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# Bridging thermal catalysis and electrocatalysis: Catalyzing CO<sub>2</sub> conversion with carbon-based materials

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Abstract: Understanding the differences between reactions driven by elevated temperature or electric potential remains challenging, largely due to materials incompatibilities between thermal catalytic and electrocatalytic environments. We show that Ni, N-doped carbon (NiPACN), an electrocatalyst for the reduction of CO<sub>2</sub> to CO (CO2R), can also selectively catalyze thermal CO<sub>2</sub> to CO via the reverse water gas shift (RWGS) representing a direct analogy between catalytic phenomena across the two reaction environments. Advanced characterization techniques reveal that NiPACN likely facilitates RWGS on dispersed Ni sites in agreement with CO2R active site studies. Finally, we construct a generalized reaction driving-force that includes temperature and potential and suggest that NiPACN could facilitate faster kinetics in CO2R relative to RWGS due to lower intrinsic barriers. This report motivates further studies that quantitatively link catalytic phenomena across disparate reaction environments.

#### Introduction

Developing catalysts that use renewable energy to convert plentiful feedstocks like H<sub>2</sub>O, N<sub>2</sub>, and CO<sub>2</sub> to value-added products could enable a sustainable global economy.<sup>[1],[2]</sup> Optimal catalysts exhibit high activity, high selectivity towards a desired product, low cost, and long-term stability to achieve economical industrial operation.<sup>[3]</sup> Research on catalysis to this end is varied and diverse; catalysts can be embodied as biological enzymes, homogeneous, molecular complexes or as solid, heterogeneous surfaces. In particular, heterogeneous catalysis can be broadly divided into two categories: *thermal catalysis*, reactions driven by temperature; and *electrochemical catalysis*, reactions driven by an applied electric potential. Scaling up processes that take advantage of these driving forces may face different challenges. For example, electrochemical reduction of  $CO_2$  (**Eq. 1**,  $CO_2R$ ) has been extensively studied as a carbon-neutral route to fuels and chemicals using renewable electricity.<sup>[1]</sup> A recent technoeconomic analysis suggested that state-of-the-art  $CO_2R$  catalysts need significant improvements in activity and stability before  $CO_2R$  electrolyzers can be industrially viable.<sup>[4]</sup> Similarly, a technoeconomic study of the thermal catalytic conversion of  $CO_2$  to CO by the reverse water gas shift reaction (**Eq. 2**, RWGS) revealed that high operating and equipment costs are required because of the high temperatures (>800°C) necessary to achieving the desired kinetics and thermodynamics for  $CO_2$  conversion on existing catalysts.<sup>[5]</sup>

Thus, the discovery and design of novel catalysts with improved performance is a primary research goal. Many approaches have been employed for both thermal and electrochemical catalysis, including trial and error<sup>[6]</sup>, high-throughput materials screening<sup>[7]</sup>, density functional theory guided predictions<sup>[8]</sup>, and machine learning and data science.<sup>[9]</sup> In both catalysis subfields, champion catalysts are discovered and rationalized by achieving the optimal binding energetics of reactants and key intermediates on the catalyst surface.<sup>[10]</sup>

**CO**<sub>2</sub>**R:** 
$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$$
 **Eq. 1**

**RWGS:**  $CO_2 + H_2 \rightarrow CO + H_2O$  **Eq. 2** 

While knowledge is sometimes leveraged across the two communities, the respective scientific efforts operate largely independently. Part of this disconnect can be attributed to physical differences between the reaction environments, such as the electrified metal-solution interface in electrochemical

environments which can impact reaction kinetics<sup>[11]</sup> in a way not observed in typical gas-phase thermal reactions. However, the earliest foundational work bridging thermal catalysis and electrocatalysis can be traced back to independent studies in the 1970s of hydrogen/Pt<sup>[12]</sup> and carbon monoxide/Pt<sup>[13]</sup> systems that pointed to significant commonalities in mechanisms, binding modes, and turnover frequencies between the reaction environments. More recently, MoS<sub>2</sub> has been widely studied as a hydrodesulfurization (HDS) catalyst<sup>[14]</sup> and an electrochemical hydrogen evolution reaction (HER) catalyst<sup>[15]</sup>, both reactions where hydrogen atom adsorption is critical. Researchers have shown that edge MoS<sub>2</sub> sites are likely active sites for both HDS<sup>[16]</sup> and HER<sup>[17]</sup>, demonstrating a direct structural link between the two reactions.

