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Uncovering Cooperative Redox Enhancement Effects in Bimetallic Catalysis

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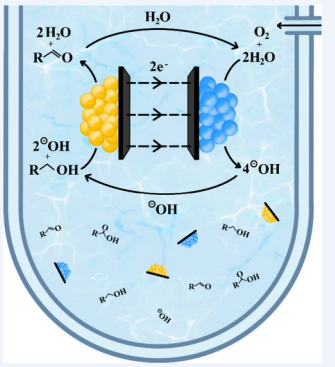
CONSPECTUS: Electro- and thermo-catalysis are frequently considered as disparate fields of research. The former is critical for the future electrified green chemical industry where renewable electrical energy will power production in place of fossil-derived sources; however, the necessary scale-up from the laboratory to commodity chemical production is in its infancy. In contrast, thermo-catalysis is at the heart of the modern chemical industry with the associated capital investments in infrastructure and technology. It is, however, far more energy intensive and typically requires the use of elevated temperatures and pressures to obtain economically viable productivity. Our recent discovery of a new approach to catalyst design, termed Cooperative Redox Enhancement (CORE), bridges the gap between these traditionally distinct fields. In this Account, we outline how CORE can facilitate a unifying approach to these fields and describe how electrochemical methods can provide detailed thermochemical mechanistic information.



Industrial heterogeneous catalysts often comprise supported precious metal nanoparticles with alloys frequently providing superior performance over monometallic counterparts. However, we have found that spatial separation of the two metals on an electronically conductive support leads to substantial enhancement in activity through electrochemical coupling. This CORE effect demonstrates that thermochemical redox reactions can, and often do, operate like nanoscale electrochemical fuel cells. The electrochemical coupling in systems containing at least two discrete active sites accelerates both half reactions in a mechanism analogous to galvanic coupling in corrosion science. CORE demonstrates that leveraging electrocatalytic approaches is a key tool for the development of the next generation of thermochemical catalysts and vice versa.

Here, our primary aim is to provide a critical overview of CORE effects that are exhibited in thermocatalytic redox reactions over bimetallic catalysts. We will provide a chronological timeline of the research in this area that led to this discovery. This will include comparing CORE to other effects which are commonly exhibited by bimetallic catalysts, e.g., the synergistic electronic and geometric effects observed through the formation of nanoalloys. We will provide a detailed overview of CORE, how it can be studied, and how thermochemical enhancements can be predicted by utilizing electrochemical methods. Specifically, we will discuss the importance of using linear sweep voltammetry, Tafel analysis, and mixed potential theory to acquire a host of new electrochemical terms that we have defined, such as E^{CORE} (operating mixed potential for bimetallic catalysts) and j^{CORE} (operating current density for bimetallic catalysts), which underpin the electrochemical study of CORE. Primarily, the discussion will be centered on the CORE effects observed in coupled systems that involve dehydrogenation and oxygen reduction, as this is the primary model system we have studied to date. However, we also include examples of how CORE has relevance in other redox reactions, demonstrating the generality of the effect. Finally, we provide a short perspective on the future directions of this field and the impact that can be expected on catalysis over the coming decade.

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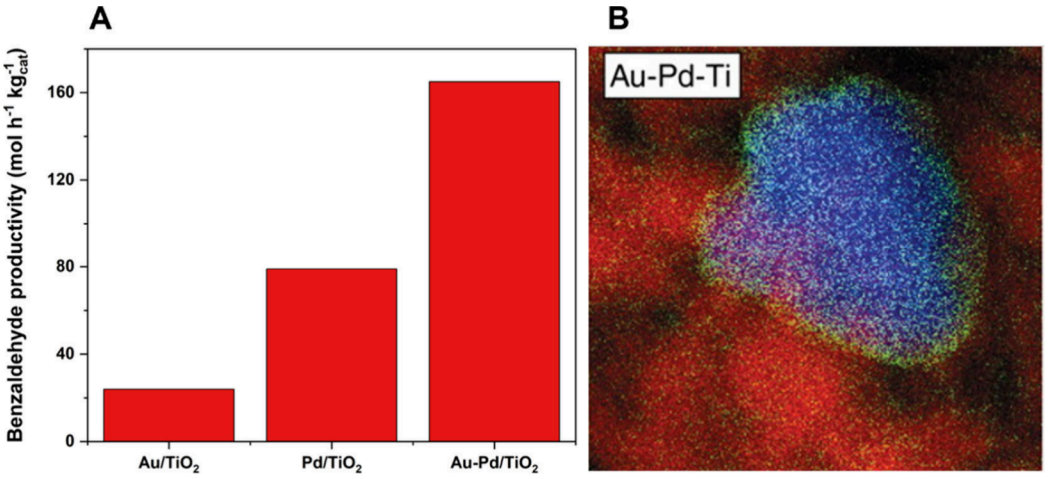

Figure 1. (A) The catalytic productivity during benzyl alcohol oxidation of Au/TiO_2, Pd/TiO_2 and alloyed $Au–Pd/TiO_2$. Conditions: 2.5 wt % Au/TiO_2, 2.5 wt % Pd/TiO_2, 2.5 wt % Au–2.5 wt % Pd/TiO_2, benzyl alcohol (40 mL), 100 °C, 2 bar pO_2, 1500 rpm, 8 h. (B) STEM-XEDS map of $Au–Pd/TiO_2$ with Ti, red; Au, blue; and Pd, green. Adapted with permission from Enache et al.[19] 19 Copyright 2006 AAAS.

- Daniel, I. T.; Zhao, L.; Bethell, D.; Douthwaite, M.; Pattisson, S.; Lewis, R. J.; Akdim, O.; Morgan, D. J.; McIntosh, S.; Hutchings, G. J. Kinetic Analysis to Describe Co-Operative Redox Enhancement Effects Exhibited by Bimetallic Au–Pd Systems in Aerobic Oxidation. *Catal. Sci. Technol.* **2023**, *13*, 47–55.[2] *Here, we derive kinetic equations that describe the thermocatalytic behavior of both monometallic and PM Au–Pd catalytic systems. The accuracy of the kinetic model provides further evidence in support of the CORE mechanism.*
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- Kim, B.; Daniel, I. T.; Douthwaite, M.; Pattisson, S.; Hutchings G. J.; McIntosh S. Tafel Analysis Predicts Cooperative Redox Enhancement Effects in Thermocatalytic Alcohol Dehydrogenation. *ACS Catal.* **2024**, *14* (11), 8488–8493.[4] *In this paper, we demonstrate the importance of accounting for competitive adsorption when considering electrochemical approaches that describe thermochemical scenarios and show how Tafel analysis gives an accurate prediction of bimetallic thermochemical rates.*

INTRODUCTION

The modern chemical industry is inherently reliant on catalysis and as such, progression of fundamental catalytic understanding is vital, enabling more optimal use of active materials. This is crucial, as even metals considered abundant today will soon be under increasing demand with the push to industrial electrification intensifying and utilization of nonprecious metals increasing. With this shift, electrocatalysis is likely to grow in importance. Already, this field provides mechanistic insights into the catalyst/reactant interface;[5–8] information which is challenging to study with methods conventionally used in heterogeneous catalysis.

