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FULL PAPER

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Mechanistic study of CO/CO₂ conversion catalyzed by a biomimetic Ni(II)-iminothiolate complex

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Abstract

We investigate the CO oxidation into CO_2 catalyzed by a biomimetic Ni(II)-iminothiolate complex in the presence of the sacrificial oxidizing agent methylviologen. We propose a catalytic mechanism supported by the density functional theory analysis of reaction intermediates that agrees with available experimental observations and kinetic data. We rule out a fivecoordinate Ni(II) species as well as a Ni(III) intermediate which was previously proposed and instead identify a key four-coordinate Ni(II) carbonyl species. We find that the turnoverlimiting step is likely the formation of the Ni(II) carboxylic acid species, although if a worse oxidant were used or if the concentration was less, then the oxidation of the Ni(I) species would be the turnover-limiting step. The reported findings should enable the design of better catalysts to favor one of the two competing pathways for CO to CO_2 conversion as catalyzed by this particular complex.

KEYWORDS

catalytic mechanism, CO oxidation, CO₂ conversion, DFT, nickel catalyst

1 | INTRODUCTION

 CO/CO_2 conversion is central to a wide range of reaction mechanisms from carbon metabolism in biology to H₂ production in industrial applications based on the water-gas shift reaction.^[1] The conversion mechanism could also provide meaningful insights into the reverse reaction that converts the greenhouse gas CO_2 into CO, a key intermediate on the path to liquid fuels.^[2-4] In Nature, reversible CO/CO_2 conversion is catalyzed by the natural enzyme carbon monoxide dehydrogenase (CODH) which has a catalytically active Ni(II) center,^[5-8] We focus on a Ni(II)-iminothiolate catalyst, proposed and synthesized by Crabtree and coworkers as a functional biomimetic CODH model system (Scheme 1). The Ni(II)-iminothiolate complex converts CO to CO_2 at room temperature in the water/methanol mixed solvent (Scheme 2) in the presence of the oxidizing agent methylviologen (mv²⁺) and acetate (AcO⁻) as a weak base.^[9,10]

A five-step catalytic cycle has been suggested for the mechanism of CO to CO_2 conversion,^[9,10] in which the decarboxylation of LNi¹-CO₂ is the turnover limiting step, as supported by the overall reaction rate dependence on P_{CO} , $[mv^{2+}]$, $[H_2O]$, [Ni], and solution pH. However, the proposed intermediates have yet to be supported (or, otherwise ruled out) by spectroscopic and theoretical studies.

Herein, we carry out a theoretical analysis of the catalytic mechanism at the density functional theory (DFT) level. The reported findings provide valuable insights into the reaction intermediates as well as guidelines for computational design of molecular catalysts for CO₂/CO conversion in this class of compounds, using inverse design methodologies demonstrated for other systems.^[11]

Yueshen Wu and Benjamin Rudshteyn contributed equally to this study.





2 | COMPUTATIONAL METHODS

We employ DFT^[12-14] with the B3LYP hybrid density functional, which includes Becke's three parameter exchange^[15] and the Lee, Yang, and Parr correlation^[16] to identify and characterize the lowest-energy intermediates for each step of the catalytic cycle, as implemented in the Gaussian 09 software package.^[17] The B3LYP functional has been used extensively to study reaction mechanisms catalyzed by transition metal complexes^[18–20] including free energy calculations of redox potentials and pK_a values.^[21–24] For optimizations, normal mode analysis, spin densities, and thermochemistry (T = 298.15 K), we used the basis set def2SVP^[25] for all nontransition metal atoms except for O, for which we used the 6–31 + G(d,p) basis,^[26,27] which reproduced well the crystallographic structure of the dimer (Supporting Information Figure S1 and Table S1).^[28] Single point calculations for more accurate energies were performed with the basis set def2TZVP^[25] for all nontransition metal atoms except for O, for which we used for O, for which we used 6–311 + G(d,p).^[26,29] All calculations were performed in a dielectric continuum model of methanol, using the SMD model^[30] as commonly applied in studies of redox and acid-base reactions in solution.^[31–34]

The pK_a of intermediates HA were calculated relative to the pK_a of acetic acid, according to the following reactions:

 $HA(solv) + AcO^{-}(solv) \rightleftharpoons A^{-}(solv) + AcOH(solv)$

$$AcOH(solv) \rightleftharpoons AcO^{-}(solv) + H^{+}(solv)$$

The calculation thus circumvents the need of computing the proton solvation free energy, as follows:

$$pK_{a,HA} = \frac{\Delta G_r(solv)}{2.303 \text{ RT}} + pK_{AcOH}$$

where $pK_{a,AcOH}$ is the experimental value of the pK_a of acetic acid (AcOH) in water (4.75)^[34] and ΔG_r (solv) is the free energy change of deprotonation of HA in solution, *R* is the ideal gas constant, and *T* is the standard temperature 298.15 K. High-spin complexes (triplet or quartet as appropriate) were considered, which could be important for Ni complexes.^[35] We found high-spin states generally higher in energy except for **1-TS**, which along with **4'-TS**, turns out to be a transition state for a side reaction, so they were not considered further (Supporting Information Table S2).

