

PAPER

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Leveraging co-operative redox enhancement (CORE) for efficient electrochemical production

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The shift from traditional fossil-fuel-based chemical production to a renewable e-chemical industry requires innovation in the design of catalytic and electrocatalytic systems for both initial production of platform hydrocarbons and their subsequent upgrading to a core suite of feedstocks and chemical intermediates. To this end, we require selective and efficient catalytic systems that operate under relatively mild conditions. We have recently developed a new approach, termed Co-Operative Redox Enhancement (CORE), to the design of catalytic systems that leverage electrocatalytic driving forces to substantially enhance the activity of what, at first glance, would be considered a thermal catalytic process. Dissimilar, physically separated but electrochemically connected catalytic nanoparticles will establish a spontaneous, nanoscale, electrochemical gradient between them due to differences in the electrocatalytic selectivity of each particle towards the desired half reactions. This leads to polarization of the nanoparticles and associated enhancement in their selectivity and activity towards the half reactions, driving an overall increase in catalytic turnover. The extent of polarization is quantifiable and the impact on overall catalytic turnover is predictable through an electrochemical approach based on modified corrosion theory. This new approach to the design of catalytic systems has wide-ranging implications for the design of thermal and electrocatalytic systems for the e-chemical industry and beyond. In this work, we discuss the oxidative dehydrogenation of benzyl alcohol utilizing coupled Au/C and Pd/C catalysts as an exemplar of CORE. The role of CORE is demonstrated through a combination of thermocatalytic and electrocatalytic experiments, pointing towards CORE as an approach to design and implement both thermal and electrochemical catalytic systems for efficient e-chemical production.

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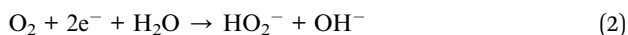
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Introduction

The fields of thermal catalysis and electrocatalysis are frequently considered entirely separable. Where thermal catalytic reactions are driven by temperature and pressure, electrocatalytic reactions occur upon the external application of an additional electrochemical potential driving force. As such, we traditionally consider electrochemical driving forces to influence electrocatalytic reactions when we explicitly design and include electrodes in the system. In contrast to this, corrosion reactions occur through the spontaneous establishment of electrochemical gradients between dissimilar metals with associated separation of the reduction and oxidation half reactions between the metals.¹ We have recently demonstrated that analogous spontaneous electrochemical driving forces can be established in apparently thermal catalytic systems through a process termed cooperative redox enhancement (CORE).^{2–8} Herein, we build upon these prior reports and present further discussion and illustration of the CORE mechanism through its application to oxidative dehydrogenation of benzyl alcohol.

The selective oxidative dehydrogenation (ODH) of alcohols to aldehydes and acids while avoiding overoxidation to carbon dioxide and water is a critical process that yields high-value aldehyde and acid products utilized in products ranging from cosmetics to pharmaceuticals.^{9–12} As we shift towards decarbonization of the chemical industry, we require new, efficient, electrochemical pathways to perform these critical reaction steps.¹³ In this work, we examine the ODH of benzyl alcohol (BZA) to benzaldehyde (BZALD) and benzoic acid (BZAC) as an exemplar CORE catalytic reaction.

The overall ODH reaction of BZA to form BZALD in alkaline media can be written as two half-reactions; the benzyl alcohol oxidation reaction (BZAOR), eqn (1), coupled with either the two- or four-electron oxygen reduction reaction (ORR), eqn (2) and (3), that sum to yield the overall reaction, eqn (4). The product BZALD can then undergo a second oxidation step of the benzaldehyde oxidation reaction (BZAHOR) to form BZAC, eqn (5). This is again coupled with the ORR to yield the overall aldehyde oxidative reduction reaction, eqn (6).



