issues, if any, are relatively limited (Deutz and Barlow, 2021). According to calculations on carbon balance, Jonge et al. carried out LCA studies on a NaOH absorption DAC system, with a special focus on the life cycle carbon efficiency. Their results also showed that the energy source is very important to the emission reduction benefits of DAC. In general, the utilization of renewable energy is the simplest and most significant way to improve the carbon efficiency of DAC at this stage (de Jonge et al., 2019).

Terlouw and co-workers (2021b) proposed that it is necessary to incorporate CO\(_2\) storage into the DAC’s LCA pro-
cess in order to fully reflect the emission reduction benefits and other environmental impacts of DAC. Based on this idea, the authors compared and studied the environmental impact of direct air capture and storage (DACCS) under different power/heat sources and a variety of technology combinations. It was found that although a negative carbon effect can be achieved in several scenarios, it is necessary to select the best energy supply mode according to the energy infrastructure of different countries and regions. This is of pivotal importance to the emission reduction capability and the environmental impact of DAC (Terlouw et al., 2021a).

It should be mentioned that DAC technology is still very immature, so there are significant challenges in technology evaluation. Terlouw et al. (2021b) systematically summarized the current LCA works for carbon-negative technologies and pointed out that existing methods may induce confusion between avoided emission and negative emission, resulting in misleading conclusions. In order to better support the development of DAC technology in the future, it is necessary to strengthen the comprehensiveness of the evaluation and the transparency of the methods.

3. Flexible metal-organic frameworks (MOFs) and ultra-low cost CO₂ capture technology

3.1. Flexible MOFs as CO₂ adsorbents

Metal-organic frameworks (MOFs) are one of the emerging and rapidly growing focuses in material science. These materials are constructed from complexation of metal ions or metal ion clusters with bridging organic linkers, which exhibit regular crystalline lattices with high surface area and well-defined pore structures (Furukawa et al., 2013; Yuan et al., 2018). In MOFs, both the metal nodes and the organic linkers can be readily adjusted. This offers an effective approach for the customization and delicate adjusting of the materials’ pore structure and functionalities. Therefore, MOFs can be widely applied in separation and catalysis science. In recent years, it was found that due to the dynamic properties of the framework component, MOFs that are responsive to external stimuli (pressure, temperature, ultraviolet light, etc.) can be synthesized (Matsuda, 2014). Based on this, construction of a reversible phase transformable CO₂ adsorption material can be realized to achieve an ultra-low cost CO₂ capture process (Schneemann et al., 2014) (Table 2). It should be noted that the energy consumption of the existing carbon capture process is relatively high, often accounting for 70% of the entire CCUS technology chain.

3.2. Light-responsive MOFs for CO₂ adsorption

One of the general strategies to construct flexible MOFs is to use organic linkers with light-responsive function groups as subunits for the framework. Modrow et al. constructed the first porous MOF (CAU-5) with photo-switchable linker molecules (3-azo-phenyl-4,4’-bipyridine). Under the irradiation of UV light (365 nm), the azo-functionality switches from its thermodynamically stable trans-isomer to cis-isomer (Modrow et al., 2011). Similarly, CO₂ adsorption behavior can be reversibly altered upon photochemical or thermal treatment in an MOF (PCN-123) with an azobenzene functional group, which can switch its conformation (Park et al., 2012). Sensharma et al. reported the synthesis and characterization of a photoactive MOF (TCM-15), which revealed a dynamic response upon UV irradiation, leading to instant desorption of pre-adsorbed CO₂. Based on FT-IR experiments and DFT calculations, the author verified that such release of CO₂ could be attributed to the structural flexibility of the materials (Sensharma et al., 2019). Lydon et al. synthesized an MOF loaded with azo-type light-responsive groups. The material showed rapid response towards CO₂ adsorption during the light on-and-off switching cycles. This work directly verified the possibility of developing ultra-low energy consumption carbon capture technology based on flexible framework materials (Fig. 4) (Lydon et al., 2013).

3.3. Guest-responsive MOFs for CO₂ adsorption

Interaction between MOFs and guest molecules is an important way to stimulate flexibility. As early as 2003, Kitaura et al. introduced displacement freedom during the self-assembly process of rigid motifs, and they proved experimentally that the obtained material has a “gate-opening pressure” for different gases, which caused the MOF material to transition from a crystalline “closed” form into an “open” form. The authors suggest that the reason for this flexibility is the displacement of π-π stacked moieties in the material.

Table 2. Properties before and after breathing-MOF.

| Reference                | Sample       | Trigger of flexibility | Properties alteration upon flexibility                                                                 |
|--------------------------|--------------|------------------------|---------------------------------------------------------------------------------------------------------|
| (Park et al., 2012)      | PCN-123      | UV irradiation         | At 1 bar pressure, CO₂ adsorption decreased from 21 to 10 cm³ g⁻¹ after UV irradiation.                |
| (Lyndon et al., 2013)    | Zn(AzDC)     | UV irradiation         | Dynamic exclusion of CO₂ during UV on-and-off switching cycles.                                          |
| (Dong et al., 2021)      | (4,4′-BPE)0.5NTU-65 | Temperature           | C₂H₄ adsorption capacity (1 bar pressure) decreased from 90 to 0 cm³ g⁻¹ when increase temperature from 195 to 263 K. |
| (Marks et al., 2020)     | CPL-2 and CPL-5 | Rotation of the         | Due to lattice expansion, CO₂ adsorption increased rapidly at pressure lower than 20 bar.              |
|                          |              | pillar ligands         |                                                                                                         |
| (Taylor et al., 2018)    | Co(bdp)      | Formation of CO₂       | At appropriate pressure, CH₄ can be largely excluded from the pores, leading to high CO₂/CH₄ adsorption selectivity. |
At the same time, due to the different interactions between different gas molecules and materials, the gate-opening pressure also varied in different atmospheres. For CO\textsubscript{2}, the opening and closing pressure are only 0.4 and 0.2 bar, respectively (Kitaura et al., 2003). Stavitski et al. prepared amino-modified NH\textsubscript{2}-MIL-53(Al) and found that the modified material has excellent CO\textsubscript{2} adsorption properties compared with the unmodified counterpart. Very interestingly, it was found that instead of binding CO\textsubscript{2} chemically, the introduced amino groups actually played a role in adjusting the framework flexibility. In this way, the CO\textsubscript{2} adsorption capacity could be enhanced while the physical adsorption nature was not altered, and therefore, a significant increase in energy consumption for desorption was avoided (Stavitski et al., 2011). Using Cu as the metal center, 2,3-pyrazinedicarboxylic acid (pzdc) as the ligand, and 4,4′-bipyridine (bpy) and 1,2-di(4-pyridil)-ethylen (bpe) as the pillar, CPL-2 (Cu\textsubscript{2}(pzdc\textsubscript{2})(bpy)) and CPL-5 (Cu\textsubscript{2}(pzdc\textsubscript{2})(bpe)) were prepared, respectively. Both samples showed excellent CO\textsubscript{2} adsorption capacity and selectivity, and based on in situ synchrotron X-ray diffraction experiments, the authors showed that the chemical interaction between CO\textsubscript{2} and the materials triggered rotation of the pillar ligands. This distortion further introduced expansion of the framework lattice, which is the key factor for the high CO\textsubscript{2} adsorption performance (Marks et al., 2020).

Taylor and co-workers prepared a Co (bdp) (bdp\textsuperscript{2}= 1, 4 benzenedipyrazolate) MOF material with a flexible framework, which showed excellent adsorption selectivity for the separation of CO\textsubscript{2} and CH\textsubscript{4}. Based on in situ X-ray Powder Diffraction (XRD) measurements, the authors suggest that the high selectivity originates from a “reversible guest templating” effect. That is, in the adsorption process, the framework expanded to form CO\textsubscript{2} clathrates, and the expended framework collapsed back to the non-templated phase in the subsequent desorption process. Based on such a mechanism, CH\textsubscript{4} was completely removed during adsorption of a 1:1 CO\textsubscript{2}/CH\textsubscript{4} mixture (Fig. 3) (Taylor et al., 2018).

### 3.4. Regulating the flexibility of MOFs for CO\textsubscript{2} adsorption

Although flexible MOFs have shown many advantages in CO\textsubscript{2} adsorption, how to regulate their flexibility to match practical conditions is still a challenging question.

