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Variable Rate Hydroxylamine Derivatization to Determine of Formaldehyde's Role and Kinetics in CO_2 Reduction to Methanol on Cobalt Phthalocyanine

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KEYWORDS: CO_2 reduction, cobalt phthalocyanine, catalysis, methanol, formaldehyde, hydroxylamine

ABSTRACT

Heterogenized cobalt phthalocyanine (CoPc) catalyzes electrochemical CO_2 reduction (CO_2R) to methanol. While it is clear that CO is a reaction intermediate, the role of formaldehyde, a sometimes-observed trace product, is less well-understood. Here, we gain insight into the methanol formation mechanism by selectively trapping formaldehyde. Using a simple preparation of CoPc heterogenized on multiwalled carbon nanotubes as the electrocatalyst, we employed three hydroxylamines which react with formaldehyde in the electrolyte to form stable, unreactive oximes at different rates: pentafluorobenzylhydroxylamine [PFBHA] (slowest), ethylhydroxylamine [EHA], and hydroxylamine [HA] (fastest). PFBHA has only a small effect on the methanol/formaldehyde selectivity, while EHA and HA (and higher concentrations of EHA) both reduce methanol molar selectivity by 25%, with a corresponding carbon-balanced increase in formaldehyde selectivity. Unbound formaldehyde thus is a relatively (compared to CO) short-lived intermediate responsible for only a quarter of the observed methanol. Extended CO_2R in PFBHA-containing electrolyte scrubs the solution of CH_2O without impacting MeOH selectivity, and we saw no noticeable difference in the rate of MeOH selectivity decline compared to control. This suggests that CH_2O is not a poison. 2D reaction-diffusion-convection simulations performed in a simplified geometry are consistent with the observed trends in methanol/formaldehyde selectivity, although derivatization rate constants larger than our experimental estimates need to be employed. We predict that hydroxylamine derivatization could be used for mechanistic analysis in other electrocatalytic networks with aldehyde intermediates.

INTRODUCTION

Electrochemical CO_2 reduction (CO_2R) is a promising approach to use renewable electricity to convert CO_2 into chemical feedstocks and fuels.[1,2] Unlike most other molecular catalysts that can only facilitate $2e^-$ reductions to CO or formate, cobalt phthalocyanine (CoPc), when heterogenized on carbon nanotubes (CNTs), can reduce CO_2 to methanol (MeOH).[3–6] For this reason, there is considerable interest in the mechanism by CoPc can facilitate the requisite 6 electron transfers.[7–12] Many studies, including our own, have demonstrated that CO is a key intermediate to reduction to MeOH, and that CO_2 and CO compete for CoPc sites, with CO_2 generally outcompeting CO.[12–18]

However, the steps by which CO is converted to MeOH are less clear. It is generally accepted that CO reduction to MeOH will go through a formyl/formaldehyde adduct.[8,15,19–21] However, whether formaldehyde itself is also an unbound intermediate and thus could transport to other reaction sites and compete with CO/CO_2 is still not clear. Boutin et al., who were the first to report MeOH production from heterogenized CoPc, also reported formaldehyde as a trace product and further showed that CoPc catalyzes formaldehyde reduction to MeOH. These observations suggest that formaldehyde is an intermediate to MeOH on CoPc.[7] Although CO_2R conditions that are optimized for methanol production generally have low formaldehyde yields, CO reduction can yield up to 7% Faradaic Efficiency (FE) to CH_2O.[20] While, the individual $2e^-$ steps from CO_2 to MeOH have been reported, it is not clear whether each individual reaction has to occur at the same catalyst site when doing CO_2R to MeOH. Our previous work has shown that CO is very mobile; here, we aim to answer whether formaldehyde is also mobile.