3 | RESULTS AND DISCUSSION

Scheme 3 shows the overall catalytic cycle supported by our DFT calculations.

The catalytic mechanism is initiated by conversion of 1 (the active species) into 2, after dissociation of the dimer, which lies off-cycle as shown in Figure 1.

We considered both the sequential PT/ET pathway (3 to 4 to 5 to 6), and an alternative ET/PT pathway (3 to 4' to 5' to 6, see dashed arrow). The coordination of water to Ni(II) (-8.8 kcal/mol, Figure 2) is thermodynamically favored when compared to binding of methanol (-7.6 kcal/mol, Supporting Information Figure S2). The formal oxidation state of Ni in intermediates 5' and 6 (with dative bonds to the -COO⁻ ligand) were determined by analyzing the spin densities of Ni-centers and the coordination bond lengths of Ni-ligand (Supporting Information Figure S3). Figure 3 summarizes the free energy changes of the transformations along the catalytic cycle.

The Ni(II) centers of intermediates **1** (Figure 2), **2**, **3**, and **4** (Figure 4) are four-coordinate square planar structures. Notably, Crabtree and coworkers assigned the environment around Ni(II) in **2** to be five-coordinate,^[9] partially due to the lack of precedence at the time for a four-coordinate Ni(II)-carbonyl species and the suggestion from an extended Hückel study that Ni(II)-carbonyl complexes could be pentacoordinated since

$$2 - N \longrightarrow N^+ + 2AcO^- + CO + H_2O \longrightarrow 2 - N \longrightarrow N^+ + 2AcOH + CO_2$$

SCHEME 2 Reaction that the Ni(II)-iminothiolate complex catalyzes

CUANTUM WILEY 3 of 7



SCHEME 3 Catalytic mechanism of CO/CO_2 conversion by the Ni(II) iminothiolate catalyst supported by DFT. The molecular charges and formal oxidation state of Ni are shown under each structure. The iminothiolate ligand is abbreviated as L in the chemical formula. The dashed line indicates an alternative path



FIGURE 1 DFT-optimized structures of (A) the dimer precatalyst and (B) the resulting intermediate on addition of water. Color code: gray = C, green = Ni, white = H, indigo = N, yellow = S, red = O



FIGURE 2 The DFT-optimized structure of (A) 1 (LNi^{II}H₂O) and (B) 1-TS



FIGURE 3 Calculated free energy changes along the catalytic cycle of CO oxidation by the Ni(II)-iminothiolate catalyst. All energies are reported in kcal/mol. The alternative pathway involving 4', 4'-TS, and 5' are shown in gray

such a configuration could enhance π -back bonding interactions between Ni(II) and CO.^[36] Nevertheless, the DFT level of theory does not support any Ni(II) pentacoordinated structure with the iminothiolate ligand. All structures starting with either carefully chosen trigonal bipyramidal, or square pyramidal geometries, converge to four-coordinate structures with the additional ligand (either CO or H₂O) detached from the Ni center, with or without Grimme's D3 dispersion correction.^[37] Additionally, there have been several reports since the original work investigating this catalyst that have found crystal structures of square planar Ni(II), often serving as structural models of the same CODH enzyme, albeit often distorted.^[38–40] These observations support the suggestion that the iminothiolate ligand is indeed unique in making the Ni center softer than the usual Ni(II), thus, facilitating π -backbonding to CO, yielding an interesting target for spectroscopic characterization.