Based on the excellent structural flexibility and mechanical resistance of MIL-53 series materials, Chanut et al. found that when an external force is applied to the materials, they gradually change from an open-pore form to a contracted form. More importantly, the pore size of the materials can be accurately controlled by the strength of the applied force. Based on this idea and considering specific separation objects, efficient separation of CO\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4} could be achieved under optimized external force conditions. At the same time, when the external force is unloaded, the material structure switched back to the open form, which led to gas desorption and material regeneration (Fig. 6). Clearly, such a strategy is superior to the conventional pressure-swing or temperature-swing processes (Chanut et al., 2020).

Using NH\textsubscript{2}-MIL-53(Al) as a parent material, Bitzer et al. introduced Sc, V, Cr, and Fe as a second metal node to prepare NH\textsubscript{2}-MIL-53 (Al, M). Based on systematic characterizations, the authors found that the flexibility of the framework can be effectively adjusted by the presence of the second metal, which further altered the CO\textsubscript{2} capture performance of the resulting samples. In general, the construction of poly-metallic MOFs can easily and effectively regulate the framework flexibility in a wide range, which has great potential in future applications (Bitzer et al., 2020).

Ghoufi’s calculation revealed that the flexibility of MIL-53 could be affected by the existence of an electric field in addition to the stimulation of the guest molecules, heat, and external forces, with a volume change of up to 40%. At the same time, varying the electric field strength led to the regulation of the unit cell volume. This provided a ready path for adjusting gas adsorption, which resulted in the efficient separation of CO\textsubscript{2} and CH\textsubscript{4} (Ghoufi et al., 2017).

Dong et al. prepared a flexible MOF (NTU-65), and its flexibility is sensitive to temperature. Based on this character-
istic, and together with the different gate-opening pressure of different gases, the authors successfully found a suitable operation window for the one-step separation of multi-component gases containing ethylene, ethane, and CO$_2$. High purity ethylene of polymerization grade was obtained by this method, which may find important potential in the petrochemical industries (Dong et al., 2021).

4. Integration of CO$_2$ capture and conversion (ICCC)

4.1. General basics of ICCC

Integration of CO$_2$ Capture and conversion (ICCC) refers to the connection of these two processes by their common microscopic steps, that is, the interaction between CO$_2$ and solid surface. During the new process, the captured CO$_2$ is directly converted to a value-added product without its desorption and enrichment (Fig. 7) (Zhou et al., 2020). Compared with the traditional CCUS chain, there are multiple advantages of ICCC. Firstly, it avoids the energy consumption of CO$_2$ desorption from absorbent/adsorbent in the traditional carbon capture process. Since this is one of the key factors causing the high cost of CCUS, it is thus expected that ICCC may significantly reduce the cost for CO$_2$ abatement. Besides, ICCC allows the disposal of CO$_2$ at close vicinity of its emission, which greatly reduces the demand for CO$_2$ transportation, and thus provides a solution to the source-sink matching problem. It is also possible that the products from an ICCC process can be readily used in downstream chains or even by the original emitter, leading to decarbonization of the energy and industrial system. The above advantages dictate the significant potential of ICCC in carbon neutralization scenarios. However, this technology is still in the stage of laboratory verification, and systematic investigations are needed to clarify more approaches that are suitable for the current emission sources.

4.2. ICCC for methanol production

Methanol is a very important platform chemical that is widely used as a fuel and a chemical raw material. Under the background of carbon neutrality, methanol is expected to become a renewable energy carrier that can replace fossil energy. The technology of CO$_2$ hydrogenation to methanol has attracted more and more attention in recent years, mainly because this process can greatly reduce the consumption of fossil resources for methanol synthesis, thereby bringing a significant effect of indirect reduction of carbon emission.

Reller et al. were among the earliest who investigated methanol producing ICCC process. In their work, N, N-Diethylethanolamine (DEEA) and Cu/ZnO-Al$_2$O$_3$ catalyst were mixed, and the system was in contact with high-pressure CO$_2$ (10–20 bar) and H$_2$ (50–70 bar) consecutively. As
such, CO₂ was firstly absorbed by DEEA, and then CO₂ could be activated and converted to methanol by Cu/ZnO-Al₂O₃. This experiment used high-pressure and pure CO₂ in the CO₂ capture stage, so it cannot be strictly classified as an ICCC process, but it clearly verifies the feasibility for the conversion of captured CO₂ to value-added products (Reller et al., 2014).

In 2016, Prakash’s group reported capturing CO₂ directly from the air and its conversion to methanol for the first time. They used pentaethylenehexamine as a CO₂ absorber and Ru-based Prince complex as a catalyst to convert the captured CO₂ to methanol under high-pressure H₂. With the optimal conditions, the yield of methanol reached 95% and could be recovered by distillation (Kothandaraman et al., 2016). Based on this work, a series of follow-up studies on several principal technical difficulties were performed. Firstly, in order to improve the efficiency of amine absorbent, a two-phase system was developed to simplify the separation of catalyst and amine, and thus the cycling stability of amine could be enhanced (Kar et al., 2018). Additionally, the authors also reported that either immobilized amines or metal hydroxide solutions can also be used for CO₂ capture in the process, which might provide solutions to the instability issue of amine-based absorbents (Fig. 8) (Kar et al., 2019; Sen et al., 2020).

4.3. ICCC for CO/syngas production

CO is the main component of coke-oven gas and a common reducing gas in the metallurgical industry. In addition, syngas composed of CO and H₂ is a widely used synthetic building block, which can be converted to a range of chemicals. At present, the preparation of CO and syngas mainly takes coal as the raw material through coking and gasification, respectively. The energy consumption of these processes is high, and an additional water-gas shift is needed to fulfill the downstream requirements on H₂/CO ratio for syngas, which further lowers the carbon efficiency by converting some CO to unusable CO₂. Therefore, carbon emission from CO/syngas production is huge, and relevant industries are facing severe pressures under the scenario of carbon neutrality. In recent years, some researchers have also studied the feasibility of preparing CO/syngas through the ICCC strategy by combining CO₂ capture with either its direct hydrogenation or reforming with alkanes.

Ni/CaO-Al₂O₃ mixed oxide was prepared by Li et al. by using CaO for high-temperature adsorption of CO₂ and Ni as the catalyst for CO₂-CH₄ reforming. This system can efficiently convert adsorbed CO₂ into syngas, but due to the sintering of CaO, the materials are gradually deactivated in prolonged cycles (Li et al., 2009). In Qiao’s work, γ-Al₂O₃ was successively impregnated with K-Ca double salts and Ni species, acting as the CO₂ adsorption and catalytic component, respectively. CO₂ adsorption and subsequent reforming with ethane to prepare syngas were then performed successfully (Qiao et al., 2017).

Bobadilla et al. prepared FeCrCu/K/MgO-Al₂O₃ bi-functional materials, and an ICCC process was carried out based on reverse water gas shift to produce syngas. The process can be operated stably under simulated flue gas conditions containing oxygen and steam (Bobadilla et al., 2016). Ce-doped Ni-Ca composite oxides were prepared by Sun et al., in which the oxygen vacancy on CeO₂ can significantly enhance the activation of CO₂, and thus its ICCC stability could be improved. When the Ca/Ni/Ce ratio is 1:01:0.033, the material can achieve 100% CO selectivity and 51.8% CO₂ conversion at the optimum temperature (650°C); no deactivation was observed in 20 capture-conversion cycles (Sun et al., 2019). Fe-Co-Mg-Ca multicomponent composites were prepared by Shao and co-workers. It was found that the existence of MgO can effectively lower the sintering of CaO, and the synergistic effect between MgO and CaO benefited CO₂ adsorption, whereas Fe and Co species can provide additional oxygen vacancies for CO₂ activation. Therefore, the material shows excellent ICCC performance with 90% CO₂ conversion and nearly 100% CO selectivity. The

Fig. 8. Integrated CO₂ capture and conversion to methanol [Reprinted from (Kar et al., 2019)].
authors also proposed a heterojunction redox mechanism. It was considered that the newly formed Fermi level in Fe$_5$Co$_5$Mg$_{10}$CaO significantly lowered the Fe$^{3+}$/Fe$^{2+}$ redox potential. Therefore, electron transfer became easier, which is responsible for the enhanced activity of CO$_2$ conversion in reverse water-gas shift (RWGS) reaction (Fig. 9) (Shao et al., 2021).

4.4. ICCC for CH$_4$ production

CH$_4$ has a high hydrogen content, so the carbon emission during the CH$_4$ consumption process is relatively low. Through hydrogenation reaction, CO$_2$ can be directly converted to methane under atmospheric pressure, and its reaction temperature is significantly lower than that of reforming and reverse water gas. Therefore, it can be better coupled with existing industrial emission sources to realize the ICCC process. This is also the most studied direction in the ICCC field.

