Hetero-Bimetallic Paddlewheel Complexes for Enhanced CO₂ Reduction Selectivity: A First Principles Study

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Abstract

The reduction of carbon dioxide (CO_2) into value-added feedstock materials, fine chemicals, and fuels represents a crucial approach for meeting contemporary chemical demands while reducing dependence on petrochemical sources. Optimizing catalysts for the CO_2 reduction reaction can entail employing first principles methods to identify catalysts possessing desirable attributes, including the ability to form diverse products and exhibit favorable reaction kinetics. In this study, we investigate the CO_2 reduction reaction on bimetallic Cu paddlewheel complexes, aiming to understand the impact metal doping has on bimetallic paddlewheel metal-organic frameworks (MOFs). Doping the paddlewheel with Mn results in a more catalytically active Cu center, poised to produce substantial quantities of formic acid (HCOOH) and minor quantities of methane (CH_4) with a suppressed production of C_2 products. Moreover, the presence of Mn as a dopant significantly reduces the limiting potential for CO_2 reduction from 2.22 eV on the homo-bimetallic Cu paddlewheel complex to 1.19 eV, thereby necessitating a smaller applied potential. Conversely, within the Co-doped paddlewheel complex, the Co-site emerges as the primary catalytic center, selectively yielding CH_4 as the sole reduced CO_2 product, with a limiting potential of 1.22 eV. Notably, the Co site faces substantial competition from H_2 production, attributed to a lower limiting potential of 0.81 eV for hydrogen reduction. Our examination of the Cu-Ni paddlewheel complex, featuring a Ni dopant, reveals two catalytically active centers, each promoting distinct reductive processes. Both the Ni and Cu sites exhibit a propensity for HCOOH formation, with the Ni site favoring further reduction to CH_4 , while the Cu site directs the reaction towards methanol (CH_3OH) production. This highlights the profound influence of metal dopant incorporations on the type and quantity of products generated during CO_2 reduction.

Introduction

The increasing utilization of petroleum-based fuels has contributed to a persistent and growing accumulation of greenhouse gases, notably carbon dioxide, in Earth's atmosphere.^{1–3} This surge has led to adverse consequences such as rising global temperatures, increased air pollution, and intensified extreme weather events. To mitigate this upward trend, an array of technologies collectively known as carbon capture, utilization, and sequestration (CCUS) are being developed to reduce atmospheric CO_2 levels.⁴ This entails capturing CO_2 emissions and subsequently employing them for immediate utilization or long-term storage. The process of CO_2 utilization involves its conversion into value-added materials, including various fuels (e.g., methane, methanol), fine chemicals (e.g., formaldehyde, formic acid), and feedstock materials (e.g., ethylene), thus serving as a sustainable alternative to petroleum-based resources.⁵

Several methodologies, including thermal hydrogenation^{6–8} and (photo)electrochemical reduction, 9,10 are currently under investigation for the activation and utilization of CO₂. Electrochemical reduction, in particular, offers a distinctive approach by allowing precise control over product formation through voltage modulation.¹¹ Notably, Kuhl and colleagues¹² have exemplified this phenomenon during CO₂ reduction on metallic copper surfaces. Their investigation revealed up to fifteen distinct CO₂ reduction products, whose composition significantly varied with applied voltage. At lower voltages (-0.9 V vs. RHE), the predominant products included methane, formate, CO, ethylene (C₂H₄), and H₂, while higher voltages led to the formation of C₃ products like n-propanol or acetone in addition to other C₁ and C₂ products.

In contrast to metallic surfaces, materials such as metal organic frameworks (MOFs) offer highly dispersed and well-defined active sites that bridge the gap between traditional heterogeneous and homogeneous catalysis.¹³ However, most MOFs are electrical insulators,

which historically posed challenges for electrochemical studies and CO₂ reduction. Nevertheless, recent research has demonstrated that even insulating MOFs can serve as effective electrocatalysts for CO₂ reduction.^{14–24} Building upon the seminal work of Weng *et al.*¹⁴ who demonstrated that HKUST-1 could effectively reduce CO₂ to CH₄, research by Nam *et al.*¹⁵ and Perfecto-Irigaray *et al.*¹⁶ explored the effects of structural distortions on HKUST-1 MOFs, yielding diverse CO₂ reduction products. Nam and colleagues induced MOF distortion through thermal treatments, achieving higher C₂H₄ production with a remarkable Faradaic efficiency (FE) of 45% for MOF-derived Cu cluster catalysts. Conversely, Perfecto-Irigaray *et al.* introduced metal dopants (Zn(II), Ru(III), or Pd(II)) to induce distortions to HKUST-1. They observed changes in the FE of ethanol (CH₃CH₂OH) and methanol (CH₃OH) production. However, their work revealed that a stable FE plateau was eventually reached, similar to or lower than that of the undoped MOF, irrespective of the dopant metal.



