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Integrated Carbon Capture and Conversion: a review on C_{2+} product mechanisms and mechanism-guided strategies

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Abstract

The need to reduce atmospheric CO_2 concentrations necessitates CO_2 capture technologies for conversion into stable products or long-term storage. A single pot solution that simultaneously captures and converts CO_2 could minimize additional costs and energy demands associated with CO_2 transport, compression, and transient storage. While a variety of reduction products exist, currently, only conversion to C_{2+} products including ethanol and ethylene are economically advantageous. Cu-based catalysts have the best-known performance for CO_2 electroreduction to C_{2+} products. Metal Organic Frameworks (MOFs) are touted for their carbon capture capacity. Thus, integrated Cu-based MOFs could be an ideal candidate for the one-pot capture and conversion. In this paper, we review Cu-based MOFs and MOF derivatives that have been used to synthesize C_{2+} products with the objective of understanding the mechanisms that enable synergistic capture and conversion. Furthermore, we discuss strategies based on the mechanistic insights that can be used to further enhance production. Finally, we discuss some of the challenges hindering widespread use of Cu-based MOFs and MOF derivatives along with possible solutions to overcome the challenges.

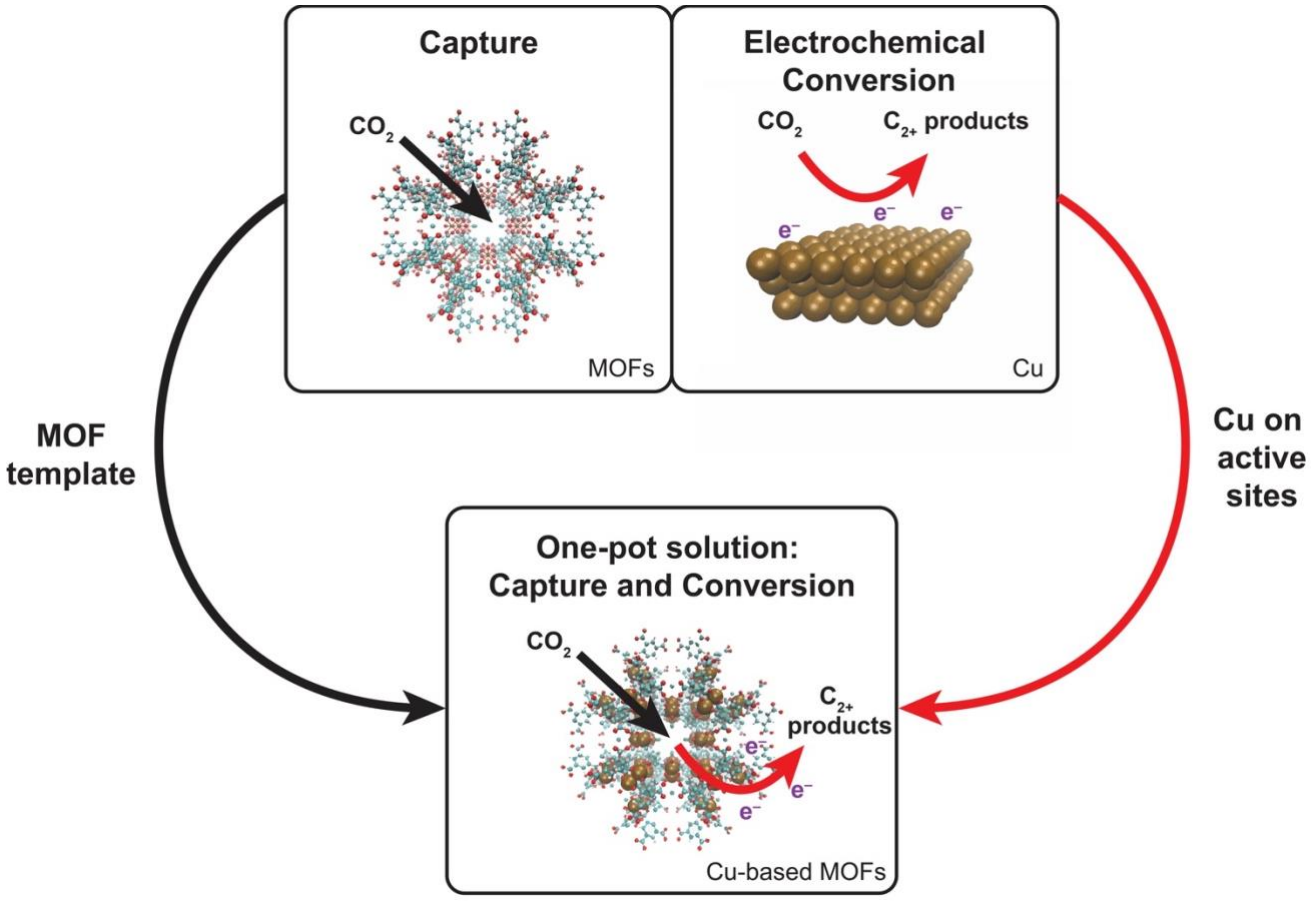

Figure TOC. A one-pot solution of combined capture and conversion represents the ideal solution with the MOFs component aiding capture and the Cu constituents supporting conversion to C_{2+} products via CO_2ER

1 Introduction

The exponential increase in greenhouse gases (GHGs) including CO_2 since the industrial revolution is the key driver of climate change (Field, Barros and on Climate Change, 2014; Sun *et al.*, 2017). Currently, the concentration of CO_2 in the atmosphere is greater than 400 ppm (Jiao *et al.*, 2019) with fossil fuels accounting for 75% of the increase in anthropogenic CO_2 emissions (Field, Barros and on Climate Change, 2014; Rafiee *et al.*, 2018). CO_2 levels are projected to increase to 685 ppm by 2050 (OECD, 2012) but CO_2 levels need to be maintained at $\leq$ 450 ppm to avoid seriously jeopardizing the environment (Metz and on Climate Change, 2007). While replacing fossil fuels with renewable sources of energy is the long-term solution, capturing CO_2 from concentrated sources and from the atmosphere is urgently needed (Birol, 2019; 'Global Energy Transformation: A Roadmap to 2050', 2018; Gielen et al., 2019). Three main separation technologies to capture CO_2 are liquid absorbents, solid adsorbents, and membranes ('Basic Research Needs for Carbon Capture: Beyond 2020: Report of the Basic Energy Sciences Workshop for Carbon Capture: Beyond 2020', 2020) but the only method currently being used in an industrial scale is absorption using aqueous amine solutions (Iyer *et al.*, 2017). However, it is fraught with issues like solvent losses and comes with a high sorbent regeneration cost. Thus, there is an ongoing search for better materials (and processes) that can achieve efficient and cost-effective carbon capture ('Basic Research Needs for Carbon Capture: Beyond 2020: Report of the Basic Energy

Sciences Workshop for Carbon Capture: Beyond 2020', 2020). In this review, we evaluate a class of solid adsorbents in more detail- Metal Organic Frameworks (MOFs). These crystalline porous materials are composed of multi-metallic units surrounded by organic linkers (Eddaoudi *et al.*, 2001; Long and Yaghi, 2009; Zhou *et al.*, 2012; "Joe" Zhou and Kitagawa, 2014; Lu *et al.*, 2014) and satisfy some of the prerequisites of an ideal CO_2 capture material: a. high selectivity towards binding CO_2, b. high capacity, c. low energy requirement for releasing CO_2, d. thermal and chemical stability along with thermal capacity, and e. good synthesizability.

The step following carbon capture is either storage or conversion. Limited known geological storage options along with associated costs of transportation and suffocation risks from potential leaks suggest that conversion and utilization should be strongly committed (Sabri *et al.*, 2021). Conversion achieves the dual objective of converting CO_2 to value-added products including urea, methane, methanol, etc., while simultaneously avoiding the risks associated with storage. Conversion of CO_2 invariably translates to CO_2 reduction. Most thermal CO_2 reduction requires harsh conditions involving high temperature and pressures, requires additional energy input and can hinder broad deployment. Depending on the energy source, it could require additional carbon-emitting fossil combustion. This can be circumvented by using CO_2 electrochemical reduction (CO_2ER) instead of thermal and pressure-driven methods (Kondratenko et al., 2013; Lu et al., 2014; Zhao et al., 2017; Jiao et al., 2019, Wang et al., 2022). Electrochemistry enables production of chemicals that are often more difficult to produce from thermal methods (Gattrell, Gupta and Co, 2006; Kondratenko *et al.*, 2013). While a wide variety of value-added products can be obtained, not all of them are economically feasible. Nitopi et al. weighed the market price of an array of value-added products against the energy required to produce them and concluded that C_{2+} products such as ethanol, ethylene, and propanol are the most economically feasible (Nitopi *et al.*, 2019). Hence, in this review, we shall focus on processes that exclusively produce C_{2+} products. Among the catalysts used for CO_2ER, Cu-based ones are unparalleled for synthesis of C_{2+} products (Nitopi *et al.*, 2019).