In the process of ICCC for CH$_4$ production, the adsorption step and conversion step can be coupled in several ways. For example, Veselovsky et al. used tandem reactors, where K$_2$CO$_3$/Al$_2$O$_3$ adsorbent was loaded in a first reactor for CO$_2$ capture, and 4% Ru/Al$_2$O$_3$ catalyst was used in a second reactor for CO$_2$ conversion after it was purged out from the first reactor via H$_2$ (Veselovsky et al., 2018). Alternatively, potassium-containing hydrotalcite and nickel-based catalyst were loaded in a single bed via a layer-by-layer way, and CO$_2$ adsorption and subsequent conversion to CH$_4$ were then achieved at 300°C – 350°C, with a yield of 2.36 mol CH$_4$ kg$^{-1}$ cat h$^{-1}$ (Miguel et al., 2017). In Sun’s work, MgO and Ru/CeO$_2$ were employed as adsorbent and catalyst, respectively, and their physical mixture was used for the ICCC to CH$_4$ process, however, the conversion rate of CO$_2$ in such a combination is relatively low (Sun et al., 2020).

In contrast to the above strategies, a combination of adsorption and catalysis sites in a single material is the most straightforward way. Farraruto’s group reported on a range of experiments based on this idea. The performances using Na, K, Mg, and Ca oxides as adsorption sites and Rh, Ru, Ni, Pt, and Co as the catalytic sites were thoroughly investigated. Meanwhile, the influences of reaction conditions and related mechanisms were also clarified (Duyar et al., 2015, 2016; Zheng et al., 2016; Arellano-Treviño et al., 2019a, b; Prolano et al., 2019).

The process of continuous abatement of CO$_2$ in simulated flue gas by ICCC was reported by Zhou et al. In their work, Ni-MgO-Al$_2$O$_3$ two-dimensional nanosheets were used as a bi-functional material. Through the optimization of reaction temperature, capture, and conversion time interval, the authors realized nearly 100% CO$_2$ capture and conversion under isothermal conditions (Fig. 10). The overall efficiency of the process has been greatly improved compared to the traditional temperature-swing and pressure-swing adsorption (Zhou et al., 2020).

5. Electro-catalytic CO$_2$ reduction (ECR)

5.1. General basics of ECR

Electro-catalytic CO$_2$ reduction (ECR) represents the processes that convert CO$_2$ via an electro-chemical way. In sharp contrast to the conventional thermal-catalytic process where high temperature and pressure are normally needed for CO$_2$ activation and conversion, ECR processes can be readily carried out in much milder conditions (atmospheric pressure and room temperature). Meanwhile, as the required energy can be largely provided in the form of electrons, the ECR processes can be directly integrated with low-grade renewables, and H$_2$O, rather than other energized molecules,
can be used as a hydrogen source. As such, ECR enables the transformation of renewable energies to chemical energies in form of fuels and/or chemicals including CO, hydrocarbons (methylene, ethylene), hydrocarbon oxygenates (formic acid, methanol, ethanol, etc.), or a mixture of them, and after their consumption, the released CO$_2$ can be recycled to close the carbon loop (Yang et al., 2016). All these merits give ECR great promise for the realization of carbon neutrality. In Table 3, we summarized several representative results from recent publications on ECR.

### 5.2. ECR to CO

Selective ECR to CO is a promising route toward industrial implementation because the produced CO can be used as a chemical feedstock to produce numerous higher-value chemicals or fuels, such as liquid fuel, low carbon olefin, and low carbon alcohol. However, direct reduction of CO$_2$ to *COO$^-$ involves a one-electron transfer process with a very negative redox potential (~1.9 V versus reversible hydrogen electrode (RHE)), which significantly inhibits the activation of CO$_2$ (Hunt et al., 2003). Therefore, suitable electrocatalysts should be developed to stabilize the *COO$^-$ intermediate, thereby reducing the activation overpotential.

Metal catalysts including Au, Ag, Zn, and Cd with both weak hydrogen and oxygen adsorption (Uesaka et al., 2018) have been widely investigated for ECR to CO. Among them, Ag exhibits extraordinary ECR to CO performance. For example, Yang’s group reported that when an Ag nanoparticle/ordered-ligand interlayer catalyst is applied in a gas-diffusion environment, a high FE of 92.6% for CO formation at a high current density of 400 mA cm$^{-2}$ could be achieved. It was verified that the interlayer structure facilitated the synergistic effect between multiple components and is responsible for such excellent performance (Kim et al., 2020a). Single-atom catalysts (SACs) with individual metal atoms dispersed on solid substrates can maximize atom utilization efficiency and thereby enhance catalytic performance. In comparison with bulk Ni metal that catalyses hydrogen evolution exclusively under ECR conditions, the Ni single-atom counterpart can selectively electrochemically reduce CO$_2$ to CO. Zhang et al. designed a methoxy group of functionalized nickel phthalocyanine (NiPc-OMe) molecules supported on carbon nanotubes, which catalyses the ECR to CO process with >99.5% selectivity. The electron-donating OMe groups could enhance the Ni-N bond strength in the Ni-N$_4$ sites and accelerate CO desorption, thereby improving the catalyst stability (Zhang et al., 2020).

Metal-free carbon-based materials were also found to be effective for ECR to CO. However, the pristine, defect-free carbon materials are less effective, and incorporating heteroatoms such as nitrogen into the carbon matrix is necessary to improve activity. Su’s group reported a N-doped CNT synthesized through the pyrolysis of mixtures of poly (diallyl dimethylammonium chloride) and oxidized CNTs. By adjusting types and contents of the used nitrogen dopants, a maxi-

### Table 3. Summary of research results on ECR catalysts.

| Reference          | Sample                        | Potential (V vs. RHE) | $j_{CO}$ (mA m$^{-2}$) | Products and FE |
|--------------------|-------------------------------|-----------------------|------------------------|-----------------|
| (Kim et al., 2020a) | Ag nanoparticles              | −0.82                 | 400                    | CO, 92.6%       |
| (Zhang et al., 2020)| NiPc-OMe                      | −0.64                 | 300                    | CO, 99.5%       |
| (Xu et al., 2016)  | N-doped CNT                   | −0.9                  | 5.8                    | CO, 90%         |
| (Dinh et al., 2018)| Cu electrocatalyst            | −0.55                 | 100                    | C$_2$H$_4$, 70% |
| (Zhong et al., 2020)| Cu-Al alloy electrocatalyst   | −1.5                  | 400                    | C$_2$H$_4$, 80% |
| (Xiong et al., 2021)| Ag@Cu$_2$O                   | −1.2                  | 178 ± 5                | CH$_4$, 74% ± 2%|
| (Yadav et al., 2022)| N-doped GQDs                 | −0.85                 | 170                    | CH$_4$, 63%     |
| (Bai et al., 2017) | Pd-Sn alloy electrocatalyst   | −0.43 V               | –                      | HCOOH, >99%     |
| (Yan et al., 2021) | s-SnLi                        | −1.2                  | 1000                   | HCOOH, 92%      |
| (Xu et al., 2020)  | Cu catalyst                   | −0.7                  | 1.8                    | C$_2$H$_5$OH, 91%|
| (Wang et al., 2020) | N-C/Cu                       | −0.68                 | 300                    | C$_2$H$_5$OH, 52% ± 1% |
| (Song et al., 2017) | N-C                          | −0.56                 | –                      | C$_3$H$_6$OH, 77% |

Fig. 10. Continuous capture and conversion of CO$_2$ to CH$_4$ [Reprinted from (Zhou et al., 2020)].
mum FE of 90% for CO formation and stable operation over 60 h with total current density and FE of 5.8 mA cm\(^{-2}\) and 85% can be achieved, respectively. During the reaction, the N-containing functionalities played an important role in stabilizing the \(^*\)COO\(^-\) intermediate, and this is the key for the sample to possess high performance (Xu et al., 2016).