Figure 1: Model paddlewheel complex used to study the CO_2 reduction reaction on HKUST-1. Color code: H (white), C (grey), O (red), Cu (brown), dopant metal (pink).

Improving upon the findings of Perfecto-Irigaray *et al.* and Nam *et al.*, this study employs first principles methods to investigate the thermodynamics of CO_2 reduction using paddlewheel cluster models of doped HKUST-1 MOFs (Figure 1). In contrast to previous studies, we explore dopant metals (Mn(II), Co(II), and Ni(II)) that are anticipated to alter the electronic structure of the adjacent Cu site while providing an alternative active site

for catalysis. Our research reveals that Mn significantly reduces the energy barrier for the initial CO₂ reduction from 2.22 eV to 1.19 eV, resulting in enhanced production of formic acid (HCOOH) and complete suppression of C₂ product formation. In contrast, the Co site of the Co-doped cluster exhibits stronger CO₂ adsorption and selective CH₄ production. However, this site also promotes more favorable hydrogen reduction to form H₂, potentially limiting CO₂ reduction efficiency. Lastly, Ni dopants yield both Ni and Cu sites with distinct reaction mechanisms, favoring HCOOH and CH₄ formation on the Ni site, while the Cu site predominantly produces HCOOH and CH₃OH. Our findings underscore the pivotal role of judicious metal dopant selection in HKUST-1, leading to significant modifications in product identity and proportions during CO₂ reduction.

Computational Details

To study the bimetallic paddlewheel MOFs, we used a truncated model of the HKUST-1 MOF composed of four acetate linkers and two metal nodes (Figure 1). This type of model has been used previously to examine multiple facets of HKUST-1.^{6,25–28} In an effort to preserve some of the inherent rigidity of the MOF material, we constrained the positions of the C atoms of the acetate linkers to their crystallographic positions, allowing all other atoms to fully relaxed during the optimization steps.^{6,25} We conducted all calculations using the M06L²⁹ density functional as implemented in the ORCA 5.0.3³⁰ software package. For basis sets, we employed def2-TZVPP for the metal atoms, def2-TZVP for the first coordination sphere around the metal atoms and the adsorbate molecules, and def2-SV(P) for all other atoms.³¹ The resolution of identity (RI)³² method was utilized to accelerate the computation of all four-index integrals with the def2/J auxiliary basis set.³³ An unrestricted Khon-Sham wavefunction was assumed for all calculations and tight criteria were used for both the SCF and geometry optimization steps. To account for dispersion effects beyond those inherent in

the MO6L density functional, we used the D3zero³⁴ method. Analytical frequency calculations were performed to ensure each structure corresponds to a local minimum and to derive thermodynamic quantities. Implicit solvation effects were considered using the continuumlike polarizable conductor model (CPCM), with H_2O as the solvent of choice.³⁵

The total energy (G) of each reactant, intermediate, and product was determined following Eq. 1, where E represents the total electronic energy, I encompasses the internal energy, accounting for zero-point energy and thermal effects, while H and S denote enthalpic and entropic contributions, respectively, evaluated at T = 298K. Additionally, eU signifies the effect of an applied potential (U) per electron (e). We considered each elementary step of the reduction reaction to proceed through a proton-coupled electron transfer (PCET) mechanism,^{36,37} entailing the addition of a hydrogen atom as a H⁺/e⁻ pair to the system. This mechanism ensures the overall charge of the system is conserved throughout the reaction. The electrochemical reaction energies were referenced relative to the reactants, which included the paddlewheel complex, a CO₂ molecule, and H⁺/e⁻ pairs representing the PCET steps. The energy of a single H⁺/e⁻ pair is set to 1/2 H₂ following the computational hydrogen electrode (CHE).^{11,38} We employed CHE as an initial approximation to elucidate the thermodynamics governing the CO₂ reduction mechanism. The limiting potential (U_L) for a given product is calculated based on the maximum difference between elementary reduction steps (ΔG_{max}) leading to the formation of that product.

$$G = E + I + H - TS - eU \tag{1}$$



Figure 2: C_1 reduction intermediates on the Cu-Cu paddlewheel complex. Arrows correspond to a reduction (PCET) step. Color code: H (white), C (grey), O (red), Cu (brown).