Furthermore, another ever-growing facet of this field is the use of bimetallic catalysts. These types of systems are a common method of increasing the efficiency and stability of active materials. They are employed in many ways, from a combination of two monometallic catalysts, to conventional alloys and multifunctional systems consisting of several distinct active species.[9–15] The success of these bimetallic systems is often attributed to vague and nondescript synergistic affects.

In this Account, we describe our recent discovery, Cooperative Redox Enhancement (CORE), which provides an alternative description of bimetallic enhancement effects.[1–4,16] Unlike conventional alloys, CORE relies upon spatially defined active sites which, when electrically connected through a conductive support in the aqueous phase, result in significant thermocatalytic rate enhancements. Intrinsic to the operation and understanding of the CORE effect is the underpinning electrochemical mechanism and we describe how sophisticated electrochemical techniques are essential in explaining the mechanistic origins of the observed rate enhancements. Finally, we provide a perspective on the future utilization of CORE and how it can be leveraged to significantly benefit the catalyst community.

"SYNERGISTIC" RATE ENHANCEMENTS USING Au AND Pd CATALYSTS

Precious or noble metals make up over 70% of the heterogeneous catalysis market.[17] Using multimetallic systems is one approach that has historically improved the performance of noble metals catalysts. These systems consistently outperform their monometallic counterparts. One of the most successful examples employs the use of Au and Pd, particularly for application in selective oxidation chemistry. Our recent Account provides an overview of our contribution to this field with reference to *in situ* generated hydrogen peroxide, as well as a useful introduction to this wide-ranging topic.[18]

Typically, bimetallic systems are considered to offer enhanced catalytic performance due to an often poorly described synergistic effect that results from the intimate mixing of the component metals. One proponent example was reported in 2006, whereby an alloyed $Au–Pd/TiO_2$ catalyst offered both

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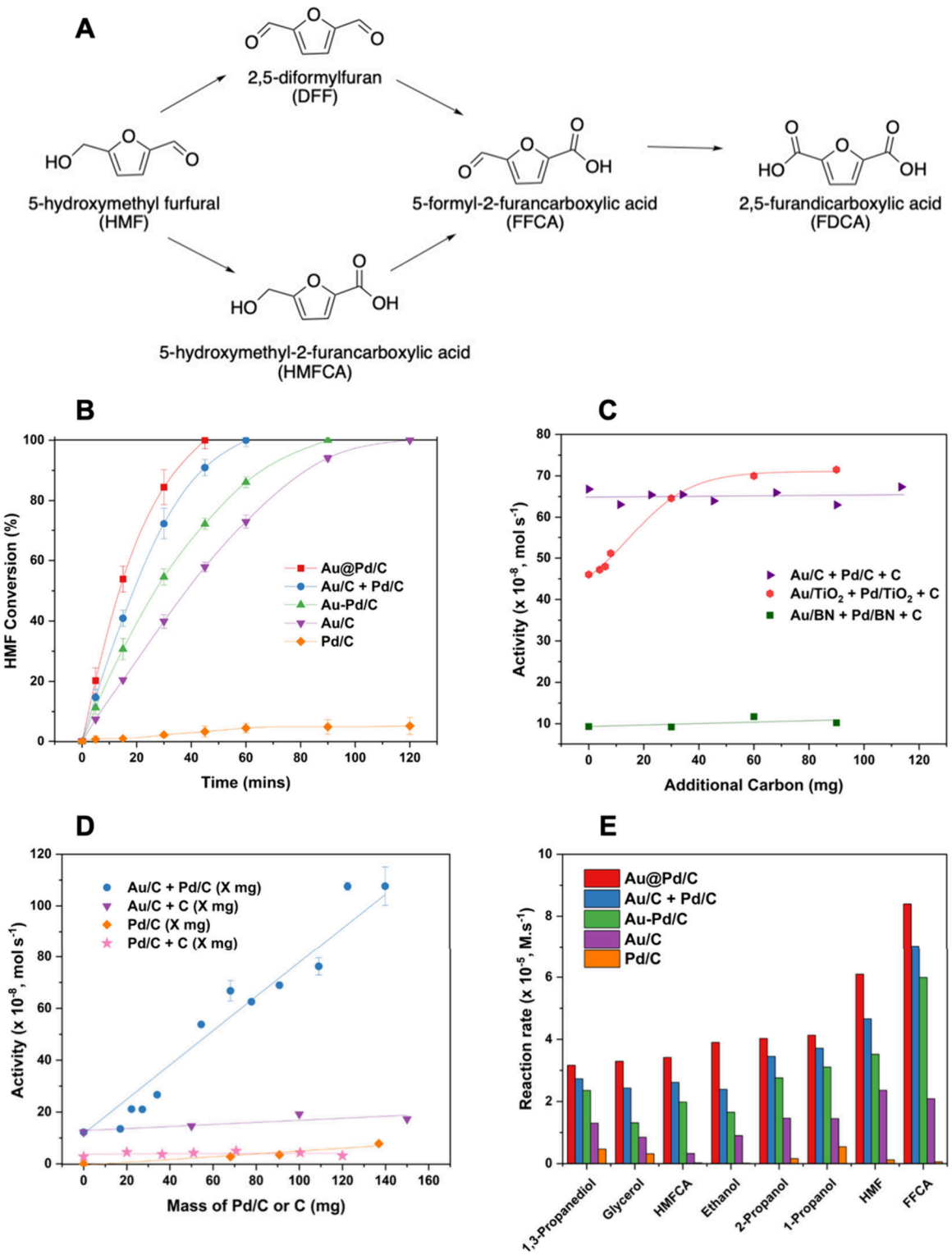

Figure 2. (A) The ODH pathway of HMF. (B) Performance of five catalyst systems for the ODH of HMF. Au@Pd/C represents a Janus-type structure, and Au−Pd/C represents an alloy structure. Au/Pd (mol/mol) = 4/1. (C) The addition of Vulcan XC72R into three PM systems on different supports. (D) The addition of 1 wt % Pd/C or Vulcan XC72R into monometallic systems. (E) Performance of the five catalytic systems from (B) for a range of alcohols and formyls. Catalyst quantities: Au@Pd/C, Au/C + Pd/C, Au−Pd/C = 143.1 mg; Au/C = 72.1 mg; Pd/C = 71 mg (when not varied). Conditions: H_2O (16 mL), HMF (0.1 M), $NaHCO_3$ (0.4 M), O_2 (3 bar), 80 °C, 30 min (for C, D, and E). Adapted from Huang et al.[1] Copyright 2022 Springer Nature.

improved activity and aldehyde selectivity for solvent-free alcohol oxidation compared to that offered by monometallic analogues.[19] At the time, the most active supported monometallic Au and Pd catalysts produced turnover frequencies (TOFs) with the respect to the aldehyde of 12500 h^{-1} and 9800 h^{-1}. The supported AuPd alloy achieved TOFs of 269000 h^{-1}, over a factor of 10 greater than the combined TOFs of the monometallic systems (Figure 1A).[20,21] Significantly, this

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bimetallic enhancement was attributed to the formation of the alloy and hence the ability of Au sites to electronically influence the catalytic properties of the Pd shell (Figure 1B).