In CO<sub>2</sub> conversion, the discovery of a Ni-Ga electrochemical CO<sub>2</sub>R catalyst<sup>[18]</sup> was inspired by a previously reported Ni-Ga CO<sub>2</sub> hydrogenation catalyst.<sup>[19]</sup> Similarly, CuZn catalysts used for electrochemical CO<sub>2</sub>R<sup>[20,21]</sup> parallel the Cu/ZnO catalysts used for thermal CO<sub>2</sub> hydrogenation.<sup>[22]</sup> However, direct comparisons remain challenging. The product distribution for both the Ni-Ga and Cu/Zn systems differ between the thermal and electrochemical reaction environments. From a materials standpoint, Cu/ZnO nanoparticle catalysts supported on Al<sub>2</sub>O<sub>3</sub> are used for thermal CO<sub>2</sub> hydrogenation,<sup>[22]</sup> while metallic CuZn films on carbon substrates are used for electrochemical CO2R.[20] Consequently, the CuZn catalysts are not directly comparable despite sharing chemical properties. The differences in active catalyst phase are typically due to the different practical requirements for each reaction environment; high thermal stability and a powdered form are necessary for thermal reactors, whereas electronic conductivity and stability to electrochemical potential changes are necessary for electrochemical cells. However, a material that can be tested for the same reaction in both environments without modification would provide valuable insight into the similarities and differences in mechanisms and energetics of the two systems.

Here, we aim to bridge these two communities using a Ni, N-doped carbon catalyst derived from polyacrylonitrile (NiPACN) [Figure 1A] that is compatible with both thermal and electrochemical reaction environments - a packed bed reactor operating at high temperature, and an electrochemical reactor operating at STP at ambient temperature and pressure with an applied potential. We discover that the exact same NiPACN catalyst is effective for both electrochemical  $CO_2 R^{[23,24]}$  and thermal CO<sub>2</sub> to CO conversion via RWGS. We hypothesize that molecular-like NiNx active sites, previously identified using time of flight mass spectrometry and dark field- scanning transmission electron microscopy as the likely electrochemical CO2R active sites<sup>[24]</sup>, are also responsible for thermal RWGS activity. We explore this active site hypothesis for RWGS through in-situ Ni Kedge X-ray absorption spectroscopy and draw comparisons between the NiPACN and a Ni phthalocyanine molecular standard to show that similar NiNx sites are maintained under RWGS reaction conditions. These results motivated us to define a generalized reaction driving force to directly compare the CO2R and RWGS catalytic rates. We find that NiPACN-catalyzed electrochemical CO<sub>2</sub>R exhibits significantly higher CO production rates than RWGS likely due to a smaller rate-determining transition state barrier in the electrochemical environment. This work shows that Ni, N-doped carbon catalysts can bridge the gap between electrochemical and thermal catalysis and motivates future studies that make quantitative comparisons across disparate reaction systems.