Results & Discussion

CO₂ Reduction on the Cu-Cu Paddlewheel Complex

To elucidate the influence of dopants on Cu-paddlewheel complexes in the context of the CO_2 reduction reaction, we start by performing an in-depth analysis of the reaction on the Cu-Cu paddlewheel complex. As previously mentioned, Nam *et al.*¹⁵ conducted studies that underscored the capacity of both Cu-acetate (CuAc) and HKUST-1 to mediate the reduction of CO_2 to products such as carbon monoxide (CO) and ethylene (C_2H_4). In our present study, we have elected to employ an acetate paddlewheel complex to model the open-metal sites (OMS) of HKUST-1. This choice is anticipated to yield slight variations, akin to those observed by Nam *et al.*, between the two materials. However, our overarching objective is to probe the potential of alternative metal dopants, not investigated by Perfecto-Irigaray *et*



Figure 3: Free energy reaction mechanism for the reduction of CO_2 on the Cu-Cu paddlewheel complex. Competing intermediates shown in red. Limiting potential values shown in blue and given in eV.

al., to enhance the CO_2 reduction reaction.

The initial step of CO_2 reduction on the Cu-Cu paddlewheel complex (Figure 2, 3) results in the formation of one of two intermediates: *OCHO for reduction at the C atom of CO_2 and *OCOH for the reduction at one of the O atoms. Here, the * symbol indicates surface adsorption of the intermediate. The *OCHO and *OCOH intermediates exhibit comparable formation energies of 2.22 and 2.34 eV, respectively. The modest difference of 0.12 eV (2.8 kcal mol⁻¹) between their formation energies suggests that both intermediates should form with a slightly higher likelihood of the *OCHO intermediate forming. Subsequently, the *OCHO intermediate can undergo further reduction to form either *HCOOH or *O and CH₂O (formaldehyde), while the *OCOH intermediate can lead to the formation of *HCOOH, *CO, or *HOCOH. In either case, the closed-shell species (*CO and *HCOOH) are more energetically favored over the open-shell species (*HOCOH and *O). The *HCOOH intermediate exhibits slightly stronger binding to the Cu site compared to *CO, although both are weakly bound (Table S1), potentially explaining the formation of both formate and CO observed by Nam *et al.* with more CO being formed.

Further reduction of both ^{*}CO and ^{*}HCOOH results in the favorable formation of ^{*}HCO

with formation energies of 1.31 and 1.63 eV, respectively. While several other intermediates are possible, they lie higher in energy and are less likely to form. Subsequent reduction steps favor the formation of the closed-shell $^{*}CH_{2}O$ species over the open-shell $^{*}HCOH$ species by 1.81 eV, limiting its expected formation. Following this, both $^{*}CH_{3}O$ and $^{*}CH_{2}OH$ intermediates are expected to form due to their similar formation energies (1.19 and 1.12 eV, respectively), but both ultimately lead to the formation of $^{*}CH_{3}OH$ in subsequent steps. The reduction process then favors the formation of the $^{*}OH$ intermediate, accompanied by the release of free CH_{4} , culminating in the formation of an adsorbed $^{*}H_{2}O$ species as the final reduced intermediate. The strong binding of both the $^{*}CH_{2}O$ and $^{*}CH_{3}OH$ intermediates to the Cu site may explain their absence in the work of Nam et al. Consequently, our results suggest that formic acid, carbon monoxide, and methane constitute the primary products of CO_{2} reduction on the Cu-Cu paddlewheel complex.