Subsequently, reports into active bimetallic Au−Pd structures have been numerous and applicable to a variety of transformations.[22−25] Typically, their improved activity relies upon the altering of geometric and/or electronic properties of the metals when combined into the new, alloyed structure.[12,13,26,27] Exploiting synergistic effects is a perfectly valid route to enhance catalyzed reaction rates, although in many cases the lack of a definitive mechanistic explanation hinders wider application and does not allow the design of a catalyst for a specific reaction. We now discuss an effect that addresses these issues. In contrast to the synergy that results from the formation of nanoalloys, CORE relies upon individual active sites retaining their inherent redox properties.

BENEFITING FROM SPATIAL SEPARATION

We first consider the model transformation that is used throughout much of this work, oxidative dehydrogenation (ODH), and specifically the mechanistic role that oxygen plays during these reactions. In 2010, in a report that was intrinsic to the design of the experiments which uncovered the CORE effect, Davis and co-workers concluded that oxygen plays an indirect role during ODH, and the direct incorporation of gaseous oxygen does not occur.[28] Isotopic labeling experiments demonstrated that hydroxide ions were the source of inserted oxygen, with alcohol oxidation proceeding through the alkoxy intermediate of the geminal diol. Therefore, molecular oxygen acts as an electron scavenger and source of hydroxide ions through the oxygen reduction reaction (ORR), and the buildup of electrons over the active site will limit the rate of hydroxide formation.

This is a crucial observation and highlights the importance of the ORR during ODH, as well as how such reactions essentially exist as two coupled half-reactions. It was our aim to apply bimetallic catalysis to this concept and thus separate the two half-reactions over two active sites. It was our hypothesis that this would alleviate some rate limiting aspects of the mechanism, including the competition for active sites between the two separate half-reactions and the accumulation of excess negative charge over the surface of the metal.

Using the ODH of 5-hydroxymethylfurfural (HMF) as the model reaction (Figure 2A),[29−32] we initially analyzed three carbon-supported, Au−Pd bimetallic systems and compared their activity to the respective monometallic systems (Figure 2B). Crucially, we observe that bimetallic catalysts with spatially defined active sites show enhanced activity compared to a conventional alloy. Specifically, a Janus-type catalyst with phase segregated Au and Pd sites demonstrated the highest activity. However, due to the affinity of the two metals, upon extended use the structure of these Janus species tends toward the alloy, coinciding with a loss in catalytic performance. What is most interesting, and perhaps the clearest demonstration of the CORE effect, comes from consideration of a physical mixture (PM) of monometallic Au and Pd catalysts (Figure 2B, blue circles). At the 30 min time point, the addition of a relatively inactive Pd catalyst into the monometallic Au/C system, results in an increase in HMF conversion by more than 30%.

Furthermore, the role of the conductive carbon support was confirmed via experiments using analogous titania and boron nitride supported catalysts. An increase in activity is observed when conductive carbon material is added into PMs of the semiconductive, titania-supported catalysts (Figure 2C). However, no such enhancement is present with carbon addition to the fully insulating, boron nitride system.[1] We propose that the fully insulating material does not facilitate any transport of electrons away from the active site, hence the absence of an effect upon addition of conductive carbon. Furthermore, we found that there is a linear relationship between the quantity of Pd/C used in the PM and the overall rate (Figure 2D). This is striking, as it clearly shows that the rate of a secondary reaction is limiting overall substrate conversion. There is no correlation between rate and the addition of bare carbon support or boron nitride-supported Pd. Although the initial mechanistic discoveries were made using HMF as the model substrate the same catalytic trends were observed with a variety of alcohols and formyls (Figure 2E).

These initial thermochemical results, along with the work of Davis and co-workers,[28] afforded the first mechanistic proposal of CORE for a PM of Au/C and Pd/C (Figure 3). In this system,

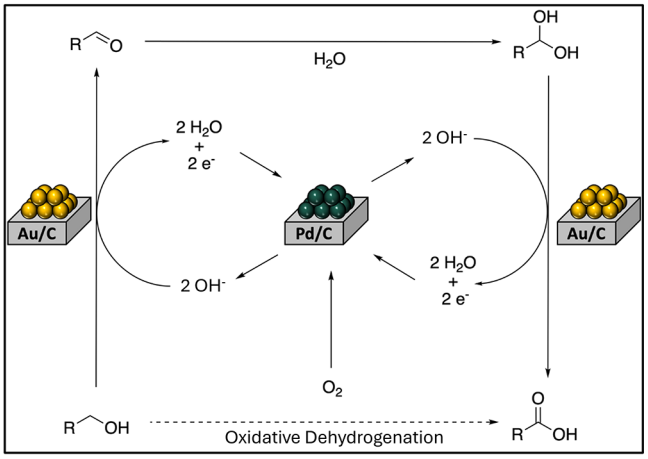

Figure 3. Proposed CORE mechanism during the catalyzed ODH of an alcohol over a PM of Au/C and Pd/C. Adapted from Huang et al.[1] Copyright 2022 Springer Nature.

anodic DH is catalyzed by Au sites liberating electrons, with Pd catalyzing cathodic oxygen reduction, and consuming electrons. The presence of (semi)conductive support is crucial for the transport of electrons, and there is some suggestion that this material can act as an electron sink.[33] This also provides one explanation why conventional alloy is less active than the PM (Figure 2A), as the individual sites do not retain their monometallic properties and subsequent activities toward the individual half-reactions. As will become clear, there are many more complexities to this system, but in essence the affinity of the different active sites toward the opposing half-reactions of the redox system results in a significant enhancement in the overall reaction rate. This is significant in the context of conventionally used bimetallic catalytic systems, as with the CORE effect we aim to avoid direct active site modification and utilize the electrochemical properties of the component catalysts.

