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Electrocatalysis at Organic-Metal Interfaces: Identification of Structure-Reactivity Relationships for CO_2 Reduction at Modified Cu Surfaces

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ABSTRACT: The limited selectivity of existing CO_2 reduction catalysts and rising levels of CO_2 in the atmosphere necessitate the identification of specific structure-reactivity relationships to inform catalyst development. Herein we develop a predictive framework to tune the selectivity of CO_2 reduction on Cu by examining a series of polymeric and molecular modifiers. We find that protic species enhance selectivity for H_2, hydrophilic species enhance formic acid formation, and cationic hydrophobic species enhance CO selectivity. ReaxFF reactive molecular dynamics simulations indicate that the hydrophilic/hydrophobic modifiers influence the formation of surface hydrides, which yield formic acid or H_2. These observations offer insights into how these modifiers influence catalytic behavior at the non-precious Cu surface and may aid in the future implementation of organic structures in CO_2 reduction devices.

INTRODUCTION

Electrocatalytic reduction of carbon dioxide (CO2R) offers an efficient strategy to reduce the presence of greenhouse gases in the atmosphere while concurrently producing valuable carbon-based products.[1,2] Existing electrocatalysts for this process, however, are insufficiently active or selective for attractive energy dense products, particularly in the face of the competing hydrogen evolution reaction (HER).[3,4] Cu surfaces, for example, have drawn interest because they are the only single-metal electrodes that produce significant amounts of hydrocarbons. However, the inability to tune the selectivity among 16 observed products, particularly under mild, aqueous conditions, poses a challenge.[3-6]

In order to address this challenge, adjustable catalytic systems need to be identified to systematically evaluate how changes in structure affect catalyst selectivity. This strategy may reveal design principles that enable development of active and selective catalysts and provide further insights into the reaction mechanism. As an example, in electrocatalytic molecular systems for CO2R, hydricity (i.e., the energy required to cleave a M-H bond to form a hydride) has been identified as a key selectivity-defining parameter.[7-10] Specifically, the initial reduction of CO_2 with two protons and two electrons can produce either CO or formic acid, with HER as a competitive side reaction. While preferential interaction of the catalytic metal center with CO_2 over protons is thought to be key to selectivity for CO, moderate hydricity facilitates migratory insertion of CO_2 into M-H bonds to yield formic acid, and strong hydride donors catalyze H_2 formation.[8-10]

While heterogeneous metal catalysts provide a more recyclable alternative to homogeneous complexes, the selectivity of heterogeneous systems has proved difficult to predictably alter.[7] Main group metals, such as In, Sn, Hg, and Pb, are selective for the synthesis of formic acid,[11] a fuel with practical applications in hydrogen storage[12,13] and direct formic acid fuel cells.[14] However, these metals often require high overpotentials.[11] In addition to formic acid, CO is also a product of interest because it serves as the intermediate towards all other observed products in electrochemical CO2R, including ethylene and ethanol, and it is currently of use in the formation of hydrocarbons through Fischer-Tropsch chemistry. However, high selectivity for CO requires metals with weak CO binding energies, such as the precious metals Au or Ag.[11]

The ability to tune the product selectivity between CO and formic acid with a non-precious metal would not only be of interest due to the practical applications of these products, but also because existing tools to control this initial bifurcation in the process of electrochemical CO2R on Cu are limited.[15-17]

Several notable, recent studies have examined product selectivity by starting with CO_2 reduction intermediates, especially with CO.[18-20] The study of the initial two proton, two electron transfer to CO_2 may open doors to tandem catalytic processes, combining multiple steps of the CO2R process, or yield insights that are applicable to further downstream processes.

In this paper, we employ organic modifiers to alter the CO2R selectivity of a single non-precious metal surface, modifying Cu surfaces to alter CO2R selectivity between CO, formic acid and H_2. Towards this goal, we first examined polymeric and molecular modifiers that feature a wide variety of functional groups (aryl, amine, amide and ether groups, for example) as well as diverse structural features (e.g., neutral or cationic, protic or aprotic). We characterized their effect on the electrocatalytic behavior of Cu at -0.7 V vs. RHE, at which the unfunctionalized Cu surface generates CO, formic acid and H_2 in roughly equivalent proportions. In the presence of organic modifiers, we observed significant changes in CO2R selectivity between these three products, with selectivities of up to 76% CO or 62% formic acid, and tuning of H_2 selectivity from 97% down to 2%. These changes allowed classification of the modifiers by the products that they promote. Examination of these classes allowed identification of the common structural characteristics that are key in influencing product selectivity.

While experimental and computational studies have examined CO2R catalysis at metal surfaces, the complexity of the catalyst/electrolyte interface makes it difficult to identify the mechanism by which a change in the catalyst affects the CO2R selectivity. As a consequence, the most commonly adopted approach has been to select specific parameters and investigate their effect on the observed selectivity.[21] In this paper, in contrast, we allow a substantial degree of freedom for the surface chemistry to provide information on relevant parameters that may have an important role in determining CO2R selectivity. Organic structures hold promise for various roles in CO2R devices, including their use as membranes,[22] electrolytes,[23-25] coatings for the preparation of nanoparticulate or surface electrodes,[26] or supports to improve electrode stability;[27] therefore, we expect that the parameters highlighted in our study will help guide the further development of CO2R catalysts and organic structures for CO2R devices.

EXPERIMENTAL METHODS

Electrode preparation: Cu foil was mechanically polished (1200G Wetordry sandpaper, 3M) and then electropolished as described in a reported procedure.[6] The two-compartment flow cell was assembled with the Cu foil, and cyclic voltammetry was run as described in previous reports in order to generate an oxide-derived Cu surface.[28,29] Specifically, an electrolyte solution of 0.05 M K_2CO_3 and 4 mM KCl was prepared. After addition of this electrolyte, three cycles of cyclic voltammetry were performed from 0.9 to -1.05V vs. RHE at a rate of 5 mV/s. This high surface area structure was chosen in order to generate greater amounts of product and facilitate product detection.

