PERSPECTIVE
https://doi.org/10.1038/s41563-020-0610-2
nature materials

Molecular enhancement of heterogeneous CO_2 reduction

Dae-Hyun Nam[1,7], Phil De Luna[1,2,3,7], Alonso Rosas-Hernández[4,5], Arnaud Thevenon[4,5], Fengwang Li[1], Theodor Agapie[4,5], Jonas C. Peters[4,5], Osama Shekhah[6], Mohamed Eddaoudi[6] and Edward H. Sargent[1] ✉

The electrocatalytic carbon dioxide reduction reaction (CO_2RR) addresses the need for storage of renewable energy in valuable carbon-based fuels and feedstocks, yet challenges remain in the improvement of electrosynthesis pathways for highly selective hydrocarbon production. To improve catalysis further, it is of increasing interest to lever synergies between heterogeneous and homogeneous approaches. Organic molecules or metal complexes adjacent to heterogeneous active sites provide additional binding interactions that may tune the stability of intermediates, improving catalytic performance by increasing Faradaic efficiency (product selectivity), as well as decreasing overpotential. We offer a forward-looking perspective on molecularly enhanced heterogeneous catalysis for CO_2RR. We discuss four categories of molecularly enhanced strategies: molecular-additive-modified heterogeneous catalysts, immobilized organometallic complex catalysts, reticular catalysts and metal-free polymer catalysts. We introduce present-day challenges in molecular strategies and describe a vision for CO_2RR electrocatalysis towards multi-carbon products. These strategies provide potential avenues to address the challenges of catalyst activity, selectivity and stability in the further development of CO_2RR.

The electrochemical carbon dioxide (CO_2) reduction reaction (CO_2RR) to fuels and chemical feedstocks, powered by renewable electricity, offers a pathway to long-term seasonal energy storage[1,2]. In CO_2RR, electrocatalysts promote the conversion of CO_2 into value-added products such as carbon monoxide (CO), formate ($HCOO^-$) or formic acid (HCOOH), methane (CH_4), ethylene (C_2H_4), and ethanol (C_2H_5OH). Today, metal-based heterogeneous catalysts commonly exhibit high activities for CO_2RR at low overpotentials[1,3]. Nevertheless, key metrics—such as product selectivity, current density as a function of applied bias, the requirement of high CO_2 concentration in the source stream, and catalyst stability—are among the factors that need to be improved in the context of renewable energy applications.

In contrast to many heterogeneous catalysts, molecular catalysts offer the advantage of synthetic control over the steric and electronic properties in the vicinity of the active site. This in turn enables mechanistic studies to address structure–function relationships that then induce rational design of new catalyst structures towards improved performance. Homogeneous catalysts have been used in the context of CO_2RR for decades[4]. These systems have shown high selectivity, with near unity product Faradaic efficiency (FE), for CO or $HCOO^-$ (HCOOH), and progress towards more reduced products such as CH_4 is emerging[5].

There has been longstanding interest in the heterogeneous catalysis community to bridge concepts from homogeneous molecular catalysis to tune heterogeneous catalysts[6]. New product profiles can emerge when organic molecules or metal complexes are interfaced with solid supports[7]. An exciting example of this bridge is metalloenzymes, which are able to mediate challenging multi-electron/proton reductive transformations at remarkably fast rates with very little applied bias[8]. This is a consequence of metalloenzyme structure, which has exploited multi-metallic active sites with ideally positioned secondary sphere interactions[9]. The catalysis research community is interested in defining and employing such design principles in artificial catalyst architectures[10]. Transferring such principles to molecularly enhanced heterogeneous catalysts represents an exciting opportunity for researchers. Introducing molecular approaches to heterogeneous CO_2RR catalysts may introduce new degrees of freedom that enable routes to enhance/alter product selectivity, increase catalyst mass activity, and lower the overpotential to drive a reaction at a desired rate. We use the term molecular approaches to refer to chemically modified electrodes—those that display motifs derived from molecular chemistry. We also note that controlling the composition of the electrolyte (water, cations and buffer species) is another critical dimension in CO_2RR, but it is a topic addressed well elsewhere[1,11].

This Perspective discusses how molecular structures can be adapted to CO_2RR electrode materials. Four main strategies are described: molecular-additive-modified heterogeneous catalysts, immobilized organometallic complex catalysts, metal–organic framework (MOF) and covalent organic framework (COF) catalysts, and metal-free polymer catalysts (Fig. 1). Molecular-based approaches to improved heterogeneous catalysis have been discussed previously[6,12,13]. This Perspective seeks to go beyond conceptualizing and classifying these ideas. Instead, it explores the extent to which the community has developed mechanistic pictures of

---

[1]Department of Electrical and Computer Engineering, University of Toronto, Toronto, Ontario, Canada. [2]Department of Materials Science and Engineering, University of Toronto, Toronto, Ontario, Canada. [3]National Research Council of Canada, Ottawa, Ontario, Canada. [4]Joint Center for Artificial Photosynthesis, California Institute of Technology, Pasadena, California, USA. [5]Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California, USA. [6]Division of Physical Sciences and Engineering, Advanced Membranes and Porous Materials Center, Functional Materials Design, Discovery and Development Research Group, King Abdullah University of Science and Technology, Thuwal, Kingdom of Saudi Arabia. [7]These authors contributed equally: Dae-Hyun Nam, Phil De Luna. ✉e-mail: ted.sargent@utoronto.ca

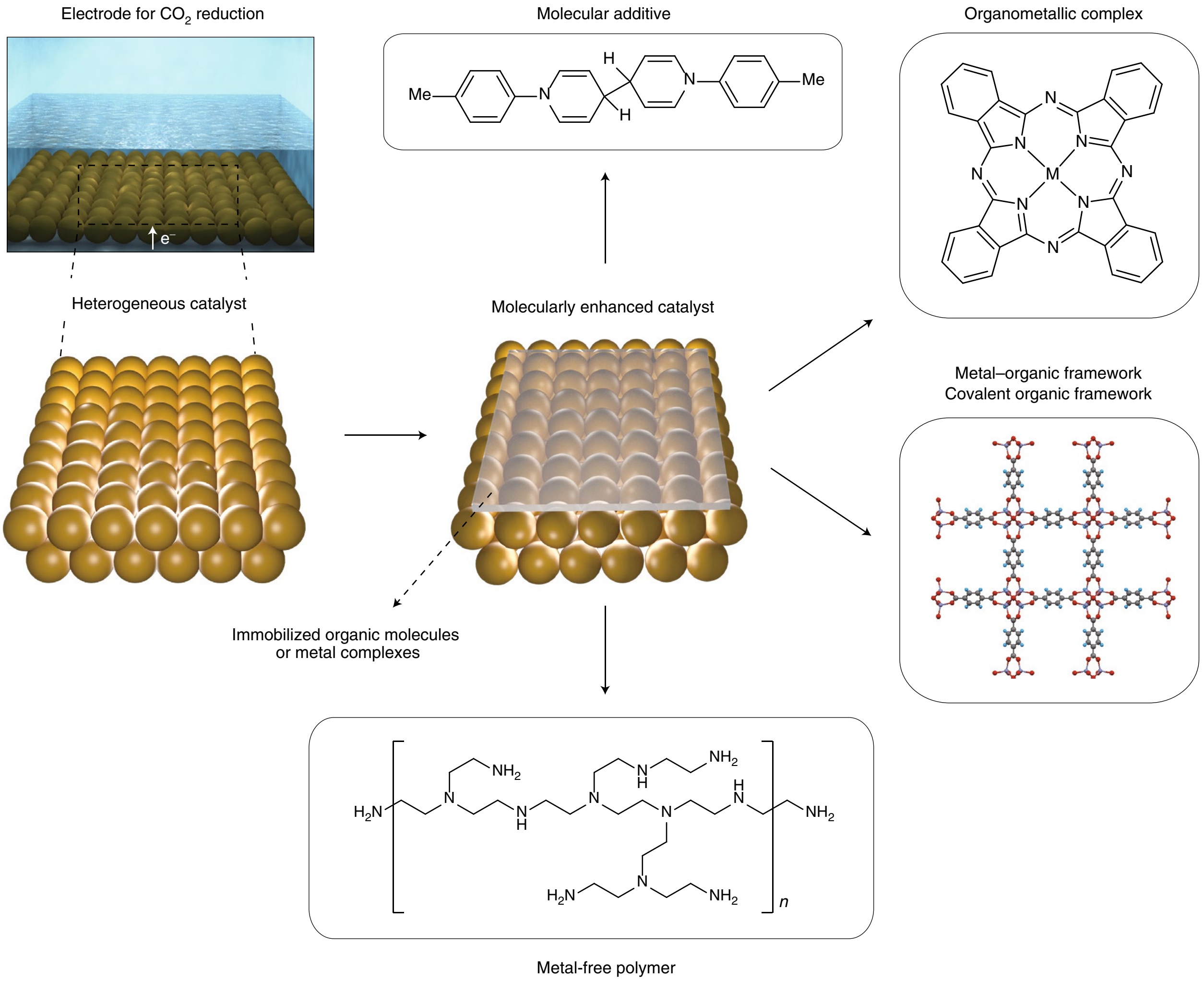

Fig. 1 | Molecularly enhanced heterogeneous CO_2RR electrocatalysts. Combining approaches such as molecular additives, organometallic complex catalysts, reticular chemistry-based MOF and COF catalysts, and metal-free polymer catalysts with electrode surfaces can offer synergies with respect to products and catalyst operating conditions.

why certain molecularly enhanced heterogeneous catalysts have improved performance; from there we speculate regarding new directions that could potentially result in further improvements in molecularly enhanced heterogeneous CO_2RR.