ORTHOGONAL CATALYTIC ROLES

The mechanism above denotes the distinct functions of Au and Pd within the ODH system. These separated roles are clearly important to the mechanism and significant investigation has been undertaken to definitively demonstrate this. As the

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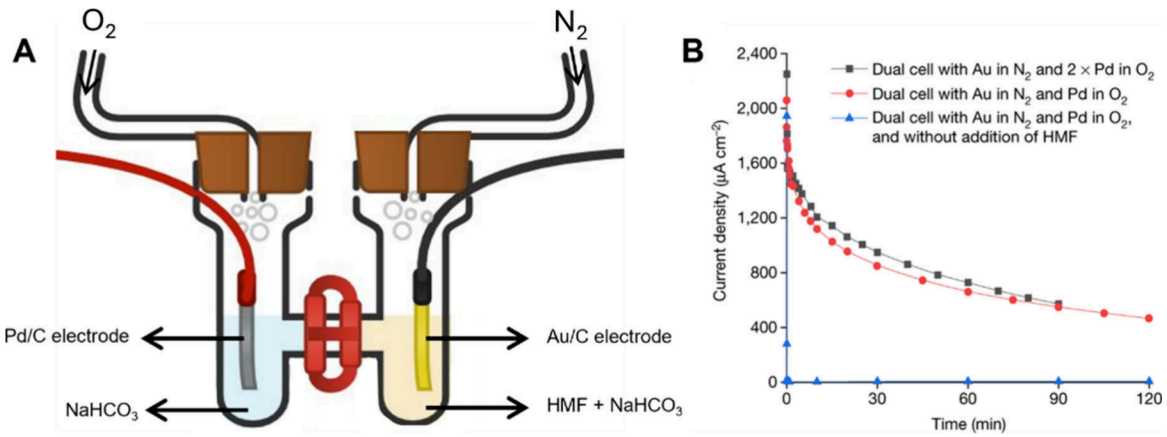

Figure 4. (A) Representation of the dual cell setup used to measure dehydrogenation and oxygen reduction half-reactions independently. (B) Data collected when the two cells from (A) are short-circuited under the conditions, demonstrating the spontaneous current flow between the two electrodes. Conditions: H_2O (35 mL), NaOH (0.1 M), HMF (0.02 M); Au (under N_2) or Pd (under O_2); 25 °C; O_2/N_2 flow 50 mL min^{-1}. Note that, in the present configuration, parameters such as pH, composition, and temperature can be independently controlled in each chamber, unlike pressure, which relies on the properties of the membrane. Adapted from Huang et al.[1] Copyright 2022 Springer Nature.

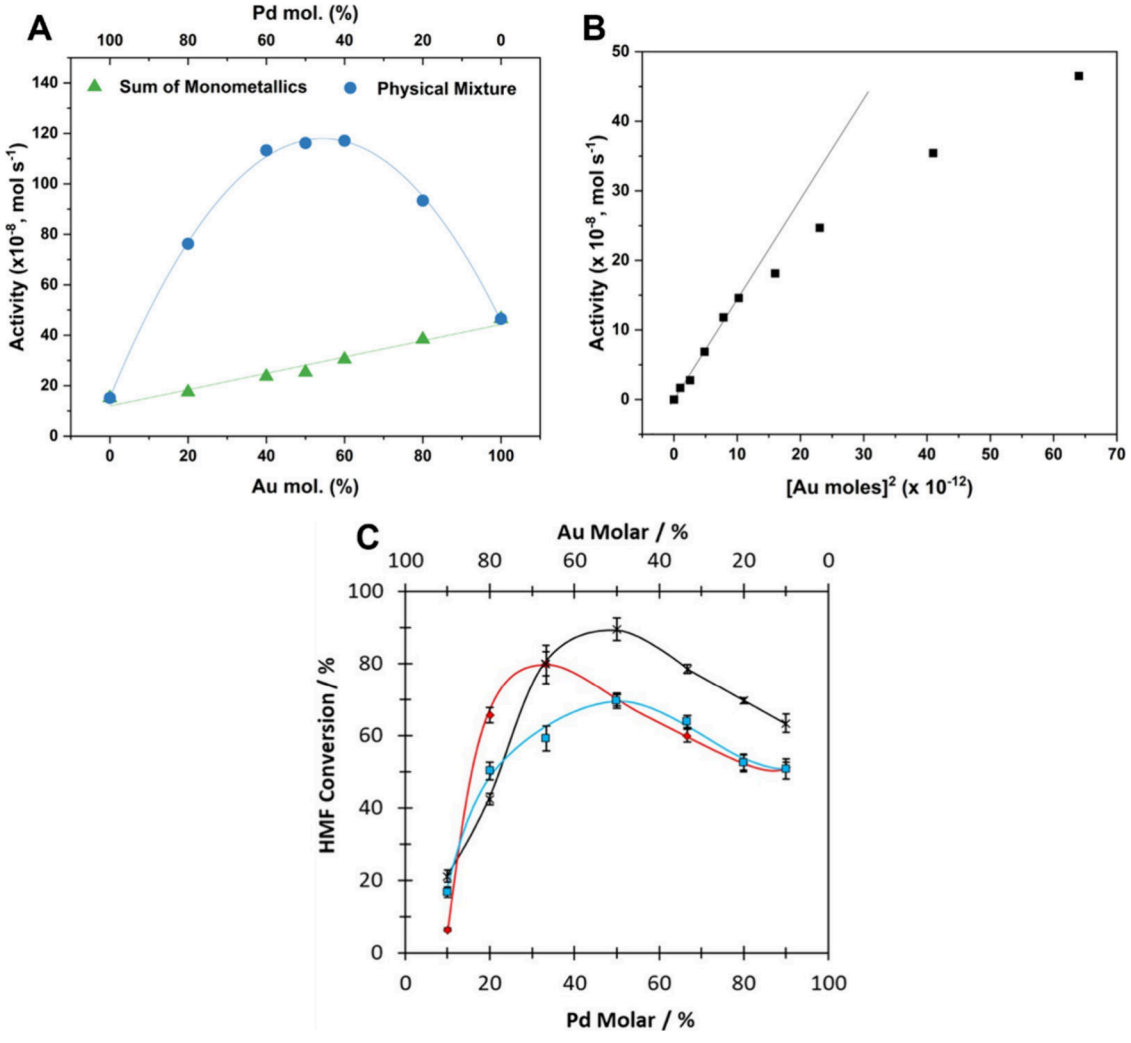

Figure 5. (A) The catalytic activity of a Au/C + Pd/C PM system at various molar ratios, compared to the sum of the monometallic activities. (B) Activity of a monometallic Au/C system against the square of the moles of Au. (C) Influence of the metal ratio on substrate conversion for three bimetallic systems with various weight loading. Key for (C): Au/C + Pd/C PM, blue squares; Au@Pd/C, red diamonds; Au−Pd/C alloy, black crosses. Conditions: 1 wt % Au/C, 1 wt % Pd/C (for (A) and (B)); H_2O (16 mL), HMF (0.1 M), $NaHCO_3$ (0.4 M), O_2 (3 bar), 80 °C, 30 min. In all bimetallic systems, HMF mol:metal mol = 200:1. Adapted from Daniel et al.[2] Copyright 2023 Royal Society of Chemistry and Zhao et al.[16] Copyright 2023 American Chemical Society.

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mechanism involves two coupled half-reactions, electrochemistry proved critical in these investigations.