#### **Results and Discussion**

We first characterized the NiPACN catalyst using annular dark field scanning transmission electron microscopy (ADF-STEM). At low magnification (**Fig 1B**), micron-sized carbon particles were observed with ~5-50 nm Ni aggregates decorating the structure. We previously hypothesized that these Ni aggregates formed at high Ni loadings after available binding sites for dispersed Ni atoms were saturated.<sup>[23]</sup> At higher magnification (**Fig 1C**), atomically dispersed Ni atoms bonded within the graphitic carbon matrix were revealed. Prior literature suggests that these Ni atoms are coordinated to nitrogen atoms and are likely present as Ni<sup>δ+</sup>.<sup>[25,26]</sup>

We used X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) to confirm these conclusions. The XRD pattern for NiPACN (**Fig 1D**) shows broad peaks at 3.5 Å and 2.1 Å that match a graphite reference pattern<sup>[27]</sup> and a series of peaks at 2.03 Å, 1.77 Å, 1.25 Å and 1.06 Å that match a Ni fcc metal reference pattern.<sup>[28]</sup> These results confirm the existence of metallic Ni aggregates in a graphitized carbon framework and show no evidence for NiO, in agreement with our prior work.<sup>[23]</sup> The XPS spectrum of the Ni 2p region (**Fig 1E**), however, shows that the dominant Ni signal is at 854.1 eV, which indicates that the majority of Ni atoms are likely in the Ni<sup>2+</sup> oxidation state.<sup>[29]</sup> This Ni<sup>2+</sup> signal observed using XPS contrasts the metallic Ni aggregates observed by XRD, and we attribute this signal to atomically dispersed Ni atoms, which would not produce crystallographic patterns.

We then investigated the catalytic activity of the NiPACN for CO2 conversion to CO under electrochemical CO2 reduction (CO<sub>2</sub>R) and thermal reverse water gas shift (RWGS) conditions to determine if the known CO2R activity of NiPACN translates to the very different operating conditions of RWGS. For electrochemical CO<sub>2</sub>R (Fig 2A), NiPACN shows high selectivity (defined as Faradaic efficiencies) versus the competing HER, agreeing with prior reports<sup>[23,26,30,31]</sup> and reaching >95% CO selectivity between -0.5V and -1.1V vs RHE, rivalling the performance of typical precious metal catalysts Au (>90% selectivity at -0.7V vs RHE)<sup>[32]</sup> and Ag (>90% selectivity at -1V vs RHE)<sup>[33]</sup>. Analogously, NiPACN showed activity (normalized to total product basis) for the RWGS, with >98% CO selectivity compared to the competing methanation reaction between 200°C and 300°C, which is reported here for the first time (Fig 2B). The high CO selectivity in both environments is surprising because metallic nickel is known to be an effective HER catalyst<sup>[34]</sup> under CO<sub>2</sub>R conditions and a selective methanation catalyst in RWGS conditions.[35]

Control experiments implicate single site Ni as the active site for RWGS, as no CO or  $CH_4$  production was observed in RWGS

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**Figure 1.** (A) Schematic of the hypothesized NiN<sub>4</sub> active site in NiPACN showing (left) thermal reverse water gas shift activity at elevated temperature and (right) electrochemical CO<sub>2</sub> reduction with an applied potential. ADF-STEM images of NiPACN at low magnification (B) and high magnification (C) with single metal atomic sites indicated with red arrows. (D) XRD pattern of NiPACN (black) compared to reference Ni (red) and graphite (blue) patterns and (E) High-resolution Ni 2p XPS of NiPACN with dashed lines showing binding energies of Ni<sup>2+</sup> (green) and metallic Ni<sup>0</sup> (red) 2p<sub>3/2</sub> peaks.

when using a metal-free PACN catalyst (SI-Figure 1A). Minimal CO was produced in the control electrochemical CO<sub>2</sub>R study and a combined STEM microscopy, secondary ion mass spectrometry study suggested NiN<sub>x</sub> electrochemical active sites.<sup>[23,24]</sup> In addition, this prior work demonstrated that carbon shells form around Ni aggregates due to Ni-catalyzed graphitization, rendering Ni aggregates inaccessible to adsorbates and catalytic reactions and explaining their apparent lack of contribution to the catalytic RWGS results<sup>[23]</sup> Thus, the presence of Ni in dispersed form is likely correlated to the active site for both reactions. This hypothesis is further supported by the high RWGS CO selectivity observed for a NiPACN sample with a lower Ni loading of 0.5 wt%, which is known to have effectively no Ni aggregates based on our prior study (SI-Figure 1B, 1C).<sup>[23]</sup> We further verified that these Ni aggregates are not the primary source of reactivity in NiPACN by comparing the reactivity to a N-free Ni/C control sample (SI-Figure 2), which showed high methanation reactivity. We also confirmed that CO is produced catalytically and not from carbon catalyst decomposition (further discussion in SI, e.g. the Boudouard reaction is not a significant competing process (SI-Figure 3)).