Recently, Li et al. ran CO_2R on CoPc in the presence of sodium bisulfite, which reacts with bulk formaldehyde to form sodium hydroxymethanesulfonate and showed that the selectivity for

methanol decreased while formaldehyde selectivity increased.[22] The MeOH (CH_2O) selectivity increased (decreased) with bisulfite concentration, and MeOH selectivity fell by a maximum of about 50% (increasing bisulfite concentration further convoluted buffer capacity in this study). From this, the authors concluded that formaldehyde is an unbound intermediate to methanol. Boutin et al., observing that the formaldehyde reduction reaction (FRR) rate (under FRR conditions) was an order of magnitude slower than the MeOH formation rate (under CO_2R conditions), argue that formyl intermediates remain adsorbed to the same cobalt site for further reduction, and that the formaldehyde desorption-readsorption pathway contributes only minimally to the overall MeOH current.[8] Additionally, formaldehyde has also been hypothesized as having two roles: an intermediate and a catalyst poison, where an oxygen-down coordination deactivates cobalt sites, and a carbon-down configuration that further reduces to CH_3OH.[23]

It is possible that different preparation methods can explain some of the conflicting results. Many studies in the CoPc literature, including our previous work, show that catalyst preparation and operating condition strongly influence catalyst behavior.[7,13,16,19,24–29] For CoPc anchored on multi-walled carbon nanotubes (MWCNTs), there are two major preparation methods: (1) where the CoPc and MWCNTs are physically mixed while in suspension and (2) where the CoPc is dissolved into a solvent (e.g. DMF) and allowed to disperse atop the CNTs.[19,24] Studies have shown that dispersed CoPc leads to stronger CO binding, but its effect on the role of formaldehyde is still unsettled.[14,16,19] We note that the 2019 study by Boutin et al. and the 2026 study by Li et al., which arrived at different conclusions, also used different CoPc preparations.[7,22]

In this study, we will investigate CoPc CO_2R in the presence of chemicals that will react with bulk formaldehyde at significantly different rates. Our goal, similar to Li et al., is to react formaldehyde with a homogenous species before it undergoes further reduction.[22] If formaldehyde

is an unbound intermediate, only reagents that react with formaldehyde faster than its characteristic transport timescale should have a significant effect on the MeOH selectivity.

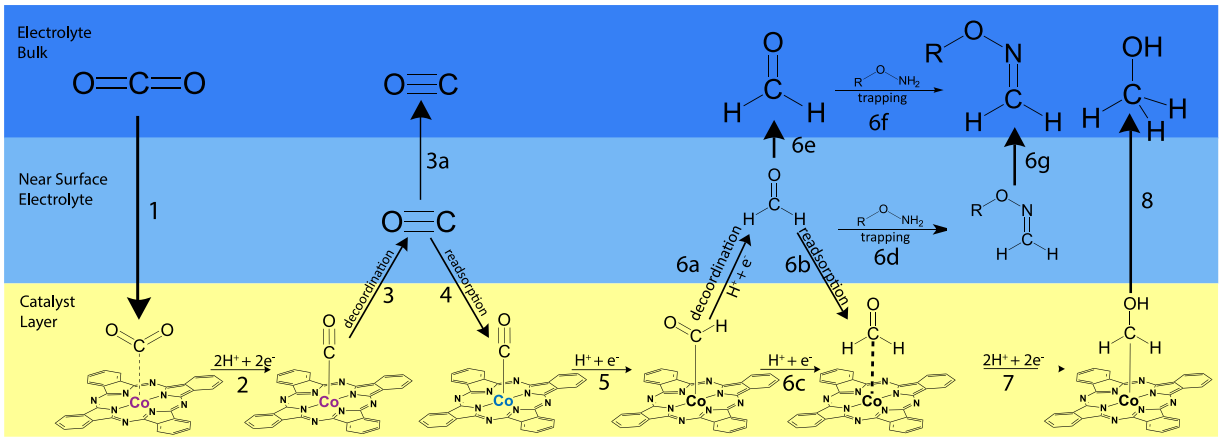
This study aims to answer three questions. Why formaldehyde is detected in small quantities in CO_2R? Does formaldehyde desorption-reabsorption play a large role, as it appears to for CO? Can formaldehyde be a poison and, if so, under what conditions? We showed in our previous work that under the optimized transport conditions, physically mixed of CoPc/MWCNT is as selective to MeOH as other preparation methods (FE ~30%).[13] Hence here we will employ physically mixed CoPc/MWCNT due to their preparative simplicity and reproducibility amongst different researchers.

