Mechanism of Ni-NHC CO₂ Reduction Catalysis Predominantly Affording Formate via Attack of Metal Hydride to CO₂

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ABSTRACT: The catalytic role of hydride intermediate in the CO₂ reduction to formate (HCOO⁻) by Ni^{II}-NHC complexes is investigated in detail by density functional theory (DFT) calculations. It is found that a Ni^{II}-hydride is sufficiently hydridic to facilitate the efficient transfer of hydride to the carbon center of CO₂, leading to the HCOO⁻ production. Importantly, the direct hydride transfer path proposed here bypasses the conventional CO₂ insertion into a metal-hydride bond. This mechanism is elucidated through a detailed analysis of the free energy changes and activation barriers, where key parameters such as reduction potentials, pK_a values, and thermodynamics of the catalytic processes are thoroughly evaluated. The thermodynamic hydricity of the Ni^{II}-hydride, calculated to be $\Delta G^{o}_{H^-} = 19.2$ kcal/mol, is in sharp contrast with the less effective Ni^{III}-hydride with $\Delta G^{o}_{H^-} = 52.4$ kcal/mol, highlighting the enhanced reactivity of Ni^{II}-hydride in formate formation. Additionally, an examination of the competitive formation of CO and H₂ reveals the preferential tendency of Ni^{II}-hydride to produce HCOO⁻ over these byproducts. Insights into the influence of the pK_a for the proton source on the feasibility of H₂ production and formate selectivity are also provided, suggesting a way to optimize reaction conditions for improved selectivity and efficiency. Our findings provide a comprehensive understanding of the CO₂ reduction to HCOO⁻ by Ni^{II}-NHC catalysts, emphasizing the direct hydride transfer mechanism rather than the classical CO₂ insertion mechanism.

INTRODUCTION

There is a strong demand to develop practically useful renewable energy cycles in order to solve the recent problems arising from the global warming and climate changes. In this regard, the artificial fuels produced by CO2 reduction catalysis is considered as one of the most promising approaches. Among various possible CO2 reduction products, a greater attention has been paid to those having a form of liquid under ambient conditions (i.e., HCOOH and MeOH) because of their high energy density together with the ease of transportation. Especially, formic acid is attractive due to its character as a hydrogen carrier. The high pressure H₂ gas formation technique has recently drawn considerable attention towards its application to hydrogen fuel cells.¹ One of our recent interests has thus concentrated on the studies leading to gain deeper mechanistic insights into the role of catalysts which predominantly yield formic acid in CO2 reduction. As for the selection of metals to be adopted in the catalytic CO₂ reduction, earth-abundant metals are highly favored in view of large-scale applications, though some molecular catalysts of a precious metal (e.g., Ru, Rh, Re and Ir) have been found to exhibit high selectivity in formate formation.^{2,3} In this context, a series of Ni^{II}-NHC catalysts (see Figure 1) developed by Albrecht and co-workers are attractive catalysts showing high selectivity in formate formation in electrocatalysis.⁴ In the report, they assumed that formate selectively forms via the attack of CO2 by a Ni^{III}-hydride



 \checkmark Selective for formate formation \checkmark High hydricity of Ni^{II}-hydride

Figure 1. Representation of Ni^{II}-NHC complexes and the key Ni^{II}-H intermediate proposed for CO_2 reduction to $HCOO^-$.

intermediate. However, the more detailed mechanistic studies are needed to fully understand the reason for the high formate selectivity by these Ni^{II} -NHC catalysts.

In this study, we conducted density functional theory (DFT) calculations to estimate the free energy changes and the activation barriers associated with the possible reaction pathways. The computational results clarify that the selective formate production is due to the formation of Ni^{II}-hydride rather than Ni^{III}-hydride as a key intermediate. Here we show that the Ni^{II}-hydride possesses a strong hydride donating ability, enabling the hydride transfer from the metal to the carbon center of CO₂. Based on the findings, we propose a more reasonable reaction pathway which was not discussed in the initial report.⁴ Additionally, competitive reactions such as CO formation and proton

Scheme 1. Two possible pathways for the reduction of CO_2 to formate by 1 [Ni^{II}L₂]. (a) Path I was proposed by Albrecht et al.⁴ (b) Path II is proposed in this work based on the DFT calculations.