In a traditional electrochemical approach, one would approach this system by designing macroscale electrodes to perform these reactions in separated chambers, electrochemically connected *via* an alkaline electrolyte and external circuit. The reactions could then be driven and controlled *via* application of an external potential to polarize the anode and cathode to accelerate the oxidation and

reduction reactions, respectively. Care would be taken to consider the associated kinetic barriers of the electrochemical reaction steps, ionic transport through electrolyte, and electron transport through the external circuit. However, these reactions are spontaneous in the direction written and, as with corrosion reactions or single-chamber electrochemical cells, a potential can be established between two reaction sites if the sites have sufficient differential selectivity towards the two half reactions. For example, the corrosion of steel is accelerated by the spontaneous polarization of an oxidizing anodic region of the surface coupled to oxygen reduction *via* the ORR at a cathodic region of the surface. Moisture from the environment serves as the electrolyte for hydroxyl ion transport between the two regions while electron transport occurs through the metal. This is the same principle that underlies CORE.

CORE occurs upon the physical separation, but electrochemical connection, of two metals with dissimilar selectivity and activity towards two redox coupled catalytic reactions. In CORE we replace this undesired oxidative corrosion reaction with, for example, the desired oxidative dehydrogenation of an alcohol. In principle, either or both half reactions can produce value added chemicals, but in this and our prior work the reduction reaction is the ORR. As with corrosion reactions, the spontaneous separation of the half reactions across sites and subsequent electrochemical polarization accelerates the overall reaction. We have shown that this CORE-enabled rate can be several times that of the sum of the individual catalyst rates.^{2–8}

The CORE mechanism leads to substantial increase in catalytic rate upon physical mixing of separate precious metal nanoparticles supported on carbon. This occurs through the spontaneous formation of electrochemical circuits at the nanoscale. For example, CORE occurs between spatially separated Au and Pd nanoparticles for the oxidative dehydrogenation of hydroxy methylfurfural (HMF) whereby HMF oxidation occurs on the Au nanoparticle, and the ORR occurs on

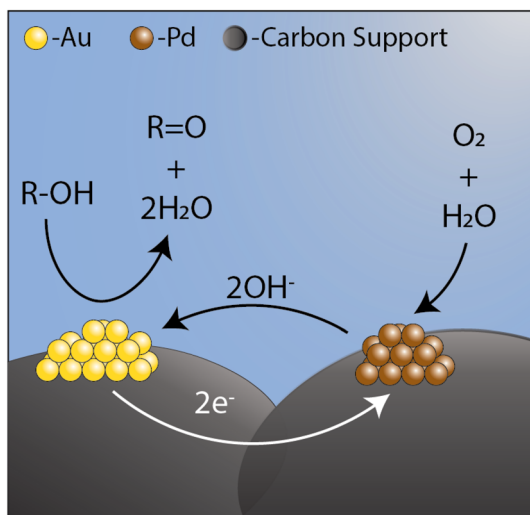


Fig. 1 Schematic representation of the CORE mechanism for oxidative dehydrogenation of an alcohol to an aldehyde.

the Pd nanoparticles (Fig. 1). In this case, the two catalytic particles are physically separated but electrically connected through a connected, aggregated, graphitic carbon support. We have demonstrated that the magnitude of CORE is strongly dependent on the electrical conductivity of the support material.² The electrochemical circuit is completed by the transport of hydroxide ions with the alkaline reaction medium serving as an electrolyte. In this example, CORE leads to a doubling of the overall rate when compared to the sum of the rates on the two individual metal catalysts.² This mechanism can be explained, confirmed, and predicted through analogous experimentation utilizing macroscale electrodes.

While our work has focused upon CORE between dissimilar metals, there is increasing awareness of how spontaneously generated electric fields influence the rate and mechanism of reactions at catalytic surfaces.^{14–28} This increased understanding can be utilized to, for example, analyze the reaction mechanisms on single-metal catalysts¹⁴ and even as a probe of surface coverage.^{25,26} For this discussion, we provide new data illustrating CORE for the ODH of benzyl alcohol utilizing physical mixtures of Au/C + Pd/C as thermocatalysts and electrocatalysts.