FIGURE 4 DFT-optimized structures of (A) 2, (B) 2-TS, (C) 3, (D) 4, (E) 5, and (F) 5-TS



FIGURE 5 DFT-optimized structure of 6



FIGURE 6 DFT-optimized structures of (A) 4', (B) 4'-TS, and (C) 5'

The experimental kinetic studies show that the reaction is first-order in p_{co} , $[H_2O]$ and $[mv^{2+}]$. Furthermore, the rate vs. pH curve has an inflection point at pH 7.6, suggesting that an intermediate with pK_a around 7.6 is involved in the steps leading to the turnover-limiting step.^[9] The DFT free energy profile of the catalytic mechanism (Figure 3) agrees with the experimental data. After dissociation of the dimer leading to intermediate **Dimer-Int** shown in Figure 1 goes through ligand substitution by CO via transition state **1-TS** (Figure 2) to yield **2** via **2-TS** and forming **3** (Figure 4) on nucleophilic attack of H_2O on CO to form the carboxylate group.

Ligand substitution (1 to 2) is slightly exergonic and the carboxylation of carbonyl ligand (2 to 3) is slightly endergonic. 2-TS is the highest confirmed transition state in terms of energy shown. Therefore, the turnover-limiting step is carboxylation step, but if the methylviologen oxidant were swapped or lower in concentration, the decarboxylation of the Ni(I) species, 6 (Figure 5), could become the turnover-limiting step. In any case, this deduction explains the dependence on the rate on the concentration of methylviologen. Regarding the pathway from 3 to 6, our calculation suggests that stepwise PT/ET is energetically preferred over the stepwise ET/PT (Figure 6) by about 15 kcal/mol. These results are consistent with EPR data^[10] supporting a Ni(I) signal with no evidence for Ni(III) intermediates, that is, supporting that the PT/ET pathway is favored over the ET/PT pathway.

Deprotonation of **3** is a very endergonic step. The free energy change (ΔG) from **3** to **4** is +11.0 kcal/mol in the presence of acetate as a weak base and +9.5 kcal/mol without acetate buffer, consistent with the very sluggish kinetics of the catalytic cycle.^[9] Interestingly, the calculated pK_a for the metal-carboxylic acid **3** is 11.3 (while the pK_a of **5**' is -5.1), in agreement with the aforementioned rate-pH profile, and supporting the stepwise PT/ET from **3** to **4** to **5** to **6** (Figure 3) and the speculation that the Ni(II)-carboxylic acid **3** is the key intermediate leading up to the turnoverlimiting step. Following deprotonation of **3**, reduction of mv²⁺ to mv⁺ provides the thermodynamic driving force to the oxidation of **4** and the oxidation of intermediate **6**, as shown in Figure 3. The original experimental kinetic study suggests that the turnover-limiting step takes place after formation of **4**, we find that after oxidation, the CO₂ spontaneously comes off suggesting a barrierless process.

4 | CONCLUSIONS

We have analyzed for the first time the catalytic mechanism of CO/CO_2 conversion by the Ni(II)-iminothiolate catalyst at the DFT level. Our results and direct comparisons to experimental data support a mechanism via a key intermediate LNi^{II}(COOH) with a pK_a of around 7.7 consistent with the experimentally observed pH-rate dependence. The Ni(II)-carbonyl intermediate is predicted to have a novel square planar four-coordinate form, rather than a pentacoordinated form as previously suggested. The turnover-limiting step is identified as related to the formation of the Ni(II) carboxylic acid species. The resulting insights on the nature of the elementary steps and identification of turnover-limiting transformations are valuable for molecular design strategies that seek to increase the catalytic efficiency by ligand design and optimization of the catalyst performance. The reported mechanistic study should thus provide a foundation for computer-aided molecular design^[11] of better catalysts in this class of compounds for CO/ CO_2 conversion.