Nam *et al.* and Perfecto Irigaray *et al.* observed the production of C_2 products, namely C_2H_4 , CH_3CH_2OH (ethanol), and CH_3COOH (acetic acid), during CO_2 reduction. The formation of C_2 products results from the coupling of less strongly bound C_1 products on the catalyst surface. In the case of the Cu-Cu paddlewheel complex, intermediates that may lead to the formation of ethylene, ethanol, and acetic acid encompass *OCOH and *CH₂OH (Figure 2). These C_1 intermediates do not directly lead to the formation of the C_2 products, but instead require subsequent reduction: two equivalents of *CH₂OH followed by two reduction steps can lead to both ethanol (Eq. 2) and ethylene (Eq. 3) formation, while the coupling of *CH₂OH and *OCOH followed by two reduction steps, may result in the formation of acetic acid (Eq. 4).

$$2CH_2OH \to (CH_2OH)_2 \xrightarrow{H^+/e^-} CH_2CH_2OH + H_2O \xrightarrow{H^+/e^-} CH_3CH_2OH + H_2O \quad (2)$$

$$2CH_2OH \to (CH_2OH)_2 \xrightarrow{H^+/e^-} CH_2CH_2OH + H_2O \xrightarrow{H^+/e^-} C_2H_4 + 2H_2O$$
(3)

$$OCOH + CH_2OH \to HOCH_2CO_2H \xrightarrow{H^+/e^-} CH_2COOH + H_2O \xrightarrow{H^+/e^-} CH_3COOH + H_2O$$

$$(4)$$

The precursor for the formation of ethanol and ethylene is $(CH_2OH)_2$ (ethylene glycol), while the precursor for acetic acid is HOCH₂CO₂H (glycolic acid). The formation of these precursors is both thermodynamically and electrochemically favorable. The reduction of glycolic acid favors the formation of the ^{*}CH₂COOH and ^{*}OH intermediates, featuring small formation energies of 0.74 and 0.87 eV, respectively. The formation of the ^{*}OH intermediate coincides with the production of free acetic acid and necessitates subsequent reduction to yield H₂O, while the ^{*}CH₂COOH intermediate requires the further reduction of the methylene C to yield acetic acid, both processes being energetically favorable. Similarly, the initial reduction of ethylene glycol leads to the formation of ^{*}CH₂CH₂OH with a formation energy of 0.82 eV, which can be further reduced to both ^{*}C₂H₄ and ^{*}CH₃CH₂OH. ^{*}C₂H₄ is formed upon the reduction of the O atom of ^{*}CH₂CH₂OH, while ^{*}CH₃CH₂OH is formed following the reduction of the methylene C atom. Both of these reduction steps are energetically favorable, with a 0.15 eV (3.5 kcal mol⁻¹) difference, indicating the likelihood of both C₂H₄ and CH₃CH₂OH formation on the Cu-Cu paddlewheel complex.

Building upon this analysis, we seek to elucidate how the introduction of Mn(II), Co(II), or Ni(II) as dopants to the Cu-Cu paddlewheel complex affects CO_2 reduction. We will emphasize the changes in the electronic structure of the Cu(II) site induced by the doped metal and how that affects the CO_2 reduction reaction, as well as how CO_2 reduction proceeds on the doped metal site.

Electronic Structure of Doped Paddlewheel Complexes

The relatively short inter-metallic distances inherent to the paddlewheel complexes often give rise to complex electronic structures. An illustrative example is observed in the Cu-Cu paddlewheel complex, where an antiferromagnetically coupled singlet ground spin state emerges as a consequence of the antiparallel spins on the Cu sites.³⁹ Consequently, a comprehensive understanding of the electronic structure of the doped paddlewheel complexes is imperative for an insightful examination of the CO_2 reduction reaction. To establish the ground spin state of each paddlewheel complex, we examined both ferromagnetic and antiferromagnetic spin states with varying spin multiplicities. In our examination, we also observed variations in the structure of the paddlewheel complexes (Table S2).

For the Cu-Mn paddlewheel complex, we considered both a ferromagnetic septet and antiferromagnetically coupled quintet spin state (see Table S3 for spin populations). These states correspond to parallel and antiparallel spins between the two centers, consisting of a five unpaired electrons on the Mn site (S = 5/2) and one unpaired electron on the Cu site (S = 1/2). We considered only the possibility of a spin flip on the Cu site for the quintet state as the half-filled nature of the d-orbitals on the Mn site would preclude an energetically favorable intermediate spin state. The energy difference between these states was determined to be 1.3 kcal mol⁻¹, which is slightly smaller than the energy difference calculated between the antiferromagnetically coupled singlet and ferromagnetic triplet states of the Cu-Cu paddlewheel complex (1.7 kcal mol⁻¹). Consequently, we anticipate that the CO₂ reduction reaction will predominantly occur on the quintet spin state surface.