We chose three different hydroxylamines (Pentafluorobenzylhydroxylamine [PFBHA], ethylhydroxylamine [EHA], and hydroxylamine [HA]) as reactants, all of which form stable oximes upon formaldehyde reaction. For this work, we will use HA to refer to the specific hydroxylamine chemical, and we will use hydroxylamine(s) to refer to chemicals that contain the hydroxylamine functional group generally. PFBHA has been used for decades as a derivatization agent for aldehyde detection, as its fluorinated groups stabilize the derivatized product and increase molecular stability for subsequent detection via electron impact mass spectrometry.[30,31] It is used in standard Environmental Protection Agency (EPA) methods for formaldehyde quantification.[32] EHA is less commonly used for trace analytical detection but has been used to study sugars.[33] HA has the least steric hinderance and reacts the fastest.

Choosing the appropriate concentration of hydroxylamine is important for this study. We need hydroxylamine in excess of the expected methanol concentration, while also not strongly impacting the bicarbonate concentration and buffer capacity, as each hydroxylamine is paired to a hydrochloride which introduces an acidic proton. Bisulfite significantly impacting electrolyte

buffer capacity was a challenge in Li's previous study.[22] In our case, we primarily used 4 mM hydroxylamine in 0.1 M bicarbonate but also ran selected experiments with 12 mM hydroxylamine.

We show in Scheme 1 a simplified hypothesized pathway towards methanol that shows key intermediates of CO and the various pathways formaldehyde can take in the presence of the hydroxylamine. If formaldehyde desorbed and readsorbed to adjacent CoPc sites, we expect that faster hydroxylamine reaction kinetics should decrease methanol selectivity while correspondingly increasing formaldehyde selectivity. We should also expect that, if formaldehyde is a poison, catalyst degradation should significantly decrease in the presence of a hydroxylamine.



Scheme 1. Simplified reaction network of CO_2R on CoPc with the presence of a hydroxylamine in the electrolyte. We show CO_2 adsorption from the bulk (1), which then gets reduced to CO (2). Adsorbed CO can desorb into the near surface electrolyte, (3) after which it can either diffuse into the bulk (3a) or get readsorbed (4). After another reduction, a formyl is formed on the CoPc (5). This can decoordinate after another reduction step (6a) or can create a coordinated formaldehyde in the catalyst layer (6b, not bound as the carbon already has a full octet). The decoordinated formaldehyde can rebind (6b), diffuse into the bulk (6e, where it will react with the hydroxylamine,

6f) or be reacted with the hydroxylamine in the near surface (6d), where the reduction is then terminated. The coordinated formaldehyde can also undergo further reduction (7) to MeOH (8).

EXPERIMENTAL

Catalyst Preparation and Electrochemical Testing

We followed the same procedure to preparing catalyst ink and electrodes as our previous work.[13] In this work, we focus on examining in the role of formaldehyde and hence we only use one specific preparation and operating potential. We used 1:0.6 MWCNT:CoPc ratio by mass as our catalyst, sprayed to a loading of 0.4 mg cm^{-2}. Chronoamperometry (CA) experiments were run at -1.1 V vs RHE for 52 minutes for standard experiments and for 3 hours in stability tests. CA experiments were run with and without the presence of 4 mM PFBHA, EHA, or HA in CO_2 saturated 0.1 M $KHCO_3$ to investigate the role of formaldehyde. Aliquots were removed during the stability measurement for measurement of intermediate MeOH concentrations. For specific detail on the procedure, see Detailed Experimental Methods in the SI.

Formaldehyde Analytical Chemistry

Two complementary methods were used for formaldehyde quantification. (1) For control experiments performed in the absence of any hydroxylamine, the electrolyte was mixed with the Hantzsch reagent that reacts with formaldehyde to form a colored compound (maximum absorbance at 410 nm), allowing for subsequent analysis using UV-Vis spectroscopy. (2) For experiments performed with hydroxylamine, the trapping reaction converts all the formaldehyde into the corresponding oxime. In this case, the electrolyte was directly injected into a GC-MS for formaldehyde quantification. For specific GC-MS methods and more details on derivatization and calibration, see Detailed Experimental Methods in the SI.

Qualitative hydroxylamine kinetics were obtained via FTIR: solutions of formaldehyde and the hydroxylamine were mixed over an ATR crystal and the signal was monitored every 5.8 seconds from 600 cm^{-1} to 4000 cm^{-1}. We monitored characteristic oxime peak growth or formaldehyde peak depletion to obtain qualitative kinetics for oxime formation. For specific measurement parameters and steps, see Detailed Experimental Methods in the SI.