Experimental

Sol immobilisation of 1 wt% Au/C and Pd/C

2 g batches of 1 wt% Au/C or Pd/C were synthesised *via* the following sol immobilisation procedure. Metal precursor in aqueous solution (HAuCl_4 , 12.4 mg_{Au} mL^{-1} , 1613 μL , or PdCl_2 , 6.1 mg_{Pd} mL^{-1} , 3279 μL) and polyvinyl alcohol (10 mg mL^{-1} , PVA mass : metal mass 1 : 1, 2000 μL) were added to deionised water (350 mL) and left to stir (1000 rpm) for 15 minutes. Fresh NaBH_4 (0.15 M, mol H : mol metal = 4 : 1) was added and the resulting colloidal solution stirred for 30 minutes. Carbon support (Carbon Black, Vulcan XC-72R, 1.98 g) was added at lower stirring speed (400 rpm) before stirring for a further 30 min (1000 rpm). The resulting catalyst was filtered, washed (DI water, 1 L g^{-1}) and dried under static air (110 °C, 16 h) before grinding to homogenise it with a pestle and mortar.

Thermocatalytic benzyl alcohol oxidation procedure

A glass Colaver reactor (50 mL, Colaver s.r.l.) was charged with an aqueous solution (16 mL) of benzyl alcohol (BZA, 0.1 M) and NaHCO_3 (0.4 M) or NaOH (0.6 M), which was stirred at 60 °C and ambient pressure for 10 minutes to equilibrate. Catalyst was then added in requisite amounts. The Colaver reactor was purged five times with O_2 before pressure was maintained at 3 bar, with a typical reaction time of 120 minutes. Samples were taken at intervals, with the Colaver reactor purged 3 times with O_2 after each sample before O_2 pressure was maintained at 1 bar or 3 bar. Samples were analysed using high-performance liquid chromatography (HPLC) (Agilent Technologies 1200 series) equipped with DAD detectors and a MetaCarb 87H (300 × 6.5 mm) column. The mobile phase consisted of aqueous 0.1 wt% H_3PO_4 solution and acetonitrile in a 70 : 30 split. Molar quantification, alcohol conversion and product selectivity were obtained using pre-determined response factors based on calibrations with known concentrations of products. Conversion was calculated as the moles of BZA consumed divided by the initial number of moles of BZA. Data points and error bars on the thermocatalytic data represent averages and standard deviations of three separate

experiments. Example raw HPLC data and calibration files are supplied as Fig. S5 and S6. Tabular data for product yield, conversion, and carbon balance are provided in Tables S1–S8. Carbon mass balance drops at high BZA conversion due to rapid conversion of BZALD to an unknown product, possibly through a condensation reaction as a result of the high concentrations of base present. For this reason, all rates are calculated based on the conversion of BZA and not on the total moles of product produced.

$$\text{Conversion, } t \text{ (\%)} = \frac{\text{mol}_{\text{initial}} - \text{mol}_t}{\text{mol}_{\text{initial}}} \times 100 \quad (7)$$

$$\text{Selectivity (\%)} = \frac{\text{mol}_{\text{product}}}{\text{mol}_{\text{total}}} \times 100 \quad (8)$$

$$\text{Yield (\%)} = \text{conversion (\%)} \times \frac{\text{selectivity (\%)}}{100} \quad (9)$$

$$\text{Carbon mass balance (\%)} = \frac{\sum \text{mol}_{\text{total}}}{\text{mol}_{\text{BZA initial}}} \times 100 \quad (10)$$

$$\text{Activity (mol s}^{-1}\text{)} = \frac{\text{mol}_{\text{BZA initial}} - \text{mol}_{\text{BZA, } t}}{\text{time(s)}} \quad (11)$$

All thermochemical and electrochemical reactors and tools are cleaned with diluted Alconox detergent and rinsed with deionized water at least three times. They are then rinsed with isopropanol or acetone to remove any residual impurities and dried with filtered air.