An initial demonstration of the proposed mechanism was performed using a dual chamber electrochemical cell, whereby anodic and cathodic electrodes could be short-circuited but physically separated by a permeable membrane. In this way, differing active sites can be exposed to orthogonal conditions (Figure 4A). Using this system, we were able to demonstrate that significant current flows between the electrodes when only the substrate is present in the Au chamber (i.e., no oxygen) and only oxygen is present in the Pd chamber (i.e., no reactant) (Figure 4B). This demonstrates two aspects of the mechanism: the spontaneous electron transport between sites and the defined roles of Au and Pd under these conditions.

These findings allowed us to analyze the mechanism by way of a kinetic model.[2] Utilizing ODH as a model transformation, and considering a two-barrier approach (i.e., DH and subsequently the ORR), one can define rate equations based on the roles of Au and Pd. eqs 1 and 2 show two such examples for the catalytic systems containing monometallic Au/C (eq 1) and a PM of Au/C and Pd/C (eq 2), where v_1 is the rate of HMFCA production, [M] is the mole of metal, f is the mole fraction of Au, and k_1 is the rate constant of reaction 1. The detailed explanation and derivation of the equations can be found in the associated publication.[2] These equations predict that the rate of reactant turnover is dependent on the ratio between Au and Pd (represented by f and $1\text{-}f$ in eqs 1 and 2). Thus, far, the work discussed has employed Au and Pd catalysts in a fixed molar ratio of 4/1, but a range of molar ratios were subsequently examined.

$$\frac{v_1}{[M]} = \frac{k_1^{A} f \cdot k_2^{A} f}{k_{-1}} \quad (1)$$

$$\frac{v_1}{[M]} = \frac{k_1^{A} f \cdot k_2^{P} (1-f)}{k_{-1}} \quad (2)$$

By varying the quantity of catalyst used to alter the metal molar ratio, catalyst properties will be consistent, and we demonstrate a volcano-type activity relationship, with a maximum at a 1/1 molar ratio (Figure 5A). This optimum ratio will be dependent on the reaction system and physical catalyst properties, as will be discussed shortly. In terms of the CORE effect, this indicates that an equal number of active sites per half-reaction results in the greatest enhancement relative to expected activity, if the reaction rate of both half reactions is similar. This result aligns with the predictions from eq 2 of the kinetic model, showing the accuracy of this model and the mechanism it is based upon.

Interestingly, considering the case of monometallic Au/C (eq 1), the kinetic model predicts a squared relationship, i.e., the relationship between metal quantity and rate will not increase linearly. Experimental data confirms this at low Au quantities ($<3.2 \times 10^{-6}$ mol_{Au}) (Figure 5B), and this result suggests that additional Au sites increase the activity of each Au site within the reaction. We suggest that this indicates coupling between two Au sites, with some preferentially performing DH and others of different physicochemical composition performing OR.

If we consider the effect of altering the metal molar ratio by changing the metal loading of the catalysts, then the mass of each catalyst used is kept consistent. As such, physical properties of the catalysts will be affected, such as the particle size.[34,35] Therefore, as metal ratio is varied, different bimetallic structures (at constant metal content) show maxima in activity enhancement at different molar ratios (Figure 5C). For example, an alloyed species (Figure 5C, black crosses) and a PM (Figure 5C, blue squares) of Au and Pd show maximum activity at a 1/1 molar ratio, whereas a Janus-type system gives maximum activity at a 2/1 molar ratio (Figure 5C, red diamonds). The hypothesis of the different optimal molar ratios was distinct ORR pathways. A dominant two-electron ORR pathway on Au was observed, producing hydrogen peroxide as a product, which can be easily consumed by Pd.[16] It is important to note that other explanations, such as the spillover of hydroxyl groups from the Pd, can be possible, and further investigation on the Janus-type catalysts and more (e.g., high entropy alloys) would benefit the field. Additionally, we determine that when Pd is in excess (i.e., weight loadings that achieve a Au/Pd molar ratio of <1), Pd sites can preferentially catalyze DH and Au sites can preferentially catalyze OR, i.e., the inverse of that seen thus far. A CORE effect is still observed, but this importantly indicates that either catalytic site can perform either half-reaction, depending on the conditions and catalyst properties. This means that CORE may occur where any type of electrical contact between two catalysts that hold preferential activity toward each half reaction exists. Indeed, beyond the carbon-linked systems utilized for ODH, which have been the focus of our studies, one may expect CORE effects in a range of alternative systems where disparate sites are responsible for individual half reactions. Notably, the enhanced activity of elementally segregated systems (above that achieved by alloy or core−shell variants), has been reported for nanocrystal aerogels when applied to glucose oxidation. It is important to note that the authors of these works ascribe the enhanced performance of these segregated systems to strain effects. However, the similarity to CORE is remarkable.[36,37]

Overall, the investigations into the kinetics and effect of the catalytic molar ratio provide clear evidence in support of the proposed CORE mechanism (Figure 3). By drawing on both theoretical and electrochemical principles, we were able to demonstrate the defined roles of Au and Pd, and how these are dependent on physical properties of the catalyst system. The specific effect of the molar ratio will clearly be different depending on the catalysts employed and with multiple products possible, there are also selectivity aspects to consider. Crucially, these studies provided a primary indication that CORE effects are not specific to a certain reaction and catalyst.

THE ELECTROCHEMICAL FRAMEWORK AND GENERALITY OF CORE

Electrocatalytic analysis has been used in recent years to provide key mechanistic detail regarding the catalyst/reactant interface. In 1999, Mallat and Baiker used catalyst potential measurements to demonstrate how Pt catalyzes two electrochemical reactions in liquid phase alcohol oxidation.[8] This important study was one of the first to document how electrochemical steady state potential measurements can be used to assess the surface concentration of reactants and products in heterogeneous catalysis.

More recently, interest in the crossover between electro- and thermo-catalysis has begun to gain popularity, with our investigation into CORE effects being a primary example of this. In a related external example, component half-reactions are considered to occur over distinct metal nanoparticles during the catalyzed production of H_2O_2, which is treated as a short-circuited electrochemical cell.[7] By measuring the rates of OR and hydrogen evolution, the overall operating potential can be predicted using mixed potential theory (MPT).[38] Briefly, the

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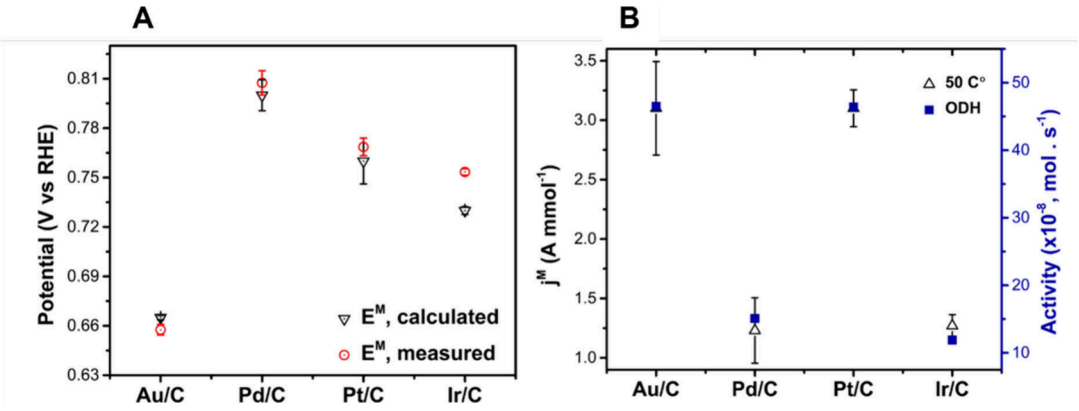

