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Letter

Tafel Analysis Predicts Cooperative Redox Enhancement Effects in Thermocatalytic Alcohol Dehydrogenation

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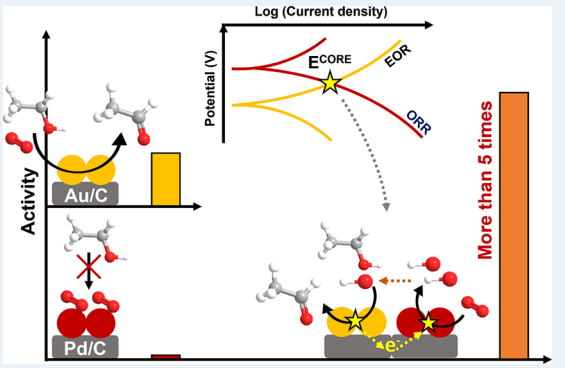
ABSTRACT: Cooperative redox enhancement (CORE) between physically separated but electrochemically connected catalysts promotes thermocatalytic reactions. Using the oxidative dehydrogenation of ethanol as a model reaction, we showcase two electrochemical approaches that predict monometallic and (CORE-enabled) bimetallic thermocatalytic activities. The common approach of linear sweep voltammetry can accurately determine the activity of individual half-reactions but does not account for competitive adsorption. This can lead to the underprediction of thermocatalytic rates and to overlooking the possibility of leveraging CORE effects. In contrast, adapting utilizing the Tafel method, with both reactants present, can accurately predict thermocatalytic rates and the coupling between separated catalysts.



KEYWORDS: *bimetallic catalysis, redox, electron transfer, oxidative dehydrogenation, electrochemical method, rate enhancement*

As the chemical industry shifts toward a more sustainable future, the direct integration of renewable energy sources will become increasingly important. The use of electrocatalysis in place of traditionally used heterogeneous catalysis will be crucial to this transition.[1,2] While these two disciplines are traditionally considered to be separate, recent work has demonstrated that electrocatalytic concepts can provide important insights into the behavior of thermocatalysts.[3−11] For example, Thejas et al.[12] presented that the OCP of the catalyst during a thermochemical reaction can provide mechanistic insights into the reaction. Their results indicate quantitively similar trends of reaction rate and increase in OCP because of the enhancement of interfacial electrostatic effects. Yuanya et al.[13] introduced a numerical model to predict the kinetic parameters of a thermocatalytic reaction based on electrochemical evaluations.

In prior work, we used the oxidative dehydrogenation (ODH) of 5-hydroxymethylfurfural (HMF) in alkaline media to demonstrate that electrochemical redox coupling can occur between two catalysts. The physical separation of active sites on a conductive support leads to substantial thermocatalytic rate enhancement.[3−6] This promotional effect, termed cooperative redox enhancement (CORE), is attributed to the dissimilar activity and selectivity of the two disparate (but coupled) metals toward the half-reactions. The resulting polarization of the two catalysts via galvanic coupling drives the overall reaction at a higher rate than that which is possible on monometallic equivalents.[6] Herein, we expand the methodologies used to study CORE, using the selective ODH of ethanol as our model reaction. We illustrate the experimental approaches necessary to characterize the CORE phenomenon and translate electrocatalytic measurements into thermocatalytic systems, to predict thermocatalytic behavior.

Ethanol ODH can be separated into two half-reactions: the ethanol oxidation reaction (EOR) and the oxygen reduction reaction (ORR):

$$CH_3CH_2OH + \frac{1}{2}O_2 \rightarrow CH_3CHO + H_2O \quad \text{(Ethanol ODH)} \tag{1}$$

$$CH_3CH_2OH + 2OH^- \rightarrow CH_3CHO + 2e^- + 2H_2O \ \text{(EOR)} \tag{2}$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \ \text{(four-electron ORR)} \tag{3}$$

Acetaldehyde is highly reactive, and it can easily be oxidized to acetic acid by the following reaction.