Electrochemical measurements

Electrodes are prepared by brush-coating on carbon cloth. Firstly, carbon cloth was sonicated with acetone, isopropanol and water for 15 min each. Catalyst ink for Au/C and Pd/C was prepared by mixing water, isopropanol and Nafion ionomer. The total amount of catalysts was measured to give a specific concentration ($0.04 \mu\text{mol cm}^{-2}$) and the prepared catalyst ink was brush-coated onto the cloth on a 50°C hot plate.

A miniature electrochemical cell (4–6 mL volume, StonyLab) was used for Tafel and single-chamber short-circuit testing. A rubber seal wrapped with Teflon tape was employed to ensure an airtight environment at elevated temperatures. For all experiments, the temperature was maintained at 60°C with an oxygen pressure of 1 bar. Note that while the oxygen pressure can be quite readily varied in the thermocatalytic experiments, challenges around sealing the more complex experimental systems for electrocatalytic experiments limit these to a maximum pressure of 1 bar. Stainless steel electrode holders were applied to hold the catalyst-coated carbon-cloth electrodes. The active surface area of each electrode was 1 cm^2 for experiments conducted at pH 14 and pH 8.4. Temperature was controlled using a silicone oil bath. For experiments under pressure conditions, the cell was purged five times to establish a fully oxygenated environment and to minimize any CO_2 contamination. Additionally, the internal solution of the reference electrode (Hg/HgO) was replaced after each pressurized experiment.

The Hg/HgO reference electrode potential varied by less than 10 mV between room temperature and 60 °C and was converted to the Reversible Hydrogen Electrode (RHE) potential and corrected for pH change using standard approaches. For short-circuit testing, the galvanic corrosion program from Gamry Framework was applied. For Tafel analysis, the catalyst was rested at open circuit potential until stabilized before the measurement with a scan rate of 0.1 mV s⁻¹. Data fitting to extract numerical values from the electrochemical data was performed utilizing the Gamry Echem Analyst software package.

Results and discussion

Fig. 2A shows the BZA conversion as a function of time for Au/C, Pd/C and physically mixed Au/C + Pd/C catalysts at a pH of 8.4. While Au/C shows reasonable BZA conversion reaching 68% conversion after 120 minutes, Pd/C alone is quite inactive providing only 4% conversion in the same period. The impact of the CORE mechanism is clearly observed when comparing the individual catalysts to the physical mixture of the two, with the Au/C + Pd/C catalysts reaching 100% conversion of BZA at 120 minutes. The activities of each catalyst were calculated after 15 minutes of reaction as 2.5×10^{-7} , 1.1×10^{-8} and 8.4×10^{-7} mol_{BZA}·s⁻¹ for the Au/C, Pd/C and Au/C + Pd/C catalysts, respectively. The rate observed for the physically mixed catalyst is three times greater than the sum of the individual catalyst rates, indicating the presence of the cooperative mechanism, in agreement with our previous observations that CORE substantially enhances the rate of oxidative dehydrogenation for a range of substrates.^{2,4-6} We have previously demonstrated that the two types of catalytic nanoparticle remain distinct during reaction and that alloy or mixed composition particles are not formed.²

Examining the product yield as a function of time for each catalyst (Fig. 2B), shows that Au/C is active for both the initial ODH step to form BZALD and the