Figure 6. For four monometallic catalysts, (A) a comparison between the calculated and measured E^M values at 50 °C and (B) alignment between the mixed current density and activity at 80 °C. Calculated E^M values are obtained by measurement of individual half-reactions, DH and ORR. Conditions for DH, ORR, and measured E^M: $NaHCO_3$ (0.4 M), HMF (0.1 M, for measured E^M and DH), and N_2 (for ORR) or O_2 (otherwise) (50 mL min^{-1}). Thermocatalytic reaction conditions can be found in the caption for Figure 7. Adapted from Daniel et al.[3] 3 Copyright 2023 American Chemical Society.

mixed potential of a system occurs where there is conservation of charge, i.e., the rates of cathodic and anodic half-reactions are balanced.[3] Thus, it is shown that by increasing the rate of one-half-reaction, the complete H_2O_2 reaction rate can be increased.

Almost concurrently to this work, Surendranath and co-workers reported on the aerobic oxidation of small organic molecules (e.g., methanol) using a similar analysis.[6] Building on this, the role of the conductive carbon support during thermocatalysis was detailed, with reference to a band-mediated mechanism that supports the system of two coupled half-reactions.[33] Later on, the Surendranath group presented a bimetallic enhancement effect in a nitrate hydrogenation system, indicating that the CORE-type mechanism is not limited to ODH reactions.[39] Additionally, An et al.[40] showed that during nitrophenol hydrogenation, coadsorption of reactants is not a necessity and that almost identical reaction rates are achieved in single- and dual-cell systems, where reactants are separated but connected via a membrane. The similarity of these works with the CORE mechanism is obvious and the success of these analyses indicates the utility of MPT.

The results discussed have enabled an understanding of how two active sites work in co-operation during a redox reaction. However, it is important to consider *why* this co-operation results in such significant activity enhancements. To investigate this, we employed the use of mixed potential theory, as discussed above. The mixed potential (E^M), where the rate of anodic (DH) and cathodic (ORR) reactions are balanced, gives a corresponding current density that is a direct measure of activity.

We performed two sets of initial electrochemical measurements using linear sweep voltammetry (LSV) and four monometallic catalysts: Au/C, Pd/C, Ir/C and Pt/C, retaining the ODH of HMF as a model reaction.[3] First, we predicted the value of E^M for each of these systems, by measuring the component half-reactions independently, i.e., in the absence of a coreagent (either HMF or O_2). We directly measured the value of E^M for the four catalysts, in the presence of both coreagents and therefore with both half-reactions occurring simultaneously. Not only do the predicted and measured E^M align, but the thermochemical monometallic activity demonstrates an almost perfect qualitative association (Figure 6). This is significant, as it is definitive evidence that this reaction system (ODH) consists of two coupled half-reactions and shows that E^M and j^M are accurate thermochemical activity descriptors, even at a conditions gap.

This determination allowed us to apply the same electrochemical analysis to bimetallic systems. The four catalysts were analyzed thermochemically in five separate PM systems at a range of molar ratios. Each system showed varying degrees of rate enhancement relative to their monometallic counterparts (Figure 7). Notably, these Pt-containing systems do not show rate enhancements, which we attributed to the alloying of the separated metal sites during exposure to reaction conditions and thus a removal of the two distinct active sites.[3] Given the coexistence of single-atom Pt and Pt clusters (1.4 ± 0.3 nm), this behavior might also be influenced by the nanoscale redox couple within disparate Pt species. Further study is necessary to understand the extent to which the activity and electrode potential of the single atom and cluster are different.

Inspired by galvanic corrosion, we can define new electrochemical descriptors, E^{CORE} and j^{CORE} that describe the operating potential and current density of the bimetallic systems, respectively. In the case of the PM systems that show a rate enhancement, the bimetallic E^{CORE} falls between the monometallic operating potentials. Hence, if we consider an example LSV plot for the independent half reactions, it is possible to observe that E^{CORE} increases the relative current density for the oxidative and reductive half-reactions (Figure 8A). Overall, this drives the increase in thermochemical reaction rate, and it is this polarization that we define as being the origin of the CORE effect. One can see that both Ir-containing systems show a polarized E^{CORE} (and therefore increased j^{CORE}) (Figure 8B), and both display thermochemical rate enhancements (Figure 7A and B). In the case of Pt, the bimetallic values of E^{CORE} are similar to that of monometallic Pt, which as discussed, is due to Pt dominating both half-reactions. We consider this to be a general description that can be applied across multiple catalytic formulations.

Having broadened the scope of CORE to include catalysts containing multiple metal formulations and in turn defined a specific origin of the effect, we can propose a set of conditions that must be satisfied if CORE is to be observed: *(1) CORE potential between the mixed potentials of the two catalysts; (2) the disparate active sites toward oxidation and reaction half reactions; (3) overlapped potential range where both oxidation and reduction simultaneously happens without side reactions; and (4) catalyst*