The cell was disassembled, the electrode was dried under N_2 flow and solutions of the organic modifier were dropcast onto the Cu surface. Once dry, a solution of Nafion binder was dropcast onto the Cu surface. The electrode, once dry, was reassembled in the flow cell for electrochemical analyses.

Chronoamperometry (CA) and product detection experiments: CA experiments were conducted in the cell with a CO_2 flow rate of 5 sccm using a Biologic potentiostat (SP-300). Prior to CA experiments, linear scan voltammetry was conducted from the open circuit potential to -1.05V vs. RHE at a scan rate of 20 mV/s in order to reduce any oxidized Cu. The impedance was then measured and correction for the ohmic resistance was applied to the CA experiment as described in a reported procedure.[30] Each trial was run at -0.7 V vs. RHE for 65 minutes. The outlet of the electrochemical cell was connected to an in-line gas chromatograph (GC), and the gaseous products were injected into the chromatograph at 15, 30, 45 and 60 minutes after the beginning of the experiment. The average values from the four injections are reported. At the end of the experiment, the liquid from both the cathode and anode were analyzed via high performance liquid chromatography (HPLC) to quantify the amount of formic acid produced, including formate that had diffused through the membrane during the experiment. Product selectivities and activities in terms of Faradaic efficiencies (%) and partial current densities (mA/cm^2) are reported with error calculated via standard error of the mean and standard deviations; standard error of the mean is used in the main text.

Measurement of the contact angle of water: Cu foil was electropolished, and the organic modifiers were dropcast onto the Cu foil at the same loadings as were used in the CA experiments. Once dry, the sample was placed on the goniometer, and 3 μL droplets of water were dropped onto the sample. The right and left angles of the droplet with the Cu surface were measured, and the average of at least five droplets is reported.

ReaxFF MD simulation: All of the ReaxFF MD simulations were carried out using LAMMPS Molecular Dynamics Simulator. The force field parameters are supplied in the Supplementary Information. The simulation models consist of 1440 Cu atoms [4×18×20 Cu(111) surface], 2000 water molecules, 26 cations and 26 bromide anions, making the system neutral. The dimension of the simulation box is 4.60 nm × 4.42 nm × 5.00 nm. Energy optimizations were first carried out to relax the interface structure with a force converge criteria of 10^{-6} kcal/mol·Å. Constant temperature, constant volume (NVT) simulations were carried out at room temperature (298K) with Nose-Hoover thermostat for 5 ns with a time step of 0.25 fs.

The binding energies of hydrogen were calculated at a coverage of 1M.

$$\Delta E_{\mathrm{H*}} = \frac{E_{\mathrm{1ML\ H*}} - E_{\mathrm{sur}}}{n_{\mathrm{sites}}} - 0.5E_{\mathrm{H_2}}$$

Here, $n_{\mathrm{sites}} = 360$ (18×20) for 1ML H*.

The formation energy of HCOOH is calculated as follows:

$$\Delta E_{\mathrm{HCOOH}} = E_{\mathrm{1ML\ H*+HCOOH}} - E_{\mathrm{1ML\ H*}} - (E_{\mathrm{H_2}} + E_{\mathrm{CO_2}} + 2\Delta E_{\mathrm{H*}})$$

RESULTS AND DISCUSSION

Structurally diverse organic modifiers result in divergent catalytic behavior from Cu: We tested a series of organic polymeric and molecular structures on Cu electrodes (**Fig. 1** and section **SA** in Supplementary Information). Oxide-derived Cu surfaces were prepared as described in a reported procedure.[28] The organic modifier of interest was dissolved in a volatile organic solvent and dropcast onto the Cu surface (**Fig. 1a**). In order to focus on interactions at the electrode/electrolyte interface, we studied surface modifiers with relatively low water solubility, such as polymeric species and molecular species with long hydrocarbon chains. Once the Cu electrode with the organic modifier was prepared, a solution of Nafion was dropcast onto the electrode. Nafion was found to act as an effective binder for the modifier without influencing the CO2R selectivity (see **SB**). The electrode was placed in a two-chamber flow cell of a reported cell design,[29] and the CO2R behavior was evaluated by conducting a chronoamperometry (CA) experiment at -0.7 V vs. RHE for 65 minutes. During the experiment, gaseous products were characterized via injections with an in-line gas chromatograph (GC), while liquid products were characterized via high performance liquid chromatography (HPLC) after the CA experiment.

In examining the effects of organic modifiers on the CO2R behavior of Cu, we discovered that the relative formation of H_2, formic acid or CO could be altered by varying the modifier. **Fig. 1b** illustrates three representative modifiers that demonstrate enhanced selectivity or activity for these products. We chose these modifiers to discuss and analyze in detail due to their structural diversity. Polyvinylpyrrolidone (**1**) is a neutral polymer that is often used as a ligand in nanoparticle synthesis.[31] Tetrahexadecylammonium bromide (**2**) is a cationic salt with low solubility in water, which aids in binding the modifier to the electrode. Polyallylamine (**3**) is a neutral polymer with primary amine groups, which can participate in hydrogen bonding interactions.