RESULTS AND DISCUSSION

Derivatizing overview and controls

We used attenuated total reflectance (ATR) Fourier transform infrared spectroscopy to qualitatively determine the reaction kinetics of the hydroxylamines with formaldehyde. The relative derivatization rates supported our intuitive assessment of relative kinetics (Figures S10-15, see SI for more detailed methods). We found that PFBHA, EHA, and HA had second order rate constants on the order of 0.1, 1, and 3 M^{-1} s^{-1} respectively.

We also showed that hydroxylamines are stable under reductive conditions in our control experiments. Figure S4-6 show chromatograms of hydroxylamine containing electrolyte after electrolysis on a Pt electrode over the same experiment time using in the trapping experiments. The chromatograms do not show their respective oxime peaks, meaning that reduction did not produce a false positive, giving us confidence that oxime peaks will arise from formaldehyde. We also did control experiments to show that the hydroxylamines were effective at reacting with the vast majority (at least 97%) of formaldehyde (details in SI), which made us confident in our methods.

We did consider the possibility of hydroxylamines reacting with surface bound formyl groups. We believe this to be unlikely due to steric and geometric reasons. The large phthalocyanine ligand and the relative steric bulk of the hydroxylamines (compared to surface bound small carbon

molecules) inhibits facile reaction with surface intermediates. The near surface bulk is also a much greater region for reaction than compared to the proportion of molecules that make it to the surface.

Effect on Methanol Selectivity

We now examine the effect of the hydroxylamines on the methanol and formaldehyde selectivity. For all our conditions, methanol is the dominant liquid product. Figure 1a shows that formaldehyde FE (as measured by post-run concentration of oxime or derivative, see SI for methods and Figure S7-9 for example post electrolysis chromatograms) remains small relative to MeOH (5% maximum CH_2O FE compared to 19% maximum MeOH FE). Addition of either EHA and HA decrease the methanol FE by from 19% to 14%, whereas using PFBHA only had small effect. Also, increasing the EHA concentration from 4 mM to 12 mM did not cause further changes in the MeOH FE. While Figure 1a shows the electron selectivity, Figure 1b shows the molar selectivity for formaldehyde and MeOH, which lets us compare whether CH_2O selectivity increases are directly accounted for by MeOH selectivity increases. For all the conditions tested, the total molar selectivity towards liquid products (MeOH and CH_2O) remained unchanged (constant molar selectivity in Figure 1b across the conditions). That is, the methanol selectivity decrease is compensated by a carbon-balanced increase in formaldehyde production. Addition of PFBHA does not lead to a difference in formaldehyde only a very small decrease in MeOH selectivity, whereas for EHA and HA (and 12 mM EHA), MeOH selectivity fell from 7.5% to 5.5% and CH_2O selectivity increased from 0.5% to 2.5%.

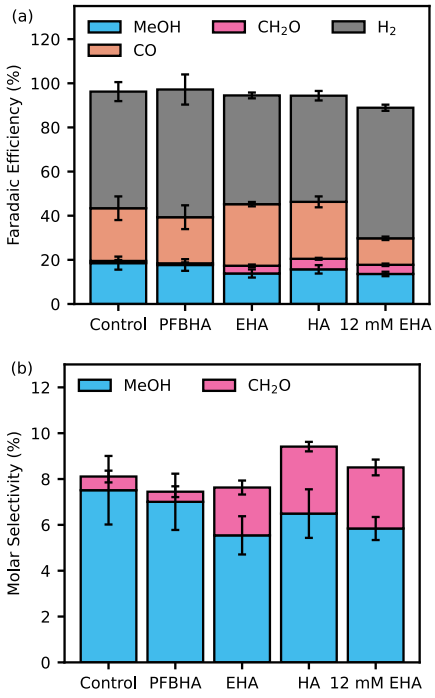


Figure 1. (a) FE of CO_2R products: control (CO_2 0.1 M $KHCO_3$), electrolyte containing 4 mM of PFBHA, EHA, and HA, and electrolyte containing 12 mM of EHA (b) molar selectivity of liquid products CH_2O and MeOH. Electrolyte flow rate was maintained at 8.5 cm/min, and the potential was maintained at -1.1 V vs RHE for 52 min. Formaldehyde was quantified by measuring the oxime concentration in the electrolyte post-run, and derivatized post-run in the case of the control (see SI for detailed methods). Error bars are 85% confidence intervals over 4 to 8 trials.