Prior literature reports have shown that, analogous to the active site in electrochemical CO2R,24 oxidized, dispersed Ni species (Ni<sup> $\delta$ +</sup>) are selective for RWGS,<sup>[36,37],[38]</sup> which suggests that these species might be a RWGS active site due to (1) the lack of adjacent surface sites necessary for C-H bond formation. or (2) the intrinsic electronic structure of Ni<sup> $\delta$ +</sup> sites. We conclude that NiPACN can be used to draw direct comparisons between thermal and electrochemical catalytic behavior because (1) it can be tested in both environments without modifying the catalyst and (2) it has demonstrated similar selectivity in converting CO<sub>2</sub> to CO in both environments.



Figure 2. (A) Selectivity to CO (filled red squares) and H<sub>2</sub> (open red triangles) of NiPACN under electrochemical CO2 reduction (CO2R) conditions in 3compartment 0.1 KHCO<sub>3</sub> testing at 0.2 mg/cm<sup>2</sup> catalyst loading (B) Selectivity to CO (filled black squares) and CH4 (open black triangles) of NiPACN under thermal reverse water gas shift (RWGS) conditions.

The above analysis represents, to the best of our knowledge, the first report of RWGS activity for Ni, N-doped carbon catalysts and the first attribution of RWGS activity to atomically dispersed metal sites in M-N-C materials. This discovery invited further characterization of the structure and stability of the NiPACN catalyst under RWGS conditions-necessary properties for practical catalysts.<sup>[23]</sup> Preliminary durability studies revealed negligible losses in activity and selectivity for the RWGS (SI-Figure 4) over 20 h of reaction. Scanning transmission electron microscopy with energy dispersive X-ray spectroscopy (STEM-EDS) mapping on the as-prepared (Fig 3A) and post-RWGS (Fig 3B) NiPACN further illustrates the unchanging catalyst structure. The similar spatial distribution of Ni, with regions of dispersed (region 1) and aggregate (region 2) Ni signal, shows that irreversible aggregation of dispersed Ni atoms does not occur under RWGS conditions. These images also suggest that NiPACN undergoes minimal reconstruction during reaction, but in-situ techniques are necessary to conclusively determine the nature of the dispersed Ni sites under reaction conditions.

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In-situ Ni K-edge X-ray absorption spectroscopy (XAS) was performed in the X-ray absorption near edge spectroscopic (XANES) region and the extended X-ray absorption fine structure (EXAFS) region to probe the binding configuration of Ni atoms in RWGS the as-prepared catalyst, under conditions (RWGS@300°C), and inert conditions (He@300°C). The XANES spectra (SI-Figure 5A) show a strong resemblance to a molecular square-planar Ni phthalocyanine (NiPc) reference, indicating a four-coordinate Ni-N geometry (further discussion in SI-Supplementary Text and SI-Figure 6).[23,39,40] We did not observe any features characteristic of metallic Ni or NiO upon heating or introduction of reactant gases in either the XANES or EXAFS spectra (SI-Figure 5B), suggesting that minimal aggregation occurs.