In the case of the Cu-Co paddlewheel complex, we examined four distinct spin states: ferromagnetic quintet and triplet spin states, as well as antiferromagnetically coupled triplet and singlet spin states. These states arise from the possibility of high spin (S = 3/2) and low spin (S = 1/2) states on the Co site, in conjunction with the prospect of a spin flip occurring on the Cu site. The ferromagnetic triplet spin state emerged as the ground spin state, characterized by a spin of S = 1/2 on both the Co and Cu sites, featuring parallel spins. The next highest spin state is the antiferromagnetically coupled singlet, lying 1.0 kcal mol⁻¹ above in energy, and corresponding to both sites having antiparallel, S = 1/2 spins. Lastly, the ground spin state of the Cu-Ni paddlewheel complex was determined to be a ferromagnetic doublet with an S = 0 Ni site.

Hydrogen Reduction

The reduction of hydrogen to produce H_2 often occurs concurrently with and competes against CO_2 reduction, particularly when high voltages are applied. Our investigation reveals that the formation of metal hydrides on the paddlewheel complexes is generally thermodynamically unfavorable, with energy requirements ranging from 0.81 eV to 2.29 eV. Figure 4 provides an overview of the formation energies associated with these metal hydrides and the subsequent formation of H₂. Among the various Cu sites, the introduction of Mn as a dopant results in a notable change in the metal hydride formation energy, reducing it from 2.29 eV to 1.67 eV. Conversely, when the paddlewheel complex incorporates Co or Ni, the impact on the formation energy is relatively modest, with changes of only 0.08 eV and 0.28 eV, respectively. However, the dopant metal itself exhibits significant variations, with the formation of a Co-hydride being the most energetically favorable at 0.81 eV, while the Mn- and Ni-hydrides necessitate 1.10 eV and 1.67 eV, respectively. As a catalyst solely for hydrogen reduction, the Co-doped paddlewheel complex demonstrates the smallest limiting potential and is therefore expected to reduce hydrogen with smaller applied voltages. Consequently, the introduction of dopants into the Cu paddlewheel complexes results in significantly more favorable hydrogen reduction, potentially impacting the overall efficiency of $\rm CO_2$ reduction. Figure 4: Reaction mechanism diagram for the reduction of hydrogen to H_2 on the paddlewheel complexes. Values shown in eV. Bold text indicates the adsorption site.



Cu-Mn Paddlewheel Complex

Our investigations revealed significant electronic structure variations in the doped paddlewheel complexes, with perhaps the largest impact observed when Mn is introduced. This disparity can be attributed to the distinct electronic configurations of the Mn and Cu sites; the former favors a high spin configuration characterized by half-filled d-orbitals, while the latter can only accommodate a single unpaired electron due to its d⁹ configuration. These significant variations in the electronic structures of the metal sites are reflected in the binding energy of CO₂, with a substantial 0.38 eV difference between them. Notably, the Mn site exhibits a stronger interaction CO₂, making it more favorable for CO₂ reduction.

During the initial reduction of CO_2 (Figure 5), the formation of *OCHO is strongly favored over *OCOH, with a notable energy difference of 1.11 eV, limiting the formation of *OCOH and, consequently, *CO. Similar to the Cu-Cu paddlewheel complex, closed-shell intermediates are more favored here, leading to the formation of *HCOOH over *O (and CH_2O) or *OCH₂O. The energy required for the formation of *HCOOH on the Mn site is



Figure 5: Free energy reaction mechanism for the reduction of CO_2 on the Mn site of the Cu-Mn paddlewheel complex. Competing intermediates shown in red. Limiting potential values shown in blue and given in eV.

relatively low at 0.61 eV, indicating that only a small applied voltage would be required to reduce CO_2 to HCOOH. However, the strong binding of ^{*}HCOOH on the Mn site suggests limited desorption.