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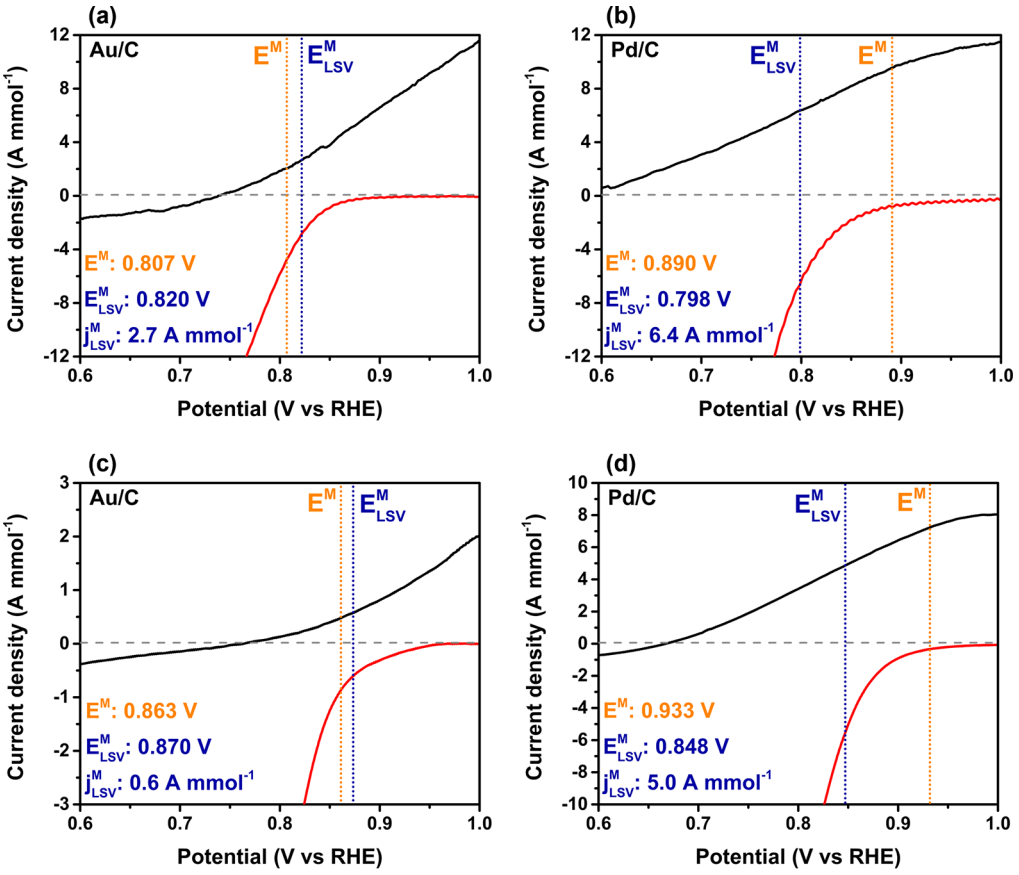

Figure 1. LSV curves of (a) Au/C and (b) Pd/C for EOR (black line) and ORR (red line) at 50 °C. The same experiments were conducted at RT with (c) Au/C and (d) Pd/C. The values of E^{M}_{LSV} and j^{M}_{LSV} are shown in the figure indicated as navy color. E^{M} was measured from an independent experiment but present in the same place for comparison. Reaction conditions (EOR, black line): 0.8 M ethanol, 1.6 M Na_2CO_3, 50 mL min^{-1} of nitrogen. Reaction conditions (ORR, red line): 1.6 M Na_2CO_3, 50 mL min^{-1} of oxygen, Reaction conditions (E^{M}): 0.8 M ethanol, 1.6 M Na_2CO_3, 50 mL min^{-1} of oxygen. Note that the E^{M} for Au/C and Pd/C is above the O_2 diffusion-limited potential range determined for our electrodes, Figure S2.

$$CH_3CHO + 2OH^- \rightarrow CH_3COOH + 2e^- + H_2O \text{ (Aldehyde OR)} \quad (4)$$

For continuity with our previous work,[3−6] we utilize a Au/C and Pd/C catalytic couple in this system. Physically separated Au and Pd nanoparticles on Vulcan carbon were synthesized following the same procedure in our prior publications.[5,6] As we have previously shown, the Au and Pd remain as separated nanoparticles and do not form an alloys under experimental conditions.[5,6] Au/C is a well-established catalyst for the thermocatalytic reaction, and both electrocatalytic half-reactions.[14−17] In contrast, despite the fact that the EOR and ORR electrocatalytic activity of Pd/C has been demonstrated,[18−21] the thermocatalytic oxidation of ethanol over Pd appears to have been overlooked.