In this review, we focus on the conversion part of the capture and conversion process because the former is a process driven by thermodynamics and is a very well-studied topic on its own (Eddaoudi *et al.*, 2001; Long and Yaghi, 2009; Zhou *et al.*, 2012; "Joe" Zhou and Kitagawa, 2014; Lu *et al.*, 2014). Here, we wanted to showcase the impact of electrocatalysis on CO_2 reduction within the framework of a conversion material. We explore mechanisms for CO_2ER to C_{2+} products in Cu-based electrodes to develop insights into the process. Such mechanistic knowledge shall guide different strategies that enhance C_{2+} product formation by optimizing the catalyst and reaction conditions. We then highlight the emerging potential of having a one-pot solution that combines capture and conversion. This has been demonstrated with Cu-based MOF derivatives where the constituent MOFs adsorb CO_2 and provide a nice framework for constituent Cu sites to act as catalytic sites for CO_2ER. Furthermore, the structure of MOF enhances catalytic activity via synergistic effects in addition to CO_2 capture. While some of the mechanistic insights and improvement strategies in Cu electrocatalysis are transferable, we also discuss the additional requirements that are mandated by the one-pot Cu-based MOF solution. Finally, we discuss challenges hindering commercial use of these materials and how they can be overcome, paving the way for using these materials as suitable candidates for broad deployment of CO_2 reduction systems.

2 CO_2 conversion

Catalysts used to fabricate electrodes are broadly classified into four groups based on the selectivity of their CO_2 reduction products: a. formate; b. CO; c. H_2; and d. hydrocarbon, aldehydes, and alcohols. The formate producers are metals such as Pb, Hg, Tl, and In, while some metals such as Au, Ag, and Zn primarily produce CO. A few metals including Ni, Fe, Pt, and Ti reduce water to H_2 and are termed H_2 producing. Cu is the only metal belonging to the fourth category making it ideal for producing C_{2+} products. This is heavily attributed to the unique characteristic of Cu of having a negative adsorption energy for CO while maintaining a positive one for H species. This translates to the ability to retain and eventually reduce CO while preventing the hydrogen evolution reaction (HER). The adsorption characteristics of CO play an instrumental role because reduction to CO is the first reaction step in CO_2ER to C_{2+} products (Nitopi *et al.*, 2019). CO production is enhanced in the presence of catalysts such as Ag and they have been increasingly used to design bi-metallic catalysts with increased reduction to C_{2+} products (Nitopi *et al.*, 2019).

While electrodes fabricated from Cu can synthesize a variety of products such as CO, formate, C_2H_4, and CH_4, we are primarily interested in producing C_{2+} products given their high benefit-to-cost ratio. In specific, formation of the C-C bond in C_{2+} is the critical first reaction for oligomerization into a range of materials, chemicals, and fuels, enabling CO_2 to serve as a primary industrial building block. Many processes exist to maximize the production of C_{2+} products but from a reduction pathway perspective, they broadly result in these effects: a. increasing the availability of CO and b. enhancing CO dimerization reactions. The first tier of products synthesized after two electron transfer from CO_2 in the CO_2ER reduction pathway consists of formate and CO (Nitopi *et al.*, 2019). The former is a terminal product, implying that it does not undergo further reduction. Thus, for C_{2+} production, we need to drive the reduction process to CO, not formate. Increasing the adsorption, transport, and overall availability of CO can enhance formation of C_{2+} products. This is the principle behind employing metals that selectively produce CO such as Ag, Au, and Zn as a co-catalyst (Nitopi *et al.*, 2019). For example, a study found Cu-Ag bimetallic electrodes resulted in higher production of CH_3CHO and C_2H_4 compared to pure Cu electrode (Ishimaru, Shiratsuchi and Nogami, 2000). The second process is based on a reaction pathway that involves enhancing CO dimerization reactions (Nitopi *et al.*, 2019). Cu (100) is observed to amplify those reactions and is reported to be one of the surfaces with a high selectivity for C_2H_4 over CH_4 (Hori *et al.*, 1995). There are other strategies to boost C_{2+} products, the most important and widespread one is increasing the electrochemically-active surface area (ECSA). Some methods for increasing ECSA include using Cu nanostructures and stepped Cu surfaces. For example, Manthiram et al. observed fourfold higher current density along with a faradaic efficiency of 80% for CH_4 production on Cu nanoparticles with an initial size of 7 nm as compared to polycrystalline Cu foil (Manthiram, Beberwyck and Alivisatos, 2014). These processes are depicted in **Figure 1**.

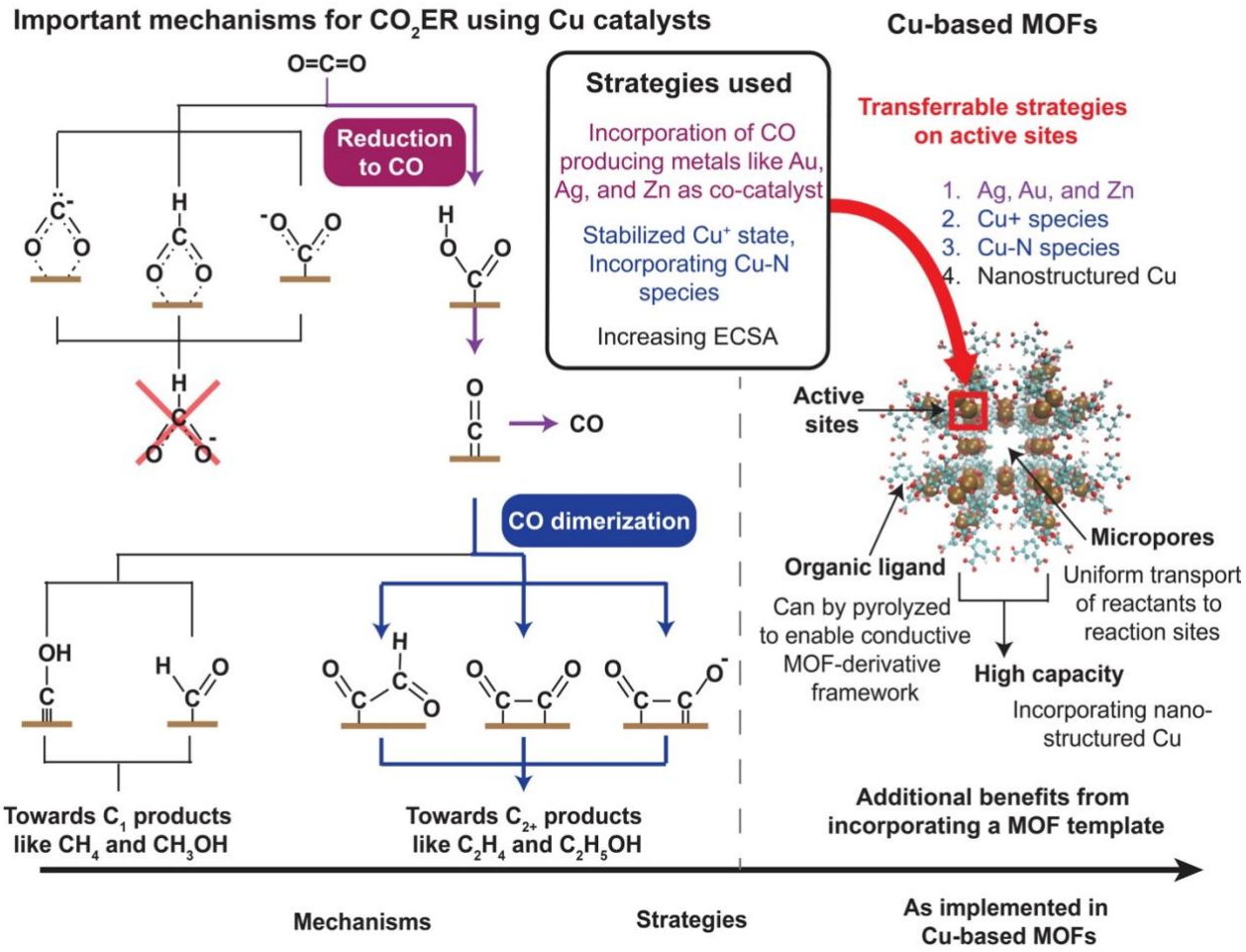

Figure 1. A partial CO_2ER pathway indicating major reactions process (Hori *et al.*, 1994, 1997; Peterson *et al.*, 2010; Kuhl *et al.*, 2012; Cheng, Xiao and Goddard, 2015; Kortlever *et al.*, 2015; Montoya *et al.*, 2015; Feaster *et al.*, 2017; Chernyshova, Somasundaran and Ponnurangam, 2018; Garza, Bell and Head-Gordon, 2018; Lum *et al.*, 2018; Liu *et al.*, 2019; Nitopi *et al.*, 2019). Mechanisms that play a critical role in the production on C_{2+} products via CO_2ER on Cu-based catalysts along with strategies used to enhance them are specifically highlighted. These strategies can be implemented in a Cu-based MOF system; the chemically tunable active sites along with additional advantages of a MOF template for catalysis highlights the ability of Cu-based MOFs to produce C_{2+} products via CO_2ER

3 Integrated CO_2 capture and conversion

Carbon conversion is preceded by carbon capture, but such sequential treatment suffers from the additional cost required for compression and transportation. For transportation, CO_2 needs to be compressed up to 150 bar which translates to at least around 360 kJ/kg CO_2 of work (Huck *et al.*, 2014). Other challenges with compression include the removal of residual moisture to avoid creating corrosive conditions in the tank and dissipation of heat during the compression process. These costs can be avoided if both processes occur in the same plant location, termed an integrated cascade system (Sabri

et al., 2021). The extremely optimistic end of this spectrum is simultaneous capture and conversion. Often, this is achieved by materials that function as both CO_2 adsorbers and CO_2 reduction catalysts.