Figure 2. Calculated energy diagram of the hypothesized reaction route (**Path I**) for CO₂ reduction to formate by the Ni^{II}-NHC catalyst via the Ni^{III}-hydride intermediate, as suggested by Albrecht et al.⁴ All the calculations are conducted by applying the potential of -2.45 V vs. Fc/Fc⁺ in the presence of TFE (pK_a = 35.4 in MeCN).

reduction during electrocatalytic CO₂ reduction by the Ni^{II}-NHC catalysts will also be discussed. Our results provide valuable insights into the reaction pathway involved in the formation of HCOO⁻ by such Ni^{II}-NHC catalysts.

RESULTS AND DISCUSSION

To streamline our calculations, we chose a complex with the simplest structure, where R = Ph and R' = H, as illustrated in **Figure 1**. Our initial calculations focused on the reaction pathway hypothesized by Albrecht and co-workers (**Path I**, see **Scheme 1a**).⁴ They proposed that a proton-coupled electron transfer (PCET) initially takes place to form ²[**Ni**^{III}(**H**)**L**₂] from ¹[**Ni**^{II}**L**₂], and that the resulting Ni^{III}-hydride reacts with CO₂ as a key intermediate to trigger the CO₂ binding. We first accessed the validity of their proposal (**Path I**) in our DFT approach as follows.

As is obvious by the energy diagram shown in Figure 2, Path I is judged to be unfeasible due to the highly uphill nature of the initial PCET step leading to form ²[Ni^{III}(H)L₂] $(\Delta G = 29.5 \text{ kcal/mol})$ when applying the potential of -2.45V vs. Fc/Fc⁺ (reduction potential of ¹[Ni^{II}L₂]) with use of trifluoroethanol (TFE; $pK_a = 35.4$ in MeCN) as the proton source. Undoubtedly, both the PT-ET (proton transfer followed by electron transfer) and ET-PT (electron transfer followed by proton transfer) routes are unfeasible. Even if the Ni^{III}-hydride is given, the subsequent step, affording a formate bound species ²[Ni^{III}(OCOH)L₂] ($\Delta G = 3.7$ kcal/mol), suffers from a kinetic challenge with the activation barrier of $\Delta G^{\ddagger} = 21.3$ kcal/mol. The release of formate from ²[Ni^{III}(OCOH)L₂] is well thermodynamically allowed via one-electron reduction ($\Delta G = -36.8$ kcal/mol, $E_{\text{cal}} = -0.86 \text{ V} vs. \text{ Fc/Fc}^+$) followed by the release of formate $(\Delta G = -15.1 \text{ kcal/mol})$ to regenerate the initial Ni^{II} catalyst.

However, **Path I** must be ruled out due to the energetically unfeasible PCET and CO₂-binding pathways.

Alternatively, we must propose a distinct mechanism for the CO₂ reduction to formate, which provides a route to bypass the high-energy pathway (**Path I**) in **Figure 2**. The more realistic pathway realized in this study is depicted in **Figure 3**, in which ${}^{I}[Ni^{II}(H)L_{2}]^{-}$ instead of ${}^{2}[Ni^{III}(H)L_{2}]$ is ascertained to directly afford formate and the initial catalyst with a reasonably low barrier ($\Delta G^{\ddagger} = 13.4$ kcal/mol).