Compared to the unfunctionalized Cu electrode (**Ox Cu**), selectivity for formic acid (blue), CO (red), or H_2 (gray) improved in the presence of **1**, **2**, or **3**, respectively (**Fig. 1c** and **SC**). The other observed products (yellow) were present in traces at this potential and largely consisted of ethylene and ethane. In the presence of **1**, the Faradaic efficiency (i.e. the percentage of electrons that were transferred to a given product) for formic acid increased to 45% ± 2% from 34% ± 3% in the **Ox Cu** case, accompanied by an increase in H_2 selectivity to 43% ± 1% from 28% ± 2%. In the presence of **2**, CO selectivity increased slightly from 28% ± 2% in the **Ox Cu** case to 33.8% ± 0.9%. H_2 selectivity drastically increased to 97% ± 2% with the addition of **3**, as compared to 28% ± 2% with **Ox**

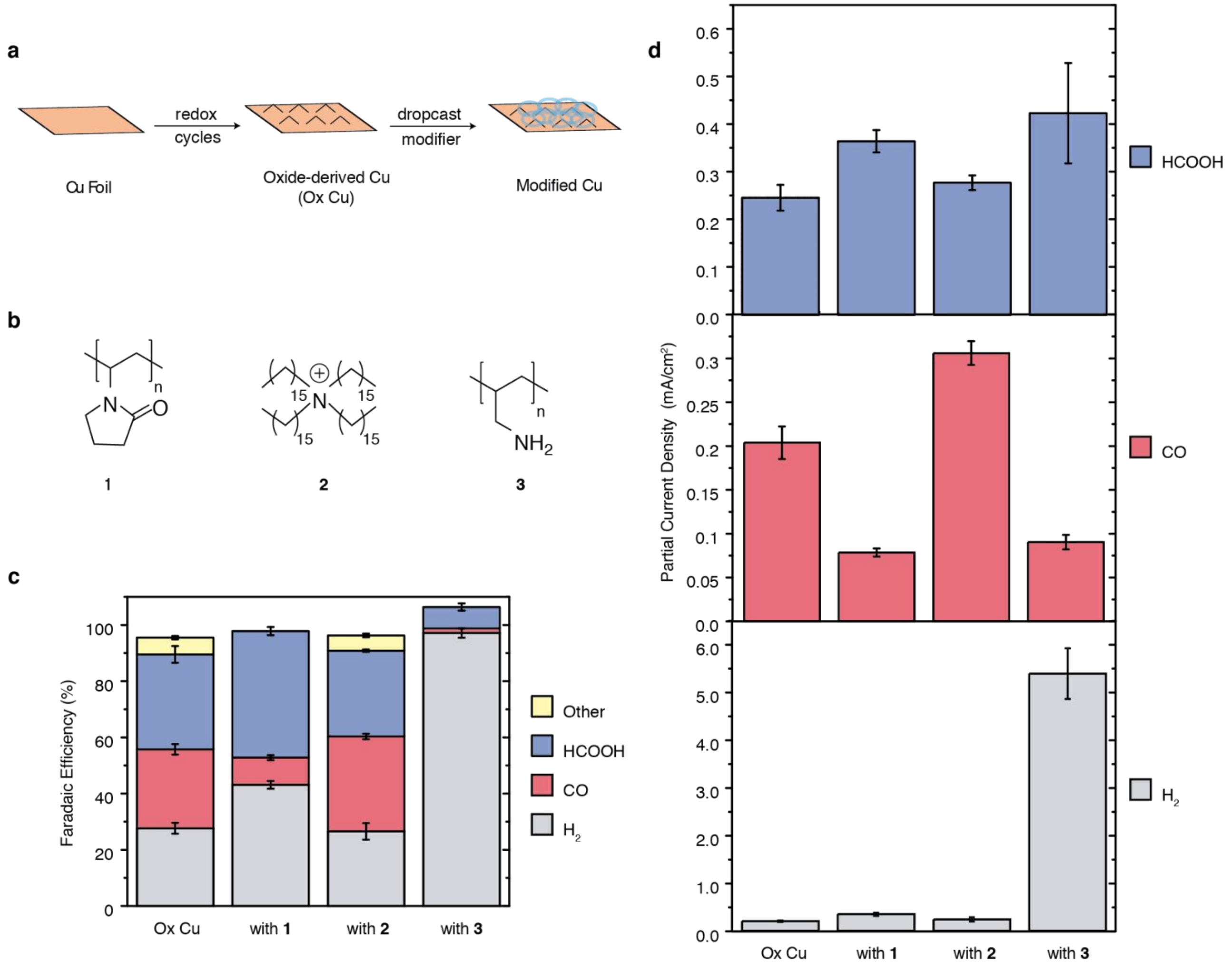


Figure 1. **Modifiers to promote H_2, CO or formic acid formation**. To readily prepare functionalized surfaces, oxide-derived Cu surfaces were generated, and the organic modifiers were then dropcast onto the surface (a). Three modifiers, namely polyvinylpyrrolidone (**1**), tetrahexadecylammonium (**2**) with bromide anion not shown, and polyallylamine (**3**), tested to promote H_2 (gray), CO (red), or formic acid (blue) formation on Cu at -0.7 V vs. RHE (b). Traces of other products (yellow) indicate the presence of ethylene and ethane. Plots of product

selectivity in terms of the Faradaic efficiencies (c) or partial current densities (d) of unfunctionalized Cu (**Ox Cu**) and of **Ox Cu** with **1**, **2**, and **3** illustrate the change in selectivity and activity with each added modifier. Values and error bars are calculated from at least three trials. Error bars are reported as standard error of the mean.

Cu.

Experiments with varying loadings of **1** and **2** demonstrate similar selectivities towards more formic acid or CO, and are described in more detail in the Supplementary Information (**SD**). In addition, similar trends were observed in experiments at higher overpotentials, with higher selectivity for formic acid, CO and H_2 obtained with **1**, **2**, and **3**, respectively (**SE**).