The constant liquid product molar selectivity between all the conditions is significant: hydroxylamines do not fundamentally alter the catalyst's intrinsic selectivity or any previous steps before the formyl/formaldehyde reduction. Instead, the hydroxylamine simply prevents the free formaldehyde it binds from undergoing further reduction. Based on the molar selectivity trends, we suggest that free formaldehyde is the intermediate to at least a quarter of the methanol produced.

We can qualitatively assess the free formaldehyde lifetime and free formaldehyde percentage based on the kinetics of the hydroxylamines. PFBHA reacts the slowest with formaldehyde as expected; hence we only observe a small decrease in methanol selectivity and little measurable difference in formaldehyde selectivity. This seems to confirm prior reports that formaldehyde, if it is an intermediate, is relatively short lived, unlike its predecessor CO which previous studies showed reacts much more slowly.[13,14,29] Use of faster complexing agents/kinetics (EHA, HA, and 12 mM EHA) adds crucial insights. We expect that HA and 12 mM EHA should have faster formaldehyde reaction kinetics compared to 4 mM EHA and hence should expect greater formaldehyde selectivity and lower methanol selectivity. Figure 1b shows that if there is any effect between the three of them, it is very small.

Comparing our assessment of formaldehyde's role and the effect of a trapping agent to other studies, we see significant differences. Boutin et al. used a similar catalyst preparation (physically mixed) as used here and found that at most 10% of the methanol originates from free formaldehyde.[8] They found that the FRR is too slow to account for MeOH formation rates by comparing formaldehyde reduction reaction rates at various CH_2O concentrations to MeOH formation rates in CO_2R/COR but did not assess the role of removing formaldehyde. Reduction of unbound formaldehyde to MeOH near the surface is complicated by higher local pH, potentially nonuniform formaldehyde hydration, and different reactant/product concentrations near the interface due to depletion and generation. This underscores the importance of removing formaldehyde during reaction to gain new insight. Li et al. instead used sodium bisulfite as their formaldehyde trapping agent and a dispersed CoPc preparation and indeed found that formaldehyde selectivity increased with its presence.[22] However, the range of trapping rates were limited by bisulfite impacting the electrolyte buffer capacity. Here, we are able to achieve fast

trapping kinetics without compromising buffer capacity and find that 25% of methanol originates from unbound formaldehyde on a physically mixed CoPc/MWCNT preparation. We showed in this work a platform to examine the role of the formaldehyde kinetics by using various trapping agents and this can be extended to other CoPc systems as well (e.g. different electrolyte or loading, or mass flow).[13,34–37]

Is formaldehyde a poison?

Yu et al reported recently that formaldehyde can have a weak poisoning effect on CoPc catalysts (dispersed preparation) by binding to the cobalt center, thereby decreasing (but not eliminating) the selectivity for methanol over the timescale of hours.[23] The authors arrived to this conclusion by showing CoPc methanol selectivity recovery when the electrolyte is replaced but, importantly, did not measure formaldehyde directly. Key to this claim is that formaldehyde has a weak and reversible poisoning effect, so its chemical potential in the bulk should strongly determine the poisoning extent and hence removal from bulk should reduce the poisoning extent. This contrasts irreversible poisoning effects like CO on Pt, where the surface will remain poisoned even when CO is removed from the system.

To see whether, with our catalyst preparation, formaldehyde has a poisoning role, we conducted 3 hr electrolysis runs with and without PFBHA, removing 1 mL aliquots for liquid analysis every 20 minutes. PFBHA reacts slowly enough as to not strongly influence the near surface reactions with CH_2O, but effectively scrubs the bulk electrolyte of formaldehyde, which should suppress the expected poisoning effect. As shown in Figure 2, MeOH FEs decline over time, but the decline is the same, within experimental uncertainty, for the control and the PFBHA experiments. While catalyst stability can be preparation dependent, in our case, formaldehyde does not appear to have a poisoning role.