The initial step is to produce the one-electron-reduced intermediate 2 [Ni^IL₂]⁻ ($\Delta G = 0$ kcal/mol), followed by the concerted proton-electron transfer (CPET)⁵ reaction to afford 1 [Ni^{II}(H)L₂]⁻ ($\Delta G = 6.1$ kcal/mol). This formally 2electron reduced species then attacks the carbon center of CO₂ to transfer a hydride to give a formate. An important realization here is the fact that the formate produced is not required to be bound to the vacant coordination site which is exposed by the loss of the hydride donor. This is because the dangling phenoxo oxygen more closely located is concertedly recoordinating to the metal center while passing over the transition state (TS). The concerted changes in the Ni-H(hydride) and Ni-O(phenoxo) distances are also clearly detailed in Figure 4 based on the results of intrinsic reaction coordinate (IRC) calculation. We think this is a good and rare example demonstrating the lack of need to once form a formate-coordinated intermediate expressed by M-OCOH. In the past, some reports suggested that formate formation proceeds via the insertion of CO2 into the metal-hydride bond (see Scheme 2a).6,7

However, many of such reaction products can be given because of intervention by the solvent as depicted in the following equation:

 $M-H + CO_2 + solv \rightarrow M-solv + HCO_2^- \rightleftharpoons M-OCOH + solv$



Figure 3. Free energy diagram for the proposed reaction route (**Path II**) for CO₂ reduction to formate by the Ni^{II}-NHC catalyst via the Ni^{II}-hydride intermediate. All the calculations are conducted by applying the potential of -2.45 V vs. Fc/Fc⁺ in the presence of TFE (p $K_a = 35.4$ in MeCN). See also **Figures S1-S3**.



Figure 4. IRC (closed-shell singlet) of the transition state for the hydride transfer process. The bond distances (Å) at some points are also shown.

Recently, this interpretation is gradually becoming clearer, due to the reports pointing out the same issues.⁸ Metal hydrides are thus regarded as nucleophilic attackers.

As for the route to ${}^{I}[Ni^{II}(H)L_{2}]^{-}$, neither the PT-ET nor ET-PT pathway is available due to the highly endergonic character, since either the one-electron reduction ($\Delta G =$ 27.7 kcal/mol) or the protonation ($\Delta G =$ 29.5 kcal/mol) of ${}^{2}[Ni^{I}L_{2}]^{-}$ is highly uphill (**Figure 3**). We thus conclude that the CPET route is the only available path to produce ${}^{I}[Ni^{II}(H)L_{2}]^{-}$ (see also **Scheme S1**).

Scheme 2. (a) Previous understanding of CO_2 insertion into a M-H bond for formate formation;^{6,7} (b) Direct hydride transfer from metal hydride to CO_2 .



As briefly discussed above, careful examination of both the reverse and forward IRC paths around the TS ¹[Ni^{II}(H···CO₂)L₂]^{-‡} allows us to better understand the structural and electronic alteration of the reaction system along the reaction coordinate. At the TS, the C...H distance (1.732 Å) achieves an obvious covalency by being much shorter than the sum of van der waals radii (2.9 Å).9 At this point, the Ni-H distance (1.559 Å) is only slightly elongated from that in the hydride precursor (1.523 Å), indicative of an associative mechanism adopted in the present formate formation step. Moving beyond the TS, the reaction proceeds with the gradual formation and eventual release of formate without showing concomitant bonding of formate oxygen to the Ni center. In summary, the Ni^{II}-hydride thus directly produces an unbound formate from CO2 in a sufficiently downhill single reaction step ($\Delta G = -24.8$ kcal/mol). As noted above, this reaction can also be interpreted as an intramolecular ligand exchange in which the hydride donor is replaced by the O(phenoxo) donor.

Extensive reviews elsewhere have thoroughly discussed the crucial role of metal hydrides in selective generation of formate over both the CO formation and the H₂ evolution.¹⁰ It has been highlighted that the thermodynamic hydricity $\Delta G^{o}_{H^{-}}$ of a metal hydride is an important parameter to predict its reactivity in hydride transfer reactions.¹¹ The $\Delta G^{o}_{H^{-}}$ denotes the free energy change when a metal hydride releases H⁻ (Scheme S2).¹⁰ In the context of formate formation process, the free energy of a hydride transfer reaction from metal hydride to CO₂ molecule can be discussed on the basis of the relative hydride donating ability of the metal hydride versus that of formate. The thermodynamic driving force for the hydride transfer reaction can be determined by the hydricities of both formate and metal hydride (see Scheme S3).