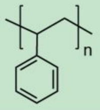
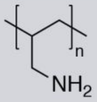
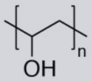
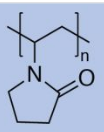
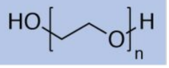
When CO_2 was replaced by N_2 under otherwise identical conditions, the absence of CO2R products was observed, thus supporting that the detected products were formed via CO2R rather than decomposition of the organic modifier (**SF**). In addition, the organic modifiers were also analyzed by ^{1}H-NMR after the hour-long CA experiment to examine whether the organic modifiers maintained their chemical structure (**SG**).

In addition to the Faradaic efficiencies, we also considered the partial current densities towards each product, which depict the amount of current transferred to generate a given product (**Fig. 1d**). These data provide more information regarding whether an increase in selectivity is due to a higher amount of product formed, or whether it is due to the selective suppression of other products caused by a decrease of the total current. **Fig. 1d** illustrates that the increase in Faradaic efficiency for H_2, CO and formic acid is accompanied by an increase in the partial current density as well. The partial current for formic acid, for example, increased from 0.25 mA/cm^2 ± 0.03 mA/cm^2 in the unfunctionalized case to 0.36 mA/cm^2 ± 0.02 mA/cm^2 with the addition of **1**, an increase of 44%. The partial current for CO increased from 0.20 mA/cm^2 ± 0.02 mA/cm^2 to 0.31 mA/cm^2 ± 0.01 mA/cm^2 with the addition of **2**, an increase of 55%. The partial current for H_2 increased 27 times from **Ox Cu** to the sample modified with **3**. These reported values are based upon geometric current densities; current densities normalized by electrochemically active surface area demonstrate similar trends (**SH**). For many of the modifiers discussed in this text, increases in selectivity are accompanied by increases in partial current densities, thus demonstrating that these organic modifiers may be used to enhance the amount of product formed.

Classification of modifiers by promoted products: The changes in product distribution with the addition of the organic modifiers in **Fig. 1** raise the question of how these changes are effected. Previous works employing organic modifiers to tune CO2R product selectivity have evoked different explanations, including interactions between modifiers with surface intermediates and effects on the local electrode environment.[19,30-33] We decided to study a diversity of structures in order to identify which common characteristics play a key role in influencing the product distribution. While a number of factors may be at play, we believe that this strategy would help ascertain which structure-reactivity relationships are the most sensitive and readily tunable.

A series of neutral organic modifiers was dropcast onto Cu electrodes as previously described. The product distribution of these samples in the CO2R reaction yielded insights into possible structure-reactivity relationships at work (**Table 1**). With the addition of polymers with protic functional groups (entries c and d, in gray), we observe a substantial increase in HER selectivity, whereas with the addition of polymers with aprotic groups (entries e and f, in blue), we observe an increase in the selectivity for formic acid. Addition of polystyrene (entry b, in green), a hydrocarbon, results in decreased selectivity for both CO and formic acid.

Table 1. Neutral polymers and their effect on CO2R selectivity at Cu. Faradaic efficiencies and total current for Cu surfaces modified with neutral polymers. Samples were prepared with the same loading of polymer by mass. CA experiments were conducted at -0.7 V vs. RHE for 65 minutes. Values represent averages of at least three trials.

Table Entry	Modifer	Modifer Number	H_2	CO	Formic Acid	Other	Total FE	Total Current (mA/cm²)
a	Ox Cu	-	28% ± 2%	28% ± 2%	34% ± 3%	6.0% ± 0.6%	96% ± 2%	0.73 ± 0.05
b		4	44.6% ± 0.6%	19% ± 2%	23.5% ± 0.8%	3.5% ± 0.7%	91% ± 2%	0.80 ± 0.13
c		3	97% ± 2%	1.63% ± 0.04%	8% ± 1%	0%	106.4% ± 0.4%	5.6 ± 0.6
d		5	71% ± 2%	15.1% ± 0.6%	17% ± 1%	0%	103% ± 1%	0.54 ± 0.06
e		1	43% ± 1%	10% ± 1%	45% ± 2%	0%	98% ± 1%	0.81 ± 0.05
f		6	44% ± 6%	16% ± 3%	38% ± 3%	0%	98% ± 2%	0.70 ± 0.08