Subsequent reduction of *HCOOH can yield four different intermediates (*HOCHOH, *HOCH₂O, *HCO, and *OH to form free CH₂O), with the formation of the Mn-OH moiety being the most favored. The *OH intermediate then requires a final reduction step to yield *H₂O and the already free CH₂O. The limiting potential for the formation of H₂O and CH₂O is 0.95 eV, higher than that of HCOOH formation, implying the need for a higher applied voltage for further *HCOOH reduction. It is expected that the Mn site favors the interaction with *H₂O rather than CH₂O due to the stronger binding energy (0.50 eV and 0.32 eV, respectively. This process ultimately results in the production of CH₂O and H₂O, but the strong binding of H₂O suggests limited catalytic activity due to significant competition with CO₂.

In contrast to the Cu-Cu paddlewheel complex, the initial CO_2 reduction on the Cu site of the Cu-Mn paddlewheel complex strongly favors the formation of *OCHO over *OCOH by 0.80 eV, inhibiting CO production and favoring HCOOH formation following a second reduc-



Figure 6: Free energy reaction mechanism for the reduction of CO_2 on the Cu site of the Cu-Mn paddlewheel complex. Competing intermediates shown in red. Limiting potential values shown in blue and given in eV.

tion step (Figure 5). The ^{*}HCOOH intermediate can then undergo a subsequent reduction to lead to the ^{*}HCO and ^{*}HOCH₂O intermediates with similar formation energies of 1.19 eV and 1.16 eV, respectively. The small energy difference between these intermediates (0.03 eV, 0.8 kcal mol⁻¹) indicates comparable likelihoods of formation. The reduction of ^{*}HCO leads to several intermediates, including ^{*}CH₂O, ^{*}CH₃O, and ^{*}CH₃OH, without competition from other lower-lying intermediates forming. The reduction of the C atom of ^{*}CH₃OH is more favorable than the O atom, yielding ^{*}OH and free CH₄. The energy difference between these two reductions is 0.66 eV. ^{*}OH is then reduced to H₂O, yielding one equivalent of CH₄ and two equivalents of H₂O from the ^{*}HCO intermediate.

While the ^{*}HCO intermediate is expected to be reduced to only ^{*}CH₂O, with no H₂O evolved during this step, the ^{*}HOCH₂O intermediate can be reduced to produce either H₂O or CH₂O. Both ^{*}H₂O and ^{*}CH₂O result in similar formation energies from ^{*}HOCH₂O and similar binding energies to the Cu site. These observations indicate that the reduction of ^{*}HOCH₂O can lead to either free CH₂O or H₂O with similar likelihoods. If H₂O is produced and ^{*}CH₂O is bound to the surface, it suggests the reduction process may continue, ultimately leading to the formation of CH₄. However, if ^{*}H₂O remains adsorbed to the Cu site, then

further reduction is unlikely to occur.

The production of CH_4 from CO_2 reduction is contingent upon the effective binding of all intermediates to the Cu site, which may not occur in the case of the Cu-Mn paddlewheel complex. Weak binding of closed-shell intermediates at the Cu site implies a reduced likelihood of subsequent reduction steps as the reaction progresses. Consequently, we anticipate a predominant proportion of HCOOH, with only limited, if any, production of CH_2O , CH_3OH , or CH_4 . This expectation contrasts with the findings of Nam *et al.*, who reported formate as only a minor product from CO_2 reduction with HKUST-1. Additionally, few C_2 products are expected due to the favorable desorption of HCOOH which hinders the coupling of C_1 intermediates. Nonetheless, our results underscore the significant influence of the Mn site on modulating the CO_2 reduction reaction in the paddlewheel complexes.

Cu-Co Paddlewheel Complex

 CO_2 exhibits a stronger interaction with the Co site of the Cu-Co paddlewheel complex, similar to the Cu-Mn paddlewheel complex. The difference in binding energy between the Cu and Co centers is slightly smaller at 0.29 eV. However, it is still substantial enough to favor interaction with the Co site. Unlike both the Cu-Cu and Cu-Mn complexes, the Co site of the Cu-Co paddlewheel complex favors the reduction of CO_2 to *OCOH over *OCHO, with a significant energy difference of 0.44 eV (Figure 7). The formation energy of *OCOH is 1.21 eV, considerably higher than that of hydrogen reduction on the site, which stands at 0.81 eV. This suggests that hydrogen reduction may compete strongly with the reduction of CO_2 on the Co site.