The in-situ XANES for RWGS@300°C shows minimal changes compared to the as-prepared catalyst, aside from a slight lowering of a post-edge peak intensity at 8352 eV (**SI-Figure 5A**). The XANES for He@300°C is nearly identical to the RWGS@300°C spectrum, demonstrating that the small differences between the as-prepared and RWGS@300°C spectra are not derived from adsorbate or reaction-induced changes and

are instead functions of sample temperature (**SI-Figure 5A and B**). There is no evidence of metallic Ni or NiO features emerging during the temperature ramp, indicating minimal aggregation occurs (**SI-Figure 5C**). These results suggest that bulk-averaged measurements of the Ni chemical state are largely probing the nature of dispersed Ni sites, which is in direct agreement with the XPS (**Fig 1E**). The lack of Ni-aggregate signatures in the XAS results are surprising given the aggregates identified via imaging and diffraction (**Fig 1B, 1D**); we attribute this to the fact that these spectra are weighted-averages based on all of the Ni environments present in the sample. Our past work on NiPACN showed that Ni aggregation occurs after full saturation of dispersed Ni sites in the material<sup>[24]</sup> suggesting that the Ni aggregates are still minority species and do not contribute substantially to the XAS/XRD spectra.

To further understand the structure of the dispersed Ni active sites, we modeled the EXAFS spectra of the as-prepared, RWGS@300°C, and He@300°C samples. In all the NiPACN catalyst samples modelled in **Fig 3C**, a single, broad peak is observed at 1.4 Å (not phase corrected) that matches



Figure 3. STEM images (left) and corresponding Ni EDS maps (right) for as-prepared (A) and post-RWGS (B) NiPACN in regions with dispersed Ni signal (region 1) and Ni aggregates (region 2). (C) Fitted in-situ EXAFS spectra (raw magnitude of EXAFS data in gray solid line, raw real component of EXAFS in colored dashed line, and fitted model in colored solid lines) of as-prepared, RWGS@300°C, and He@300°C NiPACN. Labels also indicate fitted Ni-N coordination numbers.

closely with the Ni-N scattering peak in the Ni phthalocyanine (Ni Pc) standard. EXAFS fitting was conducted to a model squareplanar NiN<sub>4</sub> complex (k-space fit of NiPACN samples, fit to NiPc standard sample and EXAFS fit parameters available in **SI-Figure 7**, **SI-Figure 8**, and **SI-Table 1**). We found that the fitted Ni-N coordination for all three samples is ~4, supporting our hypothesis of an averaged four-coordinate geometry that is stable under reaction conditions. While our work on measuring in-situ electrochemical CO<sub>2</sub>R Ni K-edge XAS is ongoing, our preliminary evidence on the basis of STEM imaging suggests that dispersed Ni sites are stable under electrochemical conditions as well. <sup>[24]</sup>

The RWGS@300°C spectrum shows no evidence of Ni-Ni coordination, which appears at ~2.2 Å in the *fcc* Ni standard, further indicating that the Ni aggregates are a minor species compared to single site Ni. This result is consistent with XPS characterization showing primarily oxidized Ni, attributed to single site Ni species, and confirms the hypothesis from STEM-EDS mapping (**Fig 3B**) that minimal aggregation occurs under reaction conditions. The primary change in the EXAFS spectra under reaction conditions is a small reduction in the intensity of the

secondary shell peaks at 1.9-2.4 Å, which is also observed in the He@300°C conditions and attributed to carbon framework relaxation or water desorption (figure and further discussion in **SI-Figure 5C**).

Having established the stability of the dispersed Ni sites in NiPACN, we next probed the mechanism of RWGS on NiPACN by measuring RWGS reaction rate orders with respect to P<sub>H2</sub> and  $P_{CO2}$  (SI-Figure 9). A CO<sub>2</sub> rate order of 0.13 ± 0.01 and H<sub>2</sub> rate order of 0.52 ± 0.01 were measured. We developed a simple kinetic model (SI-Figure 10, derivation and further discussion in SI-Supplemental Text) that suggests that these experimental rate orders are consistent with a rate determining step (RDS) involving the addition of adsorbed hydrogen atom to adsorbed CO2. We note that this proposed RWGS mechanism is directly analogous to mechanisms proposed for Ni-N-C catalysts used in for electrochemical CO<sub>2</sub>R, where the formation of a COOH\* intermediate after facile CO<sub>2</sub> adsorption is the most frequently predicted pathway.<sup>[25,30,41,42]</sup> Although this data is consistent with proposed mechanisms in the literature, we are unable to conclusively state that a particular pathway is occurring. Our

results suggest, however, that there may be parallels in the reaction steps that future work could describe in greater detail.