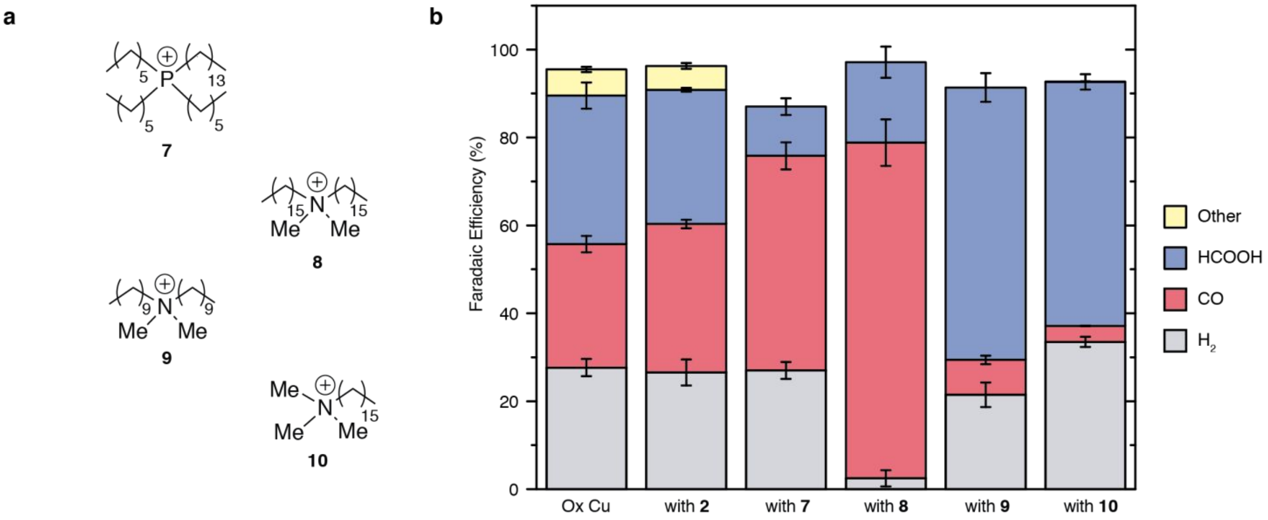


Figure 2. Study of cationic modifiers. Quaternary cationic modifiers, namely trihexyltetradecylphosphonium (**7**), dihexadecyldimethylammonium (**8**), didecyldimethylammonium (**9**), and cetyltrimethylammonium (**10**), were tested in CO2R on Cu at -0.7 V vs. RHE (a). For all of these cases, the bromide of the salt was used. The Faradaic efficiencies of **Ox Cu** and the Cu surfaces modified with cationic species are compared (b). Data and error bars in bar graphs are calculated from at least three trials. Error bars are reported as standard error of the mean.

While primary amines such as **3** have been reported to form carbamates,[34] we hypothesize that the protic functionality is responsible for this observed catalytic behavior. The enhancement of HER with the addition of protic functional groups is consistent with precedents in both homogeneous and heterogeneous HER catalysis. In addition to molecular examples,[35] primary amines have also been used to promote HER on heterogeneous Pt catalysts and has recently also been reported with 3 on Cu.[36,37] Our hypothesis is also supported by the enhancement in HER selectivity with **5**. It is possible that the protic groups act as proton shuttles, as previously suggested, or possibly that these groups have an electronic effect that promotes HER. These results suggest that protic functional groups should be avoided in the design of organic structures for CO2R devices due to this observed tendency to promote HER.

We were intrigued by the enhanced selectivity for formic acid observed with aprotic species. Therefore, we increased the diversity of examined structures to better understand this phenomenon. In addition to the functional groups exemplified by these neutral polymers, we applied the strategy outlined in **Fig. 1a** to probe cationic species. In the literature, cationic species have been employed to influence CO2R behavior at various metals.[23-25,30] In these precedents, the cationic species employed are often N-containing heterocyclic compounds, which have been theorized to influence catalytic behavior via a number of possible molecular orientations at the electrode.[24] These heterocycles have also demonstrated ancillary reactivity or fragmented under electrochemically reducing conditions, adding to the uncertainty regarding which species is responsible for observed changes in catalytic behavior.[25] Therefore, we chose to test acylic quaternary ammonium and phosphonium salts to provide structural simplicity, mitigate the potential for the modifier to be directly involved in electron transfer processes, and to readily allow for stepwise changes in structure.

In addition to the previously discussed tetrahexadecylammonium salt **2**, we tested a series of ammonium salts with varying hydrocarbon chain lengths (**Fig. 2a**) to ascertain how this structural change affects the influence of these modifiers. We had previously observed that the addition of **2**, which features four 16-carbon chains, slightly increased selectivity for CO. Changing these hydrocarbon substituents to feature three methyl groups and a C-16 chain, as in cetyltrimethylammonium bromide (**10**), yields more formic acid (**Fig. 2b**).

Unexpectedly, salts with intermediate hydrocarbon content also demonstrated a stark difference in selectivity. Didecyldimethylammonium bromide (**9**) increased formic acid selectivity, while dihexadecyldimethylammonium bromide (**8**) increased CO selectivity. The observed products for **2**, **8, 9** and **10** appear to fit a trend in which salts with greater hydrocarbon content improve selectivity for CO, while those with less improve formic acid selectivity. To further probe this observation, a phosphonium salt with relatively high hydrocarbon content (trihexyltetradecylphosphonium bromide, **7**) was also tested and found to enhance CO selectivity. Notably, the breaking point in the selectivity trend between two dimethyl substituted ammonium salts suggests that steric hindrance about the heteroatom center is not the sole root of the observed selectivity changes. In order to better understand this overall trend observed with these modifiers, we conducted additional experimental and theoretical studies to delve into the mechanism of this effect, particularly as observed with modifiers **8** and **9**, as described below.

Proposed mechanisms of influence of organic modifiers on CO2R selectivity: Faced with this unexpected relationship between the organic modifiers and the observed product distribution, we first carried out multiscale ReaxFF reactive molecular dynamics (RMD) simulations to model the morphology of the two dimethyl substituted ammonium salts, **8** and **9**, at the Cu electrode (**Fig 3a-b**). We chose these two cases because they led to dramatically different product distributions.