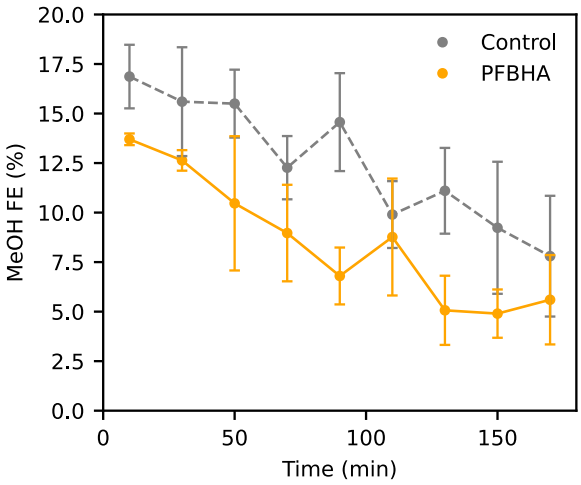


Figure 2. FE of methanol during the aliquot period during electrolysis. The FE is only associated with the MeOH formed during the last 20-minute period and does not represent a cumulative measurement. Linear flow rate was maintained at 8.5 cm/min, and the potential was maintained at -1.1 V vs RHE for the duration of the experiment. 1 mL aliquot of electrolyte is removed every 20 minutes for analysis. Error bars are standard deviations of 3 repeats per condition.

Continuum reaction-diffusion-convection model

A simplified reaction-transport model was constructed to examine the role of unbound formaldehyde. We use a 2D microkinetic model (kinetics + transport in 2D), where we assume that methanol is formed through an unbound formaldehyde intermediate, which is formed from an unbound CO intermediate (Figure 3a, more model details in SI and Figure S17). We assigned first order heterogenous rate constants for the three relevant reactions based on the experimentally observed CO, CH_2O, and MeOH fluxes. We specifically excluded step 6c from Scheme 1 (direct CO reduction without formaldehyde desorption) for this model in order to examine just the unbound formaldehyde hypothesis. We then introduced the hydroxylamine as a homogenous

species at 4 mM in the bulk with a second order rate constant k_{trap} which can be varied to examine its effect on the observed formaldehyde and methanol fluxes.

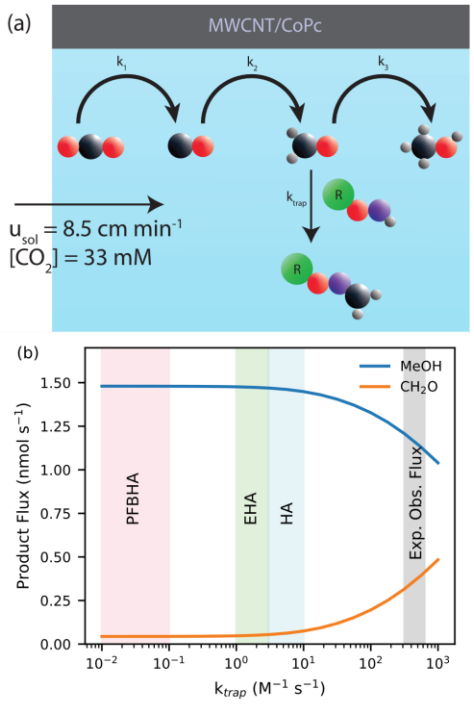


Figure 3. (a) Reaction-transport model. MeOH is formed by sequential 2e$^-$ reductions with 3 different respective heterogenous first order rate constants k_1, k_2, k_3. The hydroxylamine is accounted for by adding a bulk second order rate constant k_{trap} (b) The resulting fluxes of MeOH and formaldehyde (in the oxime form) as a function of k_{trap}. Shaded area represents approximate ranges for the rate constant of each of the hydroxylamines. Gray shaded area represents the observed MeOH and CH_2O fluxes in presence of EHA.