Based on mixed potential theory, the observed potential is realized when the rate of anodic and cathodic reactions are balanced, which is widely accepted in a corrosion-type reaction.[22−24] The catalytic activity of each half-reaction can be independently characterized electrochemically via the current density and converted into a molar rate using Faraday's law. Simple thermochemical aerobic oxidations on monometallic or alloy catalysts have been evaluated by these electrochemical approaches revealing reasonable predictions.[7−9,25] Furthermore, CORE operates through galvanic coupling, a well-known electrochemical phenomenon.[6,22,23,26] Thus, it was considered logical to draw from this body of literature to develop methods of accurately interpreting thermocatalytic systems using electrocatalytic approaches.

It is relatively straightforward to measure the mixed potential, E^{M}, for individual catalysts with both ethanol and oxygen present, Figure S1a. With no applied electrochemical driving force, this potential is equivalent to that which occurs during an analogous thermocatalytic reaction. This is the OCP at which the rates of electron generation and consumption by the EOR and the ORR, respectively, are balanced through an effective electrical short-circuit through the conductive support. The electrocatalytic rates of each half-reaction can be independently measured by exposing the catalyst to only one reactant and performing linear sweep voltammetry (LSV), Figure S1b. From this, it is then possible to predict a mixed potential where the anodic and cathodic reactions are balanced, denoted as E^{M}_{LSV} with corresponding current density j^{M}_{LSV}, Figure S1b. If the two reactants interact with the catalyst surface completely independently and both are present with no other kinetic barriers, the two mixed potentials should be the same, i.e., E^{M}_{LSV} should equal E^{M}.

This is the approach previously leveraged by Ryu et al.[7] to interpret aerobic oxidation over single or alloy catalysts and has provided a basis for how we can interpret the CORE mechanism.[6] Despite the excellent agreement of the approach in the previous reports, combining independent half-reaction

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measurements cannot always predict the performance in the mixed reactant system. We illustrate this by examining Au/C and Pd/C for ethanol ODH, Figure 1.

Over Au/C, there is good consistency with the idealized theory at both 50 °C and room temperature (RT), Figure 1**a and** 1**c**. The individual LSV curves for the EOR and ORR indicate that Au/C is active for both half-reactions, aligning with studies reporting that Au-based catalysts exhibit high thermocatalytic activity for the ODH of ethanol.[15,17] When combined, the predicted mixed potential, E^{M}_{LSV}, is within experimental reproducibility of the mixed potential from OCP measurements, E^{M}. The mixed current density, j^{M}_{LSV}, at 50 °C can be converted to an equivalent thermocatalytic rate of 0.6×10^{-7} mol s^{-1}. Considering the conditional differences and loss of active surface area upon incorporating nanoparticles onto an electrode, it shows a remarkable correlation with the ODH activity, $1.23 \pm 0.232 \times 10^{-7}$ mol s^{-1}. Evidently, in this example, the LSV approach is robust and facilitates the quantification of the thermocatalytic activity.