Materials for molecular-enhanced CO_2RR

We introduce molecular-additive-modified heterogeneous catalysts, immobilized organometallic complex catalysts, reticular chemistry-based MOF and COF catalysts, and polymer-based metal-free catalysts as materials for molecular-enhanced CO_2RR. Examples for each strategy are summarized in Fig. 2 and Table 1.

Molecular-additive-modified heterogeneous catalysts. Electrochemical CO_2RR is complex, with multiple proton-coupled electron transfer reactions depending on the nature of the product. It has been proposed that the overpotential is determined by the binding energies of intermediates associated with each of the multiple reaction steps along the pathway[14] (Fig. 3). To move in the direction of programming reaction outcome, it is important to understand the relationship between the intermediates in proposed reaction pathways[15–18]. Lowering overpotentials is difficult because the binding energy of one intermediate is typically correlated to others through thermodynamic scaling relations. Scaling relations are established by *d*-band theory, originating from the interaction between adsorbed intermediate and metal *d*-states[12]. For decreased overpotential and enhanced product selectivity of CO_2RR, strategies are required to break scaling relations and control the direction of reaction pathways toward a specific product.

It has been proposed that organic additives or coatings, such as cysteamine[19], thiols[19,20], amine[20,21], polypyrrole[22], *N*-heterocyclic carbenes (NHCs)[23], 4-pyridylethylmercaptan (4-PEM)[24], glycine[25] and *N*-substituted tetrahydro-bipyridine[26,27], may control the binding energy of CO_2RR intermediates such as *COOH, *CO and *HCOO (Fig. 2a). These reports suggest that tuning the organics to impart desired selectivities is possible. Further studies addressing structure–function correlations are needed for improved control and for accessing new reaction products.

Molecular-additive-modified heterogeneous catalysts have been investigated for the CO_2-to-CO electroconversion, where the reaction pathway is affected by altering the binding energies of *COOH and *CO intermediates (Fig. 3a)—both are supposed to be critical intermediates along the CO pathway. For instance, it has been proposed, with support from density functional theory (DFT) studies, that anchoring cysteamine molecules to Ag nanoparticles (NPs) leads to an increase of the unpaired electron localization at the surface of the NPs[19]. This is believed to result in preferential

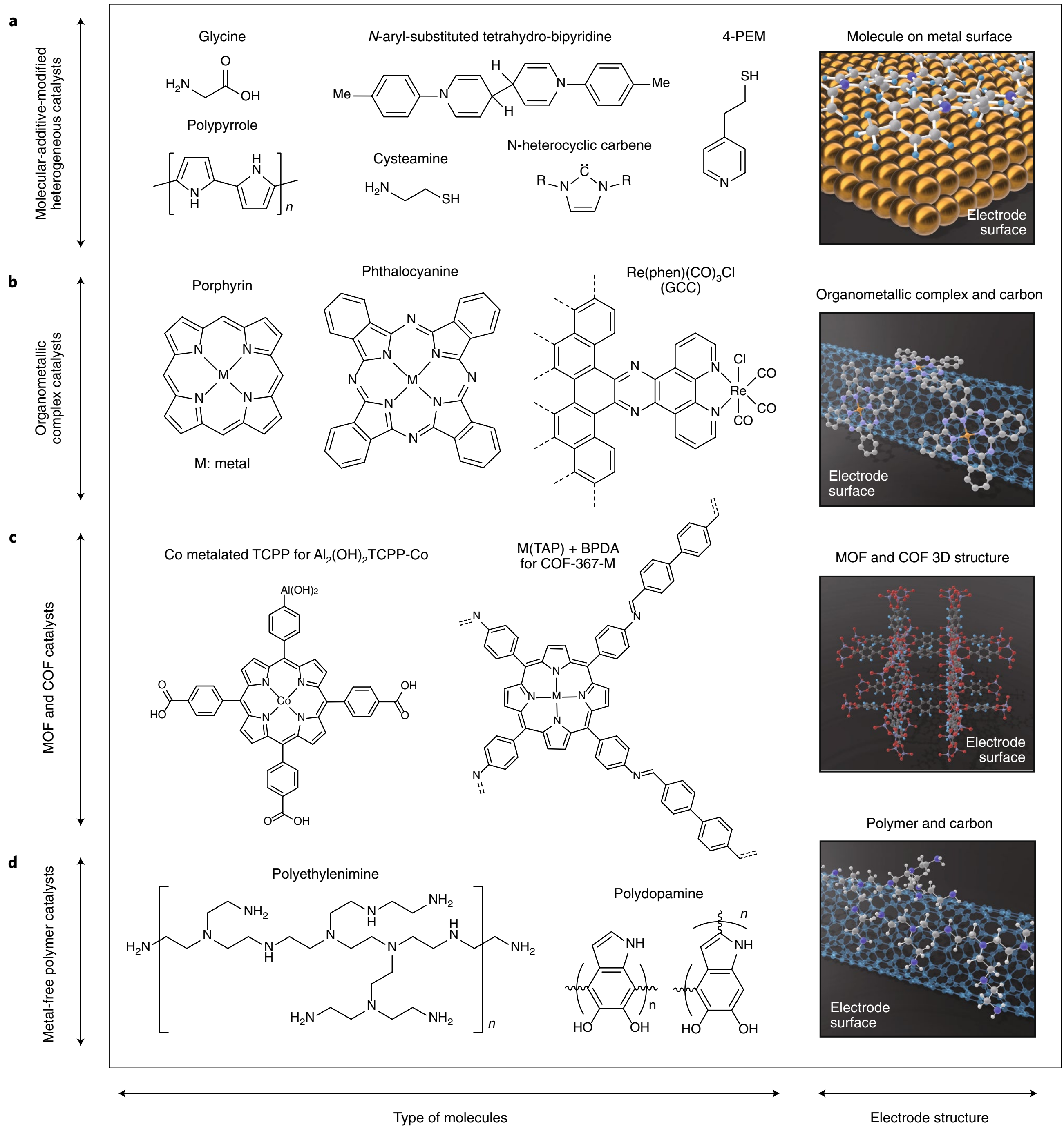

Fig. 2 | Classification of molecularly enhanced heterogeneous CO$_2$RR electrocatalysts. a, Molecular-additive-modified heterogeneous catalysts. **b**, Immobilized organometallic complex catalysts. **c**, MOF and COF catalysts. **d**, Metal-free polymer catalysts.

stabilization of the *COOH intermediate at the Ag surface, while the *CO binding energy is proposed to be less affected[19]. A similar strategy was further applied to Ag NPs modified by amine-capped cysteamine[20].

Functionalization of heterogeneous surfaces using molecular additives has also been shown to tune C$_1$ product selectivity via control over the binding energy of *COOH and *HCOO intermediates, which are proposed by DFT calculations to steer reaction pathways toward CO and HCOO$^-$ (HCOOH), respectively (Fig. 3a)[23,24]. For example, it has been suggested that the chelating NHC ligands bound to a Pd electrode can make an electron-rich Pd surface via the strong σ-donation from the NHCs ligands to Pd, favouring the formation of HCOO$^-$ product (Fig. 3a)[23]. In another approach, it was proposed that—by matching the pKa (proton donating ability) with CO$_2$RR product selectivity—self-assembled monolayers (SAMs) of 4-PEM can facilitate proton transfer from the ligand to CO$_2$ (ref. [24]).

Beyond C$_1$ products, organic functionalization of metal catalysts has also been employed to tune selectivities towards multicarbon products. For C$_{\geq 2}$ products, lowering the activation energy of CO–CO dimerization is proposed to be necessary to switch C$_1$ pathways to C$_2$ pathways (Fig. 3b). One demonstration of this tuning is the modification of Cu surfaces with an electrodeposited tetrahydro-bipyridine film generated from the reductive

Table 1 | CO_2RR performance of molecular-additive-modified heterogeneous catalysts, organometallic complex catalysts, 3D reticular catalysts and polymer-based metal-free catalysts.