Nevertheless, the subsequent reduction of *OCOH favors the formation of both *CO and *HCOOH with similar formation energies. Subsequent reductions then yield *HCO, *CH₂O, *CH₃O, and *CH₃OH, following a pattern identical to that observed on the Cu site of the Cu-Mn paddlewheel complex. Each of the intermediates strongly interacts with the Co site,



Figure 7: Free energy reaction mechanism for the reduction of CO_2 on the Co site of the Cu-Co paddlewheel complex. Limiting potential values shown in red and given in eV.

changing two aspects of the reduction reaction by limiting the desorption of closed-shell intermediates and inhibiting coupling of open-shell intermediates to form C_2 products.

Further reduction of ${}^{*}CH_{3}OH$ at both the C and O atoms lead to the formation of the ${}^{*}OH$ and ${}^{*}CH_{3}$ intermediates with similar formation energies of -0.01 eV and 0.08 eV, respectively. It is more favorable for the ${}^{*}OH$ intermediate to form, but both ultimately result in the formation of CH_{4} , either adsorbed following the reduction of ${}^{*}CH_{3}$ or as a free gaseous product following the formation of ${}^{*}OH$. The strong binding of intermediates to the Co site is expected to then lead to the selective reduction of CO_{2} to CH_{4} , in contrast to the sites of both the Cu-Mn and Cu-Cu paddlewheel complexes. Furthermore, $H_{2}O$ exhibits weaker binding to the Co site compared to the Mn site, reducing the likelihood of strong $H_{2}O$ adsorption that could compete with CO_{2} reduction.

The reduction of CO_2 on the Cu site within the Cu-Co paddlewheel complex is anticipated to be less favorable than on the Co site (Figure S1). This difference primarily arises from several factors, with the foremost being the weaker binding of CO_2 to the Cu site. Additionally, the limiting potential for CO_2 reduction is substantially higher on the Cu site than on the Co site, with values of 1.21 eV and 1.72 eV, respectively. This significant energy difference of 0.51 eV is considerably larger than that observed for the sites within the Cu-Mn paddlewheel complex (0.61 eV and 1.00 eV for Mn and Cu, respectively). Consequently, a higher potential must be applied to initiate CO_2 reduction on the Cu site of the Cu-Co paddlewheel complex, while also competing with the adsorption of CO_2 itself to the site. Therefore, our expectation is that the Co site serves as the catalytically active site for the reduction of CO_2 on the Cu-Co paddlewheel complex.

Cu-Ni Paddlewheel Complex

The adsorption behavior of CO_2 on the individual sites of the Cu-Mn and Cu-Co paddlewheel complexes exhibits significant differences, unlike the Cu-Ni paddlewheel complex, where the difference in binding energy between the Cu and Ni sites is merely 0.10 eV. This smaller energy difference implies that both Cu and Ni sites are likely involved in the CO_2 reduction reaction (Figures 8, 9). Both sites exhibit a preference for reducing CO_2 to *OCHO rather than *OCOH, with comparable limiting potentials (1.55 eV and 1.37 eV for Cu and Ni, respectively). However, the energy differences between the two reduced intermediates differ significantly, standing at 0.74 eV for Cu and 0.31 eV for Ni. Moreover, the *OCHO intermediate is favorably reduced to *HCOOH, following the trends observed for the other complexes.

Differences in electronic structures between the two sites becomes more pronounced after the reduction of *HCOOH. On the Ni site (Figure 8), the formation of *HCO is preferred, whereas on the Cu site, *HOCHOH formation is favored. Subsequent reductions of *HCO on the Ni site lead to the formation of *CH₂O, *CH₂OH, *CH₃OH, *OH, and *H₂O, ultimately culminating in the production of CH₄. Unlike the Mn and Co sites of their respective paddlewheel complexes, the Ni site does not exhibit strong binding of closed-shell intermediates. The adsorption energies of *HCOOH, *CH₂O, and *CH₃OH to the Ni site align with those observed in the Cu-Cu paddlewheel complex. Consequently, the Cu-Ni paddlewheel



Figure 8: Free energy reaction mechanism for the reduction of CO_2 on the Ni site of the Cu-Ni paddlewheel complex. Limiting potential values shown in red and given in eV.

complex is expected to produce a large proportion of HCOOH with a smaller amount of CH_4 produced as well. Additionally, the Ni site is expected to inhibit the coupling of C_1 intermediates and thus, C_2 products are not expected to form.