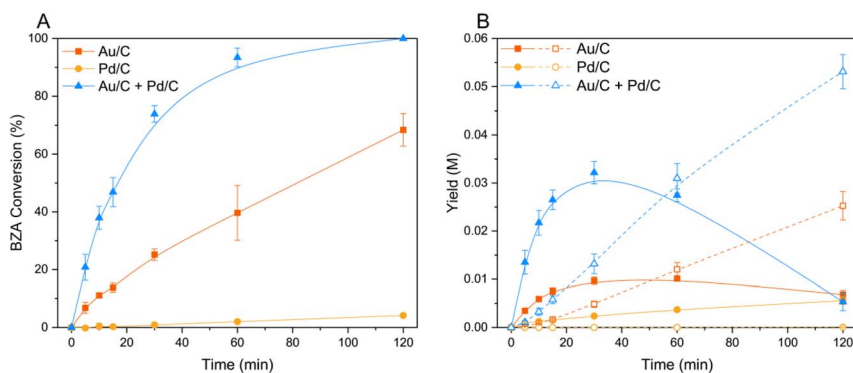


Fig. 2 Benzyl alcohol (BZA) conversion (A) and benzaldehyde (BZALD, solid lines) and benzoic acid (BZAC, dashed lines) product yields (B) as a function of time in thermocatalytic oxidative dehydrogenation with Au/C, Pd/C and physically mixed Au/C + Pd/C catalysts. The reaction was performed at 60 °C with 3 bar O₂ and at a pH of 8.4, set by the presence of 0.4 M NaHCO₃ in the aqueous phase. The initial BZA concentration was 0.1 M with 1 wt% Au/C (103 mg), 1 wt% Pd/C (55 mg), and Au/C + Pd/C (103 + 55 mg).

subsequent ODH of BZALD to form BZAC. In contrast, Pd/C appears active only for the initial ODH to BZALD. The yield profile of the Au/C + Pd/C follows the classic shape for a sequential reaction with the yield of BZALD peaking after 30 minutes prior to decreasing as the yield of the secondary reaction product, BZAC, increases. An initial observation is that this activity for both BZA and BZALD mirrors that of Au/C but occurs at a higher rate, indicating that the Au/C component is likely the active component for BZA and BZALD ODH half reactions and that Pd/C may be less active for the oxidative dehydrogenation of aldehydes. Similar trends are observed at 1 bar O₂ (Fig. S1).

Fig. 3 shows the comparable BZA conversion and product selectivity as a function of time for Au/C, Pd/C and physically mixed Au/C + Pd/C catalysts at a pH of 14. The trends observed at lower pH still hold, with the Au/C + Pd/C reaching almost 100% conversion of BZA after 15 minutes and complete conversion of the intermediate BZALD to BZAC after 30 minutes. Au/C reaches 100% conversion by 60 minutes and similarly shows complete conversion of the BZALD intermediate to BZAC. In contrast, Pd/C does not fully convert the BZA within the 120 minutes experimental period and yields a mixture of BZALD and BZAC. The activities of each catalyst were calculated after 10 minutes of reaction as 1.1×10^{-6} , 4.4×10^{-7} , and 1.8×10^{-6} mol_{BZA} s⁻¹ for the Au/C, Pd/C and Au/C + Pd/C catalysts, respectively. Similar trends are observed at 1 bar O₂ (Fig. S2). Note that while the physical mixture catalyst clearly shows an increased rate, the complete conversion of the BZA within this initial period means that the true rate and CORE enhancement is somewhat masked. As such, these experiments were repeated with one sixth catalyst loading to more accurately determine the rate for the Au/C, Pd/C and physical mixture as 8.3×10^{-7} , 1.1×10^{-6} and 2.2×10^{-7} mol_{BZA} s⁻¹, respectively, after 5 minutes of reaction time (Fig. S4). At the lower loading, at both 1 and 3 bar O₂ pressure (Fig. S3 and S4) Au/C shows lower activity, as expected, but Pd/C shows greater activity, even reaching near-100% conversion of BZA after 30 minutes. This is not fully understood, and remains an area for