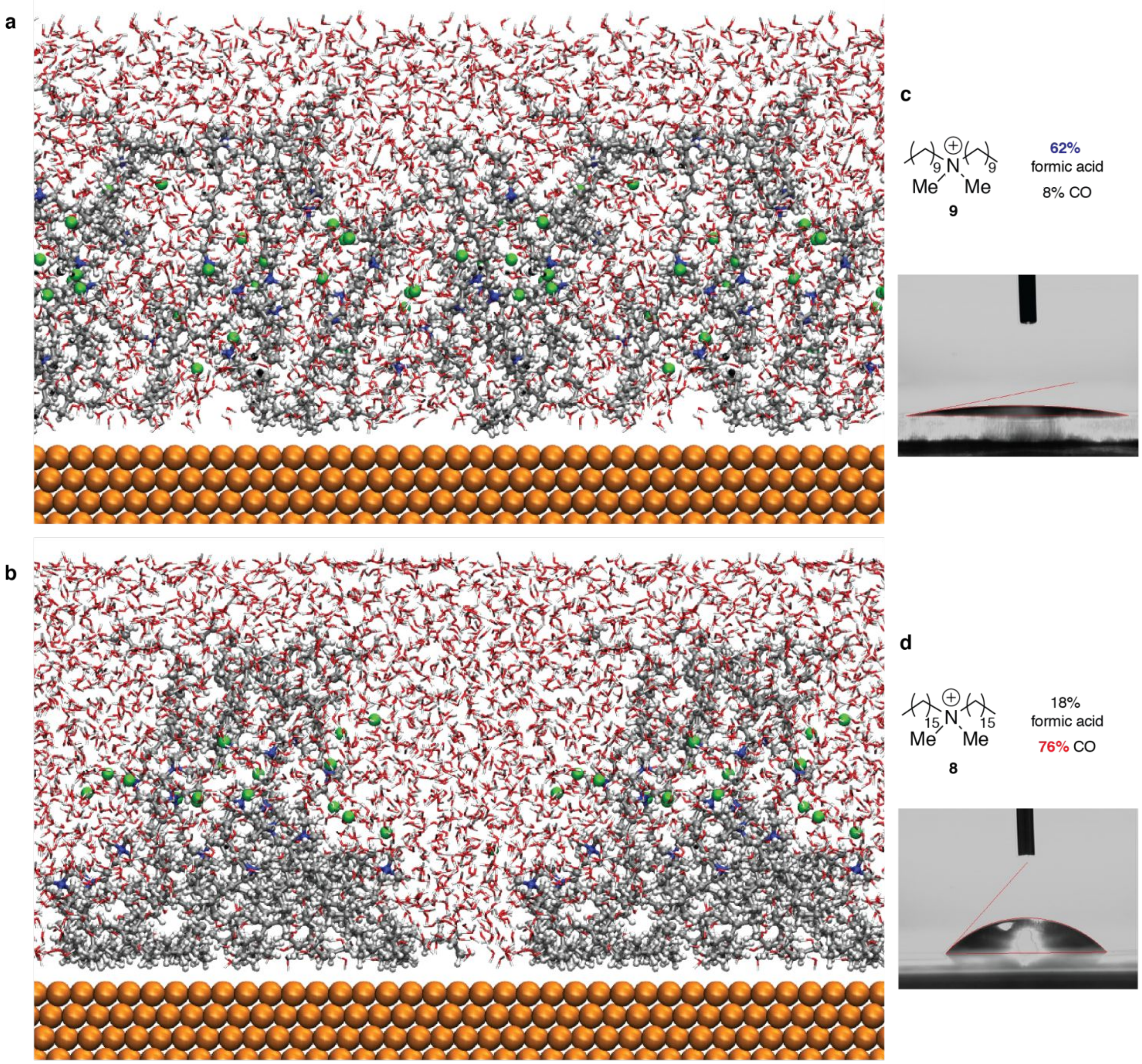


Figure 3. Study of Cu surfaces modified with 8 and 9. The last snapshot of the interface between Cu, water, and hydrophilic species **9** (a) and hydrophobic species **8** (b), extracted from 5 ns of RMD canonical ensemble (NVT) simulations at 298 K to equilibrate the interface. The colors are N in blue, C in gray, O in red, H in white, and Br in green. The contact angle between a 3 μL drop of water and Cu surfaces modified with **9** (c) and **8** (d).

For **9**, the surfactant molecules are well solvated in the electrolyte and widely distributed on the Cu electrode, forming a dispersed network (**Fig. 3a)**. For **8**, the surfactant assembles into larger clusters on the Cu electrode with the ammoniums exposed to the solvent and hydrocarbon chains inside (**Fig. 3b)**.

This difference in behavior was also probed experimentally by characterizing how Cu surfaces modified with **8** and **9** interact with water. We measured the contact angle of a 3 μL drop of water on the two modified surfaces (**Fig. 3c-d** and **SI**). We found that **9** yielded a smaller contact angle with water, indicating that the surface is relatively hydrophilic, while **8 y**ielded a larger contact angle, indicating that the surface is more hydrophobic. Intrigued by this effect, we expanded the contact angle measurements to include previously examined species (**Fig. 4a** and **SI**). In addition, we analyzed the increase in product selectivity as a function of the contact angle (**Fig. 4b** and **SJ**). Modifiers that enhanced the formation of formic acid were more hydrophilic than the unmodified Cu surface, and those that enhanced the formation of CO were more hydrophobic. We also find that the maximum selectivity for CO is obtained with **8**, which is slightly more hydrophobic than **Ox Cu**, and that this selectivity for CO decreases as the hydrophobicity further increases. In line with this observation, the most hydrophobic species studied here- polystyrene- did not yield more CO than **Ox Cu**, but rather yielded slightly more H_2. Polystyrene and **2** are also outliers in **Fig 4b**. The observation that substantial increases in hydrophobicity result in decreasing, or loss of, selectivity for CO and increased selectivity for formic acid and H_2, may further support the importance of complex surface interactions with water at the molecular scale in the CO2R mechanism. Specifically, we