Approach	Material	Product FE (%)						Electrolyte	*E* versus RHE (V)	Ref.
		H_2	CO	CH_4	$HCOO^-$	C_2H_4	C_2H_5OH			
Molecular additive modified heterogeneous catalysts	Pd		23		3			0.5 M $KHCO_3$	−0.57	[23]
	Pd + timtmb Me (NHC)		4		82			0.5 M $KHCO_3$	−0.57	
	Cu	42.8	1.7	20.2	4.7	12.4	7.2	0.1 M $KHCO_3$	−1.1	[26]
	Cu + tetrahydro-bipyridine	15.5	1.8	1.0	6.5	40.5	30.6	0.1 M $KHCO_3$	−1.1	
	Au		52					0.1 M $KHCO_3$	−0.7	[21]
	Au + OLA		73					0.1 M $KHCO_3$	−0.7	
	Co-C	95	5					0.1 M $KHCO_3$	−0.6	[22]
	Co-C + PPy	8	80					0.1 M $KHCO_3$	−0.6	
	Au	50	34		12.5			0.1 M $KHCO_3$	−1.02	[24]
	Au + 4-PEM	47	14		22.5			0.1 M $KHCO_3$	−1.05	
	Ag/C + OLA		92.6					0.5 M $KHCO_3$	−0.75	[20]
	Ag/C + OA		87.8					0.5 M $KHCO_3$	−0.75	
	Cu NW	76.2	0.7			5.9		0.1 M $KHCO_3$	−1.2	[25]
	Cu NW + Glycine	52.2	0.9			12.7		0.1 M $KHCO_3$	−1.2	
	Ag		70					0.5 M $KHCO_3$	−1.1	[19]
	Ag + Cysteamine		83					0.5 M $KHCO_3$	−0.72	
Organometallic catalysts	Cu phthalocyanine + CNT	34		66				0.5 M $KHCO_3$	−1.06	[35]
	Co phthalocyanine + CN + CNT	3.3	98					0.1 M $KHCO_3$	−0.63	[37]
	Mn (bipyridine) + CNT	45	35					0.5 M $KHCO_3$	−1.1	[34]
	Cu porphyrin + C		10	27	17			0.5 M $KHCO_3$	−0.976	[32]
	Co protoporphyrin + graphite		60					0.1 M $HClO_4$	−0.6	[36]
MOF/COF catalysts	HKUST-1	7	24			45		1 M KOH	−1.97	[53]
	ZIF-8-Zn$(NO_3)_2$		65					0.5 M NaCl	−1.8 (versus SCE)	[81]
	COF-M-Co	12	88					0.5 M $KHCO_3$	−0.86	[50]
	Co porphyrin MOF	24	76					0.5 M $KHCO_3$	−0.7	[48]
Metal-free polymer catalysts	Polydopamine	12	7		77			0.1 M TBA-PF_6	−0.86 (versus NHE)	[54]
	Polyethylenimine				87			0.1 M $KHCO_3$	−1.8 (versus SCE)	[57]

OLA, oleylamine; PPy, polypyrrole; 4-PEM, 4-pyridylethylmercaptan; OA, oleic acid; TBA-PF_6, Tetrabutylammonium hexafluorophosphate.

coupling of *N*-arylpyridinium salts, which lowers the partial current densities for H_2 and CH_4, and increases selectivity for $C_{\geq 2}$ products[26]. The modification of Cu surface with glycine is reported also to enhance C_2 hydrocarbon production compared with the case of bare Cu (Table 1)[25].

Surface modification of electrodes with organic compounds is a simple, inexpensive and versatile approach to tune the selectivity profile of CO_2RR. Acquiring an increasingly detailed understanding of the interactions with the electrode and CO_2RR substrate/intermediates is especially important. In particular for Cu, several theoretical reports suggest that tuning the adsorption energy of *CCH and/or *CHCHOH intermediates allows control over selectivity between C_2H_4 and C_2H_5OH (Fig. 3b). The added degree of freedom by organic modification of Cu electrodes can potentially be impactful

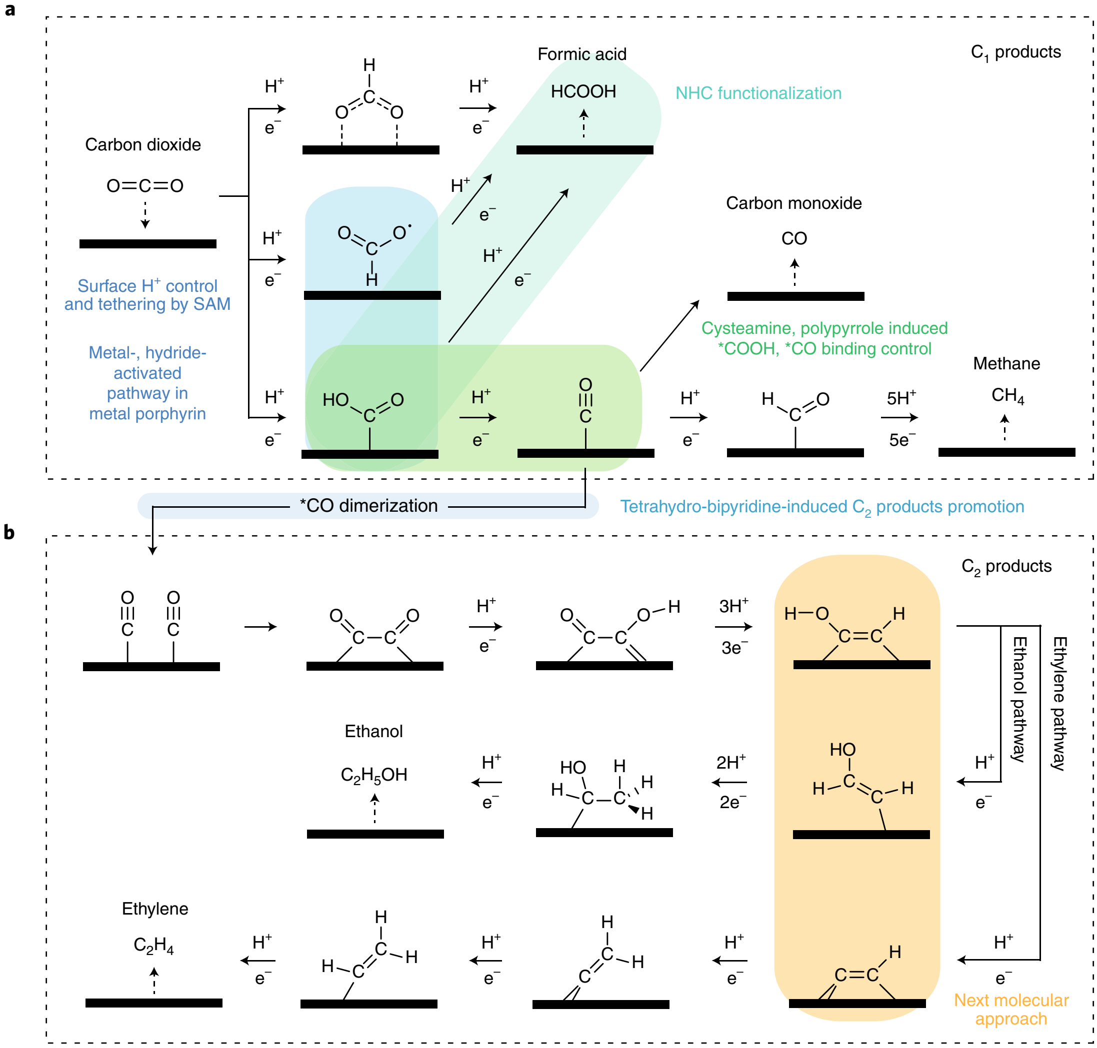

Fig. 3 | Examples of action modes of molecular approaches on heterogeneous CO_2RR catalysts. Theoretical CO_2 reduction mechanism with the proposed role of molecular additives in the stabilization of certain adsorbed intermediates[15–18]. **a**, Reaction pathway for C_1 products (carbon monoxide, formic acid, methane) impacted by the types of molecular additives highlighted via the coloured text[19–24,31]. **b**, Reaction pathway for C_2 products (ethylene, ethanol) impacted by a film of tetrahydro-bipyridine from an electrodeposited *N*-substituted pyridinium additive[26]. Figure adapted with permission from ref. [15], American Chemical Society; ref. [16], American Chemical Society; ref. [17], American Chemical Society; and ref. [18], Springer Nature Ltd.

to tune C_2 product selectivities. We envisage, beyond the above theoretical proposals or rationalizations, that the role of the molecular additives needs to be investigated further experimentally, such as by detecting CO_2RR intermediates using in situ/operando spectroscopies such as Raman, X-ray photoelectron spectroscopy (XPS) and surface enhanced infrared absorption spectroscopy (SEIRAS). Recently, the effect of an *N*-arylpyridinium-derived molecular-additive layer on the Cu electrode has been investigated by using SEIRAS during CO_2RR[28]. It has been revealed that the molecular-additive layer can control the pH gradient or block the active sites according to the chemical structure of the *N*-arylpyridinium group. This approach will provide more insight to the research community.