In contrast, over the Pd/C, Figure 1b, the values for E^{M}_{LSV} and E^{M} do not align (0.798 V vs 0.890 V, respectively), with LSV predicting a thermocatalytic reaction rate of 1.33×10^{-7} mol s^{-1} at 50 °C, 19 times higher than the observed thermocatalytic rate of $0.077 \pm 0.232 \times 10^{-7}$ mol s^{-1}. It is worth noting that the E^{M} is far closer to the ORR onset potential of 0.910 V (at 0.5 A $mmol^{-1}$), which suggests that surface-adsorbed oxygen may block sites and inhibit interactions between ethanol and Pd, when both reactants are present. The poor prediction of the thermocatalytic activity from the j^{M}_{LSV} is rationalized by the disagreement of E^{M}_{LSV} and E^{M}. The lack of alignment between the mixed potentials for Pd/C suggests that the two-half reactions do not occur on independent catalytic sites and that competitive adsorption may be a factor. Two sets of step change measurements, Figure S3 and Figure S4, were conducted for both catalysts. For Au/C, the equilibration to the same potential, irrespective of the direction of approach, suggests that both oxygen and ethanol actively interact simultaneously with the Au/C surface. In the case of Pd/C, after the injection of oxygen, the rise in potential above the E^{M}_{LSV} and toward the ORR onset potential suggests the displacement of adsorbed ethanol by oxygen, which is in agreement with several studies.[20,27,28] Additionally, competitive adsorption on Pd, and respective alloys, in the presence of oxygen has been extensively studied in fuel cell catalysis.[29−31] It is well established that even small proportions of Pd species can inhibit the influence of ethanol that can be crossed over from the anodic side, achieving excellent ORR stability in the ethanol fuel cell.[32]

A H-Cell was utilized at 50 °C to determine the EOR products of Au/C and Pd/C when holding the anode at the E^{M} determined from Figure 1. Acetic acid was formed with a faradaic efficiency of 89.9% for Au/C and 96.4% for Pd/C. Similar results were obtained from thermochemical tests, Figure S7. This indicates the primary oxidation route on Au/C and Pd/C for both thermo- and electrochemical tests is through acetaldehyde and its further oxidation to acetic acid. Note that the E^{M} of Pd/C is higher than the onset potential of Pd oxide further indicating that cycling of Pd between Pd^{0} and Pd^{2+} is likely a key step in the catalytic cycle.[3] XPS analysis of these catalysts,[6] confirmed the existence of Pd^{2+} in pre- and postreaction catalysts. It should also be noted that a small amount of acetaldehyde is likely lost during these experiments to its low boiling point of 20.2 °C.

Tafel plot analysis is a possible alternative approach to measure overall reaction rates, Figure S5.[33,34] Crucially, the measurement is conducted in the presence of both the reductant and oxidant, accounting for the competitive adsorption behavior of reactants. Herein, we denote the obtained Tafel potential as E^{M}_{Tafel}, and Tafel current density as j^{M}_{Tafel}, by Tafel extrapolation, Figure 2 **and** Figure S6. While

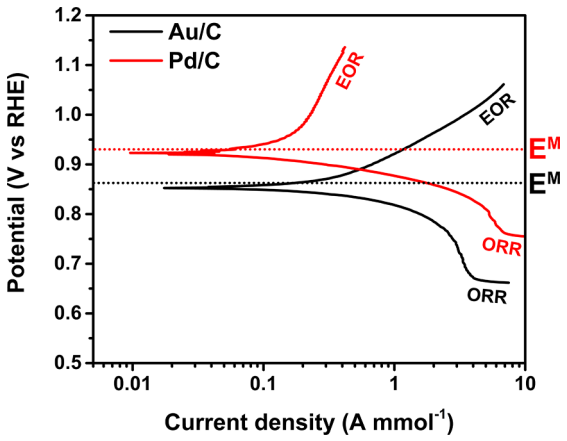

Figure 2. Tafel slopes of (a) Au/C and Pd/C. The dotted black and red lines indicate the E^{M} of Au/C and Pd/C, respectively. Reaction conditions (Tafel, E^{M}): 0.8 M ethanol, 1.6 M Na_2CO_3, 50 mL min^{-1} of oxygen, RT.

these experiments were conducted at room temperature to simplify the experimental system, as shown in Figure 1 and our prior work,[6] room temperature experiments are excellent predictors for the elevated temperature activity and presence of the CORE phenomenon.