These findings motivated us to perform a more detailed mechanistic analysis of CO<sub>2</sub>R and RWGS to further compare CO<sub>2</sub> conversion mechanisms across reaction environments. We used Tafel slope analysis to assess the extent to which an applied overpotential lowers the transition state energy<sup>[43]</sup> and extracted a value of  $\alpha n = 0.54 \pm 0.17$ , representing the charge transfer coefficient of the RDS, using a series resistor model to account for mass transport limitations apparent at higher overpotentials (**Fig 4A**). This  $\alpha n$  value corresponds to a ~110 mV/decade Tafel slope at 298 K, which is comparable to the theoretical value of 120 mV/decade attributed to a first electron transfer RDS, i.e., the likely RDS produces the first adsorbed CO<sub>2</sub> intermediate (CO<sub>2</sub><sup>-</sup> or COOH).<sup>[43]</sup> Analogously for thermal catalysis, we extracted an apparent activation energy E<sub>A,RWGS</sub> = 66 ± 2 kJ/mol (**Fig 4B**) for RWGS on NiPACN using an Arrhenius plot.

We note that an exponential dependence of rate on each respective driving force ( $\eta$  for CO<sub>2</sub>R and 1/T for RWGS) is expected and motivates the direct comparison between CO production rates on NiPACN in electrochemical and thermal environments. This comparison is justified by the fact that the same NiPACN catalyst powder was employed in both systems, keeping active site density and structure constant to a first approximation. We define D as a generalized reaction driving force applicable to either system (**Eq. 3, 4**). This parameter combines the effect of changing temperature or overpotential with R = ideal gas constant, F = Faraday's constant, T = absolute temperature, A = a reaction pre-factor that contains the reactant concentration terms and transition state theory pre-factors, and the fitted parameters  $E_A$  or  $\alpha n$ .

 $rate = Ae^{D}$ 

$$D = \left(-\frac{1}{RT}\right) (E_A - \alpha n F \eta)$$
 Eq. 4

We also defined D<sub>0</sub> as the reference driving force at T = 200°C for RWGS and  $\eta = 0.4V$  for CO<sub>2</sub>R with corresponding rates, R<sub>0</sub>, for the conditions of catalytic onset in each system (defined as the conditions where the lowest measurable CO rate was recorded). We then analyzed the dependence of approximate turnover frequency (TOF, measured as CO/Ni/s, using total Ni content for normalization within each reaction system) as a function of D-D<sub>0</sub>, the driving force relative to D<sub>0</sub> (**Fig. 4C**). A y = x relationship at low driving forces for both electrochemical and thermal reactivity is observed, as expected based on **Eq. 3**, **4**. Deviations at larger relative driving forces in the electrochemical data are attributed to the onset of transport limitations.

We then compared the absolute CO production rates versus D to quantitatively compare the activity of NiPACN for RWGS and CO<sub>2</sub>R. In order to determine D for CO<sub>2</sub>R, an estimate of the activation energy of  $CO_2R$ ,  $E_{A,CO2R}$ , is needed (Eq. 4). Temperature-dependent measurements of CO<sub>2</sub>R activity are a frontier-research area because typical CO2R electrochemical cells are not equipped for precise temperature control.<sup>[44]</sup> Here, we used an electrochemical CO<sub>2</sub>R cell with a recirculating electrolyte connected to an external, temperature-controlled reservoir (SI-Figure 11 and SI-Methods) to extract EA, CO2R = 45 ± 5 kJ/mol, estimated using a Butler-Volmer expression to account for overpotential<sup>[45]</sup>, and compare the absolute CO production rates versus D (Fig 4D). We note that these experiments were conducted in a 2-compartment electrochemical cell, in contrast to the gas-fed, 3-compartment cell used in the CO<sub>2</sub>R data presented in Figures 2A and 4A, which is unlikely to strongly affect the CO<sub>2</sub>R mechanism (further discussion in SI-Methods).<sup>[45]</sup>