5.3. ECR to hydrocarbons

With the combination of hydrogen from water, CO\(_2\) can be electrocatalytically converted to hydrocarbons, mainly containing methane (CH\(_4\)) and ethylene (C\(_2\)H\(_4\)), via eight electron-proton and twelve electron-proton reaction processes, respectively. Cu-based nanoparticles can produce hydrocarbons at moderate overpotentials. This is attributed to the appropriate strength of CO chemisorption on Cu, and protonation or dimerization of CO is considered to be a key step towards the formation of single- (CH\(_2\)) or multi-carbon (C\(_n\)H\(_{2n}\)) hydrocarbons (Peterson et al., 2010) (Kortlever et al., 2015). During the above mechanism, the \(^*\)CO coverage on the catalysts can significantly influence the ECR activity and selectivity. A high \(^*\)CO coverage can readily trigger C-C coupling that enhances C\(_2\)H\(_4\) formation, while less \(^*\)CO on the catalyst surface might not be competitive enough over hydrogen evolution reaction (Huang et al., 2017).

In the past several years, significant progress has been made in ECR to C\(_2\)H\(_4\) conversion, including catalysts, electrolytes, and electrodes. A typical example was reported by Sargent’s group where a Cu electrocatalyst at an abrupt reaction interface in an alkaline electrolyte (7 M KOH) reduces CO\(_2\) to C\(_2\)H\(_4\) with 70% FE at a potential of \(-0.55\) V vs. RHE. The remarkable performance is correlated to hydroxide ions on or near the Cu surface, which lowered the activation energy barriers of ECR and C-C coupling (Dinh et al., 2018). A graphite/carbon NPs/Cu/PTFE electrode was further constructed to prevent flooding problems and stabilize the Cu catalyst surface, thereby resulting in enhanced stability over the prolonged operation for 150 h. Afterwards, they developed a Cu-Al alloy electrocatalyst to further improve the FE of C\(_2\)H\(_4\) to 80% at a current density of 400 mA cm\(^{-2}\) in 1 M KOH electrolyte. They suggested that the Cu-Al alloys provide multiple sites and surface orientations with near-optimal CO binding for both efficient and selective ECR (Zhong et al., 2020).

The progress on ECR to CH\(_4\) has which has the highest heating value of 55.5 MJ kg\(^{-1}\) among all the ECR products, is far behind that of C\(_2\)H\(_4\). There is still a lack of applicable catalysts with satisfactory CH\(_4\) selectivity. Only very recently, Xiong et al. fabricated an Ag@Cu\(_2\)O core-shell structure. By fixing the Ag core and adjusting the Cu\(_2\)O envelope size, the \(^*\)CO coverage and \(^*\)H adsorption at the Cu surface can be modulated to steer the ECR pathway towards CH\(_4\). The optimal catalyst delivered a high CH\(_4\) FE of 74% ± 2% and a partial current density of 178 ± 5 mA cm\(^{-2}\) at \(-1.2\) V vs. RHE (Xiong et al., 2021). Yadav and co-workers reported an amine functionalized N-doped GQDs for efficient ECR to CH\(_4\). It revealed that the CH\(_4\) yield (partial current density) increased linearly with amino group (NH\(_2\)) content. Consequently, a maximum CH\(_4\) FE of 63% could be obtained over the catalyst with the maximum NH\(_2\) content of 9.07 atomic concentration (%) (Yadav et al., 2022).

5.4. ECR to oxygenates

Investigations on ECR to oxygenates mainly focus on formic acid (or formate) and ethanol via two electron-proton and twelve electron-proton reaction processes, respectively. Formic acid is an important product from ECR that has been widely explored as a hydrogen carrier. The common strategy for industrial production of formic acid is carboxylation of methanol, which, however, requires intensive energy input. It is thus highly desired to directly convert CO\(_2\) to formic acid via the ECR process, which was predicted to have a production potential of 475 kt yr\(^{-1}\) by 2030 globally. (Contentful, 2021).

Several metals, including Sn, In, and Bi, have been investigated as electro-catalysts for selective ECR to formic acid or formate. Among these metals, Sn commands the most attention for its low toxicity and cost. Bai and some of the co-authors of this paper developed a Pd-Sn alloy electrocatalyst for exclusive formic acid formation (FE>99%) in a 0.5 M KHCO\(_3\) solution. The presence of Pd modified the electronic configuration and oxygen affinity of Sn, which stabilized the HCOO* intermediate and the subsequent formic acid formation (Bai et al., 2017). Recently, Zheng’s group developed a surface-Li-doped Sn (s-SnLi) catalyst, which exhibited a high FE of 92% and a partial current density of 1.0 A cm\(^{-2}\) for producing formate. The introduction of Li dopants into the Sn lattice enabled the localization of negative charges and lattice strains to their neighbouring Sn atoms; thereby, both activity and selectivity of ECR to formate were enhanced (Fig. 11) (Yan et al., 2021).

Ethanol, a kind of clean and renewable liquid fuel with a heating value of \(-1366.8\) kJ mol\(^{-1}\), is a preferred product from ECR. Owing to the higher energy density and ease of storage and transportation compared to gas products, ethanol has also been considered as one of the optimal candidate fuels that substitute or supplement fossils in many applications (Shih et al., 2018). Moreover, ethanol is also an important and widely used common chemical feedstock for organic chemicals and medical disinfectants. Based on the considerable market demand, direct conversion of CO\(_2\) to ethanol using only water and driven by renewable energy is highly desired.

Cu is the only reported metal so far that can electrochemically catalyse ECR to ethanol. However, the selectivity is extremely low due to its moderate binding energy with most reaction intermediates. To promote the selectivity towards ethanol, manipulation of the binding strength of reaction intermediates on Cu is a commonly used strategy. Xu et al. reported a carbon-supported Cu catalyst via an amalgamated Cu–Li method, by which most Cu is atomically dispersed on the carbon surface. The high initial dispersion of single Cu atoms favors the selective ECR to ethanol with FE reaching \(-91%\) at \(-0.7\) V vs. RHE and outstanding durability of
16 h. However, the current density (around 1.8 mA cm\(^{-2}\)) is still below the industrial level (Xu et al., 2020). Based on recent investigations, the improvement of current density is at the expense of ethanol FE. For instance, Sargent’s group coated a nitrogen-doped carbon (N-C) layer on a Cu surface to build a confined reaction volume, which promoted C-C coupling and suppressed the breaking of the C-O bond in HOCCH\(^*\), thereby promoting ethanol selectivity in ECR. Under a current density of 300 mA cm\(^{-2}\), an ethanol FE of (52 ± 1) % is achieved on 34% N-C/Cu (Wang et al., 2020). Metal-free nitrogen-doped carbon materials have also been recently reported to be capable of ethanol production from ECR, which delivered comparable catalytic activities to Cu-based catalysts and even better durability. Song and co-workers developed a metal-free cylindrical mesoporous nitrogen-doped carbon as a robust catalyst for selective ECR to ethanol. The synergy of nitrogen heteroatoms and highly uniform cylindrical channel structures dramatically boosted C–C bond formation in ECR. Therefore, the catalyst enabled efficient production of ethanol with a high FE of 77% at −0.56 V vs. RHE in 0.1 M KHCO\(_3\) (Song et al., 2017). Inspired by the potential of adjusting the nanostructure of

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**Fig. 11.** Scheme illustrations of (a) electrochemical lithiation preparation of the s-SnLi catalyst, and (b) its function mechanism for ECR to formate [Reprinted from (Yan et al., 2021)].

**Fig. 12.** The demonstration system of CO\(_2\) electrolysis for syngas production [Reprinted from (Carbon Energy Technology Co. LTD, 2020)].
the catalyst to acquire multi-carbon compounds, the group further developed a hierarchical porous N-doped carbon with micropores embedded in the channel walls of N-doped ordered mesoporous carbon. By controlling the micropore content, the ethanol formation rate is improved by one order of magnitude compared to that of the counterpart without medium micropores. These reports have provided new insights for designing highly efficient electrocatalysts for ECR to ethanol in the future (Song et al., 2020).

6. Summary

Clearly, CCUS will play an important role in reaching the carbon neutrality target, not just at its current stage, but more so after future development. In particular, deep decarbonization requires a considerable revolution of the current energy and industrial infrastructure. Therefore, cutting-edge /disruptive CCUS technologies are becoming increasingly important and influential.

In this paper, we reviewed four technologies that are regarded as frontiers of CCUS. In Table 4, their relevance to carbon neutrality over other low-carbon technologies, advantages over regular CCUS technologies, and difficulties for future development are summarized.