Given that these measurements are acquired in the same chemical environment, the E^{M}_{Tafel} are in near-perfect agreement with the previously determined E^{M} for both catalysts. Examining the EOR branch of both Tafel plots, Au/C demonstrates a substantially higher EOR rate in the presence of oxygen (3.51 A $mmol^{-1}$ at 1.0 V) than Pd/C (0.23 A $mmol^{-1}$ at 1.0 V) in agreement with the trend in measured thermocatalytic activities for the overall reaction. Crucially, Tafel analysis accounts for the oxygen inhibition, which influences the EOR rate. This is effectively illustrated by the lower Tafel current density and high Tafel slope for the EOR branch of the Pd/C Tafel curve and indicates that there is a lower thermocatalytic rate for ethanol ODH on Pd/C than on Au/C. It is however important to note that the LSV approach remains valid when competitive factors are not rate-limiting, or when one wishes to determine the activities of the individual half-cell reactions alone.

In our previously reported description of CORE effects,[6] the separation of the anodic and cathodic half reactions between catalysts and the polarization of both active sites form a new mixed potential, denoted as E^{CORE}, which is measured as an open circuit potential of the mixed catalyst with both reactants present. The cathodic polarization of one metal and the anodic polarization of the other accelerate the overall thermocatalytic rate. This coupling is analogous to active galvanic corrosion, where the corrosion rate (anodic oxidation reaction) of one metal is accelerated by electrochemical polarization when coupled to a dissimilar metal performing the cathodic ORR.[35−37] In CORE, the anodic corrosion reaction is replaced with a selective electrochemical oxidation, previously demon-

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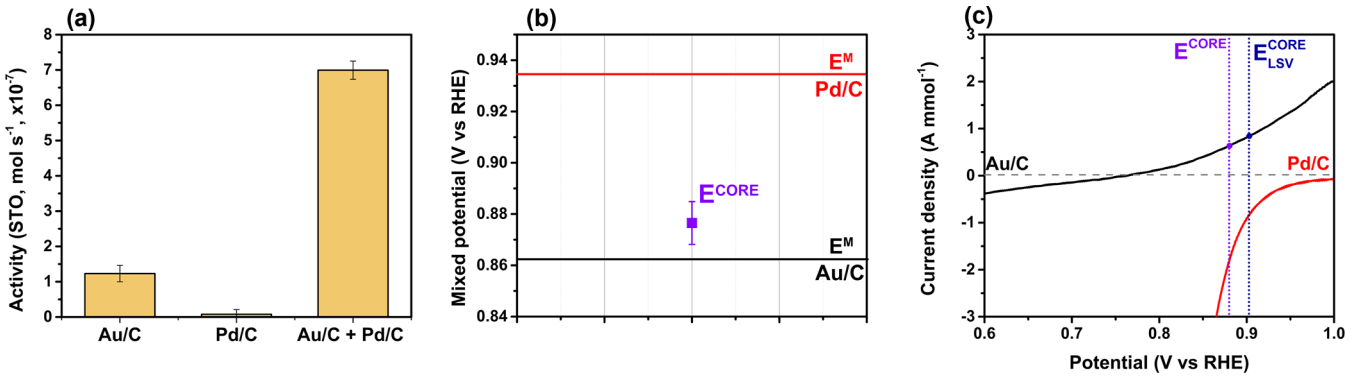

Figure 3. (a) Activity of ODH of ethanol on Au/C, Pd/C, and Au/C + Pd/C after 30 min. (b) Comparison of E^{M} of Au/C and Pd/C and its mixture Au/C + Pd/C, E^{CORE}, obtained from the OCP measurements. (c) LSV curves of Au/C (black line, HMFOR) and Pd/C (red line, ORR). Reaction conditions of the thermocatalytic reaction: 0.8 M ethanol, 1.6 M Na_2CO_3, 3 bar of oxygen, 60 °C. Reaction conditions of the OCP measurements: 0.8 M ethanol, 1.6 M Na_2CO_3, 50 mL min^{-1} of oxygen, RT. The reaction conditions of Figure 3c are given in Figure 1.

strated with the HMF dehydrogenation (DH) and herein with the ethanol DH.[6]