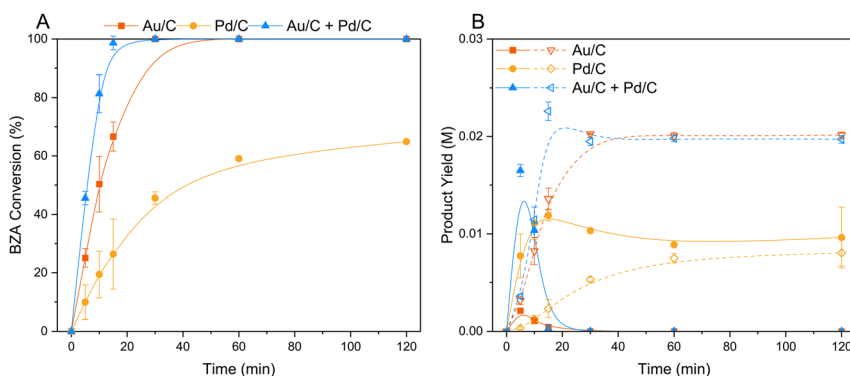


Fig. 3 Benzyl alcohol (BZA) conversion (A) and benzaldehyde (BZALD, solid lines) and benzoic acid (BZAC, dashed lines) product yields (B) as a function of time in thermocatalytic oxidative dehydrogenation with Au/C, Pd/C and physically mixed Au/C + Pd/C catalysts. The reaction was performed at 60 °C with 3 bar O₂ at a pH of 14, set by the presence of 0.6 M NaOH in the aqueous phase. The initial BZA concentration was 0.1 M with 1 wt% Au/C (103 mg), 1 wt% Pd/C (55 mg), and Au/C + Pd/C (103 + 55 mg).

future study. As with the lower pH data, the trends in alcohol and aldehyde oxidation of the physically mixed Au/C + Pd/C catalyst generally follow those of the Au/C but at substantially increased rate, facilitated by the presence of Pd/C.

The CORE mechanism operates through the spontaneous generation of nanoscale electrochemical cells within the physically mixed catalytic system. In this case, it is important to note that we observe significant flocculation and aggregation of the carbon-supported catalysts within the aqueous reaction medium (Fig. S7). This aggregation is key to achieving the electrical connectivity between the Au/C and Pd/C nanoparticles that, in combination with hydroxide ion transport through the alkaline electrolyte, completes the CORE circuit.

The proposed CORE mechanism can be confirmed *via* electrochemical measurements utilizing macroscale electrodes. This requires close coordination between the preparation of catalysts for both thermocatalytic and electrocatalytic experiments. Challenges remain in directly matching catalytic turnover. The two catalyst systems cannot be precisely matched as catalyst deposition onto a support, often using a binding agent, can lead to agglomeration, buried interfaces, and diffusion limitations in the electrochemical experiments that are not present in the thermocatalytic system. Alternative preparation of the catalyst directly onto a macroscale electrode can lead to substantial differences in catalyst morphology and particle size. Nevertheless, we have shown direct correlation between the thermocatalytic activity and electrocatalytic activity of the materials.⁴

One method to examine the electrocatalytic activity of the catalysts for these half reactions is *via* linear scan voltammetry (LSV) curves measured in the presence of only one of the reactants, for example, measuring the electrode response for the alcohol oxidation reaction in the absence of molecular oxygen.^{5,8} While this can be effective, it excludes the possibility that competitive adsorption between reactants can alter the electrocatalytic response. Ignoring this possibility can lead to failure to correlate the electrocatalytic measurement to the thermocatalytic behavior that is, by necessity, measured for the overall reaction in the presence of both reactants.

A more appropriate approach is to measure the response of the catalyst in the presence of both reactants to yield a Tafel curve. Fig. 4 shows illustrative Tafel curves for two hypothetical catalysts. Starting with Catalyst I, the Tafel response shows a symmetric current response upon polarization in both oxidation and reduction directions. The symmetric central potential in the curve is the mixed potential of the electrocatalyst where the rates of oxidation and reduction reactions are equilibrated. This point can be measured as the open circuit potential of the catalyst at rest in solution. For oxidative dehydrogenation reactions as discussed herein, the oxidative branch of the Tafel curve is the electrocatalyst response when the electrode is polarized to favor the alcohol or aldehyde oxidation half reactions, eqn (10) and (11). As expected the rate of the reaction, measured as a current density, increases upon increasing the potential, which reduces the electrochemical potential of the electrons in the electrode and thus drives the oxidation of the substrate. The opposite occurs upon decreasing the potential for the reductive branch driving the ORR, eqn (8) or (9). We can measure an exchange current density, denoted here as j^{Tafel} , through extrapolation from the linear regions of the oxidative and reductive branches. This exchange current density indicates the inherent rate of the two half reactions at the equilibrium mixed potential and can be considered as an indication of the overall reaction rate