As seen in Figure 3b, increasing k_{trap} decreases the methanol flux and concomitantly increases the formaldehyde flux (see Figures S18-S19 for concentration profiles for all the species at a low and high k_{trap}). In our experiments, we observed a 25% reduction in the methanol molar flux due to the hydroxylamine. Our continuum model predicts that this should happen at rate constants around 10^2-10^3 M^{-1} s^{-1} (see gray shaded area on Figure 3b), about 2 orders of magnitude higher

than the estimated rate constants for the hydroxylamines. Given the simplicity of the model and the method used to estimate the rate constants, we did not expect quantitative agreement. Our measured rate constants are necessarily lower bounds as imperfect mixing in our FTIR experiments will lower the observed k_{trap}. Also, local pH increases during electrolysis can also increase the effective k_{trap}. Hydration effects could also play a role if unbound formaldehyde generated by CoPc reacts before full hydration. The model also assumes a smooth electrode; a rougher electrode can have a lower k_3 which should lead to a larger effect for a given k_{trap}. We also considered a surface bound pathway. However, adding a surface bound (6c) pathway alone does not qualitatively change our interpretation as shown in Figure S20, where we added path 6c with rate constants chosen such that 25% of the MeOH originate from the unbound pathway. This model thus provides a qualitative framework for connecting the kinetics of the trapping agents to the kinetics of formaldehyde reduction and formation.

LIMITATIONS AND OUTLOOK

In this study we showed a chemical method for trapping formaldehydes at various kinetic timescales to examine the role of formaldehyde in CoPc without significantly altering the relevant chemical environment for CO_2R. While we developed a model to connect trapping rate constant to formaldehyde formation/conversion rates, its quantitative utility was limited by some key assumptions. Future models should consider the pH dependence of k_{trap}, and account for the roughness of these catalysts (they are very rough). More precise kinetic measurements could be done with stop-flow techniques; the pH dependence could also be examined. In the case of PFBHA, NMR could be used to quantify the kinetics, noting that it has been used before for other bulky hydroxylamine reactions.[38]

Aldehydes have complex aqueous chemistry: they can form acetals, hemiacetals, and hydrates with alcohols and water, react with themselves, undergo aldol additions and condensations, etc. Aldehyde chemistry is also relevant to other electrocatalytic CO_2R pathways. On Cu, acetaldehyde is both an observed product and sometimes a hypothesized intermediate towards ethanol, but as in the case with formaldehyde and methanol in this study, its exact role is still debated.[39–41] Hydroxylamines can also react with other aldehydes (albeit slower than formaldehyde).[38,42] We thus suggest that the methods developed in this work could be applied to study other systems where aldehyde chemistry might play a role. This can include studying the effect of electrolyte or CoPc preparation on the lifetime/role of formaldehyde, or studying study the acetaldehyde lifetime in Cu and examine whether ethanol selectivity is affected, among others.

CONCLUSIONS

We used three different hydroxylamines with varying steric bulk (and hence varying kinetics) as trapping agents to react (and remove from further reduction) unbound formaldehyde to oximes during CO_2R to MeOH on CoPc. This allowed for a large variation in the trapping rate without significantly altering the buffer capacity of the electrolyte. We found that on our physically mixed preparation of CoPc, unbound formaldehyde is an intermediate to at least 25% of the MeOH, which is more than previously thought. The slower-reacting PFBHA did not affect MeOH selectivity whereas the faster EHA, HA, and 12 mM EHA (3x concentration) reduced MeOH selectivity by a quarter, confirming that formaldehyde is a short lived intermediate (compared to CO). We also found no evidence that formaldehyde is a poison. A simplified continuum-microkinetic model assuming sequential $2e^-$ reductions is in qualitative agreement with the experiments. We discussed the possibility of using the same technique to study the role of acetaldehyde in electrocatalytic CO_2R on Cu.

ASSOCIATED CONTENT

[#] The co-first authors reserve the right to put their name first on their resumes and CVs.

Supporting Information. Detailed Experimental Methods, Details of Continuum Modeling, Supplemental Figures and Tables, Supplemental References

Data availability. The raw data will be uploaded to a public repository upon publishing.

Author Contributions. AS, CK, and JA jointly conceptualized the paper. AS and CK performed electrochemistry experiments, the analytical chemistry, and wrote the original draft. AD, JWA, and CK performed continuum simulations. HZ and AS performed IR experiments. All authors were involved in draft revisions.

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Conflicts of interest

No conflicts of interest to report.

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