Such corrosion couples are typically analyzed via a Tafel plot, as in Figure 2. The crossover in Pd/C ORR and Au/C EOR Tafel curves is directly analogous to the crossover expected for active galvanic corrosion of dissimilar metals, hence predicting that we will observe CORE effect in this case. Considering the thermocatalytic data, Figure 3a, the ethanol ODH rate observed for the physically mixed Au/C + Pd/C catalyst is 5.35 times higher than the direct summation of the rates observed on Au/C and Pd/C, with the same total metal loading, Figure 3a. As discussed above, the overall rate of Pd/C is very low due to the high oxygen coverage on the surface, however, Pd/C is active for the ORR. Measuring the CORE potential of the Au/C + Pd/C catalyst system yields an E^{CORE} of 0.877 ± 0.01 V, Figure 3b, which lies between the E^{M} values of the individual catalysts, as predicted by the crossover point in the Tafel plots, Figure 2. This confirms that through coupling, both catalytic sites are polarized, enhancing the rate of each half-reaction.

By combining the LSV curves for the ORR on Pd/C and EOR on Au/C, we can examine an idealized scenario where the ORR occurs exclusively on Pd/C and the EOR exclusively on Au/C, Figure 3c. Determining the potential of equal cathodic and anodic current density yields an LSV-predicted CORE potential, E_{LSV}^{CORE}, of 0.902 V at a current density of 0.85 A $mmol^{-1}$. Alternatively, the E^{CORE} determined by OCP measurement, 0.877 V, yields a slightly lower current density of 0.63 A $mmol^{-1}$. The CORE potential and current density from LSV tests and OCP measurements are, as expected, close to the crossover point in the Tafel plots, 0.889 V and 0.536 A $mmol^{-1}$, Figure 2.

The slight differences in E^{CORE} values among the Tafel, LSV, and OCP approaches are reasonable considering that the complete separation of the half-reactions assumed from the LSV method is not feasible in actual thermocatalytic reactions. While we can predict that there will be a significant separation between half-reactions using electrochemical measurements, the thermocatalytic system is far more complex. In the Au/C + Pd/C thermocatalytic system, we must expect incomplete separation due to the random nature of the catalyst particle distribution. Despite this, we have demonstrated that the active, CORE-derived, spontaneous polarization of the two metals separates the half-reactions to a significant extent, accelerating both half-reactions, and leading to a greater than 5-fold increase in the observed thermocatalytic reaction rate. In the case discussed herein, we leverage CORE to enable the high ORR activity of Pd/C without requiring the EOR to occur on this oxygen-dominated surface. Half-reaction separation due to CORE can circumvent limitations of competitive adsorption that otherwise limit the overall rates on monometallic catalysts.

In summary, we have described the advantages of utilizing the Tafel approach to predict thermocatalytic reaction rates. The LSV method, designed to capture individual half-cell reaction activities in an isolated electrochemical cell, is clearly limited when competitive adsorption between reactants plays a significant role in limiting the reaction rate. Tafel measurements are conducted in the presence of both reactants and thus more accurately reflect the thermocatalytic reaction conditions. Thus, while LSV is useful to understand the rates of individual half-reactions, the Tafel approach is necessary to fully translate this to the thermocatalytic rates for both monometallic and CORE-enabled bimetallic catalysts. The Tafel method can predict the presence of CORE between Au/C and Pd/C, and demonstrate that this enhanced rate is due to the separation of half-reactions between electrochemically coupled physically separated catalysts.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.3c06103.

Schematics explaining the electrochemical experimental setup. Electrochemical analysis for monitoring the adsorption trends of the catalysts. Thermochemical activity and carbon balance data. Materials and methods for electrochemical and thermochemical analysis, and catalyst synthesis. Supplementary references (PDF)

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Author Contributions

[§]B.K. and I.T.D. contributed equally. B.K., I.T.D., M.D., S.P., G.J.H., and S.M. conceived and conceptualized the project. B.K. and I.T.D. conducted the experimental investigation and performed the data analysis. M.D., S.P., G.J.H., and S.M. provided project supervision. G.J.H. and S.M. provided funding acquisition. The manuscript was finalized and edited through the contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

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