Immobilized organometallic complex catalysts. Organometallic complexes, whose design is inspired by metalloenzyme active sites, such as those in CO dehydrogenase (CODH), feature a metal centre supported by a ligand framework that tunes the reactivity of the metal by affecting its local environment[29]. The ligand and metal centre affect the complex's catalytic properties by the tuning of molecular geometry, electronic states and intermediate binding, as well as the second coordination sphere interactions, such as hydrogen bonding and electrostatic interactions[30,31]. Immobilization strategies have been investigated for a wide range of metal complexes, including ligand platforms such as porphyrins[32], bipyridines[33,34], cyclams[35], protoporphyrin[36] and phthalocyanine[37] (Fig. 2b).

Porphyrin- and phthalocyanine-based organometallic complexes have been studied as effective homogeneous catalysts for CO_2RR in organic media[4]. The immobilization of these molecular catalysts enables CO_2RR in aqueous media. For instance, a hybrid material composed of Co phthalocyanine (CoPc) complexes anchored on carbon nanotubes (CNTs) performed the selective electroreduction of CO_2 to CO with FE over 90% in aqueous potassium bicarbonate ($KHCO_3$) solution, showing a turnover frequency of 2.7 s^{-1} and a 10-h stability[37]. Interestingly, beyond CO production, the immobilized Co protoporphyrin systems are also able to produce a trace amount of more reduced products such as CH_4 at lower pH[36].

With the aim of obtaining more reduced products, researchers have also explored Cu-based coordination compounds. For instance, when a Cu phthalocyanine (CuPc) complex was supported on multi-walled CNTs, the resulting hybrid material displayed a FE of 66% for the production of CH_4 in aqueous electrolyte[35]. In situ X-ray absorption spectroscopy (XAS) studies suggest that the CuPc undergoes reversible structural and redox changes to form small, metallic copper particles with a size of ~2 nm. The molecular species appears to serve as a precursor to form Cu(0) that is the presumed active catalyst for CO_2RR.

Organometallic complexes are usually immobilized onto support materials (for example, graphite, graphene and CNTs) via interactions such as covalent bonding, π–π stacking interactions, electropolymerization and grafting[13,33]. In these hybrid systems, the electrochemical and catalytic behaviours of the immobilized metal catalyst resemble that of the corresponding homogeneous species, though some shifts of redox processes are often observed. The immobilized complexes act as the redox-active centres that mediate the activation of substrate (for example, CO_2) via their own oxidation or reduction processes. This behaviour is likely to be due to the weak electronic communications between the immobilized metal catalyst and the support, resulting in a tunnelling barrier to electron transfers in these systems.

In contrast, the Surendranath group has recently reported molecular catalysts electronically linked to a graphitic electrode through conjugated aromatic pyrazine linkages. The authors found distinct electron transfer behaviours compared with those observed in weakly-immobilized systems[38,39]. Unlike homogeneous molecular catalysts with stepwise electron transfer and substrate activation, this graphite conjugated catalyst (GCC) induces concerted electron transfer and substrate activation[38]. The conductive pyrazine linkages also provide strong electronic coupling that minimizes the potential drop between the electrode and the metal complex.

The metal active site in GCCs exists inside the electrical double layer. As the Fermi energy level of electrode (E_F) is shifted, the redox potential of the metal active centre is shifted together and there is no change in the driving force for electron transfer between graphite and metallic active centre in GCCs. No outer-sphere electron transfer or reduction of metal active centre is observed in GCCs[38,39]. A potential drop between the GCC site and the solution was found, which induces ion transfers coupled with electron transfers between them[38]. The applied potential modulates the driving force for substrate activation[39,40].

The electrolyte environment also has an effect on the catalytic behaviours of the immobilized molecular catalysts. In CO_2RR using bicarbonate (HCO_3^-) electrolyte, there exists an equilibrium of CO_2 (aq) + $H_2O \leftrightarrow H^+$ (aq) + HCO_3^- (aq)[13]. It has been reported that CO_2RR using organometallic complexes with weak electronic coupling, such as CoPc on CNT, relies on both electron transfer and an ion–electron transfer step[13,41]. In low [HCO_3^-], electron transfer induces reduction from Co(II) to Co(I) and COO^- adsorption at the Co centre. In high [HCO_3^-], coupled ion–electron transfer becomes a rate-determining step, and HCO_3^- acts as a proton donor. CO_2RR of GCCs is expected to proceed with coupled ion–electron transfer for substrate activation. It has been reported that strong electronic coupling enhances turnover frequency compared to weak electronic coupling[40].

An emerging class of materials that is receiving significant attention is single-atom catalysts (SACs). N-doped conducting carbon materials can provide a matrix for SACs where discrete metal centres are embedded within the N ligand field, mimicking the local environment of metallic centres in organometallic complexes[42]. SACs have proven to be successful materials to perform CO_2RR at lower overpotentials with high efficiencies for C_1 products. An example of DFT modelling has proposed that N-coordinated active metal centre promotes *COOH binding, leading to a high selectivity for C_1 products[43]. The pyrolysis of MOF materials has also been employed for the fabrication of SACs, which has allowed for a fine control of the spatial separation among metal atomic sites with N coordination[44]. In SACs, the metal atomic centre is directly incorporated within the carbon support, and these are expected to be close to the case of strong electronic coupling. Investigating the oxidation states of the metal active centre by operando XAS will be helpful to understand the electronic coupling in SACs[45]. Further research on CO_2RR mechanistics in the context of SACs is required.

Related to molecular catalyst heterogenization, the immobilization of enzymatic catalysts represents a related emerging strategy for electrochemical CO_2RR. The potential for high selectivity and specificity for complex products at low applied bias is an important advantage of biocatalysts[46]. Increasing CO_2RR selectivity and activity for highly reduced products, accessing alternative reduction products, and increasing the stability of the protein under electrochemical conditions and electrolyte pH, are current challenges in this area.

Reticular chemistry-based MOFs and COFs catalysts. Reticular chemistry provides access to three-dimensional (3D) porous materials that can immobilize molecular catalysts at well-defined positions. MOFs (organic linkers and metal nodes) and COFs (covalently connected organic molecules) exhibit properties such as high surface area, tunable porosity, diversity in metal and functional groups, confinement effects and periodic metal arrangements[47]. These properties make MOFs and COFs attractive for use as catalysts. These reticular systems have several properties suitable for their use as catalysts in CO_2RR[47,48]. Coordinatively unsaturated metal sites, functionalized organic linkers and periodic defects may all serve as active sites[49]. Certain MOFs and COFs can be integrated without immobilization anchoring materials. They promote the uniform distribution of the metal active centre without agglomeration (Fig. 2c). Because of their inherent pore confinement properties, these can induce local CO_2 concentration enhancement and this may allow for CO_2RR catalysis in dilute CO_2 environments.

Porphyrin-based MOFs and COFs have been widely investigated as CO_2RR electrocatalysts for C_1 products[48,50]. Co-metalated porphyrin-based Al-MOFs ($Al_2(OH)_2$TCPP-Co) exhibit high CO selectivity and activity, in which Co(I), formed by the reduction of Co(II) during CO_2RR, is supposed to be the formal catalytic active site[48]. In another example, Co-metalated porphyrin-based COFs exhibit FE values up to 90% for CO with a turnover frequency of 9,400 h^{-1} (ref. [50]). By exploiting a layer-by-layer MOF synthesis, two-dimensional (2D) MOF thin films on substrates have been studied, and reticular chemistry used to control the preferred orientation of the MOF[51,52].

Recently, it was revealed that undercoordinated Cu sites in HKUST-1 could be afforded by detaching the carboxylate moieties. According to the degree of thermal calcination at a specific temperature, the degree of Cu dimer distortion towards an asymmetric structure was controlled. This Cu dimer control in the secondary building unit induced the formation of coordinate structure-controlled Cu clusters. Distortion of the Cu dimer resulted in the formation of Cu clusters with lower Cu–Cu coordination numbers, and an overall catalyst material that exhibited a C_2H_4 FE of 45%[53].

Despite these initial promising results, research on MOFs and COFs CO_2RR electrocatalysts is still nascent and currently shows relatively lower current density than conventional metal heterogeneous catalysts. A major challenge for MOFs is their low electrical conductivity, which limits the ability for charges to be carried to the active sites within the periodic structure. Continued efforts to enhance electrical conductivity, robustness under high pH electrolyte, durability at negative reduction potential, generation of $C_{\geq 2}$ products, and substrate interfacing are needed for MOF and COF catalysts to rival the performance of state-of-the-art heterogeneous electrocatalysts. As efforts to address the limitations presented above continue, MOF and COF materials will be an attractive platform for the next generation of CO_2RR electrocatalysts[47].