DAC is one of the rare technologies that is able to offer negative emission, and very uniquely, DAC also provides a solution to historical emissions. Both characteristics are necessary to suppress climate change. When comparing with other CCUS technologies, localization of DAC is highly flexible. Therefore, the necessity for CO$_2$ transportation can be minimized by deployment of DAC in close vicinity of CO$_2$ emitters and/or downstream utilization/storage sites. Based on such a feature, DAC is an ideal approach for distributed, mobile, and small-scale emitters. Currently, DAC is an immature technology, and the process cost is relatively high. Efficient absorbents/adsorbents, coupling with renewable energies, process engineering, and scaling-up are among the most urgent issues to be solved.

Flexible MOFs are a type of smart materials that can potentially alter the landscape of many applications. When they are used as CO$_2$ adsorbents, their reversible breathing behavior toward external stimuli may change the fundamental thermodynamic driving force for adsorbent regeneration and thus enable less energy-intensive strategies over traditional temperature-swing and pressure-swing processes. Lowering the cost of CO$_2$ capture by flexible MOFs is of particular importance to facilitate the large-scale application of CCUS, which in turn guarantees carbon neutrality to be achieved. However, the performance of the reported flexible MOFs cannot meet the requirement of practical application. Further research, including design of a suitable process, is needed.

ICCC technology represents a new way of carbon recycling, which may promote the formation of low-carbon models and processes of the industrial system. This is of promise as decarbonization of industrial departments is considerably difficult. Compared with existing CCUS technologies, ICCC has obvious advantages in terms of cost reduction, source-sink matching, and so forth. Nevertheless, ICCC is still in the laboratory verification stage. How CO$_2$ capture and its conversion can be efficiently combined, how value-added products can be obtained, and how the process can be adjusted to match practical application scenarios are still questionable at this stage.

Recently, ECR has been one of the most eye-catching areas in catalysis. Due to its natural connection with renewable electricity, the process manages to close the carbon loop of fuels and chemicals by storing the low-grade renewable energy. Therefore, large-scale deployment of ECR can effectively avoid consumption of fossil fuels and thus contribute carbon reduction in an indirect way. Compared with other CO$_2$ conversion technologies, the ECR process can be carried out under very mild conditions. Additionally, ECR can be readily modularized, which greatly facilitates its scaling-up. The primary technical difficulties of ECR include the design and preparation of the catalyst with high activity and selectivity and engineering challenges related to coupling

| Technology  | Relevance to carbon neutrality over other low-carbon technologies | Advantages over regular CCUS technologies | Technological difficulties |
|-------------|---------------------------------------------------------------|------------------------------------------|---------------------------|
| DAC         | • Negative emission effects • Solution to historical emissions | • Flexibility in localization • Minimize transportation demand • Solution to dispersed and small-scale emission sources | • High-performance adsorbents/adsorbents • Coupling with renewable energies • Process engineering • Scaling-up |
| Flexibilt MOFs | • Enable low-cost CCUS for carbon neutrality • A new way of carbon recycling • Re-shape industrial system | • Lowering energy consumption for carbon capture • Lowering CCUS cost • Source-sink matching | • High-performance materials • Process engineering • Efficient coupling of absorption and conversion process • Extension of products • Matching with application scenarios • High-performance catalysts • Coupling with low-grade renewable energy |
| ICCC        | • Avoiding fossil fuels • Storing low-grade renewable energies | • Milder conditions • Easy to scale-up | |
| ECR         | | | |
with low-grade renewable energy.

7. Outlook

CCUS technology is the only approach that can achieve large-scale and low-carbon utilization of fossil energy and resources, which will surely play an important role in coping with climate change. However, under the new goal of carbon neutrality, the positioning of CCUS technology has changed significantly, and the application scenarios of some cutting-edge/disruptive CCUS technologies have been greatly expanded, which is expected to constitute inevitable carbon reduction solutions for the energy and industrial system.

The CCUS technologies reviewed in this paper have attracted widespread attention from both the academia and industrial sectors, and their feasibility has been well verified, with some technologies having been demonstrated on a certain scale. In the future, it will be necessary to further strengthen related investigations on materials, mechanisms, processes, and engineering. These will lead to the lowering of process costs and clarification of application scenarios, eventually promoting the practical application of the technologies. It should be noted that in recent years, research on CCUS and related fields has progressed very rapidly, and this paper is not comprehensive as it only lists a limited number of examples. Facing the future, cutting-edge/disruptive CCUS technologies will continue to emerge and develop, and we anticipate they will offer important contributions to carbon neutrality.

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REFERENCES

Arellano-Treviño, M. A., N. Kanani, C. W. Jeong-Potter, and R. J. Farrauto, 2019a: Bimetallic catalysts for CO2 capture and hydrogenation at simulated flue gas conditions. Chemical Engineering Journal, 375, 121953, https://doi.org/10.1016/j.cej.2019.121953.

Arellano-Treviño, M. A., Z. Y. He, M. C. Libby, and R. J. Farrauto, 2019b: Catalysts and adsorbents for CO2 capture and conversion with dual function materials: Limitations of Ni-containing DFM for flue gas applications. Journal of CO2 Utilization, 31, 143–151, https://doi.org/10.1016/j.jcou.2019.03.009.

Bai, X. F., W. Chen, C. C. Zhao, S. G. Li, Y. F. Song, R. P. Ge, W. Wei, and Y. H. Sun, 2017: Exclusive formation of formic acid from CO2 electroreduction by a tunable Pd-Sn alloy. Angewandte Chemie International Edition, 56, 12,219–12,223, https://doi.org/10.1002/anie.201707098.

Bhatt, P. M., Y. Belmabkhout, A. Cadiou, K. Adil, O. Shekhahe, A. Shkurenko, L. J. Barbou, and M. Eddaoudi, 2016: A fine-tuned fluorinated MOF addresses the needs for trace CO2 removal and air capture using physisorption. Journal of the American Chemical Society, 138, 9301–9307, https://doi.org/10.1021/jacs.6b05345.

Bitzer, J., S.-L. Heck, and W. Kleist, 2020: Tailoring the breathing behavior of functionalized MIL-53(AlM)-NH2 materials by using the mixed-metal concept. Microporous and Mesoporous Materials, 308, 110329, https://doi.org/10.1016/j.micromeso.2020.110329.

Bobadilla, L. F., J. M. Riesco-García, G. Penelás-Pérez, and A. Urakawa, 2016: Enabling continuous capture and catalytic conversion of flue gas CO2 to syngas in one process. Journal of CO2 Utilization, 14, 106–111, https://doi.org/10.1016/j.jcou.2016.04.003.

Brethome, F. M., N. J. Williams, C. A. Seipp, M. K. Kidder, and R. Custelcean, 2018: Direct air capture of CO2 via aqueous-phase absorption and crystalline-phase release using concentrated solar power. Nature Energy, 3, 553–559, https://doi.org/10.1038/s41560-018-0150-z.

Cavalcanti, L. P., G. N. Kalantzopoulos, J. Eckert, K. D. Knudsen, and J. O. Fossum, 2018: A nano-silicate material with exceptional capacity for CO2 capture and storage at room temperature. Scientific Reports, 8, 11287, https://doi.org/10.1038/s41598-018-10283-2.

Chanut, N., A. Ghoufi, M.-V. Coulet, S. Bourrelly, B. Kuchta, G. Maurin, and P. L. Llewellyn, 2020: Tailoring the separation properties of flexible metal-organic frameworks using mechanical pressure. Nature Communications, 11, 1216, https://doi.org/10.1038/s41467-020-15036-y.

Choi, S., M. L. Gray, and C. W. Jones, 2011: Amine-tethered solid adsorbents coupling high adsorption capacity and regenerability for CO2 capture from ambient air. ChemSusChem, 4, 628–635, https://doi.org/10.1002/cssc.201000355.

Climeworks, 2021: Direct air capture: a technology to remove CO2. Available from https://climeworks.com/co2-removal.

Custelcean, R., 2021: Direct air capture of CO2 via crystal engineering. Chemical Science, 12, 12, 518–12, 528, https://doi.org/10.1039/D1SC04097A.

de Jonge, M. M. J., J. Daemen, J. M. Loriaux, Z. J. N. Steinmann, and M. A. J. Huijbregts, 2019: Life cycle carbon efficiency of Direct Air Capture systems with strong hydroxide sorphents. International Journal of Greenhouse Gas Control, 80, 25–31, https://doi.org/10.1016/j.ijggc.2018.11.011.

Deutz, S., and A. Bardow, 2021: Life-cycle assessment of an industrial direct air capture process based on temperature–vacuum swing adsorption. Nature Energy, 6, 203–213, https://doi.org/10.1038/s41560-020-00771-9.