In acetonitrile, the hydricity of formate anion has been estimated as $\Delta G^{o}_{H^-} = 44.2 \text{ kcal/mol}.^{12,13}$ Thus, hydrides with ΔG^{o}_{H-} < 44.2 kcal/mol are poised to produce formate in the presence of 1 atm CO2.10,11 For the Ni^{II}-hydride ¹[Ni^{II}(H)L₂]⁻, its hydricity is calculated to be $\Delta G^{o}_{H^-} = 19.2$ kcal/mol, indicating that the hydride transfer to CO2 is about 25 kcal/mol downhill under these conditions (see Table 1). This clearly indicates that the Ni^{II}-hydride is sufficiently hydridic, making it thermodynamically favorable for the reduction of CO2 to give formate. Remarkably, the hydricity of Ni^{III}-hydride ²[Ni^{III}(H)L₂] is estimated to be $\Delta G^{o}_{H^-}$ = 52.4 kcal/mol, revealing that the ²[Ni^{III}(H)L₂] is a poor hydride donor and is disfavored for the formate production (Table 1). Therefore, to enable the hydride transfer to CO₂, the Ni^{III}-hydride requires an additional one-electron reduction, transforming it into the much more hydridic Ni^{II}hydride species.

The relationship between the one-electron reduction potential and the hydricity, as highlighted by DuBois and co-workers,13 is particularly important to understand the behaviors of metal hydride. For Ni^{II}-NHC complexes, the strong electron-donating ability of the NHC ligands significantly increases the electron density around the Ni center, leading to a cathodic shift in the $\mathrm{Ni}^{\mathrm{II/I}}$ reduction potential. This is likely the key factor allowing the Ni-NHC hydrides to exhibit high efficiency and selectivity in CO2 reduction to formate. In contrast, other nickel catalysts such as [HNi^{II}(diphosphine)₂]⁺ catalysts,¹⁴ exhibit lower hydricity with the thermodynamic hydricity in the range of 51-66 kcal/mol (Table 1). As a result, these complexes are generally more effective in catalyzing the reverse reaction of formate formation, i.e., hydride transfer from formate to nickel complex to give CO2 and Ni-hydride.15,16 Such significantly different catalytic properties of nickel catalysts including the Ni-NHCs underscore the importance of controlling the electronic properties of the ligand in order to achieve desirable reactivity and selectivity of metal hydride for the CO₂-to-HCOOH conversion.

It is also well-established that the direct CO₂ binding to a metal center often results in CO formation,^{17,18} with a minor exception.¹⁹ In the context of Ni^{II}-NHC complexes, their notable selectivity for formate formation over CO arises from the easier formation of [Ni^{II}(H)L₂]⁻, where the metal-

Table 1. Thermodynamic hydricities of nickel hydrides and their corresponding free energies for a hydride transfer reaction to form formate.

Compounds	p <i>K</i> a	ΔG^{o}_{H-} (kcal/mol) in MeCN	ΔG°_{rxn} (formate) (kcal/mol) ^a	ref
HCOO-	_	44.2 ^b	-	12, 13
[HNi ^{II} (diphosphine) ₂] ⁺	8-18	51-66 ^c	7-22	14
[Ni ^{III} (H)(L) ₂]	13.8	52.4	8.2	tw ^d
[Ni"(H)(L) ₂] ⁻	51.2	19.2	-25.0	tw ^d

^aRelative free energy to produce formate. ^bBased on a hydride transfer equilibrium between CO₂ and [Pt(depe)₂H]]⁺. ^cDetermined by potential- pK_a method.^{20 d}tw, this work, calculated value.