Polymer-based metal-free catalysts. Metal-free conjugated and conductive polymers have been used directly as CO_2RR electrocatalysts[54–56]. Semiconducting polymers, such as polypyrrole

(62% for CH_3COOH, 41% for HCOOH and 2% HCHO) and polyaniline (78% for CH_3COOH and 12% for HCOOH), were applied as heterogeneous electrocatalysts using a $CH_3OH/LiClO_4/H^+/H_2O$ electrolyte[55,56]. It was proposed that CO_2 adsorption occurs via hydrogen bonding interactions. Polydopamine (PDA), which contains significantly more hydrogen bonding sites per repeating unit, has shown selectivity for C_1 products[54] (Fig. 2d). It was proposed that these conductive polymers activate CO_2 sequentially at the carbonyl and amide groups. This catalyst exhibited CO FE over 80% and showed stability over 16 h in non-aqueous electrolytes[54]. In another example, the amine moieties of polyethylenimine was proposed to stabilize CO_2RR intermediates via hydrogen bonding interactions and therefore promote CO_2-to-$HCOO^-$ conversion on N-doped CNT[57] (Fig. 2d). Adsorbed CO_2 is reduced to $CO_2^{\bullet-}$ at the N site, and stabilized via hydrogen bonding in polyethylenimine. It has been proposed that bonded $CO_2^{\bullet-}$ is protonated and forms $HCOO^-$ (ref. [57]).

Graphene and CNTs have been actively studied as different types of metal-free carbon-based CO_2RR electrocatalysts. Studies related to catalytic activity as a function of N doping (pyridinic, graphitic, pyrrolic N) and B doping have been carried out, and most have shown the production of CO and $HCOO^-$ to be favoured (graphitic N-doped CNT: 90% for CO[58], N-doped graphene: 73% for $HCOO^-$ (ref. [59])). It has been reported that N-doped graphene quantum dots, which contain a higher density of pyridinic N-edge sites, exhibited 31% C_2H_4 FE[60]. DFT calculations point to the importance of N-doped edges in converting CO_2 into C_2 products[61]. Research in carbon-based materials should be cautious, because trace metals such as Ni, Fe, Mn and Cu can be present as impurities in carbon-based materials such as graphite, graphene oxide and CNTs. Specifically, Cu in graphene oxide has been reported to promote CH_4 formation in CO_2RR[62]. Furthermore, by taking advantage of the reduction of dissolved Cu ions in the electrolyte, CH_4 production can be optimized[62]. This reveals that trace metals, even at low concentrations, can be effective in tuning the CO_2RR activity of carbon-based materials.

Metal-free catalysts for CO_2RR are appealing given the low-cost of such materials and the potential diversity of structure and reactivity available. However, challenges include the synthesis of well-defined, functionalized polymers suitable for structure–function studies to gain insight into the mechanism(s) of CO_2RR. Features that would be of interest to explore in this context are the molecular weight, dispersity and monomer content of the polymer[63]. This could be achieved, for example, by targeting bifunctional copolymers made of semiconducting blocks for electron delivery and blocks designed to activate CO_2 through weak secondary interactions.

Future directions and strategies

Here we turn to new approaches that rely on the molecular enhancement of heterogeneous catalysts to address challenges in CO_2RR. Activity amplification and product selectivity increase are essential for practical applications. A significant aspect in the implementation of these molecular approaches is the need for systematic structure–function studies that provide insight into the nature of the active species and mechanism(s) of catalysis. These studies are essential for the rational improvement of the catalyst systems.

Second coordination sphere interactions. With inspiration from enzyme active sites, control of interactions of intermediates with groups in close proximity can increase activity and selectivity for CO_2RR[64]. Secondary coordination sphere interactions with motifs such as pendant amine donors[65], hydrogenase mimics[66] and hangman porphyrins[67] have received attention for electrocatalysts. Designing pendant groups that can engage as hydrogen bonding and Lewis acid interactions is expected to have significant effects on catalysis (Fig. 4a). Lewis acids can help to shift the redox potential for CO_2RR by promoting CO_2 binding and activation[9]. In Fig. 4b, solid-state structure (left, protein data bank (PDB): 4UDX) and schematic representation (right) of the CO_2-bound NiFe-CODH active site explain the role of different interactions in CO_2 activation: redox active metal, Lewis acidic metal and hydrogen bonding with functionalized pendant groups[64]. The correct positioning of groups that can interact with intermediates in CO_2RR relative to the electrode surface is a significant challenge for this approach, but will be instrumental for reactivity.

Tandem catalysis. Coupling of multiple catalysts that perform successive steps in CO_2RR has been employed in molecular systems[68]. This approach can be used to perform CO_2RR to CO at more positive potentials with a molecular catalyst, followed by subsequent reduction of CO to multi-carbon products on a Cu electrode. Overall, such an approach provides access to a system that performs the reduction of CO_2 to $C_{\geq 2}$ species with lower overpotentials[69]. Alternatively, a molecular catalyst could be employed to perform orthogonal chemistry (Fig. 4c). For example, the catalytic dimerization or oligomerization of C_2H_4 could result in a C_4, C_6 or a statistical distribution of C_{2n} olefins, depending on the type of catalyst employed[70] (Fig. 4d). A Ni-based MOF has been applied for carbon upgrading from C_2H_4 to 1-butene (C_4H_8) (ref. [71]). Access to catalysts for tandem chemistry that are compatible with electrochemistry on Cu may represent a significant opportunity.

Control of proton inventory. The chemistry of CO_2 in aqueous systems has the additional complication of non-redox reactivity due to the pH-dependent equilibrium among dissolved CO_2, HCO_3^-, and carbonate (CO_3^{2-}). Although a neutral pH electrolyte is advantageous to avoid carbonate formation, $C_{\geq 2}$ production on Cu electrodes is favoured in microenvironments in which the pH is high[72], which limits the concentration of protons at the electrode and translates to more C–C coupling chemistry. Therefore, in addition to electron transfer, an important aspect of controlling the selectivity profile of CO_2RR is proton transfer[73,74] (Fig. 4e). For example, DFT calculations offer an explanation of how pH determines C_1 and C_2 product pathways at the well-defined Cu (111) surface[72] (Fig. 4f). In real catalysts, the electrode surface structure, as well as mass transport, will affect CO_2RR, and computational insight needs to be accompanied by further experiment investigations. This approach has already been proven to be effective for controlling proton transfer in the oxygen reduction reaction with supported molecular Cu electrocatalysts within a hybrid bilayer membrane[75]. Analogously, a membrane-like layer generated by molecular additives on Cu could control the flow of protons and thereby improve CO_2RR selectivity for $C_{\geq 2}$ products. A challenge here will be the development of appropriate preparation methodologies to avoid blocking of active sites on the Cu catalyst.

Selective inhibition. Molecular additives can serve as promoters of certain reaction pathways or as inhibitors. Towards targeting $C_{\geq 2}$ products, selective inhibitors for the generation of CH_4 and other C_1 by-products are desirable (Fig. 4g). For example, electrodes modified by deposited films of tetrahydro-bipyridine molecules with low steric hindrance in the *para* position of the phenyl ring (flat structure; Fig. 4h) have been shown to enhance CO_2RR towards $C_{\geq 2}$ products, while *tert*-butyl substitution increases H_2 generation and decreases $C_{\geq 2}$ products[26]. This shows that the steric profile of the pyridinium additive can affect the CO_2RR product reaction pathway[26]. Proposed mechanisms for the effect on selectivity include selective inhibition of sites primarily responsible for CH_4 formation, the activation of sites responsible for $C_{\geq 2}$ formation, and inhibition of proton transfer (via a pH gradient). The development of a range of additives that result in low C_1 production, as well as more detailed insights into the fundamental basis of such selectivity, remain areas of much interest.