Interestingly, metal organic frameworks (MOFs) which belong to the category of solid adsorbers can serve as both an adsorbent for CO_2 capture as well as a catalyst for CO_2 conversion. Some of the attractive features of MOFs that make it ideal for CO_2 capture include a. porous structure, b. chemically tunability, c. compatibility with other materials, d. structural flexibility, and e. hydrophobicity (Ding *et al.*, 2019). The open metal sites and organic linkers serve as Lewis acid and basic sites, respectively, both of which can coordinate and bind CO_2 (Ding *et al.*, 2019). For example, M-MOF-74 (M: Mg, Ni, Co, Zn) coordinates CO_2 via the metal sites (Kong *et al.*, 2012; Queen *et al.*, 2014) while IRMOF uses its N-containing Lewis base (amines) as the site for binding CO_2 (Millward and Yaghi, 2005). Moreover, CO_2 capture is enhanced with linkers functionalized with polar functional groups like -F, -Br, $-NO_2$, and $-SO_3$ as the additional dipole interacts with the quadrupole of CO_2 (Debatin *et al.*, 2010; Gassensmith *et al.*, 2011; Zhang *et al.*, 2016; Mosca *et al.*, 2018; Ding *et al.*, 2019). Additionally, the chemical features can be altered by easily functionalizing the linkers and modifying metal centers. These sites and modifications enhance CO_2 capture via synergistic effects. Lastly, the pore size and flexibility of these hydrophobic structures are tunable (Ding *et al.*, 2019).

Synthesizing C_{2+} products via electroreduction of CO_2 calls for Cu-based electrodes to serve as catalysts. The easily tunable characteristic of MOFs translates to the ability to incorporate Cu within the framework (as shown in **Figure 1**). Cu-based MOFs such as HKUST-1 exist that exhibit selectivity for C_{2+} products when used as an electrochemical catalyst (Han *et al.*, 2021a). **Table 1** highlights the catalysts, products, and synthesis efficiency. More importantly, we believe that it is important to highlight that not only do Cu-based MOFs combine both capture and conversion capabilities, but the combination increases the performance of both processes.

First, the availability of uniformly dispersed active sites and high surface area already makes MOFs an excellent catalyst template in general while the constituent micropores ensure uniform transport of reactants to the catalytic sites (Ding *et al.*, 2019). MOFs have been used for thermal reduction of CO_2 to synthesize organic products via cycloaddition, carboxylation, and cyclization reactions (Zalomaeva *et al.*, 2013; Liu *et al.*, 2015; Zhang *et al.*, 2016; Liang *et al.*, 2017; Xiong *et al.*, 2017; Nguyen *et al.*, 2018; Wang *et al.*, 2018). For example, MMCF-2 has been shown to provide a 95% yield for cycloaddition of CO_2 with propylene oxide in the presence of a co-catalyst (Gao *et al.*, 2014).

Table 1: List of Cu-based materials used as electrodes for CO_2ER to C_{2+} products

Adsorber	Material category	Conductive component	Electrolyte	Reactor cell type	Potential (V vs SHE)	Potential (V vs RHE)	Products	Efficiency (%)	Current density (mA/cm^2)	Reference
Cu	Metal	Metal	0.1 M $KHCO_3$	H-type pyrex cell	-1.44	-1.05	C_2H_4	25.5	-5	(Hori *et al.*, 1995; Hori, 2008)
							C_2H_5OH	5.7		
							C_3H_7OH	3		
Cu (100)					-1.4	-1	C_2H_4	40.4		
							Alcohol	12		
							Aldehyde	4.4		
Cu (110)					-1.55	-1.15	C_2H_4	15.1		
							Alcohol	7.4		
							Aldehyde	3.1		
Cu (111)					-1.55	-1.15	C_2H_4	8.3		
							Alcohol	3.3		
							Aldehyde	2.7		
Cu-BTC	MOF	Glassy carbon electrode	0.1 M KCl	Three electrode singles compartment electrochemical cell	-2.27		Oxalic acid	51	19.22	(Senthil Kumar, Senthil Kumar and Anbu Kulandainathan, 2012)
Cu-BTC			0.5 M $KHCO_3$	Micro Flow cell, ElectroCell A/S	-0.28		C_2H_5OH	10.3	10	(Albo *et al.*, 2017)
HKUST-1		Carbon paper	0.1 M $KHCO_3$	H-type cell		-0.98	C_2H_4, C_2H_5OH	58.6	19.2	(Han *et al.*, 2021)
MOF-Cu_3(HITP)$_2$		Conducting support	0.1 M $KHCO_3$	Two compartment H-cell	-1.56		C_2H_4	48	48	(Sun *et al.*, 2021)
HKUST-1				Micro Flow cell, ElectroCell A/S			C_2H_5OH	15.9	10	(Albo *et al.*, 2017)
CuAdeAce								1.2		

CuDTA MOA								6		
CuZnDTA MOA								9.9		
Cs^+ modified Cu,Zn MOF (Zr_{12} BPDC)							C_2H_5OH			(An *et al.*, 2019)
Cu(II)/ade-MOF				H-type cell		-1.4	C_2H_4	34	8.5	(Yang *et al.*, 2019)
MOF-Cu_3(HITP)$_2$		Conducting support		H-cell, flow-cell			C_2H_4	60-70		(Sun *et al.*, 2021)
OD Cu/C HKUST-1	MOF derivatives via pyrolysis	Carbonized structure	0.1 M $KHCO_3$	Two bath cell		-0.1	C_2H_5OH	45.2-71.2		(Zhao *et al.*, 2017)
HKUST-1 with desymmetrized Cu dimer			1 M KOH	Flow cell	-1.07		C_2H_4	45	262	(Nam *et al.*, 2018)
Cu MOF-NC; BEN-Cu BTC			0.1 M $KHCO_3$	H-cell		-1.01	C_2H_4	11.2	8	(Yao *et al.*, 2020)
							C_2H_5OH	18.4		
Cu@CuxO-MOF HKUST-1			0.1 M $KHCO_3$	Flow cell		-1.58	C_2H_4	51	150	(Yao *et al.*, 2020)
HKUST-MOF derived $Cu_xO_yC_z$			1M KOH	Three compartment cell			C_2H_4, C_2H_6, C_2H_5OH, C_3H_7OH	54	80	(Sikdar *et al.*, 2021)
CuZn-NC MOF-74			0.1 M $KHCO_3$	H-type compression cell		-1	C_2H_4, C_2H_5OH	25	12	(Juntrapirom *et al.*, 2021)
Cu_2O/Cu@NC **Cu-NBDC**			0.1 M $KHCO_3$			-1.6	C_2H_4	23.9		(Jin *et al.*, 2021)
Cu-GNC-VL			0.5 M $KHCO_3$	H-type cell		-0.87	C_2H_5OH	70.53	10.4	(Zhang *et al.*, 2020)
Ag/Cu on HKUST			1 M KOH	Three compartment glass cell		-0.28	C_2H_4, C_2H_6, C_2H_5OH, C_3H_7OH	21	120	(Sikdar *et al.*, 2022)
Cu/Cu_2O@NG (HKUST-1 and N-doped graphene)	MOF derivatives via electrochemical reaction	N-doped graphene	0.2 M KI	Single compartment gas diffusion cell		-1.9	C_2H_4, C_2H_5OH, C_3H_7OH	56	19	(Zhi *et al.*, 2021)
HKUST-1-derived Cu nanosheet		Cu foil	0.1 M $KHCO_3$	H-type cell		-1.03	C_2 products	56		(Wang *et al.*, 2021)

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Second, nanostructured Cu has been shown to display a higher catalytic activity compared to its bulk counterpart owing to a higher ECSA (Nitopi *et al.*, 2019) arising from the structural increase in steps, facets, and edge atoms. Moreover, grain boundaries are found to promote C-C coupling reactions while suppressing HER (Sun *et al.*, 2021). This effect can be readily exploited in MOFs and they provide an opportunity of significantly enhancing ECSA by incorporating Cu nanostructures and single atoms. For example, Cu-based MOFs such as HKUST-1 have been shown to produce C_2H_4 and C_2H_5OH at 59% efficiency (Han *et al.*, 2021a). Moreover, a Cu-based HKUST-1 embedded on carbon catalysts via an electrochemical reaction resulted in ~10-fold increase in faradaic efficiency for synthesizing C_{2+} products compared to a pristine Cu foil (Wang *et al.*, 2021). This enhancement was attributed to the stepped surfaces, facets, and edges that contributed to the 1.24-fold higher ECSA observed compared to the Cu foil. Cu nanocrystallites were generated in MOF-$Cu_3(HITP)_2$ and the rich grain boundaries aided in C-C coupling reactions resulting in producing C_2H_4 with 60-70% efficiency (Sun *et al.*, 2021).

Third and most importantly, MOFs provide a structure where additional chemical species can be easily incorporated among the plethora of active sites available. From studies done on Cu electrodes, a variety of additions were found to enhance CO_2 conversion that holds true for Cu-based MOFs as well, and are well-suited to be adapted within the MOF structure (**Figure 1**). One of the primary chemical modifications that enhances C_{2+} product formation is the addition of metals that produce CO such as Au, Ag, and Zn as co-catalysts. As mentioned in section 1, Au nanoparticles dispersed on a polycrystalline Cu foil results in a 100x higher reduction rate to C_{2+} products compared to Cu alone (Morales-Guio *et al.*, 2018). This effect is also observed in CuZn bimetallic material embedded in a carbonized MOF, where the influence of Zn led to a 5-fold increase in faradaic efficiency in producing C_2H_4 and C_2H_5OH (Juntrapirom *et al.*, 2021). A similar effect was also seen in Ag/Cu bimetallic catalysts based on a Cu-based MOF derivative where many C_{2+} products were produced with an efficiency of 21% (Sikdar et al., 2022).