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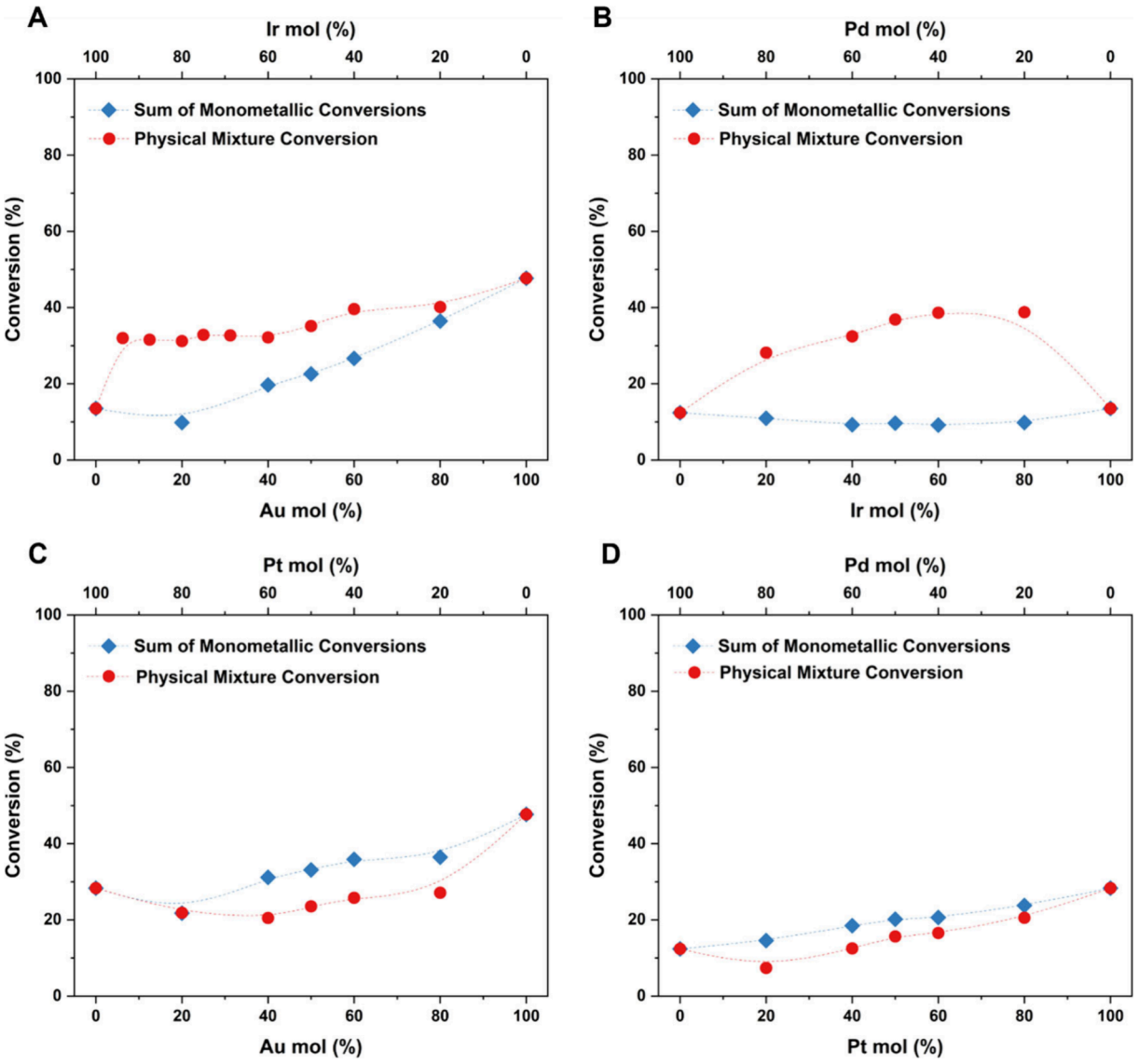

Figure 7. Substrate conversion exhibited by PM systems vs the sum of the monometallic conversions at respective molar quantities for (A) Au/C + Ir/C, (B) Pd/C + Ir/C, (C) Au/C + Pt/C, and (D) Pd/C + Pt/C. All catalysts are approximately 1 wt %. Each data point represents a constant total metal content = HMF mol:metal mol = 200:1. Conditions: 1000 rpm, H_2O (16 mL), HMF (0.1 M), $NaHCO_3$ (0.4 M), 3 bar O_2, 80 °C, 30 min. Adapted from Daniel et al.[3] Copyright 2023 American Chemical Society.

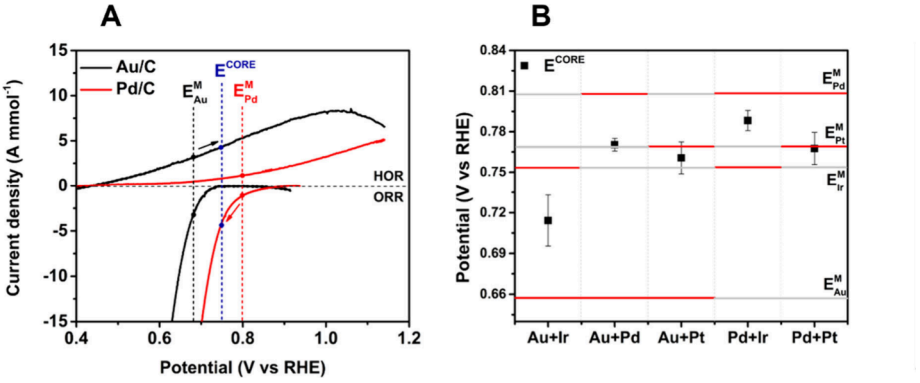

Figure 8. (A) Individually measured LSV curves for Au/C (black) and Pd/C (red) for the DH and ORR half reactions, coplotted on the same axis with the individual and new bimetallic (E^{CORE}) mixed potentials highlighted. (B) E^{CORE} for the five catalytic systems calculated through the method shown in (A), compared to the respective monometallic mixed potential values highlighted in red. Conditions: $NaHCO_3$ (0.4 M), HMF (0.1 M, for DH), and N_2 or O_2 (for DH) (50 mL min^{-1}), 50 °C. Adapted from Daniel et al.[3] Copyright 2023 American Chemical Society.

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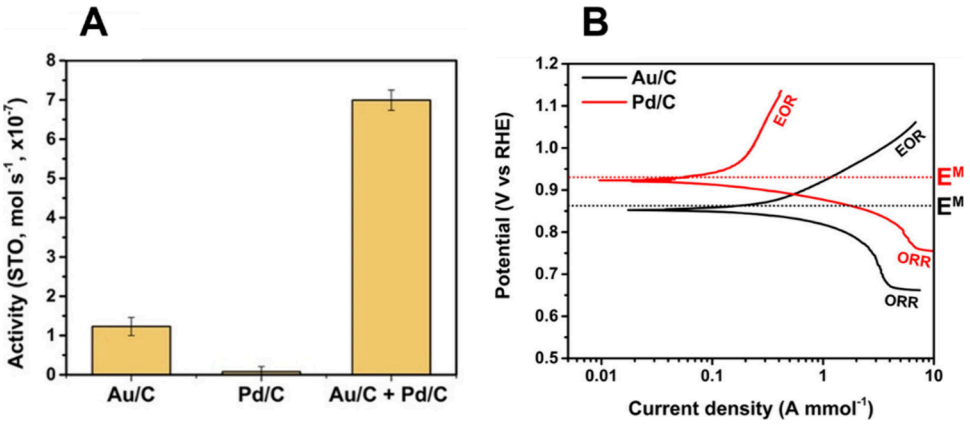

Figure 9. (A) Thermocatalytic activity of ethanol ODH for Au/C, Pd/C, and Au/C + Pd/C. Conditions: H_2O (16 mL), ethanol (0.8 M), Na_2CO_3 (1.6 M), O_2 (3 bar), 60 °C. (B) Tafel slopes for Au/C and Pd/C; dotted lines show agreement with measured E^M. Conditions: Ethanol (0.8 M), Na_2CO_3 (1.6 M), O_2 (50 mL min^{-1}), RT. Adapted from Kim et al.[4] Copyright 2024 American Chemical Society.

stability under reaction conditions for maintaining spatial separation.[3]

A MPT-derived short-circuit model accurately depicts the operation of thermochemical reaction systems; however, it is not without its drawbacks. There are some clear examples where electrocatalytic and thermocatalytic activities align extremely well, such as in Figure 6. However, when measuring individual half-reactions, we assume that there is perfect separation of the two half-reactions in the thermochemical system. This is often not the case, as with a thermochemical mixed reactant and catalytic system, there can be issues of competitive adsorption.