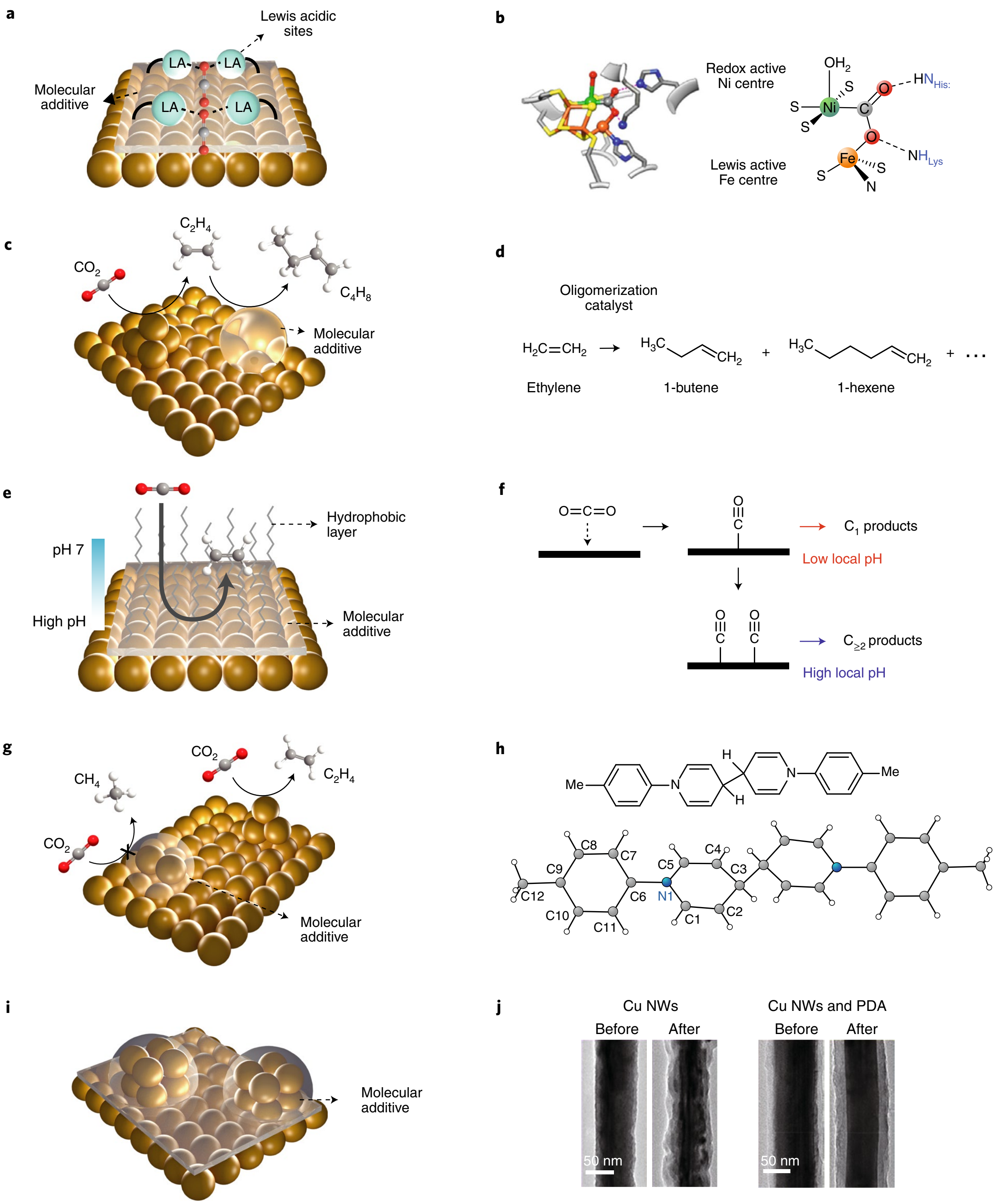

Fig. 4 | Future challenges for molecular strategies. a, Second coordination sphere interaction. **b**, Schematic of a multi-metallic metalloenzyme active site with secondary sphere interactions. **c**, Tandem catalyst for a multi-carbon product. **d**, Example of ethylene oligomerization. **e**, Control of proton inventory during electrochemical CO_2RR. **f**, CO_2RR pathway according to local pH. **g**, Selective inhibition of undesired products. **h**, Example of a molecular additive that forms a film on a copper electrode for selective inhibition of methane and hydrogen. **i**, Stabilization of surface morphology of the electrode by molecular additive. **j**, Example of polydopamine-based stability enhancement of Cu. Figure reproduced with permission from ref. [64], American Chemical Society (**b**); ref. [82], Elsevier (**d**); and ref. [72], American Chemical Society (**f**); and adapted with permission from ref. [26], American Chemical Society (**h**); and ref. [76], Wiley (**j**).

Stabilization of electrode microstructure. It has been established that certain Cu crystal facets and morphologies favour $C_{\geq 2}$ products[3]. Surface reorganization during electrocatalysis can affect CO_2RR selectivity. Molecular additives and coatings may serve as ligands to stabilize the surface of the electrode against severe reconstruction[27] (Fig. 4i). When the Cu surface was functionalized with polydopamine, surface reorganization was prevented during CO_2RR (Fig. 4j). Polydopamine led to highly stable CO_2RR to CH_4 by Cu over 14 h without a decrease in current density, while CO_2RR by bare Cu ceased within 3 h (ref. [76]). Amine groups in polydopamine may assist in the protonation of *CO at the Cu surface. Polymer-based metal surface modification thus can contribute not only to stability, but also to high selectivity towards the formation of specific CO_2RR products. Furthermore, for the utilization of discrete Cu active sites displaying mononuclear, dinuclear Cu or oxo-bridged Cu in CO_2RR, the development of robust molecular catalysts is desirable for both practical applications and mechanistic studies.

Challenges

At present, most mechanistic studies regarding the role of organic molecules and metal complexes on electrode surfaces are based on the binding energy between intermediates and the electrode surface, and rely on calculation. To deepen understanding of CO_2RR among molecularly enhanced heterogeneous catalysts, fundamental studies of the electrochemical electrode/electrolyte interface, electron transfer kinetics and mass transport of chemical species such as CO_2 (aq), HCO_3^-, CO_3^{2-} and OH^- near the electrode require experimental elucidation[77,78]. There is a lack of knowledge about the effect of surface coverage and electroactive surface area of molecularly enhanced electrodes as well as the chemical state and the real structure of organic molecules and metal complexes during CO_2RR. Investigating the effects of such molecular approaches on heterogeneous catalysts should take into account electron–proton coupled/decoupled pathways, the surface structure of modified electrodes, the interfacial electric field and transport limitations imposed by the surface molecular layer.

Given the complexity of these systems, gaining fundamental insight into their function is likely to require concerted multidisciplinary efforts including areas of catalysis, synthesis, spectroscopy and theory. There exist challenges related to lifetime, activity, selectivity and identity of the active sites. While the ability to tailor the microenvironment (the local environment near the metal active site) of hybrid catalyst structures may lead to improved selectivities and rates through carefully designed interactions, a major concern of such structures is that they can degrade/evolve such that the original rational design has been lost[79]. For the stability of heterogenized molecular catalysts, aggregation, leaching and demetallation must be prevented[13]. Covalent grafting of organometallic complexes on electrode surfaces can enhance their stability and performance[80]. Research on heterogenized molecular catalyst stability will benefit from in situ/operando spectroscopy. In particular, in situ/operando XAS provides a probe of oxidation states and the local coordination environment of the metal centre in an organometallic complex, and MOF and COF heterogeneous catalysts during reaction. ^{13}C labelling experiments must be performed to ensure that the reduced carbon products are derived from CO_2 rather than via degradation of the catalyst or additives. Conductivity is another major challenge that needs to be addressed. Molecular-based approaches can only be effective if the electron can travel from the conductive substrate to the tailored active site.

Conclusion and outlook

This Perspective has highlighted the potential of applying molecular strategies to enhance heterogeneous electrochemical CO_2RR. These strategies can, at least in principle, offer precise control of catalyst active sites. The use of well-defined organic molecules and metal complexes for metal surface modification can alter the binding energy of CO_2RR intermediates, and thereby lead to product selectivity control by breaking scaling relations. A distinct advantage of molecular enhancement approaches is that structure–function relationships can be more precisely defined. Such relationships can provide mechanistic insights essential to rational catalyst improvement. Molecularly enhanced heterogeneous CO_2RR catalysts offer the potential to overcome major challenges in tunability and stability as a frontier opportunity for CO_2RR electrocatalysis.