Didas, S. A., S. Choi, W. Chakittisilp, and C. W. Jones, 2015: Amine-oxide hybrid materials for CO2 capture from ambient air. Accounts of Chemical Research, 48, 2680–2687, https://
Duyar, M. S., M. A. A. Treviño, and R. J. Farrauto, 2015: Dual function materials for CO₂ capture and conversion using renewable H₂. Applied Catalysis B: Environmental, 168–169, 370–376, https://doi.org/10.1016/j.apcatab.2014.12.025.

Duyar, M. S., S. X. Wang, M. A. Arellano-Treviño, and R. J. Farrauto, 2016: CO₂ utilization with a novel dual function material (DFM) for capture and catalytic conversion to synthetic natural gas: An update. Journal of CO₂ Utilization, 15, 65–71, https://doi.org/10.1016/j.jcou.2016.05.003.

Energy & Climate Intelligence Unit, 2021: Net zero emissions race. [Available from https://eciu.net/netzerotracker].

Engineering, C., 2021: Carbon engineering deployment timeline. [Available from https://carbonengineering.com/our-story].

Franchi, R. S., P. J. E. Harlick, and A. Sayari, 2005: Applications of pore-expanded mesoporous silica. 2. Development of a high-capacity, water-tolerant adsorbent for CO₂. Industrial & Engineering Chemistry Research, 44, 8007–8013, https://doi.org/10.1021/ie0504194.

Furukawa, H., K. E. Cordova, M. O’Keeffe, and O. M. Yaghi, 2013: The chemistry and applications of metal-organic frameworks. Science, 341, 1230444, https://doi.org/10.1126/science.1230444.

Ghoufi, A., K. Benhamed, L. Boukli-Hacene, and G. Maurin, 2017: Electrically induced breathing of the MIL-53(Cr) metal–organic framework. ACS Central Science, 3, 394–398, https://doi.org/10.1021/acscentsci.6b00392.

Goeppert, A., M. Czau, R. B. May, G. K. S. Prakash, G. A. Olah, and S. R. Narayanan, 2011: Carbon dioxide capture from the air using a polyanime based regenerable solid adsorbent. Journal of the American Chemical Society, 133, 20 164–20 167, https://doi.org/10.1021/ja2100005.

Goglio, P., A. G. Williams, N. Balta-Ozkan, N. R. P. Harris, P. Williamson, D. Huising, Z. Zhang, and M. Tavoni, 2020: Advances and challenges of life cycle assessment (LCA) of greenhouse gas removal technologies to fight climate changes. Journal of Cleaner Production, 244, 118896, https://doi.org/10.1016/j.jclepro.2019.118896.

Gong, Q., and Coauthors, 2019: Structural defects on converted bismuth oxide nanotubes enable highly active electrocatalysis of carbon dioxide reduction. Nature Communications, 10, 2807, https://doi.org/10.1038/s41467-019-10819-4.

Hepburn, C., and Coauthors, 2019: The technological and economic prospects for CO₂ utilization and removal. Nature, 575, 87–97, https://doi.org/10.1038/s41586-019-1681-6.

Hicks, J. C., J. H. Drese, D. J. Fauth, M. L. Gray, G. G. Qi, and C. W. Jones, 2008: Designing adsorbents for CO₂ capture from flue gas-hyperbranched aminosilicas capable of capturing CO₂ reversibly. The Journal of the American Chemical Society, 130, 2902–2903, https://doi.org/10.1021/ja077795v.

Huang, Y., A. D. Handoko, P. Hirunisit, and B. S. Yeo, 2017: Electrocatalytic reduction of CO₂ using copper single-crystal surfaces: Effects of CO* coverage on the selective formation of ethylene. ACS Catalysis, 7, 1749–1756, https://doi.org/10.1021/acscatal.6b03147.

Hunt, P., D. R. Worrall, F. Wilkinson, and S. N. Batchelor, 2003: Quantitative rate constants for the reaction of dyes and alkenes with α-hydroxalkyl radicals, measured by laser flash photolysis. Photochemical & Photobiological Sciences, 2, 518–523, https://doi.org/10.1039/B212051H.

IEA, 2020a: World energy outlook 2020. 171 pp.

IEA, 2020b: Energy technology perspectives 2020. 461 pp.

Inagaki, F., C. Matsumoto, T. Iwata, and C. Mukai, 2017: CO₂-selective absorbents in air: Reverse lipil bilayer structure forming neutral carboxamic acid in water without hydration. Journal of the American Chemical Society, 139, 4639–4642, https://doi.org/10.1021/jacs.7b01049.

IPCC, 2014: Climate Change 2014: Synthesis Report, contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. IPCC, Geneva, Switzerland, 151 pp.

IPCC, 2018: Global Warming of 1.5°C. World Meteorological Organization, Geneva, Switzerland, 32 pp.

Kar, S., R. Sen, A. Goeppert, and G. K. S. Prakash, 2018: Integrative CO₂ capture and hydrogenation to methanol with reusable catalyst and amine: Toward a carbon neutral methanol economy. Journal of the American Chemical Society, 140, 1580–1583, https://doi.org/10.1021/jacs.7b12183.

Kar, S., A. Goeppert, and G. K. S. Prakash, 2019: Integrated CO₂ capture and conversion to formate and methanol: Connecting two threads. Accounts of Chemical Research, 52, 2892–2903, https://doi.org/10.1021/acs.accounts.9b00324.

Keith, D. W., G. Holmes, D. S. Angelo, and K. Heidel, 2018: A process for capturing CO₂ from the atmosphere. Joule, 2, 1573–1594, https://doi.org/10.1016/j.joule.2018.05.006.

Keller, L., B. Ols, J. Lenhart, L. Abdul, P. Blanke, and M. Wessling, 2018: High capacity polyethyleneimine impregnated microtubes made of carbon nanotubes for CO₂ capture. Carbon, 126, 338–345, https://doi.org/10.1016/j.carbon.2017.10.023.

Kim, D., and Coauthors, 2020a: Selective CO₂ electrocatalysis at the pseudocapacitive nanoparticle/ordered-ligand interlayer. Nature Energy, 5, 1032–1042, https://doi.org/10.1038/s41560-020-00730-4.

Kim, E. J., and Coauthors, 2020b: Cooperative carbon capture and steam regeneration with tetraamine-appended metal-organic frameworks. Science, 369, 392–396, https://doi.org/10.1126/science.abb3976.

Kitaura, R., K. Seki, G. Akiyama, and S. Kitagawa, 2003: Porous coordination-polymer crystals with gated channels specific for supercritical gases. Angewandte Chemie International Edition, 42, 428–431, https://doi.org/10.1016/S0003-3804(03)01170-0.

Kortlever, R., J. Shen, K. J. P. Schouten, F. Calle-Vallejo, and M. Kitaura, 2003: Porous metal coordination-polymer crystals with gated channels specific for supercritical gases. Angewandte Chemie International Edition, 42, 428–431, https://doi.org/10.1016/S0003-3804(03)01170-0.

Kortlever, R., J. Shen, K. J. P. Schouten, F. Calle-Vallejo, and M. T. Koper, 2015: Catalysts and reaction pathways for the electrochemical reduction of carbon dioxide. The Journal of Physical Chemistry Letters, 6, 4073–4082, https://doi.org/10.1021/acs.jpclett.5b01559.

Kothandaraman, J., A. Goeppert, M. Czau, G. A. Olah, and G. K. S. Prakash, 2016: Conversion of CO₂ from air into methanol using a polyanime and a homogeneous ruthenium catalyst. Journal of the American Chemical Society, 138, 778–781, https://doi.org/10.1021/jacs.5b12354.

Kumar, A., D. G. Madden, M. Lusi, K. J. Chen, E. A. Daniels, T. Curtin, J. J. Perry IV, and M. J. Zaworotko, 2015: Direct air
capture of CO₂ by physisorbent materials. Angewandte Chemie International Edition, 54, 14 372−14 377, https://doi.org/10.1002/anie.201506952.

Kumar, A., C. Hua, D. G. Madden, D. O’Nolan, K.-J. Chen, L.-A. J. Keane, J. J. Perry IV, and M. J. Zaworotko, 2017: Hybrid ultramicroporous materials (HUMs) with enhanced stability and trace carbon capture performance. Chemical Communications, 53, 5946−5949, https://doi.org/10.1039/C3CC2289A.