Eq. 3

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Figure 4. (A) Logarithm of CO production rate under electrochemical CO2R conditions normalized to total Ni atoms versus non-dimensionalized overpotential with a dashed curve showing fit to a series resistor model. (B) Arrhenius plot of the logarithm of CO production under RWGS conditions versus inverse temperature. (C) Normalized CO production R/R0 versus D-D0 with R being production rate of CO and D being driving force and with R0/D0 referring to lowest driving force case for RWGS/CO2R. (D) Logarithm of absolute CO production for CO2R and RWGS vs D (Eq 3,4).

We found that the absolute reaction rates for RWGS are substantially lower than the CO<sub>2</sub>R rates, by factors of ~50-100 in these experiments, but are roughly colinear when plotted versus D. This data suggests that the higher intrinsic catalytic rates in the electrochemical environment compared to the thermal, gas-phase environment could be directly explained by the higher driving force (i.e., lower energy barrier) imposed on the electrochemical system, enabled by the lower  $E_A$  for  $CO_2R$  and the strong effect of overpotential on rate (Fig 4D). Thus, we have used the same Ni, N-doped carbon catalyst material to (1) demonstrate analogous reactivity across thermal and electrochemical systems, (2) identify similar likely active sites responsible for this catalysis in both systems and (3) give preliminary, quantitative interpretations to the disparate reaction rates in the two environments and bridge the two environments by showing that faster reaction rates in the electrochemical environments could be derived from lower intrinsic barriers in the CO<sub>2</sub>R system. This finding is consistent with recent theoretical and experimental work that suggests that electric field effects<sup>[46–48]</sup> and solvation<sup>[49]</sup> likely play a strong role in stabilizing adsorbates during CO<sub>2</sub>R in electrochemical systems.



**Figure 5.** (A) Schematized reaction coordinate diagram for CO<sub>2</sub> conversion to CO via RWGS at 25°C and 300°C and via electrochemical CO<sub>2</sub>R at  $\eta$ =0 mV and  $\eta$ =600 mV overpotentials. (B) Experimental CO production rates in log-scale, normalized to total Ni content, for the four cases depicted in (A).

To summarize these findings, we constructed a schematized reaction coordinate diagram for both the electrochemical CO<sub>2</sub>R and thermal RWGS that illustrates the different effects of temperature and overpotential on reaction thermochemistry (Fig 5A, based on experimental enthalpic transition state barriers and tabulated enthalpies of formation<sup>[50]</sup>). The energies of the reactants, RDS energy barriers (here, equal to D), and products are expressed as enthalpy normalized to RT in order to encompass the effect of increased temperature in kinetic expressions (Eq. 4) and to reflect that measured EA values are formally enthalpic transition state barriers based on transition state theory.<sup>[51]</sup> Increasing temperature in RWGS results in a moderate decrease in the reaction barrier relative to the thermal energy of the environment, leading to a modest increase reaction rate. In addition to the already-lower EA barrier in the electrochemical environment, the application of an overpotential for electrochemical CO<sub>2</sub>R causes a linear decrease in reaction energetics as a function of electrode potential, resulting in a more substantial decrease to the transition state barrier. The combination of the lower intrinsic barrier for CO<sub>2</sub>R (45 ± 5 kJ/mol) relative to RWGS (66 ± 2 kJ/mol) and the assumed linear effect of potential on the transition state barrier results in significantly greater predicted rates for NiPACN-catalyzed  $CO_2R$  relative to RWGS which is agrees with the experimentally-observed rates (**Fig 5B**).