Received: 16 January 2019; Accepted: 8 January 2020;
Published online: 25 February 2020

References

1. Hori, Y. In *Modern Aspects of Electrochemistry* (eds. Vayenas, C. G., White, R. E. & Gamboa-Aldeco, M. E.) 89–189 (Springer, 2008).
2. Thang-Dinh, C. et al. CO_2 electroreduction to ethylene via hydroxide-mediated copper catalysis at an abrupt interface. *Science* **360**, 783–787 (2018).
3. Nitopi, S. et al. Progress and perspectives of electrochemical CO_2 reduction on copper in aqueous electrolyte. *Chem. Rev.* **119**, 7610–7672 (2019).
4. Benson, E. E., Kubiak, C. P., Sathrum, A. J. & Smieja, J. M. Electrocatalytic and homogeneous approaches to conversion of CO_2 to liquid fuels. *Chem. Soc. Rev.* **38**, 89–99 (2009).
5. Qiao, J., Liu, Y., Hong, F. & Zhang, J. A review of catalysts for the electroreduction of carbon dioxide to produce low-carbon fuels. *Chem. Soc. Rev.* **43**, 631–675 (2014).
6. Cui, X., Li, W., Ryabchuk, P., Junge, K. & Beller, M. Bridging homogeneous and heterogeneous catalysis by heterogeneous single-metal-site catalysts. *Nat. Catal.* **1**, 385–397 (2018).
7. Copéret, C. et al. Bridging the gap between industrial and well-defined supported catalysts. *Angew. Chem. Int. Ed.* **57**, 6398–6440 (2018).
8. Armstrong, F. A. & Hirst, J. Reversibility and efficiency in electrocatalytic energy conversion and lessons from enzymes. *Proc. Natl Acad. Sci. USA* **108**, 14049–14054 (2011).
9. Fesseler, J., Jeoung, J.-H. & Dobbek, H. How the [$NiFe_4S_4$] cluster of CO dehydrogenase activates CO_2 and NCO^-. *Angew. Chem. Int. Ed.* **54**, 8560–8564 (2015).
10. Thomas, J. M., Raja, R. & Lewis, D. W. Single-site heterogeneous catalysts. *Angew. Chem. Int. Ed.* **44**, 6456–6482 (2005).
11. Singh, M. R., Kwon, Y., Lum, Y., Ager, J. W. & Bell, A. T. Hydrolysis of electrolyte cations enhances the electrochemical reduction of CO_2 over Ag and Cu. *J. Am. Chem. Soc.* **138**, 13006–13012 (2016).
12. Li, Y. & Sun, Q. Recent advances in breaking scaling relations for effective electrochemical conversion of CO_2. *Adv. Energy Mater.* **6**, 1600463 (2016).
13. Corbin, N., Zeng, J., Williams, K. & Manthiram, K. Heterogeneous molecular catalysts for electrocatalytic CO_2 reduction. *Nano Res.* **12**, 2093–2125 (2019).
14. Peterson, A. A. & Nørskov, J. K. Activity descriptors for CO_2 electroreduction to methane on transition-metal catalysts. *J. Phys. Chem. Lett.* **3**, 251–258 (2012).
15. Kortlever, R., Shen, J., Schouten, K. J. P., Calle-Vallejo, F. & Koper, M. T. M. Catalysts and reaction pathways for the electrochemical reduction of carbon dioxide. *J. Phys. Chem. Lett.* **6**, 4073–4082 (2015).
16. Xiao, H., Cheng, T. & Goddard, W. A. Atomistic mechanisms underlying selectivities in C_1 and C_2 products from electrochemical reduction of CO on Cu(111). *J. Am. Chem. Soc.* **139**, 130–136 (2017).
17. Lum, Y., Cheng, T., Goddard, W. A. & Ager, J. W. Electrochemical CO reduction builds solvent water into oxygenate products. *J. Am. Chem. Soc.* **140**, 9337–9340 (2018).
18. Liu, X. et al. pH effects on the electrochemical reduction of $CO_{(2)}$ towards C_2 products on stepped copper. *Nat. Commun.* **10**, 32 (2019).
19. Kim, C. et al. Achieving selective and efficient electrocatalytic activity for CO_2 reduction using immobilized silver nanoparticles. *J. Am. Chem. Soc.* **137**, 13844–13850 (2015).
20. Kim, C. et al. Insight into electrochemical CO_2 reduction on surface-molecule-mediated Ag nanoparticles. *ACS Catal.* **7**, 779–785 (2017).
21. Zhao, Y., Wang, C., Liu, Y., MacFarlane, D. R. & Wallace, G. G. Engineering surface amine modifiers of ultrasmall gold nanoparticles supported on reduced graphene oxide for improved electrochemical CO_2 reduction. *Adv. Energy Mater.* **8**, 1801400 (2018).
22. Mun, Y. et al. A novel strategy to develop non-noble metal catalyst for CO_2 electroreduction: Hybridization of metal-organic polymer. *Appl. Catal. B Environ.* **236**, 154–161 (2018).
23. Cao, Z. et al. Chelating N-heterocyclic carbene ligands enable tuning of electrocatalytic CO_2 reduction to formate and carbon monoxide: Surface organometallic chemistry. *Angew. Chem. Int. Ed.* **57**, 4981–4985 (2018).
24. Fang, Y. & Flake, J. C. Electrochemical reduction of CO_2 at functionalized Au electrodes. *J. Am. Chem. Soc.* **139**, 3399–3405 (2017).
25. Xie, M. S. et al. Amino acid modified copper electrodes for the enhanced selective electroreduction of carbon dioxide towards hydrocarbons. *Energy Environ. Sci.* **9**, 1687–1695 (2016).
26. Han, Z., Kortlever, R., Chen, H.-Y., Peters, J. C. & Agapie, T. CO_2 reduction selective for $C \geq 2$ products on polycrystalline copper with N-substituted pyridinium additives. *ACS Cent. Sci.* **3**, 853–859 (2017).
27. Thevenon, A., Rosas-Hernández, A., Peters, J. C. & Agapie, T. In-situ nanostructuring and stabilization of polycrystalline copper by an organic salt additive promotes electrocatalytic CO_2 reduction to ethylene. *Angew. Chem. Int. Ed.* **58**, 16952–16958 (2019).