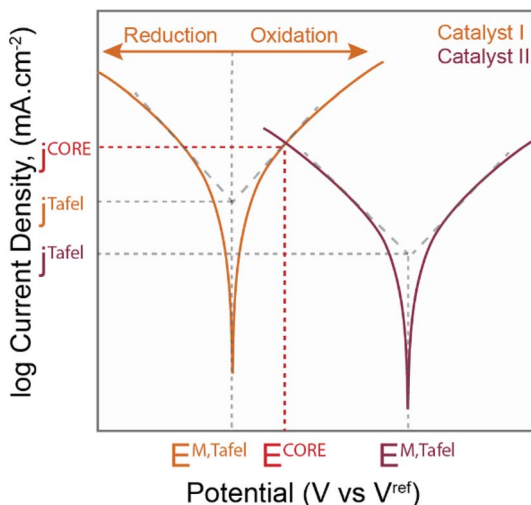


Fig. 4 Illustrative Tafel plot for two catalysts showing the individual catalyst Tafel curves and associated calculation of the individual catalyst mixed potentials, $E^{M,Tafel}$, and exchange current densities, j^{Tafel} . The catalyst curves are color coded with the oxidative and reductive branches for Catalyst I labeled. The spontaneously formed CORE potential, E^{CORE} and associated increase in overall rate, j^{CORE} , are illustrated in red.

that we may expect from a thermocatalytic reaction with the same catalyst. The performance of Catalyst II is similarly illustrated, noting that the catalyst equilibrates at a higher potential and provides a lower exchange current density.

CORE occurs when we electrochemically connect these two catalysts and they establish a new equilibrium potential at E^{CORE} that lies between the two individual metal mixed potentials. This potential is calculated as the point where the oxidative branch of Catalyst I crosses the reductive branch of Catalyst II. This infers that the oxidation half reaction now occurs on Catalyst I and the reduction half reaction occurs on Catalyst II. As such, it is somewhat analogous to the potential derived from mixed potential theory for multiple redox couples occurring on a single catalyst;^{27,28} however, in this case, we have two distinctly different catalysts.

Note that this mutual polarization leads to an increase in the associated overall rate to j^{CORE} ; this is the origin of CORE. Catalyst I with the lower mixed potential is polarized to a higher potential, driving the oxidation reaction on this catalyst, while Catalyst II with the higher mixed potential is polarized to lower potential, driving the reduction reaction on this catalyst. This mechanistic understanding is directly adapted from the long-standing understanding of corrosion science.¹ Beyond understanding the mechanism, this can provide a predictive capability for the CORE mechanism based on Tafel analysis prior to undertaking thermocatalytic experiments.

We have previously demonstrated remarkable correlation between the CORE thermocatalytic rate of physically mixed precious metal catalysts and calculated j^{CORE} by combining the individual catalyst Tafel and LSV curves for a range of mixed precious metal catalysts in the oxidative dehydrogenation of alcohols.⁴ Similarly, we find direct agreement between the open circuit potential of

electrodes with physically mixed catalysts and E^{CORE} calculated from the individual catalyst Tafel and LSV curves.^{4,5} These clear correlations demonstrate that CORE polarization occurs in these physical mixtures and directly leads to enhancement in thermocatalytic rate.