MOFs can also incorporate non-metals within its framework. Appending N-containing Cu-N species is credited to amplify formation of C_{2+} products and lend higher stability. The former is attributed to the more stable adsorption of the CH_2 intermediate species and inhibition of HER (Jin *et al.*, 2021). This is cited as the reason for the Cu_2O/Cu@NC catalyst made from Cu-NBDC MOF showing 24% efficiency in forming C_2H_4 in direct contrast to the Cu_2O/Cu@C catalyst (no N content) which did not produce any C_2H_4 (Jin *et al.*, 2021). N, N dimethylformamide (DMF) was used in Cu-BTC and it was found to increase dimerization reactions producing oxalic acid with an efficiency of 51% (Senthil Kumar, Senthil Kumar and Anbu Kulandainathan, 2012). Similarly, N-containing ligands in Cu(II)/ade-MOFs augmented C_2H_4 generation with a 45% efficiency (Yang *et al.*, 2019). An N-containing BEN-Cu-BTC derivative displayed efficiencies of 18% and 11% for C_2H_5OH and C_2H_4, respectively (Cheng *et al.*, 2019). As seen from section 2, adding N-containing species is also a strategy used to increase CO_2 capture as these groups interact with CO_2 to enhance adsorption making this a dual-purpose addition for both capture and conversion.

Furthermore, stabilizing the Cu^+ state was shown to boost synthesis of C_{2+} products via enhancing CO dimerization. This effect was observed in HKUST-1 where the high Cu^+ /Cu^0 ratio resulted in

producing C_2H_4 and C_2H_5OH with efficiency of 59% (Han *et al.*, 2021a). For similar reasons, the Cu@Cu_xO structure in a Cu-based MOF derivative created C_2H_4 with 51% efficiency (Yao *et al.*, 2020).

While MOFs contain a plethora of advantages for CO_2ER, they are also plagued by some disadvantages. Some of them are the lack of conductivity and stability. This necessitates the addition of conductive supports that can in turn, complicate manufacturability. To truly enhance the catalytic activity to the maximum limit, we need to explore methods of making the MOF conductive on its own. Fortuitously, this can be achieved by pyrolyzing the MOFs to create MOF derivatives that not only are stable and conducting because of the carbonization of the organic linkers at high temperatures, but the process also creates additional active sites (Chen *et al.*, 2018). These reasons led to oxide-derived Cu/carbon catalyst generated from HKUST-1 via pyrolysis displaying a very low overpotential (-0.1 V vs RHE) for production of C_2H_5OH (Zhao *et al.*, 2017). Other such Cu-based MOF derivatives are listed in **Table 1** with the products and their efficiencies. These examples demonstrate that Cu-based MOF derivatives are well suited for CO_2ER to C_{2+} products.

4 Conclusion

An integrated carbon capture and conversion process is urgently needed to address atmospheric GHG concentrations. A one-pot solution avoids the additional cost, energy burden, and risks of compression and transportation that is associated with the CO_2 storage (and succeeding conversion). Only conversion to C_{2+} products is reported to be economically feasible. Since electrochemical reduction can be achieved under milder temperature and pressure conditions, they are preferred over thermal reduction. Cu-based catalysts are the gold standard for CO_2ER to synthesize C_{2+} products while MOFs are renowned for their CO_2 capture abilities. The chemical tunability of MOFs makes it possible to make Cu-based MOFs which fit perfectly with the requirement of the one-pot solution to enable CO_2 capture and CO_2ER synthesis of C_{2+} products. A series of Cu-based MOFs were explored and their performance in converting CO_2 to C_{2+} products were summarized (**Table 1**). We also delved deeper into the mechanisms that are involved in C_{2+} product formation and various strategies that can be used to enhance it. Notable among these processes are incorporating Ag/Au/Zn as co-catalysts to increase CO yield, as converting CO_2 to CO is the first step in the CO_2ER pathway. Another strategy is increasing the ECSA of the catalyst, which is the principle behind using nanostructured Cu instead of polycrystalline Cu foil. Moreover, these Cu nanoclusters can be embedded into MOFs as well. We also explored one critical disadvantage of MOFs for electrocatalysis: their low electrical conductivity, which necessitates using conductive supports. However, using pyrolyzed MOFs is an easy way to achieve the requisite electrical conductivity while also boosting stability. These materials classes are highlighted in **Figure 2**. We believe that this one-pot solution can be used for cleaned and reacted flue gas with the added advantage of avoiding energies involved in pressurization and collection. This has been reported in a few studies (D'Alessandro *et al.*, 2010; Kong *et al.*, 2012; McDonald *et al.*, 2012). Moreover, we want to highlight that this technology is in its conceptual stage and is not a working technology yet. Transformation to a full-fledged technology would require detailed evaluation of the scientific and engineering challenges such as separation of the reduction product from electrolyte and optimizing extended operation. A technoeconomic analysis would be useful to determine the scalability and to direct the implementation towards viable pathways.

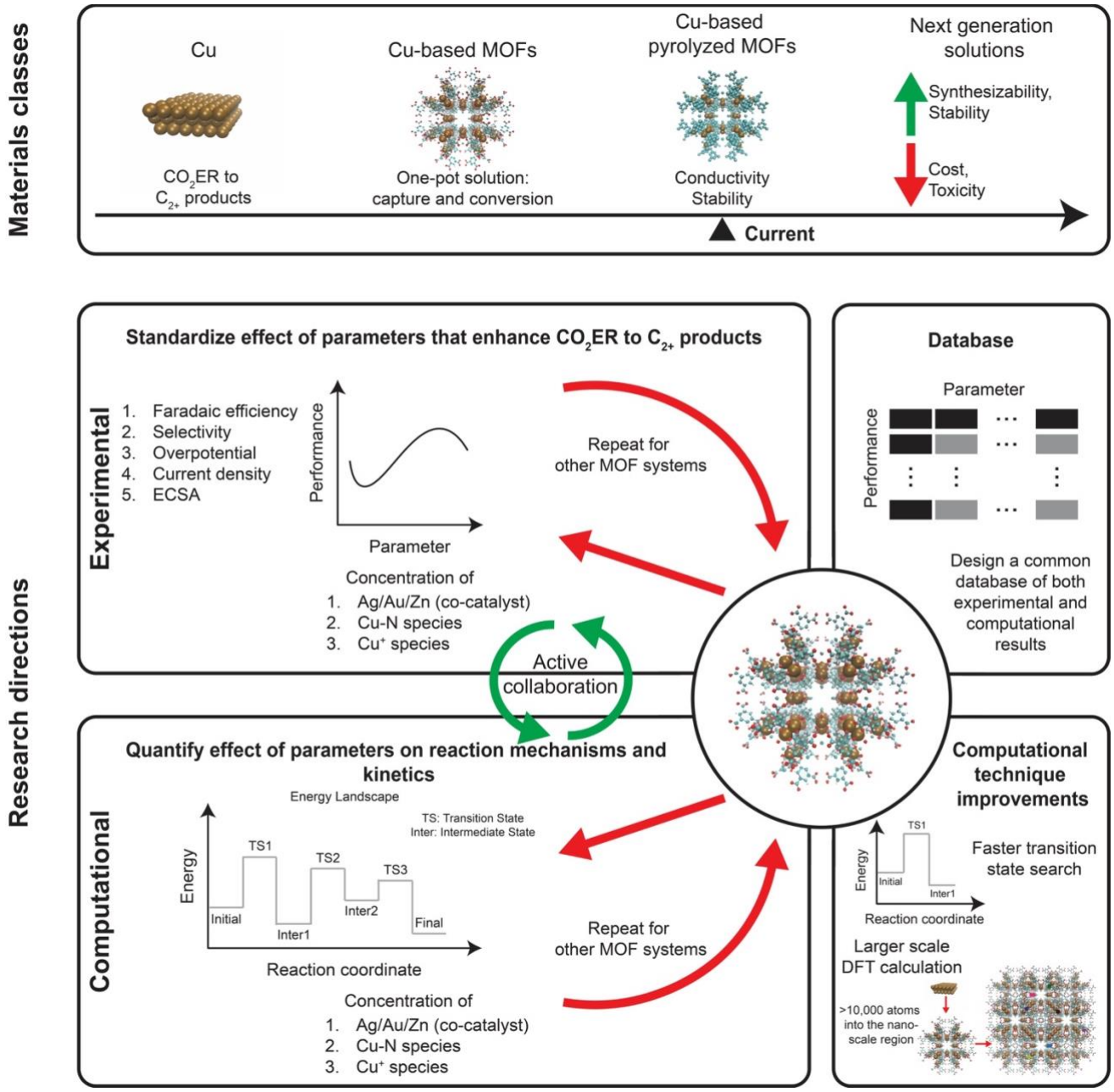

Figure 2. The materials classes involved in the CO_2ER to C_{2+} products: each successive progression highlights an improvement over the prior group. Future research directions are depicted.