28. Ovalle, V. J. & Waegele, M. M. Understanding the impact of N-Arylpyridinium ions on the selectivity of CO_2 reduction at the Cu/electrolyte interface. *J. Phys. Chem. C.* **123**, 24453–24460 (2019).
29. Francke, R., Schille, B. & Roemelt, M. Homogeneously catalyzed electroreduction of carbon dioxide—Methods, mechanisms, and catalysts. *Chem. Rev.* **118**, 4631–4701 (2018).
30. Chapovetsky, A. et al. Pendant hydrogen-bond donors in cobalt catalysts independently enhance CO_2 reduction. *ACS Cent. Sci.* **4**, 397–404 (2018).
31. Göttle, A. J. & Koper, M. T. M. Determinant role of electrogenerated reactive nucleophilic species on selectivity during reduction of CO_2 catalyzed by metalloporphyrins. *J. Am. Chem. Soc.* **140**, 4826–4834 (2018).
32. Weng, Z. et al. Electrochemical CO_2 reduction to hydrocarbons on a heterogeneous molecular Cu catalyst in aqueous solution. *J. Am. Chem. Soc.* **138**, 8076–8079 (2016).
33. Willkomm, J. et al. Grafting of a molecular rhenium CO_2 reduction catalyst onto colloid-imprinted carbon. *ACS Appl. Energy Mater.* **2**, 2414–2418 (2019).
34. Reuillard, B. et al. Tuning product selectivity for aqueous CO_2 reduction with a Mn(bipyridine)-pyrene catalyst immobilized on a carbon nanotube electrode. *J. Am. Chem. Soc.* **139**, 14425–14435 (2017).
35. Weng, Z. et al. Active sites of copper-complex catalytic materials for electrochemical carbon dioxide reduction. *Nat. Commun.* **9**, 415 (2018).
36. Shen, J. et al. Electrocatalytic reduction of carbon dioxide to carbon monoxide and methane at an immobilized cobalt protoporphyrin. *Nat. Commun.* **6**, 8177 (2015).
37. Zhang, X. et al. Highly selective and active CO_2 reduction electrocatalysts based on cobalt phthalocyanine/carbon nanotube hybrid structures. *Nat. Commun.* **8**, 14675 (2017).
38. Jackson, M. N. et al. Strong electronic coupling of molecular sites to graphitic electrodes via pyrazine conjugation. *J. Am. Chem. Soc.* **140**, 1004–1010 (2018).
39. Oh, S., Gallagher, J. R., Miller, J. T. & Surendranath, Y. Graphite-conjugated rhenium catalysts for carbon dioxide reduction. *J. Am. Chem. Soc.* **138**, 1820–1823 (2016).
40. Kaminsky, C. J., Wright, J. & Surendranath, Y. Graphite-Conjugation Enhances Porphyrin Electrocatalysis. *ACS Catal.* **9**, 3667–3671 (2019).
41. Zhu, M., Ye, R., Jin, K., Lazouski, N. & Manthiram, K. Elucidating the reactivity and mechanism of CO_2 electroreduction at highly dispersed cobalt phthalocyanine. *ACS Energy Lett.* **3**, 1381–1386 (2018).
42. Chen, Y. et al. Single-atom catalysts: Synthetic strategies and electrochemical applications. *Joule* **2**, 1242–1264 (2018).
43. Pan, Y. et al. Design of single-atom Co–N_5 catalytic site: A robust electrocatalyst for CO_2 reduction with nearly 100% CO selectivity and remarkable stability. *J. Am. Chem. Soc.* **140**, 4218–4221 (2018).
44. Sun, T., Xu, L., Wang, D. & Li, Y. Metal organic frameworks derived single atom catalysts for electrocatalytic energy conversion. *Nano Res.* **12**, 2067–2080 (2019).
45. Gu, J., Hsu, C.-S., Bai, L., Chen, H. M. & Hu, X. Atomically dispersed Fe^{3+} sites catalyze efficient CO_2 electroreduction to CO. *Science* **364**, 1091–1094 (2019).
46. Reda, T., Plugge, C. M., Abram, N. J. & Hirst, J. Reversible interconversion of carbon dioxide and formate by an electroactive enzyme. *Proc. Natl Acad. Sci.* **105**, 10654–10658 (2008).
47. Diercks, C. S., Liu, Y., Cordova, K. E. & Yaghi, O. M. The role of reticular chemistry in the design of CO_2 reduction catalysts. *Nat. Mater.* **17**, 301–307 (2018).
48. Kornienko, N. et al. Metal–organic frameworks for electrocatalytic reduction of carbon dioxide. *J. Am. Chem. Soc.* **137**, 14129–14135 (2015).
49. Jiao, L., Wang, Y., Jiang, H.-L. & Xu, Q. Metal–organic frameworks as platforms for catalytic applications. *Adv. Mater.* **30**, 1703663 (2017).
50. Lin, S. et al. Covalent organic frameworks comprising cobalt porphyrins for catalytic CO_2 reduction in water. *Science* **349**, 1208–1213 (2015).
51. Diercks, C. S. et al. Reticular electronic tuning of porphyrin active sites in covalent organic frameworks for electrocatalytic carbon dioxide reduction. *J. Am. Chem. Soc.* **140**, 1116–1122 (2018).
52. De Luna, P. et al. Metal–organic framework thin films on high-curvature nanostructures toward tandem electrocatalysis. *ACS Appl. Mater. Interfaces* **10**, 31225–31232 (2018).
53. Nam, D.-H. et al. Metal-organic frameworks mediate Cu coordination for selective CO_2 electroreduction. *J. Am. Chem. Soc.* **140**, 11378–11386 (2018).
54. Coskun, H. et al. Biofunctionalized conductive polymers enable efficient CO_2 electroreduction. *Sci. Adv.* **3**, e1700686 (2017).
55. Aydin, R. & Köleli, F. Electrocatalytic conversion of CO_2 on a polypyrrole electrode under high pressure in methanol. *Synth. Met.* **144**, 75–80 (2004).
56. Köleli, F., Röpke, T. & Hamann, C. H. The reduction of CO_2 on polyaniline electrode in a membrane cell. *Synth. Met.* **140**, 65–68 (2004).
57. Zhang, S. et al. Polyethylenimine-enhanced electrocatalytic reduction of CO_2 to formate at nitrogen-doped carbon nanomaterials. *J. Am. Chem. Soc.* **136**, 7845–7848 (2014).
58. Xu, J. et al. Revealing the origin of activity in nitrogen-doped nanocarbons towards electrocatalytic reduction of carbon dioxide. *ChemSusChem* **9**, 1085–1089 (2016).
59. Wang, H., Chen, Y., Hou, X., Ma, C. & Tan, T. Nitrogen-doped graphenes as efficient electrocatalysts for the selective reduction of carbon dioxide to formate in aqueous solution. *Green. Chem.* **18**, 3250–3256 (2016).
60. Wu, J. et al. A metal-free electrocatalyst for carbon dioxide reduction to multi-carbon hydrocarbons and oxygenates. *Nat. Commun.* **7**, 13869 (2016).
61. Zou, X. et al. How nitrogen-doped graphene quantum dots catalyze electroreduction of CO_2 to hydrocarbons and oxygenates. *ACS Catal.* **7**, 6245–6250 (2017).
62. Lum, Y. et al. Trace levels of copper in carbon materials show significant electrochemical CO_2 reduction activity. *ACS Catal.* **6**, 202–209 (2016).
63. Gentekos, D. T. & Fors, B. P. Molecular weight distribution shape as a versatile approach to tailoring block copolymer phase behavior. *ACS Macro Lett.* **7**, 677–682 (2018).
64. Buss, J. A., VanderVelde, D. G. & Agapie, T. Lewis acid enhancement of proton induced CO_2 cleavage: bond weakening and ligand residence time effects. *J. Am. Chem. Soc.* **140**, 10121–10125 (2018).
65. Helm, M. L., Stewart, M. P., Bullock, R. M., DuBois, M. R. & DuBois, D. L. A synthetic nickel electrocatalyst with a turnover frequency above $100{,}000^{-1}$ for H_2 production. *Science* **333**, 863–866 (2011).
66. Zhao, Y., Cao, X. & Jiang, L. Bio-mimic multichannel microtubes by a facile method. *J. Am. Chem. Soc.* **129**, 764–765 (2007).
67. McGuire, R. Jr et al. Oxygen reduction reactivity of cobalt(ii) hangman porphyrins. *Chem. Sci.* **1**, 411–414 (2010).
68. Huff, C. A. & Sanford, M. S. Cascade catalysis for the homogeneous hydrogenation of CO_2 to methanol. *J. Am. Chem. Soc.* **133**, 18122–18125 (2011).
69. Morales-Guio, C. G. et al. Improved CO_2 reduction activity towards C2+ alcohols on a tandem gold on copper electrocatalyst. *Nat. Catal.* **1**, 764–771 (2018).
70. Hulea, V. Toward platform chemicals from bio-based ethylene: heterogeneous catalysts and processes. *ACS Catal.* **8**, 3263–3279 (2018).
71. Metzger, E. D., Brozek, C. K., Comito, R. J. & Dincă, M. Selective dimerization of ethylene to 1-butene with a porous catalyst. *ACS Cent. Sci.* **2**, 148–153 (2016).
72. Xiao, H., Cheng, T., Goddard, W. A. & Sundararaman, R. Mechanistic explanation of the pH dependence and onset potentials for hydrocarbon products from electrochemical reduction of CO on Cu (111). *J. Am. Chem. Soc.* **138**, 483–486 (2016).
73. Wuttig, A., Yaguchi, M., Motobayashi, K., Osawa, M. & Surendranath, Y. Inhibited proton transfer enhances Au-catalyzed CO_2-to-fuels selectivity. *Proc. Natl Acad. Sci. USA* **113**, E4585–E4593 (2016).
74. Weinberg, D. R. et al. Proton-coupled electron transfer. *Chem. Rev.* **112**, 4016–4093 (2012).
75. Barile, C. J. et al. Proton switch for modulating oxygen reduction by a copper electrocatalyst embedded in a hybrid bilayer membrane. *Nat. Mater.* **13**, 619–623 (2014).
76. Liu, H. et al. Polydopamine functionalized Cu nanowires for enhanced CO_2 electroreduction towards methane. *ChemElectroChem* **5**, 3991–3999 (2018).
77. Chen, S., Liu, Y. & Chen, J. Heterogeneous electron transfer at nanoscopic electrodes: importance of electronic structures and electric double layers. *Chem. Soc. Rev.* **43**, 5372–5386 (2014).
78. Raciti, D., Mao, M. & Wang, C. Mass transport modelling for the electroreduction of CO_2 on Cu nanowires. *Nanotechnology* **29**, 44001 (2017).
79. Limburg, B., Bouwman, E. & Bonnet, S. Molecular water oxidation catalysts based on transition metals and their decomposition pathways. *Coord. Chem. Rev.* **256**, 1451–1467 (2012).
80. Marianov, A. N. & Jiang, Y. Covalent ligation of Co molecular catalyst to carbon cloth for efficient electroreduction of CO_2 in water. *Appl. Catal. B Environ.* **244**, 881–888 (2019).
81. Wang, Y., Hou, P., Wang, Z. & Kang, P. Zinc imidazolate metal–organic frameworks (ZIF-8) for electrochemical reduction of CO_2 to CO. *ChemPhysChem* **18**, 3142–3147 (2017).
82. Agapie, T. Selective ethylene oligomerization: recent advances in chromium catalysis and mechanistic investigations. *Coord. Chem. Rev.* **255**, 861–880 (2011).

Acknowledgements

This work was in part supported financially by the Natural Sciences and Engineering Research Council of Canada, the Ontario Research Fund: Research Excellence Program (ORF-RE-RE08-034), the Natural Resources Canada Clean Growth Program (CGP-17-0455) and CIFAR Bio-Inspired Solar Energy Program (FL-000719). This work was also supported by the Joint Center for Artificial Photosynthesis, a DOE Energy InnovationHub, supported through the Office of Science of the US Department of Energy under award no. DESC0004993, and was also based on work supported by the King Abdullah University of Science and Technology (KAUST) Office of Sponsored Research (OSR) under award no. OSR-2018-CPF-3665-03 and OSR-2019-CCF-1972.04.

P.D.L. acknowledges the Natural Sciences and Engineering Research Council of Canada for support in the form of a Canada Graduate Scholarship and A.T. acknowledges the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie Action H2020-MSCA-IF-2017 (793471).

Competing interests

The authors declare no competing interests.

Additional information

Correspondence should be addressed to E.H.S.

Reprints and permissions information is available at www.nature.com/reprints.