Lee, W. R., S. Y. Hwang, D. W. Ryu, K. S. Lim, S. S. Han, D. Moon, J. Choi, and C. S. Hong, 2014: Diamine-functionalized metal–organic framework: Exceptionally high CO₂ capacities from ambient air and flue gas, ultrafast CO₂ uptake rate, and adsorption mechanism. Energy & Environmental Science, 7, 744−751, https://doi.org/10.1039/C3EE42328J.

Li, L. Y., D. L. King, Z. M. Nie, and C. Howard, 2009: Magnesium-stabilized calcium oxide absorbents with improved durability for high temperature CO₂ capture. Industrial & Engineering Chemistry Research, 48, 10 604−10 613, https://doi.org/10.1021/ie901166b.

Liao, P.-Q., and Coauthors, 2016: Putting an ultrahigh concentration of amine groups into a metal-organic framework for CO₂ capture at low pressures. Chemical Science, 7, 6528−6533, https://doi.org/10.1039/C6SC00836D.

Lin, J. B., and Coauthors, 2021: A scalable metal-organic framework as a durable physisorbent for carbon dioxide capture. Science, 374, 1464−1469, https://doi.org/10.1126/science.abi7281.

Lu, W., J. P. Sculley, D. Yuan, R. Krishna, and H.-C. Zhou, 2013: Porous carbon dioxide capture from air using amine-grafted porous polymer networks. The Journal of Physical Chemistry C, 117, 4057−4061, https://doi.org/10.1021/jp311512q.

Lyndon, R., K. Konstas, B. P. Ladewig, P. D. Southon, C. J. Kepert, and M. R. Hill, 2013: Dynamic photo-switching in metal–organic frameworks as a route to low-energy carbon dioxide capture and release. Angewandte Chemie International Edition, 52, 3695−3698, https://doi.org/10.1002/anie.201206359.

Ma, X. L., X. X. Wang, and C. S. Song, 2009: “Molecular Basket” sorbents for separation of CO₂ and H₂S from various gas streams. Journal of the American Chemical Society, 131, 5777−5783, https://doi.org/10.1021/ja8074105.

Marks, S. D., K. Riascos-Rodriguez, R. R. Arrieta-Pérez, A. A. Yakovenko, J. Exley, P. G. Evans, and A. J. Hernandez-Malдонado, 2020: Lattice expansion and ligand twist during CO₂ adsorption in flexible Cu bipyridine metal–organic framework. Journal of Materials Chemistry A, 8, 18 903−18 915, https://doi.org/10.1039/DOTA03298K.

Martell, J. D., P. J. Milner, R. L. Siegelman, and J. R. Long, 2020: Kinetics of cooperative CO₂ adsorption in diamine-appended variants of the metal–organic framework Mg2(dobpdc). Chemical Science, 11, 6457−6471, https://doi.org/10.1039/D8SC01087A.

Matsuda, R., 2014: Selectivity from flexibility. Nature, 509, 434−435, https://doi.org/10.1038/509434a.

McDonald, T. M., and Coauthors, 2015: Cooperative insertion of CO₂ in diamine-appended metal-organic frameworks. Nature, 519, 303−308, https://doi.org/10.1038/nature14327.

Miguel, C. V., M. A. Soria, A. Mendes, and L. M. Madeira, 2017: A sorptive reactor for CO₂ capture and conversion to renewable methane. Chemical Engineering Journal, 322, 590−602, https://doi.org/10.1016/j.cej.2017.04.024.

Modrow, A., D. Zargaran, R. Herges, and N. Stock, 2011: The first porous MOF with photoswitchable linker molecules. Dalton Transactions, 40, 4217−4222, https://doi.org/10.1039/c0dt01629b.

Carbon energy technology Co., Ltd (Beijing), 2020: The pilot project of carbon dioxide electrolysis to syngas successfully passed the on-site assessment. https://www.sohu.com/a/434528697_99809823, (in Chinese).

Mukherjee, S., and Coauthors, 2019: Trace CO₂ capture by an ultra-microporous physisorbent with low water affinity. Science Advances, 5, eaax9171, https://doi.org/10.1126/sciadv.aax9171.

Nandi, S., and Coauthors, 2015: A single-ligand ultra-microporous MOF for precombustion CO₂ capture and hydrogen purification. Science Advances, 1, e1500421, https://doi.org/10.1126 /sciadv.1500421.

Park, J., D. Q. Yuan, K. T. Pham, J.-R. Li, A. Yakovenko, and H.-C. Zhou, 2012: Reversible alteration of CO₂ adsorption upon photochemical or thermal treatment in a metal–organic framework. Journal of the American Chemical Society, 134, 99−102, https://doi.org/10.1021/ja209197f.

Peterson, A. A., F. Abild-Pedersen, F. Studt, J. Rossmeisl, and J. K. Nørskov, 2010: How copper catalyzes the electroreduction of carbon dioxide into hydrocarbon fuels. Energy & Environmental Science, 3, 1311−1315, https://doi.org/10.1039/ COEE00071J.

Potter, M. E., K. M. Cho, J. J. Lee, and C. W. Jones, 2017: Role of alumina basicty in CO₂ uptake in 3-aminopropylsilylestabilized calcium oxide sorbents. ChemSusChem, 10, 2192−2201, https://doi.org/10.1002/cssc.201700115.

Proulx, L., E. Tello, M. A. Arellano-Trevino, S. X. Wang, R. J. Farraruto, and M. Cobo, 2019: In-situ DRIFTS study of two-step CO₂ capture and catalytic methanation over Ru, “Na₂O₄/Al₂O₃” dual functional material. Applied Surface Science, 479, 25−30, https://doi.org/10.1016/j.apsusc.2019.01.281.

Qiao, Y. Q., J. Y. Wang, Y. Zhang, W. L. Gao, T. Harada, L. Huang, T. A. Hatton, and Q. Wang, 2017: Alkali nitrates molten salt modified commercial MgO for intermediate-temperature CO₂ capture: Optimization of the Li/Na/K ratio. Industrial & Engineering Chemistry Research, 56, 1509−1517, https://doi.org/10.1021/acs.iecr.6b04793.

Qu, C. F., X. Yang, D. Zhang, and X. L. Zang, 2020: Estimating health co-benefits of climate policies in China: An application of the regional emissions-air quality-climate-health (reach) FRAMEWORK. Climate Change Economics, 11, 2041004, https://doi.org/10.1142/S201007820410043.

Reller, C., M. Pöge, A. Lißner, and F. O. R. L. Mertens, 2014: Methanol from CO₂ by organo-cocatalysis: CO₂ capture and hydrogenation in one process step. Environmental Science & Technology, 48, 14 799−14 804, https://doi.org/10.1021/ es503914d.

Sabatino, F., A. Grimm, F. Gallucci, M. van Sint Annaland, G. J. Kramer, and M. Gazzani, 2021: A comparative energy and costs assessment and optimization for direct air capture technologies. Joule, 5, 2047−2076, https://doi.org/10.1016/j.joule.2021.05.023.

Sanz-Pérez, E. S., C. R. Murdock, S. A. Didas, and C. W. Jones, 2016: Direct capture of CO₂ from ambient air. Chemical Reviews, 116, 11 840−11 876, https://doi.org/10.1021/acs. chemrev.6b00173.

Sayari, A., and Y. Belmabkhout, 2010: Stabilization of amine-containing CO₂ adsorbents: Dramatic effect of water vapor. Jour-
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of the American Chemical Society, 132, 6312–6314, https://doi.org/10.1021/ja1013773.

Schneemann, A., V. Bon, I. Schwedler, I. Senkovska, S. Kaska1, and R. A. Fischer, 2014: Flexible metal–organic frameworks. Chemical Society Reviews, 43, 6062–6096, https://doi.org/10.1039/C4CS00101J.

Sen, R., A. Geepert, S. Kar, and G. K. S. Prakash, 2020: Hydroxide based integrated CO2 capture from air and conversion to methanol. Journal of the American Chemical Society, 142, 4544–4549, https://doi.org/10.1021/jacs.9b12711.

Sen, T., Y. Kawajiri, and M. J. Reaff, 2019: Adsorption process intensification through structured packing: A modeling study using zeolite 13X and a mixture of propylene and propane in hollow-fiber and packed beds. Industrial & Engineering Chemistry Research, 58, 5750–5767, https://doi.org/10.1021/acs.iecr.8b02189.

Sensharma, D., N. Y. Zhu, S. Tandon, S. Vaesen, G. W. Watson, and W. Schmitt, 2019: Flexible metal–organic frameworks for light-switchable CO2 sorption using an auxiliary ligand strategy. Inorganic Chemistry, 58, 9766–9772, https://doi.org/10.1021/acs.inorgchem.9b00768.