Figure 5. Free energy diagram for the two competitive reactions of Ni^{II}-hydride with use of TFE ($pK_a = 35.4$ in MeCN). The activation barrier for CO₂ reduction to formate (ΔG^{\ddagger} (formate)) is proposed to be lower than that for H₂ production (ΔG^{\ddagger} (H₂)) based on the LFER.

hydride is sufficiently hydridic in MeCN to reduce CO₂ into formate. Our calculations reveal that a CO₂²⁻ bound intermediate required for the CO evolution can be yielded only if the two-electron reduced intermediate is available based on the reaction: ${}^{1}[Ni^{0}L_{2}]^{2-} + CO_{2} \rightarrow$ ${}^{1}[Ni(CO_{2}^{2-})L_{2}]^{2-}$ (see Figure S4). However, this route is substantially disfavored due to the highly uphill character of the step affording ${}^{1}[Ni^{0}L_{2}]^{2-}$ ($\Delta G = 27.7$ kcal/mol; Figure 3). It is therefore concluded that the high preference for the promotion of the CPET step leading to afford the ${}^{1}[Ni^{11}HL_{2}]^{-}$ is the primary reason for the high selectivity in formate formation versus CO formation.

The reason for the experimentally observed low selectivity for H₂ production versus CO₂ reduction can be discussed as follows. Notably, the free energy change associated with the H₂ evolution by reacting ¹[Ni^{II}HL₂]⁻ with the HBase⁺ ($\Delta G^{o}_{rxn}(H_2)$) consists of three components derived from hydride release from metal hydride ($\Delta G^{o}_{H^{-}}$), protonation of free hydride yielding H₂ ($-\Delta G^{o}_{H2}$), and deprotonation from HBase⁺ ($\Delta G^{o}_{pKa} = 1.364 pK_{a}$) (Scheme **3**).¹⁰ This means that the pK_a value of the acid source used largely affects the driving force for H2 evolution because the former two parameters remain constant as far as the same catalyst produces H₂ by the similar mechanism. Figure 5 illustrates the manner how the H2 production is disfavored in terms of driving force ($\Delta G_{rxn}(H_2) = -8.5$ kcal/mol) relative to the CO₂ reduction (ΔG_{rxn} (formate) = -24.8 kcal/mol) when 1 [Ni^{II}HL₂]⁻ reacts with the acid (TFE; pK_a) = 35.4 in MeCN)) or CO₂. The activation free energy for the H₂ production ($\Delta G^{\ddagger}(H_2)$) can not be estimated, but that for the hydride transfer to CO2 leading to formate is calculated as ΔG^{\ddagger} (formate) = 13.4 kcal/mol (see below). Based on the so-called linear free energy relationship (LFER),²¹ the higher activation free energy for the H₂ production relative to the CO₂ reduction, *i.e.*, $\Delta G^{\ddagger}(H_2) \gg \Delta G^{\ddagger}(formate)$, can be

Scheme 3. Free energy change for protonation of a metal hydride to produce H_2 . $\Delta G^{o}_{H2} = 76$ kcal/mol in MeCN.

MH 🚤 M'+H	ΔG^{o}_{H-}	(1)
H⁺+H⁻ <== H ₂	$-\Lambda G^{0}$	(2)

...

HBase ⁺		H ⁺ + Base	$\Delta G^{o}{}_{pKa}$	(3)
		Z	H2 H2	• • •

 $MH + HBase^{+} \longrightarrow M^{+} + H_{2} + Base \qquad \Delta G^{o}_{rxn}(H_{2})$ (4) $\Delta G^{o}_{rxn}(H_{2}) = \Delta G^{o}_{H^{-}} - \Delta G^{o}_{H^{2}} + 1.364(pK_{a})$ (5) well rationalized, resulting in the selective formate formation in this catalytic system (see **Figure 5**).