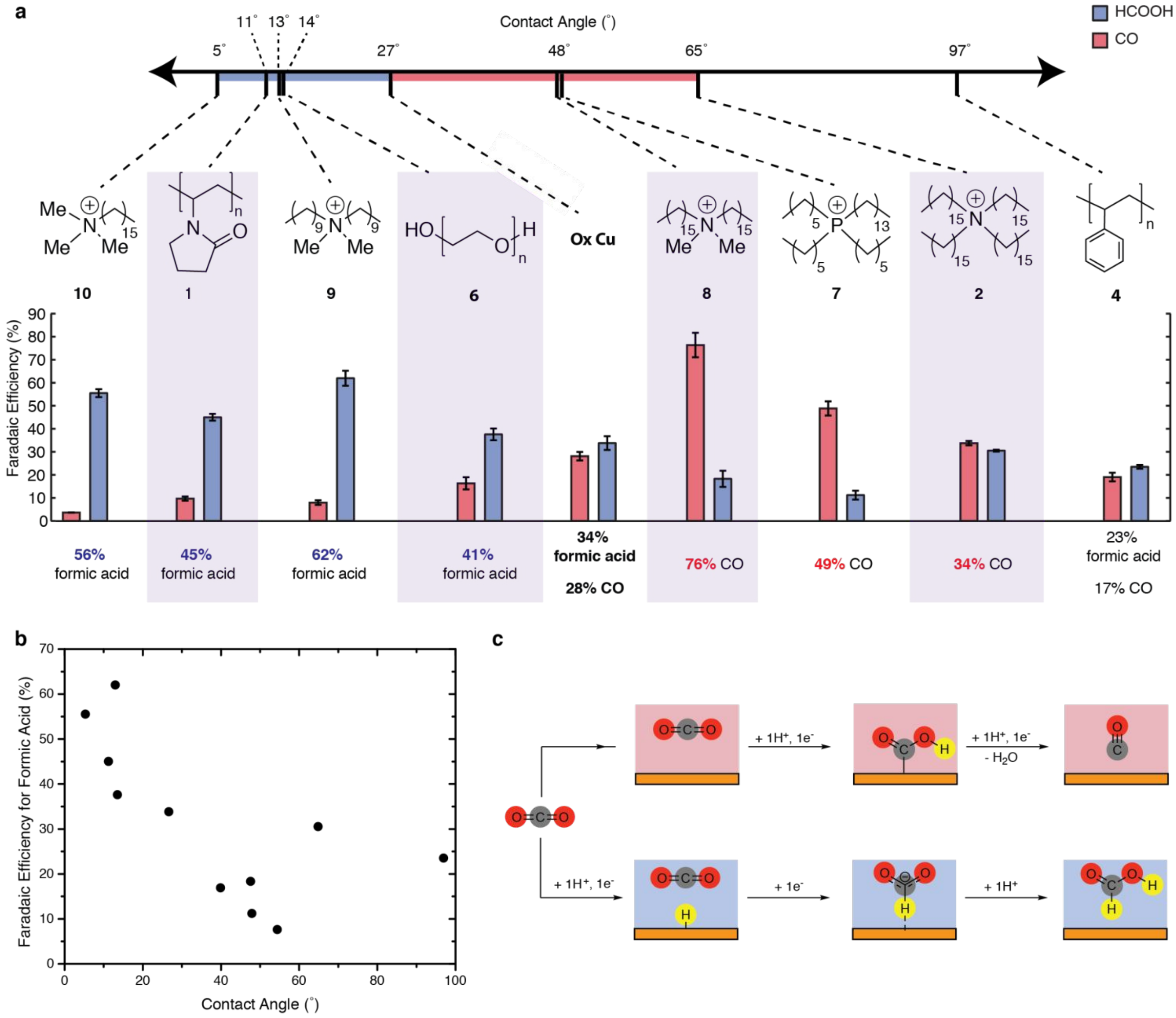


Figure 4. Relationship between hydrophilicity/phobicity and product selectivity. The contact angle was determined for Cu surfaces modified with the organic species shown. Surfaces that are more hydrophilic than **Ox Cu** were more selective for formic acid (highlighted in blue), and those that are cationic and more hydrophobic were more selective for CO. The CO, formic acid product selectivity for the modifiers is also included. Boxes are included to guide the eye. The balance of the Faradaic efficiency consisted largely of H_2 (see **SI**) (a). Plotting the selectivity towards formic acid against the contact angle yields a marked relationship, with modifiers 2 and 4 as outliers at 65˚ and 97˚, respectively (b). The mechanism for the formation of CO proceeds through a C-bound intermediate, while formic acid formation proceeds through addition to a surface hydride (c).

hypothesize that the presence of the heteroatom in modifiers **7**, **8**, **9**, and **10** plays an important role in determining these interactions with water, which are reduced in the presence of hindered ammonium salts (**2**) and the hydrocarbon polystyrene, thus explaining why these latter modifiers yield a product distribution more similar to **Ox Cu**.

These observed relationships between the organic modifier and the CO2R selectivity suggest that the effects of the modifiers involve properties that are structure non-specific (i.e. not related to the exact molecular structure). For example, the observation that two dimethyl substituted ammonium species can result in substantially different product distributions suggests that their bulk properties have a generalized effect on the local surface environment, consequently influencing chemical transformations at the Cu surface.

In order to better understand how these modifiers may influence the observed product distribution, we considered mechanisms for the formation of CO and formic acid developed from full solvent quantum mechanics (**Fig. 4c**).[38] The formation of CO proceeds via a bent CO_2 stabilized by water, which extracts an H from a H_2O molecule to form the bent carbon-bound *COOH intermediate. In turn, *COOH extracts an H from a second H_2O molecule to form aqueous

H_2O and surface bound CO. In contrast, formation of formic acid occurs via direct addition of CO_2 to a surface M-H to yield formate, followed by extraction of H from a H_2O molecule to yield formic acid. Thus, changes in the bonding of H and the availability of H2O at the surface have a strong influence on which products are formed.