Shao, B., and Coauthors, 2021: Heterojunction-redox catalysts of FeCo2Mg20Ca0 for high-temperature CO2 capture and in situ conversion in the context of green manufacturing. Energy & Environmental Science, 14, 2291–2301, https://doi.org/10.1039/D0EE03320K.

Shi, X. Y., H. Xiao, K. S. Lackner, and X. Chen, 2016: Capture CO2 from ambient air using nanofunctioned ion hydronation. Angewandte Chemie International Edition, 55, 4026–4029, https://doi.org/10.1002/anie.201507846.

Shi, X. Y., H. Xiao, H. Azarabadi, J. Z. Song, X. L. Wu, X. Chen, and K. S. Lackner, 2020: Sorbents for the direct capture of CO2 from ambient air. Angewandte Chemie International Edition, 59, 6984–7006, https://doi.org/10.1002/anie.201906756.

Shih, C. F., T. Zhang, J. H. Li, and C. L. Bai, 2018: Powering the future with liquid sunshine. Joule, 2, 1925–1949, https://doi.org/10.1016/j.joule.2018.08.016.

Song, Y. F., W. Chen, C. C. Zhao, S. G. Li, W. Wei, and Y. H. Sun, 2017: Metal-free nitrogen-doped mesoporous carbon for electroreduction of CO2 to ethanol. Angewandte Chemie International Edition, 56, 10 840–10 844, https://doi.org/10.1002/anie.201607677.

Song, Y. F., S. B. Wang, W. Chen, S. G. Li, G. H. Feng, W. Wei, and Y. H. Sun, 2020: Enhanced ethanol production from CO2 electroreduction at micropores in nitrogen-doped mesoporous carbon. ChemSusChem, 13, 293–297, https://doi.org/10.1002/cssc.201902833.

Stavitski, E., and Coauthors, 2011: Complexity behind CO2 Capture on NH2-ML-53(Al). Langmuir, 27, 3970–3976, https://doi.org/10.1021/la1045207.

Stevenson, S. A., 2019: Thermodynamic considerations in CO2 utilization. AIChE Journal, 65, e16695, https://doi.org/10.1002/aic.16695.

Sun, H. M., J. Q. Wang, J. H. Zhao, B. X. Shen, J. Shi, J. Huang, and C. F. Wu, 2019: Dual functional catalytic materials of Ni over Ce-modified CaO sorbents for integrated CO2 capture and conversion. Applied Catalysis B: Environmental, 244, 63–75, https://doi.org/10.1016/j.apcatb.2018.11.040.

Sun, H. M., Y. Zhang, S. L. Guan, J. Huang, and C. F. Wu, 2020: Direct and highly selective conversion of captured CO2 into methane through integrated carbon capture and utilization over dual functional materials. Journal of CO2 Utilization, 38, 262–272, https://doi.org/10.1016/j.jcou.2020.02.001.

Taylor, M. K., and Coauthors, 2018: Near-perfect CO2 capture from air and conversion to methanol. Journal of the American Chemical Society, 140, 10 324–10 331, https://doi.org/10.1021/jacs.8b06062.

Tertlouw, T., K. Treyer, C. Bauer, and M. Mazzotti, 2021a: Life cycle assessment of direct air carbon capture and storage with low-carbon energy sources. Environmental Science & Technology, 55, 11 397–11 411, https://doi.org/10.1021/acs.est.1c03263.

Tertlouw, T., C. Bauer, L. Rosa, and M. Mazzotti, 2021b: Life cycle assessment of carbon dioxide removal technologies: A critical review. Energy & Environmental Science, 14, 1701–1721, https://doi.org/10.1039/d0ee03757e.

Uesaka, M., Y. Saito, S. Yoshioka, Y. Domoto, M. Fujita, and Y. Inokuma, 2018: Oligooacetylacetones as shapable carbon chains and their transformation to oligoimines for construction of metal-organic architectures. Communications Chemistry, 1, 23, https://doi.org/10.1038/s42004-018-0021-3.

Veselovskaya, J. V., P. D. Parunin, O. V. Netskina, L. S. Kibis, A. I. Lysikov, and A. G. Okunev, 2018: Catalytic methanation of carbon dioxide captured from ambient air. Energy, 159, 766–773, https://doi.org/10.1016/j.energy.2018.06.180.

Wang, X., and Coauthors, 2020: Efficient electrically powered CO2-to-ethanol via suppression of deoxygenation. Nature Energy, 5, 478–486, https://doi.org/10.1038/s41560-020-0607-8.

Xiong, L. K., and Coauthors, 2021: Geometric modulation of local CO flux in Ag@CuO nanoreactors for steering the CO2RR pathway toward high-efficacy methane production. Advanced Materials, 33, 2101741, https://doi.org/10.1002/adma.202101741.

Xu, H. P., and Coauthors, 2020: Highly selective electrocatalytic CO2 reduction to ethanol by metallic clusters dynamically formed from atomically dispersed copper. Nature Energy, 5, 623–632, https://doi.org/10.1038/s41560-020-0666-x.

Xu, J. Y., and Coauthors, 2016: Revealing the origin of activity in nitrogen-doped nanocarbons towards electrocatalytic reduction of carbon dioxide. ChemSusChem, 9, 1085–1089, https://doi.org/10.1002/cssc.201600202.

Xu, X. C., C. S. Song, J. M. Andresen, B. G. Miller, and A. W. Scaroni, 2002: Novel polyethyleneimine-modified mesoporous molecular sieves of MCM-41 type as high-capacity adsorbent for CO2 capture. Energy & Fuels, 16, 1463–1469, https://doi.org/10.1021/ef020058u.

Yadav, R. M., and Coauthors, 2022: Amine-functionalized carbon nanodot electrocatalysts converting carbon dioxide to methane. Advanced Materials, 34, 2105690, https://doi.org/10.1002/adma.202105690.

Yan, S., and Coauthors, 2021: Electron localization and lattice strain induced by surface lithium doping enable amperel level electrolys of formate from CO2. Angewandte Chemie International Edition, 60, 25 741–25 745, https://doi.org/10.1002/anie.202111351.

Yang, H., M. Singh, and J. Schaefer, 2018: Humidity-swing mechanism for CO2 capture from ambient air. Chemical Communications, 54, 4915–4918, https://doi.org/10.1039/c8cc02109k.

Yang, K. D., and Coauthors, 2016: Graphene quantum sheet catalyzed silicon photocathode for selective CO2 conversion to CO. Advanced Functional Materials, 26, 233–242, https://
Yuan, S., and Coauthors, 2018: Stable metal–organic frameworks: Design, synthesis, and applications. Advanced Materials, 30, 1704303, https://doi.org/10.1002/adma.201704303.

Yue, M. C, K. Imai, Y. Miura, and Y. Hoshino, 2017: Design and preparation of thermo-responsive vinylamine-containing micro-gel particles for reversible absorption of carbon dioxide. Polymer Journal, 49, 601−606, https://doi.org/10.1038/pj.2017.28.

Zhang, X., and Coauthors, 2020: Molecular engineering of dispersed nickel phthalocyanines on carbon nanotubes for selective CO\textsubscript{2} reduction. Nature Energy, 5, 684−692, https://doi.org/10.1038/s41560-020-0667-9.

Zheng, Q. H., R. Farrauto, and A. C. Nguyen, 2016: Adsorption and methanation of flue gas CO\textsubscript{2} with dual functional catalytic materials: A parametric study. Industrial & Engineering Chemistry Research, 55, 6768–6776, https://doi.org/10.1021/acs.iecr.6b01275.

Zhong, M., and Coauthors, 2020: Accelerated discovery of CO\textsubscript{2} electrocatalysts using active machine learning. Nature, 581, 178–183, https://doi.org/10.1038/s41586-020-2242-8.

Zhou, Z. J., and Coauthors, 2020: 2D-layered Ni-MgO-Al\textsubscript{2}O\textsubscript{3} nanosheets for integrated capture and methanation of CO\textsubscript{2}. ChemSusChem, 13, 360–368, https://doi.org/10.1002/cssc.201902828.

Zhu, X. C., T. S. Ge, J. Y. Wu, F. Yang, and R. Z. Wang, 2021: Large-scale applications and challenges of adsorption-based carbon capture technologies. Chinese Science Bulletin, 66, 2861–2877, https://doi.org/10.1360/TF-2021-0017.