While Cu-based MOFs display a high potential for CO_2ER, translating it to commercial use requires us to overcome challenges associated with the scaling-up of fabrication and deployment of MOFs. Firstly, MOFs are expensive and often, the primary contributing factor is the solvent cost (DeSantis *et al.*, 2017). For example, it accounts for 40% of the cost in HKUST-1 made via solvothermal process (DeSantis *et al.*, 2017). Opting for alternative processes such as liquid assisted grinding (LAG) and aqueous synthesis has the potential to reduce the cost by 34-83% as these processes use less solvent in comparison (DeSantis *et al.*, 2017). Moreover, the presence of inorganic nano-sized metal ions that are non-biodegradable along with trapped non-aqueous solvents such as dimethylformamide (DMF) make

MOFs toxic (Kumar *et al.*, 2019). More detailed studies on the toxic effects of MOFs are required for design of less toxic MOFs. Additionally, operation of MOFs for electrocatalytic applications often subject them to exposure to harsh chemical environments making chemical stability essential for efficient operation. Stability, in turn, is a direct result of the bonding environment including interactions such as hydrogen bonding and pi stacking (Coe, 2002; Nouar *et al.*, 2008; Howarth *et al.*, 2016). Incorporating a more inert central metal ion in the MOF structure can increase chemical stability (Kang *et al.*, 2011; Leus *et al.*, 2016). MOF derivatives synthesized via pyrolysis also slow down metal nanoparticle corrosion in the electrolyte, which in turn improves stability (Xiao, Wang and Guan, 2022). Another strategy to consider would be wrapping a protecting film on the surface of MOFs and MOF derivatives (Xiao, Wang and Guan, 2022). Mechanical stability is another factor affecting operation and while strategies like interweaving MOF networks (Tan and Cheetham, 2011; Burtch, Jasuja and Walton, 2014; Katz *et al.*, 2015) are often used, this can be redundant in MOFs for CO_2ER as liquid electrolyte filling MOFs enhances its stability already (Bennett *et al.*, 2015; van de Voorde *et al.*, 2015). Thermal stability is not as important in MOFs for CO_2ER as electroreduction does not require harsh thermal conditions for CO_2 capture or conversion. Finally, the poor electrical conductivity of the organic linkers necessitates presence of conductive substrates such as carbon cloth (Xiao, Wang and Guan, 2022). As previously highlighted, MOF derivatives created via pyrolysis can provide the required conductivity with the formed carbon layers. By altering synthesis parameters, the degree of graphitization can be enhanced. By adjusting the chemistry of the MOF precursors, the degree of defect carbon structure can be tuned. Both strategies can be used to optimize the resulting MOF derivative for enhanced conductivity (Xiao, Wang and Guan, 2022).

Lastly, we summarize our review with **Figure 2** and we provide conjectures regarding research needs for the next generation one-pot carbon-neutral solutions. Future research should standardize experimental results to facilitate comparison across multiple studies, enabling the community to accelerate the discovery process (Ward *et al.*, 2022). Most of the electrochemical reductions occur at the interface of the electrode and the electrolyte. Using experimental characterization techniques can help us understand bonding and identify species participating in the reaction. Overall, investigating the solid/liquid interface using characterization techniques requires overcoming two major challenges. First, characterization techniques need to be adapted for high pressure environments, as opposed to high vacuum, to replicate the more realistic experimental conditions. Second, the region corresponding to the electrical double layer is small and sandwiched between the bulk electrode and the bulk electrolyte, requiring for Å to nm resolution. Thus, the characterization techniques need to be specifically modified to enable a focus on the solid/liquid interface. Recent developments in characterization techniques like Fourier Transform Infrared spectroscopy (FTIR), Raman spectroscopy, and Ambient-Pressure X-Ray Spectroscopy (APXPS) have been able to overcome these challenges (Tian & Ren, 2004; Zaera, 2014; Favaro *et al.*, 2017b; Salmeron, 2018; Lu *et al.*, 2019; Han *et al.*, 2021b; Radjenovic *et al.*, 2021; Ye & Liu, 2021; Hao *et al.*, 2022). Using these characterization tools could enable a deeper understanding of the mechanisms involved in the activation process (Favaro *et al.*, 2017a; Qian *et al.*, 2019; Qian *et al.*, 2020). The field will benefit from active collaboration across experimental and computational investigations with the former focused on evaluating the performance of Cu-based MOFs as a function of parameters involved in the mechanism enhancement. On the other hand, computational studies can play a key role in assessing the energy landscape involved in the conversion of CO_2 to specific products. These assessments can be accelerated by implementing larger scale density functional theory (DFT) calculations (Kronik *et al.*, 2006; Zhou *et al.*, 2006; Xu *et al.*, 2019, 2021; Motamarri *et al.*, 2020; Dogan, Liou and Chelikowsky, 2022; Hao *et al.*, 2022; Xu, Prendergast and Qian, 2022) along with a faster transition state search procedure (Koistinen *et al.*, 2017; Garrido Torres *et al.*, 2019; Meyer, Schmuck and Hauser, 2019). Eventually, a database common

to both experimental and computational work, as outlined by the Materials Project (Jain *et al.*, 2013) can be constructed which can go a long way towards helping design high performance solutions.

5 List of acronyms and abbreviations of MOFs

DOBDC	2,5-Dihydroxyterephthalate
BTC	Benzene-1,3,5-tricarboxylate
BDC	1,4-Benzenedicarboxylate
BPDC	Biphenyl-1,4-dicarboxylate
M-MOF-74	$[M_2(DOBDC)(H_2O)_2]$ ($M=Mg^{2+}$, Ni^{2+}, Co^{2+}, Zn^{2+})
IRMOF-3	$[Zn_4O(NH_2BDC)_3]$
HKUST-1	$[Cu_3(BTC)_2(H_2O)_3]$
HITP	2,3,6,7,10,11-hexaiminotriphenylene
H-CuTCPP	Helical Cu porphyrinic MOF meso-tetra (4-carboxyphenyl) porphyrin
CuAdeAce	Copper(II)–adeninate–acetate
CuDTA MOA	Copper bis-bidentate dithiooxamidate metal-organic aerogel
Cu(II)/ade-MOF	CuII/adeninato/carboxylato metal-biomolecule frameworks
Cu MOF-NC; BEN-Cu BTC	Calcination of N-containing benzimidazole-modified Cu-BTC MOFs (BEN-Cu-BTC)
Cu-NBDC	Cu 2-aminoterephthalic acid
Cu-GNC-VL	Cu/Cu_2O nanocomposite loaded on the surface of carbon derived from direct carbonization of two-dimensional cross-like zeolitic imidazolate framework-L coated vertically on graphene oxide

H_4TACTMB	1,4,7,10-tetrazazcyclododecane-N,N',N'',N'''-tetra-p-methylbenzoic acid
MMCF-2	$[Cu_2(Cu\text{-}TACTMB)(H_2O)_3(NO_3)_2]$
F-IRMOF-3	Functionalized IRMOF; NH_2 groups converted to quaternary ammonium salt though introduction of CH_3I

6 Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

7 Author Contributions

AJ and JQ contributed to the conception of the review. AJ wrote the first draft of the manuscript. All authors contributed to manuscript revision.

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10 References

Albo, J. *et al.* (2017) 'Copper-Based Metal–Organic Porous Materials for CO2 Electrocatalytic Reduction to Alcohols', *ChemSusChem*, 10(6), pp. 1100–1109. Available at: https://doi.org/10.1002/cssc.201600693.

An, B. *et al.* (2019) 'Cooperative copper centres in a metal–organic framework for selective conversion of CO2 to ethanol', *Nature Catalysis*, 2(8), pp. 709–717. Available at: https://doi.org/10.1038/s41929-019-0308-5.

355 'Basic Research Needs for Carbon Capture: Beyond 2020: Report of the Basic Energy Sciences
356 Workshop for Carbon Capture: Beyond 2020' (2020), p. 196.

357 Bennett, T.D. *et al.* (2015) 'Mechanical properties of zeolitic metal–organic frameworks:
358 mechanically flexible topologies and stabilization against structural collapse', *CrystEngComm*, 17(2),
359 pp. 286–289. Available at: https://doi.org/10.1039/C4CE02145B.

360 Birol, D.F. (2019) 'WORLD ENERGY OUTLOOK 2019', p. 810.

361 Burtch, N.C., Jasuja, H. and Walton, K.S. (2014) 'Water stability and adsorption in metal-organic
362 frameworks', *Chemical Reviews*, 114(20), pp. 10575–10612. Available at:
363 https://doi.org/10.1021/cr5002589.

364 Chen, Y.-Z. *et al.* (2018) 'Metal–organic framework-derived porous materials for catalysis',
365 *Coordination Chemistry Reviews*, 362, pp. 1–23. Available at:
366 https://doi.org/10.1016/j.ccr.2018.02.008.

367 Cheng, T., Xiao, H. and Goddard, W.A.I.I.I. (2015) 'Free-Energy Barriers and Reaction Mechanisms
368 for the Electrochemical Reduction of CO on the Cu(100) Surface, Including Multiple Layers of
369 Explicit Solvent at pH 0', *The Journal of Physical Chemistry Letters*, 6(23), pp. 4767–4773.
370 Available at: https://doi.org/10.1021/acs.jpclett.5b02247.

371 Cheng, Y.-S. *et al.* (2019) 'An MOF-derived copper@nitrogen-doped carbon composite: the
372 synergistic effects of N-types and copper on selective CO_2 electroreduction', *Catalysis Science &*
373 *Technology*, 9(20), pp. 5668–5675. Available at: https://doi.org/10.1039/C9CY01131E.

374 Chernyshova, I. v, Somasundaran, P. and Ponnurangam, S. (2018) 'On the origin of the elusive first
375 intermediate of CO2 electroreduction', *Proceedings of the National Academy of Sciences*, 115(40),
376 pp. E9261–E9270. Available at: https://doi.org/10.1073/pnas.1802256115.

377 Coe, C.G. (2002) 'Structural Effects on the Adsorptive Properties of Molecular Sieves for Air
378 Separation', in T.J. Pinnavaia and M.F. Thorpe (eds) *Access in Nanoporous Materials*. Boston, MA:
379 Springer US (Fundamental Materials Research), pp. 213–229. Available at: https://doi.org/10.1007/0-
380 306-47066-7_14.