We note that many additional factors and kinetic phenomena influence the absolute reaction rates in these systems which highlights opportunities for exciting future studies in this field. Some of these effects include: (1) differences in the accessibility of active sites under reaction conditions, (2) differences in reactant concentration, and (3) the entropic barrier in the RDS. As this class of carbon materials is effectively nonporous<sup>[52]</sup>, we contend that active site availability is similar in both the thermal and electrochemical reaction environments, suggesting that factor (1) is unlikely to cause substantial differences. Factor (1) also impacts the total NiPACN catalyst loading in the two environments; here, we use ~0.2 mg for CO<sub>2</sub>R and ~200 mg for RWGS. However, the similar CO<sub>2</sub> conversions (~0.1-1% conversion) in both systems ensure a fair comparison of conversion regimes. Factor (2) identifies that reactant concentrations could also account for differences in reaction rate; these concentrations are  $c_{CO2} = c_{H2} = 0.01$  M for RWGS, roughly similar to the  $c_{CO2} = 0.03M$ , and  $c_{HCO3-} = 0.1 M$  (the presumed proton donor) for CO2R. Thus, the effect of reactant concentrations on rate in the two environments is not fully determined, and the effect of solvent caging, which distorts the typical collision theory prediction of reaction rates, cannot be fully described. Pertaining to factor (3), our mechanistic analysis suggests a rate-determining electron-transfer CO<sub>2</sub> adsorption step for CO<sub>2</sub>R and a surface hydrogenation of a CO<sub>2</sub>-related intermediate for RWGS, which would lead to different entropic pre-factors (A in Eq. 3 in main text) in the transition-state theory framework.<sup>[51]</sup> Specifically, the large negative entropic barrier (~58 kJ/mol at 298K) for adsorption in the RDS of CO2R would lead to a significantly smaller pre-factor and thus a reduced rate at the same driving force. Thus, the fact that c<sub>CO2</sub> is comparable in both systems and entropic transition state effects would lead to a smaller electrochemical pre-factor both further point to an enthalpic transition state stabilization that underlies the higher activity observed in electrochemical CO2R. A more complete understanding of the comparison of electrochemical and thermal reaction rates over the same catalyst is desired and will necessitate nuanced and precise future studies that deconvolute the rich and complex phenomena that govern heterogeneous catalvsis.

#### Conclusion

These results show that selective  $CO_2$  to CO catalysis is facilitated by atomically dispersed Ni sites under both electrochemical and thermal driving forces when using the same Ni, N-doped carbon catalyst. Because we used the exact same catalyst powder in both systems, we were able to make direct comparisons between CO production rates in each system. We provide a framework for quantitative comparison that defines a generalized driving force that encompasses changes in both temperature and potential; this shows that electrochemical  $CO_2R$ is substantially faster than RWGS in these experimental conditions, likely due to lower intrinsic reaction barriers in the electrochemical RDS. We propose that future work in developing novel materials and quantitative comparisons between parallel

electrochemical and thermal catalytic systems are essential for unifying the study of catalytic phenomena across reaction environments. Ultimately, these efforts could bolster catalyst discovery efforts that have the potential to transform the fuels and chemicals industries through innovative, carbon-neutral, and renewable chemical transformations.

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**Keywords:** catalysis • carbon dioxide • electrochemistry • reverse water-gas shift • metal, nitrogen-doped carbon

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#### **Entry for the Table of Contents**

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Despite similar underlying phenomena, studies that directly analogize between thermal catalysis and electrocatalysis are rare. Here, we employ a Ni, N-doped carbon catalyst that is thermally stable and electronically conductive to show that high selectivity CO production is observed under both electrochemical CO<sub>2</sub> reduction conditions and thermal reverse-water gas shift environments.