Considering ethanol oxidation as a model reaction, CORE effects are clearly still evident (Figure 9A). The measured and predicted mixed potentials derived using open circuit potential and LSV measurements show excellent agreement with the thermochemical data for Au/C.[4] Given that there is a slight enforced conditions gap, there is almost quantitative alignment when the current density is converted to thermocatalytic rate. (Table 1). However, in the case of Pd/C, LSV data predicts a thermochemical ethanol oxidation rate 19 times higher than the actual value (Table 1 at 50 °C), with an onset potential approaching that of the ORR. This demonstrates that the two component half-reactions are not completely independent over the Pd/C catalyst, supported by the fact that injection of oxygen into an ethanol reaction solution raises the operating potential, as active sites are suggested to be blocked from the substrate. Due to a lack of substantive interaction between Au and oxygen, this is not observed over the Au/C under these conditions.

Table 1. Values for E^M and j^M for Au/C and Pd/C from Three Different Measurements[a]

		Au/C		Pd/C	
Thermocatalytic rate/× 10^{-7}, mol s^{-1}		1.23 ± 0.232		0.077 ± 0.232	
Electrochemical method	Descriptor	RT	50 °C	RT	50 °C
OCP	E^M/V	0.863	0.807	0.933	0.890
LSV	E^M/V	0.870	0.820	0.848	0.798
	j^M/× 10^{-7}, mol s^{-1}	0.12	0.60	1.03	1.32
Tafel	E^M/V	0.852	N.A.	0.922	N.A.
	j^M/× 10^{-7}, mol s^{-1}	0.07	N.A.	0.03	N.A.

[a]Compared to the thermocatalytic rates: (i) open circuit potential (OCP); (ii) LVS predictions; (iii) Tafel analysis.

To account for competitive adsorption, we demonstrate that Tafel analysis, where both coreagents (ethanol and oxygen) are present, is an excellent predictor of thermochemical activity over catalysts where competitive adsorption is an issue. The determined E^M values from Tafel analysis are exceptionally close to those measured for Au/C and, as it accounts for oxygen inhibition, showing that a j^M value is much closer to the thermochemical value for Pd/C (Figure 9B, Table 2). The differences between the LSV and Tafel method are attributed to the fact that LSV assumes complete separation of the half reactions. Moreover, the LSV method may face additional limitations such as capacitance current and diffusion limitations, due to higher scan rate and fast consumption of reactants on the surface during polarization. E^M values via Tafel measurements are still consistent with the thermochemical CORE effect and the origin of this through spontaneous polarization. The short-circuit model with LSVs is still a viable and accurate electrochemical method for describing thermochemical reactions, when competitive adsorption is not a factor. Tafel analysis simply enables conditions closer to the actual thermochemical system and hence a more accurate translation.

The fact that competitive adsorption is clearly a factor within catalytic oxidation systems affords another perspective of how CORE facilitates improved reaction rates: having two distinct active sites that preferably catalyze different component half reactions removes any competitive adsorption. This is why *condition (2)* is included and must be satisfied for CORE to occur.

CONCLUSIONS AND FUTURE PERSPECTIVES

Co-operative Redox Enhancement, or CORE, is a recently discovered phenomenon that shows how a thermochemical reaction can behave akin to a nanoscale electrochemical cell. If certain criteria are satisfied, two disparate active sites will catalyze individual half-reactions that collectively constitute a redox process. These active sites are electronically coupled and thus polarized, increasing the rate of each half-reaction and in turn the overall reaction rate. In contrast to the vague and encompassing term 'synergy', we have shown detailed derivations of the mechanism and origin of CORE effects, and that these effects can be general across different reaction formulations.

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Based on the in-depth foundations discussed here, there is, undoubtedly, enormous scope for further expansion of the CORE effect to demonstrate its validity for a wider range of catalytic materials. Our understanding of the operation of certain bimetallic catalytic systems can improve significantly using the electrochemical tools laid out in this Account. Nevertheless, the development of CORE and its applications is still in its nascent stages, presenting numerous avenues for future research.

A quantitative and kinetic-based investigation of the spontaneous polarization effect by CORE is warranted. A deeper understanding of the quantitative comparison between the interfacial electron flow via CORE and the actual turnover, and the kinetic study, such as the time scale required for this polarization to reach a steady state, is currently lacking. In these cases, the influence of diffusion length caused by spatial separation needs to be carefully considered. Such studies would significantly enhance our ability to utilize and design CORE more efficiently. Additionally, the structural stability of catalysts operated via CORE presents a compelling area of study, especially for Janus-type catalysts, which have been prone to alloying in our initial studies. The formation of an electrochemical double-layer, along with local potential and ion gradients, introduces additional complexities that must be considered in future catalyst design. This will necessitate the use of in situ and operando analytical techniques, which have thus far been underexplored.

Support engineering offers another important dimension for advancing CORE. By strategically introducing defects or doping elements, or using different dimensions, the support material itself can be engineered to be catalytically active. This can prevent potential alloying as well as minimize any diffusion limitations. Furthermore, leveraging the interfacial interactions between the support and the catalyst can also provide a potential strategy for fine-tuning reactant selectivity.

Crucially, the CORE effect can be extended to any redox systems that establish orthogonal functionality between two active sites. This potentially includes reaction systems based on the gas−solid, solid−solid, and liquid−solid interface. For example, inorganic/organic hybrid systems, such as using a metallic catalyst coupled with organometallic complexes, can represent a promising characteristic as the electrical contact can be made between metal centers and the redox-active organic molecules.

Ultimately, future work should focus on optimizing, or improving upon, catalytic transformations that are industrially significant. With that in mind, we recommend that subsequent studies utilize industrially applicable catalysts and operating conditions, for example, by focusing on flow-type systems.

The CORE effect changes how we approach bimetallic catalysis and with this greater fundamental understanding, catalyst design can be tailored to a much greater extent, which is extremely significant. Furthermore, the electrochemical methods presented here provide a facile and comprehensive predictive tool for thermochemical catalyst design. This will allow individual active sites to be selected based on the components of a known redox process. This will, among other aspects, afford the more efficient usage of scarce materials and contribute to reducing the demands of the energy-expensive chemical industry.

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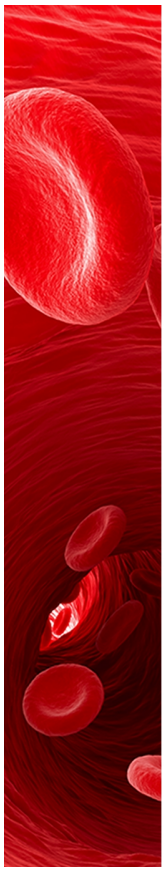

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