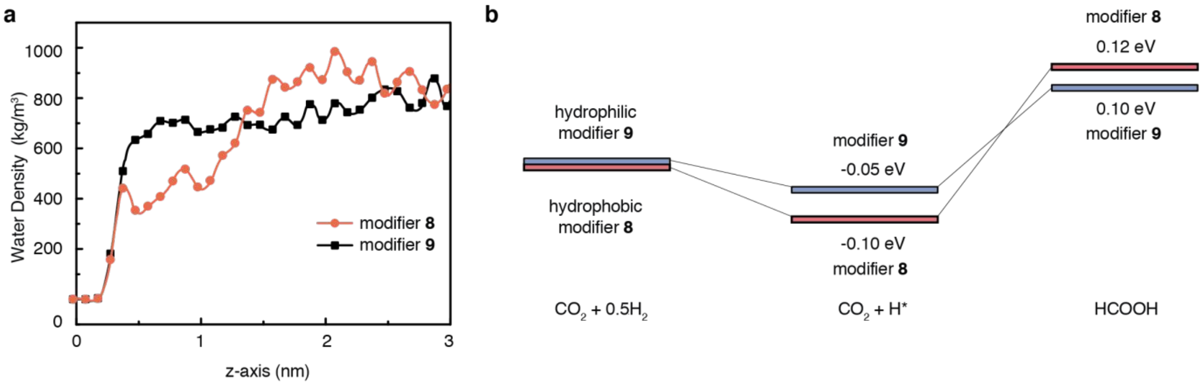


Figure 5. Role of hydrophobic modifier 8, hydrophilic modifier 9, and the surrounding water. Profile of density of water along the z axis, perpendicular to the Cu surface, on surfaces modified with **8** and **9** (a). Formation energies predicted from ReaxFF for the formation of formic acid at Cu surfaces modified with **8** and **9** (b).

The partial current densities of the modified Cu surfaces studied herein also support the intermediacy of a surface hydride species in the formation of both formic acid and H_2. The modifiers that promote formic acid formation also tend to yield more H_2, while those that generate less formic acid also tend to yield less H_2 (**SK**). This type of relationship is not observed between CO and H_2 or CO and formic acid.

While the binding strength of this surface hydride species is generally considered to be intrinsic to the metal surface, previous work from our group has demonstrated that it is sensitive to the surrounding water environment.[39] Increasing the hydrophobicity of a Pt(100) surface decreased the adsorbed water (i.e., the local density of water), reorganized the water structure and changed the hydrogen bonding energies of this water. Studies of the Pt system also demonstrated that this decrease in water adsorption on a hydrophobic surface stabilized the binding of H to the metal surface.

With these precedents in mind, we sought to understand whether the addition of hydrophilic and hydrophobic modifiers to the Cu surface may similarly influence the water at the Cu interface, and whether these changes in the local electrolyte environment may impact the formation of CO2R products. In order to understand how **8** and **9** influence the local aqueous environment, we examined the density of water at varying distances perpendicular to the copper electrode.

Consistent with the bulk measurement of the interaction of water with these modified electrodes (**Fig. 3c-d**), the availability of water at the nanometer scale is lower with **8,** the more hydrophobic molecule, than with **9,** the more hydrophilic molecule (**Fig. 5a**). From this density profile of water, we estimate that the electrode area covered by water with **9** is 1.55 times of that with **8** at a cut-off of 0.67 nm from the surface of the electrode, a distance that corresponds to about two monolayers of water.

With this understanding of how **8** and **9** influence the availability of water at the Cu interface, we examined how these changes at the electrode interface influence the binding energy of a M-H at the Cu surface, and, in turn, the formation of formic acid. As shown in **Fig. 5b**, ReaxFF calculations demonstrate that a surface hydride species is stabilized in the presence of hydrophobic species **8** compared to hydrophilic species **9**. This finding is consistent with previously described calculations conducted on Pt.[39] Addition of CO_2 to the stronger M-H bond to yield formic acid, as previously described (**Fig. 4c**), is more difficult than with the weaker M-H bond found on the hydrophilic surface. We therefore propose that the promotion of formic acid formation on the hydrophilic surface is due to this weakened M-H species, while hydrophobic species **8** results in stronger M-H bonds, suppressing formic acid formation and allowing CO formation to predominate.

CONCLUSIONS

With this study, we provide a strategy to identify important structure-reactivity relationships and tune selectivity in CO2R. We tested organic modifiers featuring a wide variety of characteristics and found that protic modifiers enhanced HER selectivity, demonstrating that aprotic species are necessary to hone CO2R selectivity. We identify structures that improve selectivity towards CO, formic acid, or H_2, reaching selectivities of up to 76% CO or 62% formic acid, and tuning the H_2 selectivity from 97% down to 2%. By comparison, Ag foil at the same potential yields less than 20% CO, only reaching 90% CO formation around -1.0 V vs. RHE,[40] while Sn foil yields around 30% formic acid at -0.7 V vs. RHE, reaching a maximum around 70% between -0.9 and -1.0 V vs. RHE.[15] Among these aprotic species, cationic hydrophobic modifiers enhanced selectivity for CO, while hydrophilic modifiers enhanced selectivity for formic acid. In addition, we find that within the tested hydrophobic modifiers, small perturbations from the **Ox Cu** wettability resulted in improved selectivity for CO, while substantially more hydrophobic species resulted in lower selectivity for CO. This ability to alternately tune between CO and formic acid, and suppress H_2 production, is unprecedented for a non-precious metal catalyst for CO2R. These structure-reactivity relationships illuminate important design principles for novel, selective CO2R electrocatalysts.

This correlation of observed products with hydrophilicity/phobicity and study of surface hydride formation demonstrates that the role of water deserves careful consideration in designing organic modifiers for CO2R. Previous works have delved into possibilities in using strategic hydrogen bonding and Lewis acidic interactions to stabilize specific intermediates and aid in tuning CO2R selectivity. Our study suggests that these modified Cu systems are sensitive to the structure of the surrounding water, and therefore, that strategies in ligand design moving forward may find interesting new avenues in targeting how the surrounding water may be manipulated.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Additional experimental details, experiments with Nafion, chronoamperometry traces, experiments with varying amounts of modifier, product distributions at more negative potentials, experiments under N_2, NMR characterization of modifiers and electrolyte, partial current densities, contact angle data, relationship between formation of different products, tables of Faradaic efficiency data (PDF)

Reactive Force Field Simulation details (TXT)

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