In addition, we also examined how the feasibility in H₂ production via ¹[Ni^{II}HL₂]⁻ varies by varying the pK_a of the proton source (**Table S1**). When MeOH ($pK_a = 39$ in MeCN) is used,²² the CPET route to the hydride itself becomes more difficult ($\Delta G = 11.0 \text{ kcal/mol}$) compared to adopting TFE ($\Delta G = 6.1 \text{ kcal/mol}$) (**Figure S5**). On the other hand, the use of phenol ($pK_a = 29.1$ in MeCN) permits a weakly downhill route to the hydride ($\Delta G = -2.4 \text{ kcal/mol}$) as well as a sufficiently downhill following H₂ evolution step ($\Delta G = -17.3 \text{ kcal/mol}$) (**Figure S5**). Considering the constant driving force for the formate formation with any acid source including phenol (ΔG_{rxn} (formate) = -24.9 kcal/mol), a lowering in the formate selectivity is expected in the same manner as discussed by Yang *et al.*²³

Scheme 4. Proposed mechanism of CO_2 reduction to formate by the Ni^{II}-NHC catalyst.



CONCLUSIONS

In summary, we have shown that the Ni^{II}-hydride rather than Ni^{III}-hydride is the most likely intermediate which undergoes nucleophilic attack to the carbon centre of CO₂, as depicted in Scheme 4. Moreover, we have also demonstrated that formate is directly released from the transition state given by the attack of the hydride to CO₂. Our results clearly point out the importance of avoiding the often-used expression "CO2 insertion" when discussing the formate formation proceeding via the direct C-H bond formation according to the mechanism described in this study. Even if the metal-O(formate) bonded species is the only detectable product, a caution is needed to avoid defining it as a CO₂ insertion, if there remains a possibility of promoting the rebound of O(formate) into the hydridereleased vacant coordination site as a subsequent step after C-H bond formation.

COMPUTATIONAL DETAILS

Reduction potentials and pK_a values were determined in conjunction with isodesmic reactions using experimentally examined reference redox and proton-dissociation processes. Therefore, the solvation free energies of individual species were directly calculated by optimizing their geometries in solution without utilizing the Born-Haber treatment, as described elsewhere.^{24,25} Calculated redox potentials were benchmarked using the experimentally and computationally obtained reduction potentials for the Ni^{II/I}-NHC couple ($E_{exp} = -2.45$ V vs. Fc/Fc⁺). Calculated pK_a values were benchmarked by adopting the experimentally and computationally obtained pK_a value of phenol ($pK_{a,exp} = 29.1$ in CH₃CN).²⁶

All the calculations were carried out using DFT as implemented in Gaussian 09 package.²⁷ Geometries of all the species have been fully optimized using the hybrid functional M06,²⁸ with the effect of solvation in acetonitrile taken into consideration using the conductor-like polarizable continuum model (C-PCM) method.²⁹ The 6-31+G** basis set was applied to the H, C, N, and O atoms, while the effective core potentials (ECPs) basis set (SDD) was applied to the Ni atom. Structures of TSs were determined using the TS option, followed by performing the IRC calculations to verify the right connections between the TS and its forward or backward minimum.

All the energy diagrams used to predict the most probable reaction pathways incorporate calculated free energy changes linked to two key processes as follows (**Scheme S4**): (i) The free energy change associated with the reduction of each intermediate was calculated under the applied electrode potential of -2.45 V vs. Fc/Fc⁺, which corresponds to the Ni^{II/I}-NHC couple studied in this report; (ii) The free energy change associated with the protonation of each intermediate was calculated according to proton transfer from the proton source TFE, using the reported pK_a value of 35.4 in MeCN.³⁰

The potential- pK_a method²⁰ was used to theoretically determine the thermodynamic hydricity ΔG^{o}_{H-} . This method involves a calculated pK_a value of Ni-hydride and two calculated reduction potentials of the conjugate hydride acceptors (see **Scheme S5**), in which the value of $\Delta G^{o}_{H-} =$ 79.6 kcal/mol reported as a thermodynamic constant for the 2-electron reduction of proton into hydride (H⁺ + 2e⁻ \rightarrow H⁻) was adopted.¹⁰ In addition, the calculated hydricity values were finally benchmarked using the experimentally and computationally obtained hydricity value of formate in acetonitrile ($\Delta G^{o}_{H-} = 44.2$ kcal/mol).¹²

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NOTES

The authors declare no competing interests.

ASSOCIATED CONTENT

Supporting Information

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

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