381 D'Alessandro, D. M., Smit, B., & Long, J. R. (2010) 'Carbon dioxide capture: prospects for new
382 materials', *Angewandte Chemie International Edition*, *49*(35), 6058-6082. Available at
383 https:/doi.org/10.1002/anie.201000431

384 Debatin, F. *et al.* (2010) 'In Situ Synthesis of an Imidazolate-4-amide-5-imidate Ligand and
385 Formation of a Microporous Zinc–Organic Framework with H2-and CO2-Storage Ability',
386 *Angewandte Chemie*, 122(7), pp. 1280–1284. Available at: https://doi.org/10.1002/ange.200906188.

387 DeSantis, D. *et al.* (2017) 'Techno-economic Analysis of Metal–Organic Frameworks for Hydrogen
388 and Natural Gas Storage', *Energy & Fuels*, 31(2), pp. 2024–2032. Available at:
389 https://doi.org/10.1021/acs.energyfuels.6b02510.

390 Ding, M. *et al.* (2019) 'Carbon capture and conversion using metal–organic frameworks and MOF-
391 based materials', *Chemical Society Reviews*, 48(10), pp. 2783–2828. Available at:
392 https://doi.org/10.1039/C8CS00829A.

393 Dogan, M., Liou, K.-H. and Chelikowsky, J.R. (2022) 'Real-space Methods for Electronic Structure
394 Calculations of over 100,000 Atoms'. Available at: https://doi.org/10.26153/TSW/43732.

395 Eddaoudi, M. *et al.* (2001) 'Modular Chemistry: Secondary Building Units as a Basis for the Design
396 of Highly Porous and Robust Metal−Organic Carboxylate Frameworks', *Accounts of Chemical*
397 *Research*, 34(4), pp. 319–330. Available at: https://doi.org/10.1021/ar000034b.

398 Favaro, M. *et al.* (2017a) 'Subsurface oxide plays a critical role in CO2 activation by Cu (111)
399 surfaces to form chemisorbed CO2, the first step in reduction of CO2', *Proceedings of the National*
400 *Academy of Sciences*, *114*(26), 6706-6711. Available at: https://doi.org/10.1073/pnas.1701405114

401•
402 Favaro, M. *et al.* (2017b) 'Ambient-Pressure X-ray Photoelectron Spectroscopy to Characterize the
403 Solid/Liquid Interface: Probing the Electrochemical Double Layer', *Synchrotron Radiation*
404 *News*, *30*(2), 38-40. Available at: https://doi.org/ 10.1080/08940886.2017.1289806

405 Feaster, J.T. *et al.* (2017) 'Understanding Selectivity for the Electrochemical Reduction of Carbon
406 Dioxide to Formic Acid and Carbon Monoxide on Metal Electrodes', *ACS Catalysis*, 7(7), pp. 4822–
407 4827. Available at: https://doi.org/10.1021/acscatal.7b00687.

408 Field, C.B., Barros, V.R. and on Climate Change, I.P. (eds) (2014) *Climate change 2014: impacts,*
409 *adaptation, and vulnerability: Working Group II contribution to the fifth assessment report of the*
410 *Intergovernmental Panel on Climate Change*. New York, NY: Cambridge University Press.

411 Gao, W.-Y. *et al.* (2014) 'Crystal Engineering of an nbo Topology Metal–Organic Framework for
412 Chemical Fixation of CO2 under Ambient Conditions', *Angewandte Chemie International Edition*,
413 53(10), pp. 2615–2619. Available at: https://doi.org/10.1002/anie.201309778.

414 Garrido Torres, J.A. *et al.* (2019) 'Low-Scaling Algorithm for Nudged Elastic Band Calculations
415 Using a Surrogate Machine Learning Model', *Physical Review Letters*, 122(15), p. 156001. Available
416 at: https://doi.org/10.1103/PHYSREVLETT.122.156001/FIGURES/3/MEDIUM.

417 Garza, A.J., Bell, A.T. and Head-Gordon, M. (2018) 'Mechanism of CO2 Reduction at Copper
418 Surfaces: Pathways to C2 Products', *ACS Catalysis*, 8(2), pp. 1490–1499. Available at:
419 https://doi.org/10.1021/acscatal.7b03477.

420 Gassensmith, J.J. *et al.* (2011) 'Strong and Reversible Binding of Carbon Dioxide in a Green Metal–
421 Organic Framework', *Journal of the American Chemical Society*, 133(39), pp. 15312–15315.
422 Available at: https://doi.org/10.1021/ja206525x.

423 Gattrell, M., Gupta, N. and Co, A. (2006) 'A review of the aqueous electrochemical reduction of
424 CO2 to hydrocarbons at copper', *Journal of Electroanalytical Chemistry*, 594(1), pp. 1–19. Available
425 at: https://doi.org/10.1016/j.jelechem.2006.05.013.

426 Gielen, D. *et al.* (2019) 'The role of renewable energy in the global energy transformation', *Energy*
427 *Strategy Reviews*, 24, pp. 38–50. Available at: https://doi.org/10.1016/j.esr.2019.01.006.

428 'Global Energy Transformation: A Roadmap to 2050' (2018), p. 76.

Han, Y. *et al.* (2021a) 'Understanding Structure-activity Relationship on Metal-Organic-Framework-Derived Catalyst for CO2 Electroreduction to C2 Products', *ChemElectroChem*, 8(16), pp. 3174–3180. Available at: https://doi.org/10.1002/celc.202100942.

Han, Y. *et al.* (2021b) 'In situ characterization of catalysis and electrocatalysis using APXPS', *ACS Catalysis*, *11*(3), 1464-1484. Available at https:/doi.org/10.1021/acscatal.0c04251

Hao, H. *et al.* (2022) 'Chemical transformations and transport phenomena at interfaces', *Wiley Interdisciplinary Reviews: Computational Molecular Science*, p. e1639. Available at: https://doi.org/10.1002/WCMS.1639.

Hori, Y. *et al.* (1994) 'Electrocatalytic process of CO selectivity in electrochemical reduction of CO2 at metal electrodes in aqueous media', *Electrochimica Acta*, 39(11), pp. 1833–1839. Available at: https://doi.org/10.1016/0013-4686(94)85172-7.

Hori, Y. *et al.* (1995) 'Adsorption of CO accompanied with simultaneous charge transfer on copper single crystal electrodes related with electrochemical reduction of CO2 to hydrocarbons', *Surface Science*, 335, pp. 258–263. Available at: https://doi.org/10.1016/0039-6028(95)00441-6.

Hori, Y. *et al.* (1997) 'Electrochemical Reduction of CO at a Copper Electrode', *The Journal of Physical Chemistry B*, 101(36), pp. 7075–7081. Available at: https://doi.org/10.1021/jp970284i.

Hori, Y. (2008) 'Electrochemical CO2 Reduction on Metal Electrodes', in C.G. Vayenas, R.E. White, and M.E. Gamboa-Aldeco (eds) *Modern Aspects of Electrochemistry*. New York, NY: Springer (Modern Aspects of Electrochemistry), pp. 89–189. Available at: https://doi.org/10.1007/978-0-387-49489-0_3.

Howarth, A.J. *et al.* (2016) 'Chemical, thermal and mechanical stabilities of metal-organic frameworks', *Nature Reviews Materials*, 1. Available at: https://doi.org/10.1038/natrevmats.2015.18.

Huck, J.M. *et al.* (2014) 'Evaluating different classes of porous materials for carbon capture', *Energy & Environmental Science*, 7(12), pp. 4132–4146. Available at: https://doi.org/10.1039/C4EE02636E.

Ishimaru, S., Shiratsuchi, R. and Nogami, G. (2000) 'Pulsed Electroreduction of CO[sub 2] on Cu-Ag Alloy Electrodes', *Journal of The Electrochemical Society*, 147(5), p. 1864. Available at: https://doi.org/10.1149/1.1393448.

Iyer, S.S. *et al.* (2017) 'Integrated Carbon Capture and Conversion To Produce Syngas: Novel Process Design, Intensification, and Optimization', *Industrial & Engineering Chemistry Research*, 56(30), pp. 8622–8648. Available at: https://doi.org/10.1021/acs.iecr.7b01688.

Jain, A. *et al.* (2013) 'Commentary: The Materials Project: A materials genome approach to accelerating materials innovation', *APL Materials*, 1(1), p. 011002. Available at: https://doi.org/10.1063/1.4812323.

Jiao, L. *et al.* (2019) 'Toward CO2 utilization for direct power generation using an integrated system consisting of CO2 photoreduction with 3D TiO2/Ni-foam and a photocatalytic fuel cell', *Journal of Materials Chemistry A*, 7(11), pp. 6275–6284. Available at: https://doi.org/10.1039/C8TA12255E.

Jin, H. *et al.* (2021) 'Cu-Based Catalyst Derived from Nitrogen-Containing Metal Organic Frameworks for Electroreduction of CO2', *Wuli Huaxue Xuebao/ Acta Physico - Chimica Sinica*, 37(11). Available at: https://doi.org/10.3866/PKU.WHXB202006017.

"Joe" Zhou, H.-C. and Kitagawa, S. (2014) 'Metal–Organic Frameworks (MOFs)', *Chemical Society Reviews*, 43(16), pp. 5415–5418. Available at: https://doi.org/10.1039/C4CS90059F.

Juntrapirom, S. *et al.* (2021) 'Tuning CuZn interfaces in metal–organic framework-derived electrocatalysts for enhancement of CO2 conversion to C2 products', *Catalysis Science & Technology*, 11(24), pp. 8065–8078. Available at: https://doi.org/10.1039/D1CY01839F.