Conversely, the Cu site within the Cu-Ni paddlewheel complex is not expected to yield appreciable amounts of CH_4 (Figure 9). Instead, the favorable reduction of *HOCH_2OH can occur at either the O or C atoms, resulting in the formation of a free H_2O and an adsorbed *CH_2OH or free CH_3OH and an adsorbed *OH intermediate, respectively. The latter reduction is more favorable with a formation energy 0.64 eV lower than the former. This process then leads to the formation of one equivalent each of H_2O and CH_3OH on the Cu site of the Cu-Ni paddlewheel complex.

The binding of *HCOOH to the Cu site is similar to that on the Ni site and to the Cu sites of the Cu-Cu paddlewheel complex, suggesting that some proportion of CO_2 will be reduced to HCOOH as a product. Further reduction of *HCOOH is expected to lead to CH₃OH production, following the formation of a favorable *OH intermediate, which hinders the production of CH₄. The Cu-Co paddlewheel complex is anticipated to produce HCOOH, CH₃OH, and CH₄ from CO₂ reduction with no significant C₂ product formation and only a



Figure 9: Free energy reaction mechanism for the reduction of CO_2 on the Cu site of the Cu-Ni paddlewheel complex. Limiting potential values shown in red and given in eV.

minor proportion of H_2 .

Conclusions

The investigation into CO_2 reduction across various mixed-metal paddlewheel complexes has shed light on the profound influence of metal doping in hetero-bimetallic HKUST-1 materials. Initially, we conducted an in-depth analysis of the CO_2 reduction reaction within a homo-metallic Cu-Cu paddlewheel complex. This analysis provided valuable insights into the complex electronic structure, which governs the formation of both C_1 and C_2 products, including HCOOH, CO, CH₄, CH₃CH₂OH, C₂H₄, and CH₃COOH. Building upon these insights, we proceeded to investigate the same reaction on Cu paddlewheel complexes doped with Mn, Co, or Ni.

The introduction of Mn as a dopant was found to enhance the catalytic activity of the Cu site, driven by the electronic structure of the Mn dopant. This enhancement was found to inhibit the production of C_2 products through strong interactions of the Cu site with open-shell intermediates capable of coupling together. Simultaneously, it weakened interactions with closed-shell intermediates, leading to the predominance of less highly reduced products such as HCOOH and CH_2O . In contrast, the Co site of the Cu-Co paddlewheel complex demonstrated a distinct catalytic behavior, marked by stronger CO_2 adsorption and a lower limiting potential for CO_2 reduction. Consequently, this site emerged as the primary catalytic site within the Cu-Co paddlewheel complex. Selective CH_4 formation was expected to be the dominant outcome of CO_2 reduction, driven by the strong binding of all reduced intermediates. Notably, the Co site displayed a lower H_2 limiting potential of 0.81 eV, suggesting strong competition with CO_2 reduction. Lastly, the Cu-Ni paddlewheel complex showcased the coexistence of catalytically active Cu and Ni sites. The Ni site was expected to favor HCOOH and CH_4 formation with little competition for C_2 products or H_2 formation. In contrast, the Cu site directed the reaction towards HCOOH and CH_3OH production.

Incorporating diverse metal dopants into Cu-based paddlewheel complexes has, therefore, emerged as a versatile strategy for enhancing the CO_2 reduction reaction on multiple fronts. These enhancements include the inhibition of C_2 byproducts, thereby increasing the selectivity of C_1 products such as HCOOH, CH_3OH , and CH_4 . Furthermore, they influence the competitive interplay with hydrogen reduction, leading to H_2 formation. Collectively, these findings underscore the versatility of mixed-metal catalysts in tailoring CO_2 reduction reactions for diverse applications.

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Supporting Information Available

The supporting information contains additional figures that help support our findings. The file "Energy Data.xlsx" contains the energy values for each reactant, intermediate, and product. The "XYZ.zip" file contains the Cartesian coordinates for each reactant, intermediate, and product on the paddlewheel complexes.

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TOC Graphic