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REFERENCES

- [1] D. J. Evans, Coord. Chem. Rev. 2005, 249, 1582.
- [2] A. M. Appel, J. E. Bercaw, A. B. Bocarsly, H. Dobbek, D. L. DuBois, M. Dupuis, J. G. Ferry, E. Fujita, R. Hille, P. J. Kenis, Chem. Rev. 2013, 113, 6621.
- [3] S. Berardi, S. Drouet, L. Francàs, C. Gimbert-Suriñach, M. Guttentag, C. Richmond, T. Stoll, A. Llobet, Chem. Soc. Rev. 2014, 43, 7501.
- [4] J. Qiao, Y. Liu, F. Hong, J. Zhang, Chem. Soc. Rev. 2014, 43, 631.
- [5] M. Can, F. A. Armstrong, S. W. Ragsdale, Chem. Rev. 2014, 114, 4149.
- [6] P. A. Lindahl, Biochemistry 2002, 41, 2097.
- [7] D. Qiu, M. Kumar, S. W. Ragsdale, T. G. Spiro, Science 1994, 264, 817.
- [8] W. Shin, P. A. Lindahl, J. Am. Chem. Soc. 1992, 114, 9718.
- [9] Z. Lu, R. H. Crabtree, J. Am. Chem. Soc. 1995, 117, 3994.
- [10] Z. Lu, C. White, A. L. Rheingold, R. H. Crabtree, Angew. Chem. Int. Ed. 1993, 32, 92.
- [11] D. Xiao, L. A. Martini, R. C. Snoeberger, III, R. H. Crabtree, V. S. Batista, J. Am. Chem. Soc. 2011, 133, 9014.
- [12] P. Hohenberg, W. Kohn, Phys. Rev. 1964, 136, B864.
- [13] W. Kohn, L. J. Sham, Phys. Rev. 1965, 140, A1133.
- [14] R. G. Parr, W. Yang, Density Functional Theory of Atoms and Molecules, Oxford University Press, New York 1989.
- [15] A. D. Becke, J. Chem. Phys. 1993, 98, 5648.
- [16] C. Lee, W. Yang, R. G. Parr, Phys. Rev. B 1988, 37, 785.
- [17] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, *Gaussian 09, Revision D.01*, Gaussian, Inc., Wallingford, CT **2009**.
- [18] A. Bassan, M. R. Blomberg, P. E. Siegbahn, L. Que, J. Am. Chem. Soc. 2002, 124, 11056.
- [19] T. Lind, P. E. Siegbahn, R. H. Crabtree, J. Phys. Chem. B 1999, 103, 1193.
- [20] P. E. Siegbahn, R. H. Crabtree, J. Am. Chem. Soc. 1997, 119, 3103.
- [21] S. Khan, K. R. Yang, M. Z. Ertem, V. S. Batista, G. W. Brudvig, ACS Catal. 2015, 5, 7104.
- [22] I. Rivalta, K. R. Yang, G. W. Brudvig, V. S. Batista, ACS Catal. 2015, 5, 2384.
- [23] E. M. Sproviero, J. A. Gascon, J. P. McEvoy, G. W. Brudvig, V. S. Batista, J. Inorg. Biochem. 2006, 100, 786.
- [24] T. Wang, G. Brudvig, V. S. Batista, J. Chem. Theory Comput. 2010, 6, 755.
- [25] F. Weigend, R. Ahlrichs, Phys. Chem. Chem. Phys. 2005, 7, 3297.
- [26] T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. V. R. Schleyer, J. Comput. Chem. 1983, 4, 294.
- [27] W. J. Hehre, R. Ditchfield, J. A. Pople, J. Chem. Phys. 1972, 56, 2257.
- [28] Z. Lu, C. White, A. L. Rheingold, R. H. Crabtree, Inorg. Chem. 1993, 32, 3991.
- [29] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, J. Chem. Phys. 1980, 72, 650.
- [30] A. V. Marenich, C. J. Cramer, D. G. Truhlar, J. Phys. Chem. B 2009, 113, 6378.
- [31] S. J. Konezny, M. D. Doherty, O. R. Luca, R. H. Crabtree, G. L. Soloveichik, V. S. Batista, J. Phys. Chem. C 2012, 116, 6349.
- [32] D. Y. Shopov, B. Rudshteyn, J. Campos, V. S. Batista, R. H. Crabtree, B. G. W., J. Am. Chem. Soc. 2015, 137, 7243.



- [33] D. Y. Shopov, B. Rudshteyn, J. Campos, D. J. Vinyard, V. S. Batista, G. W. Brudvig, R. H. Crabtree, Chem. Sci. 2017, 8, 1642.
- [34] J. Ho, Phys. Chem. Chem. Phys. 2015, 17, 2859.
- [35] J. N. Harvey, Wiley Interdiscip. Rev. Comput. Mol. Sci. 2014, 4, 1.
- [36] S. A. Macgregor, Z. Lu, O. Eisenstein, R. H. Crabtree, Inorg. Chem. 1994, 33, 3616.
- [37] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. 2010, 132, 154104.
- [38] W.-F. Liaw, Y.-C. Horng, D.-S. Ou, C.-Y. Ching, G.-H. Lee, S.-M. Peng, J. Am. Chem. Soc. 1997, 119, 9299.
- [39] W.-F. Liaw, C.-H. Chen, C.-M. Lee, G.-H. Lee, S.-M. Peng, J. Chem. Soc. Dalton Trans. 2001, 138.
- [40] J. Forniés, A. Martín, L. Martín, B. Menjón, H. A. Kalamarides, L. F. Rhodes, C. S. Day, V. W. Day, Chem. Eur. J. 2002, 8, 4925.

SUPPORTING INFORMATION

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