Kang, I.J. *et al.* (2011) 'Chemical and Thermal Stability of Isotypic Metal–Organic Frameworks: Effect of Metal Ions', *Chemistry – A European Journal*, 17(23), pp. 6437–6442. Available at: https://doi.org/10.1002/chem.201100316.

Katz, M.J. *et al.* (2015) 'Exploiting parameter space in MOFs: A 20-fold enhancement of phosphate-ester hydrolysis with UiO-66-NH2', *Chemical Science*, 6(4), pp. 2286–2291. Available at: https://doi.org/10.1039/c4sc03613a.

Koistinen, O.P. *et al.* (2017) 'Nudged elastic band calculations accelerated with Gaussian process regression', *The Journal of Chemical Physics*, 147(15), p. 152720. Available at: https://doi.org/10.1063/1.4986787.

Kondratenko, E. v *et al.* (2013) 'Status and perspectives of CO2 conversion into fuels and chemicals by catalytic, photocatalytic and electrocatalytic processes', *Energy & Environmental Science*, 6(11), pp. 3112–3135. Available at: https://doi.org/10.1039/C3EE41272E.

Kong, X. *et al.* (2012) 'CO2 Dynamics in a Metal–Organic Framework with Open Metal Sites', *Journal of the American Chemical Society*, 134(35), pp. 14341–14344. Available at: https://doi.org/10.1021/ja306822p.

Kortlever, R. *et al.* (2015) 'Catalysts and Reaction Pathways for the Electrochemical Reduction of Carbon Dioxide', *The Journal of Physical Chemistry Letters*, 6(20), pp. 4073–4082. Available at: https://doi.org/10.1021/acs.jpclett.5b01559.

Kronik, L. *et al.* (2006) 'PARSEC – the pseudopotential algorithm for real-space electronic structure calculations: recent advances and novel applications to nano-structures', *physica status solidi (b)*, 243(5), pp. 1063–1079. Available at: https://doi.org/10.1002/PSSB.200541463.

Kuhl, K.P. *et al.* (2012) 'New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces', *Energy & Environmental Science*, 5(5), pp. 7050–7059. Available at: https://doi.org/10.1039/C2EE21234J.

Kumar, P. *et al.* (2019) 'Regeneration, degradation, and toxicity effect of MOFs: Opportunities and challenges', *Environmental Research*, 176, p. 108488. Available at: https://doi.org/10.1016/j.envres.2019.05.019.

Leus, K. *et al.* (2016) 'Systematic study of the chemical and hydrothermal stability of selected "stable" Metal Organic Frameworks', *Microporous and Mesoporous Materials*, 226, pp. 110–116. Available at: https://doi.org/10.1016/j.micromeso.2015.11.055.

Liang, L. *et al.* (2017) 'Carbon dioxide capture and conversion by an acid-base resistant metal-organic framework', *Nature Communications*, 8(1), p. 1233. Available at: https://doi.org/10.1038/s41467-017-01166-3.

Liu, X. *et al.* (2019) 'pH effects on the electrochemical reduction of CO(2) towards C2 products on stepped copper', *Nature Communications*, 10(1), p. 32. Available at: https://doi.org/10.1038/s41467-018-07970-9.

Liu, X.-H. *et al.* (2015) 'An Efficient Nanoscale Heterogeneous Catalyst for the Capture and Conversion of Carbon Dioxide at Ambient Pressure', *Angewandte Chemie International Edition*, 54(3), pp. 988–991. Available at: https://doi.org/10.1002/anie.201409103.

Long, J.R. and Yaghi, O.M. (2009) 'The pervasive chemistry of metal–organic frameworks', *Chemical Society Reviews*, 38(5), pp. 1213–1214. Available at: https://doi.org/10.1039/B903811F.

Lu, W. *et al.* (2014) 'Tuning the structure and function of metal–organic frameworks via linker design', *Chem. Soc. Rev.*, 43(16), pp. 5561–5593. Available at: https://doi.org/10.1039/C4CS00003J.

Lu, Y. H. *et al.* (2019) 'Infrared nanospectroscopy at the graphene–electrolyte interface', *Nano letters*, *19*(8), 5388-5393. Available at: https://doi.org/10.1021/acs.nanolett.9b01897

Lum, Y. *et al.* (2018) 'Electrochemical CO Reduction Builds Solvent Water into Oxygenate Products', *Journal of the American Chemical Society*, 140(30), pp. 9337–9340. Available at: https://doi.org/10.1021/jacs.8b03986.

Manthiram, K., Beberwyck, B.J. and Alivisatos, A.P. (2014) 'Enhanced Electrochemical Methanation of Carbon Dioxide with a Dispersible Nanoscale Copper Catalyst', *Journal of the American Chemical Society*, 136(38), pp. 13319–13325. Available at: https://doi.org/10.1021/ja5065284.

McDonald, T. M., Lee, W. R., Mason, J. A., Wiers, B. M., Hong, C. S., & Long, J. R. (2012). 'Capture of carbon dioxide from air and flue gas in the alkylamine-appended metal–organic framework mmen-Mg2 (dobpdc)', *Journal of the American Chemical Society*, *134*(16), 7056-7065. Available at: https://doi.org/10.1021/ja300034j

Metz, B. and on Climate Change, I.P. (eds) (2007) *Climate change 2007: mitigation of climate change: contribution of Working Group III to the Fourth assessment report of the Intergovernmental Panel on Climate Change*. Cambridge ; New York: Cambridge University Press.

Meyer, R., Schmuck, K.S. and Hauser, A.W. (2019) 'Machine Learning in Computational Chemistry: An Evaluation of Method Performance for Nudged Elastic Band Calculations', *Journal of Chemical Theory and Computation*, pp. 6513–6523. Available at: https://doi.org/10.1021/ACS.JCTC.9B00708/ASSET/IMAGES/MEDIUM/CT9B00708_M018.GIF.

Millward, A.R. and Yaghi, O.M. (2005) 'Metal−Organic Frameworks with Exceptionally High Capacity for Storage of Carbon Dioxide at Room Temperature', *Journal of the American Chemical Society*, 127(51), pp. 17998–17999. Available at: https://doi.org/10.1021/ja0570032.

Montoya, J.H. *et al.* (2015) 'Theoretical Insights into a CO Dimerization Mechanism in CO2 Electroreduction', *The Journal of Physical Chemistry Letters*, 6(11), pp. 2032–2037. Available at: https://doi.org/10.1021/acs.jpclett.5b00722.

Morales-Guio, C.G. *et al.* (2018) 'Improved CO2 reduction activity towards C2+ alcohols on a tandem gold on copper electrocatalyst', *Nature Catalysis*, 1(10), pp. 764–771. Available at: https://doi.org/10.1038/s41929-018-0139-9.

Mosca, N. *et al.* (2018) 'Nitro-Functionalized Bis(pyrazolate) Metal–Organic Frameworks as Carbon Dioxide Capture Materials under Ambient Conditions', *Chemistry – A European Journal*, 24(50), pp. 13170–13180. Available at: https://doi.org/10.1002/chem.201802240.

Motamarri, P. *et al.* (2020) 'DFT-FE – A massively parallel adaptive finite-element code for large-scale density functional theory calculations', *Computer Physics Communications*, 246, p. 106853. Available at: https://doi.org/10.1016/J.CPC.2019.07.016.

Nam, D.-H. *et al.* (2018) 'Metal–Organic Frameworks Mediate Cu Coordination for Selective CO2 Electroreduction', *Journal of the American Chemical Society*, 140(36), pp. 11378–11386. Available at: https://doi.org/10.1021/jacs.8b06407.

Nguyen, P.T.K. *et al.* (2018) 'New Metal–Organic Frameworks for Chemical Fixation of CO2', *ACS Applied Materials & Interfaces*, 10(1), pp. 733–744. Available at: https://doi.org/10.1021/acsami.7b16163.

Nitopi, S. *et al.* (2019) 'Progress and Perspectives of Electrochemical CO2 Reduction on Copper in Aqueous Electrolyte', *Chemical Reviews*, 119(12), pp. 7610–7672. Available at: https://doi.org/10.1021/acs.chemrev.8b00705.

Nouar, F. *et al.* (2008) 'Supermolecular building blocks (SBBs) for the design and synthesis of highly porous metal-organic frameworks', *Journal of the American Chemical Society*, 130(6), pp. 1833–1835. Available at: https://doi.org/10.1021/ja710123s.

OECD (2012) *OECD Environmental Outlook to 2050: The Consequences of Inaction*. Paris: Organisation for Economic Co-operation and Development. Available at: https://www.oecd-ilibrary.org/environment/oecd-environmental-outlook-to-2050_9789264122246-en.

Peterson, A.A. *et al.* (2010) 'How copper catalyzes the electroreduction of carbon dioxide into hydrocarbon fuels', *Energy & Environmental Science*, 3(9), p. 1311. Available at: https://doi.org/10.1039/c0ee00071j.

Qian, J., *et al.* (2019) 'Initial steps in forming the electrode–electrolyte interface: H2O adsorption and complex formation on the Ag (111) surface from combining quantum mechanics calculations and ambient pressure X-ray photoelectron spectroscopy', *Journal of the American Chemical Society*, *141*(17), 6946-6954. Available at https://doi.org/10.1021/jacs.8b13672

Qian, J. *et al.* (2020) 'Addressing the sensitivity of signals from solid/liquid ambient pressure XPS (APXPS) measurement', *The Journal of chemical physics*, *153*(4), 044709. Available at https://doi.org/10.1063/5.0006242

Queen, W. *et al.* (2014) 'Comprehensive study of carbon dioxide adsorption in the metal–organic frameworks M 2 (dobdc) (M = Mg, Mn, Fe, Co, Ni, Cu, Zn)', *Chemical Science*, 5(12), pp. 4569–4581. Available at: https://doi.org/10.1039/C4SC02064B.

Radjenovic, P. M. *et al.* (2021). Watching Reactions at Solid–Liquid Interfaces with in Situ Raman Spectroscopy. *The Journal of Physical Chemistry C*, *125*(48), 26285-26295. Available at: https://doi.org/10.1021/acsjpcc.1c08640

Rafiee, A. *et al.* (2018) 'Trends in CO2 conversion and utilization: A review from process systems perspective', *Journal of Environmental Chemical Engineering*, 6(5), pp. 5771–5794. Available at: https://doi.org/10.1016/j.jece.2018.08.065.

Sabri, M.A. *et al.* (2021) 'Current and future perspectives on catalytic-based integrated carbon capture and utilization', *Science of The Total Environment*, 790, p. 148081. Available at: https://doi.org/10.1016/j.scitotenv.2021.148081.

Salmeron, M. (2018) 'From surfaces to interfaces: ambient pressure XPS and beyond', *Topics in Catalysis*, *61*(20), 2044-2051. Available at: https://doi.org/ 10.1007/s11244-018-1069-0

Senthil Kumar, R., Senthil Kumar, S. and Anbu Kulandainathan, M. (2012) 'Highly selective electrochemical reduction of carbon dioxide using Cu based metal organic framework as an electrocatalyst', *Electrochemistry Communications*, 25, pp. 70–73. Available at: https://doi.org/10.1016/j.elecom.2012.09.018.

Sikdar, N. *et al.* (2021) 'A Metal–Organic Framework derived CuxOyCz Catalyst for Electrochemical CO2 Reduction and Impact of Local pH Change', *Angewandte Chemie International Edition*, 60(43), pp. 23427–23434. Available at: https://doi.org/10.1002/anie.202108313.

Sikdar, N. *et al.* (2022) 'Redox Replacement of Silver on MOF-Derived Cu/C Nanoparticles on Gas Diffusion Electrodes for Electrocatalytic CO2 Reduction', *Chemistry - A European Journal*, 28(12). Available at: https://doi.org/10.1002/chem.202104249.

Sun, H. *et al.* (2021) 'Promoting ethylene production over a wide potential window on Cu crystallites induced and stabilized via current shock and charge delocalization', *Nature Communications*, 12(1). Available at: https://doi.org/10.1038/s41467-021-27169-9.

Sun, K. *et al.* (2017) 'Ultrahigh Mass Activity for Carbon Dioxide Reduction Enabled by Gold–Iron Core–Shell Nanoparticles', *Journal of the American Chemical Society*, 139(44), pp. 15608–15611. Available at: https://doi.org/10.1021/jacs.7b09251.

Tan, J.C. and Cheetham, A.K. (2011) 'Mechanical properties of hybrid inorganic–organic framework materials: establishing fundamental structure–property relationships', *Chemical Society Reviews*, 40(2), p. 1059. Available at: https://doi.org/10.1039/c0cs00163e.

Tian, Z. Q., & Ren, B. (2004) 'Adsorption and reaction at electrochemical interfaces as probed by surface-enhanced Raman spectroscopy', *Annu. Rev. Phys. Chem.*, *55*, 197-229. Available at https://doi.org/ 10.1146/annurev.physchem.54.011002.103833

van de Voorde, B. *et al.* (2015) 'Improving the mechanical stability of zirconium-based metal-organic frameworks by incorporation of acidic modulators', *Journal of Materials Chemistry A*, 3(4), pp. 1737–1742. Available at: https://doi.org/10.1039/c4ta06396a.

Wang, D. *et al.* (2021) 'HKUST-1-derived highly ordered Cu nanosheets with enriched edge sites, stepped (211) surfaces and (200) facets for effective electrochemical CO2 reduction', *Chemosphere*, 278, p. 130408. Available at: https://doi.org/10.1016/j.chemosphere.2021.130408.

Wang, X. *et al.* (2018) 'A metal–metalloporphyrin framework based on an octatopic porphyrin ligand for chemical fixation of CO2 with aziridines', *Chemical Communications*, 54(10), pp. 1170–1173. Available at: https://doi.org/10.1039/C7CC08844B.

Wang, Y. *et al.* (2022) 'Catalytic Processes to Accelerate Decarbonization in a Net-Zero Carbon World', *ChemSusChem*, 15(24). Available at: https://doi.org/10.1002/cssc.202201290.

Ward, L. *et al.* (2022) 'Principles of the Battery Data Genome', *Joule*, 6(10), pp. 2253–2271. Available at: https://doi.org/10.1016/j.joule.2022.08.008.

Xiao, L., Wang, Z. and Guan, J. (2022) '2D MOFs and their derivatives for electrocatalytic applications: Recent advances and new challenges', *Coordination Chemistry Reviews*, 472, p. 214777. Available at: https://doi.org/10.1016/j.ccr.2022.214777.

Xiong, G. *et al.* (2017) 'Cluster-based MOFs with accelerated chemical conversion of CO2 through C–C bond formation', *Chemical Communications*, 53(44), pp. 6013–6016. Available at: https://doi.org/10.1039/C7CC01136A.

Xu, Q. *et al.* (2019) 'Ab initio electronic structure calculations using a real-space Chebyshev-filtered subspace iteration method', *Journal of Physics: Condensed Matter*, 31(45), p. 455901. Available at: https://doi.org/10.1088/1361-648X/AB2A63.

Xu, Q. *et al.* (2021) 'SPARC: Simulation Package for Ab-initio Real-space Calculations', *SoftwareX*, 15, p. 100709. Available at: https://doi.org/10.1016/J.SOFTX.2021.100709.

Xu, Q., Prendergast, D. and Qian, J. (2022) 'Real-Space Pseudopotential Method for the Calculation of 1 s Core-Level Binding Energies', *Journal of Chemical Theory and Computation*, 18(9), pp. 5471–5478. Available at: https://doi.org/10.1021/ACS.JCTC.2C00474/SUPPL_FILE/CT2C00474_SI_002.ZIP.

Yang, F. *et al.* (2019) 'Highly efficient electroconversion of carbon dioxide into hydrocarbons by cathodized copper–organic frameworks', *Chemical Science*, 10(34), pp. 7975–7981. Available at: https://doi.org/10.1039/C9SC02605C.

Yao, K. *et al.* (2020) 'Metal–organic framework derived copper catalysts for CO2 to ethylene conversion', *Journal of Materials Chemistry A*, 8(22), pp. 11117–11123. Available at: https://doi.org/10.1039/D0TA02395G.

Ye, Y., & Liu, Z. (2021) 'APXPS of Solid/Liquid Interfaces. In *Ambient Pressure Spectroscopy in Complex Chemical Environments'* (pp. 67-92). American Chemical Society. Available at https://doi.org/10.1021/bk-2021-1396.ch004

Zaera, F. (2014) 'New advances in the use of infrared absorption spectroscopy for the characterization of heterogeneous catalytic reactions' *Chemical Society Reviews*, *43*(22), 7624-7663. Available at: https://doi.org/10.1039/C3CS60374A

Zalomaeva, O. v *et al.* (2013) 'Synthesis of cyclic carbonates from epoxides or olefins and CO2 catalyzed by metal-organic frameworks and quaternary ammonium salts', *Journal of Energy Chemistry*, 22(1), pp. 130–135. Available at: https://doi.org/10.1016/S2095-4956(13)60017-0.

Zhang, G. *et al.* (2016) 'A Robust Sulfonate-Based Metal–Organic Framework with Permanent Porosity for Efficient CO2 Capture and Conversion', *Chemistry of Materials*, 28(17), pp. 6276–6281. Available at: https://doi.org/10.1021/acs.chemmater.6b02511.

Zhang, Yangyang *et al.* (2020) 'Cu/Cu _2 O Nanoparticles Supported on Vertically ZIF-L-Coated Nitrogen-Doped Graphene Nanosheets for Electroreduction of CO _2 to Ethanol', *ACS Applied Nano Materials*, 3(1), pp. 257–263. Available at: https://doi.org/10.1021/acsanm.9b01935.

Zhao, K. *et al.* (2017) 'CO2 Electroreduction at Low Overpotential on Oxide-Derived Cu/Carbons Fabricated from Metal Organic Framework', *ACS Applied Materials & Interfaces*, 9(6), pp. 5302–5311. Available at: https://doi.org/10.1021/acsami.6b15402.

Zhi, W.-Y. *et al.* (2021) 'Efficient electroreduction of CO2 to C2-C3 products on Cu/Cu2O@N-doped graphene', *Journal of CO2 Utilization*, 50, p. 101594. Available at: https://doi.org/10.1016/j.jcou.2021.101594.

Zhou, X. *et al.* (2012) 'Functionalized IRMOF-3 as efficient heterogeneous catalyst for the synthesis of cyclic carbonates', *Journal of Molecular Catalysis A: Chemical*, 361–362, pp. 12–16. Available at: https://doi.org/10.1016/j.molcata.2012.04.008.

Zhou, Y. *et al.* (2006) 'Parallel self-consistent-field calculations via Chebyshev-filtered subspace acceleration', *Physical Review E - Statistical, Nonlinear, and Soft Matter Physics*, 74(6), p. 066704. Available at: https://doi.org/10.1103/PHYSREVE.74.066704/FIGURES/3/MEDIUM.