Fig. 5A shows the Tafel curves for Au/C and Pd/C measured in 0.2 M BZA at 60 °C and 1 bar O₂ at a pH of 14. Raw data and fits used to extract numeric values are provided in Fig. S8. The Au/C electrode shows a relatively symmetric response in both oxidation and reduction directions. The Tafel curve indicates a mixed potential for Au/C of 0.863 V under these conditions, and we can calculate a Au/C exchange current density of 0.22 mA cm⁻². The Pd/C curve shows a similar symmetric response but with an indication of a possible diffusion limitation at higher overpotential on the BZ oxidation branch of the curve. The Pd Tafel curve indicates a mixed potential of 0.915 V with a corresponding exchange current density of 0.12 mA cm⁻². The crossover point of the Au/C BZA oxidation curve and Pd/C ORR curve indicates an E^{CORE} of 0.886 V, with an associated j^{CORE} of 0.23 mA cm⁻². This higher potential of Pd/C compared with Au/C indicates that the ORR will be favored on Pd/C and the alcohol oxidation steps favored on Au/C in the CORE system. The higher exchange current density of Au/C compared with Pd/C correlates with the observed higher thermocatalytic rate for Au/C vs. Pd/C (Fig. 3A and 4A). Similarly, j^{CORE} is substantially greater than the exchange current density of either catalyst alone, in agreement with the higher thermocatalytic rate for the physically mixed, CORE-coupled, thermocatalyst. Finally, we observed in Fig. 2B and 3B that the trend in BZALD and BZAC for the Au/C + Pd/C catalyst is similar to that observed for the Au/C catalyst. This further supports the conclusion from this Tafel plot analysis that Au/C primarily plays the role of an alcohol oxidation catalyst in the physically mixed catalyst.

Since these reactions are spontaneous and both catalysts spontaneously polarize upon electrochemical connection in the same mixed reactant chamber, we can anticipate that similar polarization will occur upon electrochemically connecting macroscale Au/C and Pd/C electrodes in a single chamber. We then anticipate that the electron flow that occurs at the nanoscale in the thermocatalyst

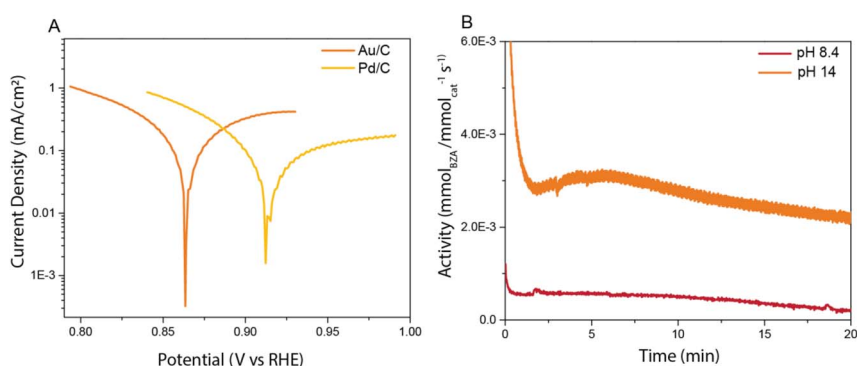


Fig. 5 (A) Tafel plots for Au/C and Pd/C electrodes at pH = 14. The reaction was performed at 60 °C with 1 bar O₂ at a pH of 14, set by the presence of 0.6 M NaOH in the aqueous phase. (B) Closed-circuit current measured between connected Au/C and Pd/C electrodes in a single chamber at a pH of 8.4 and a pH of 14 with 1 bar of O₂.

will occur at the macroscale through the connecting wire between the electrodes and, crucially, be measurable. Fig. 5B shows the current density, converted to an electrocatalytic activity, flowing between Au/C and Pd/C electrodes connected in solutions at pH of 8.4 and 14. Unscaled raw data is provided in Fig. S9. The higher rate at a pH of 14 is consistent with the increased thermocatalytic rate at the same pH for the physically mixed Au/C + Pd/C catalyst. The direction of current flow is such that the Au/C is anodic and performing alcohol oxidation, and Pd/C is cathodic and performing the ORR, as anticipated from Tafel analysis. This is again in agreement with the observation that the oxidative dehydrogenation selectivity trends in the thermocatalytic data for the Au/C + Pd/C catalyst follow that of the Au/C catalyst.

It is important to note that, even in the presence of CORE-enabled catalytic systems, not every catalytic step must necessarily occur *via* the CORE mechanism. Any disconnected or isolated catalyst may still be active towards thermal catalytic turnover of the substrate. We have previously utilized closed-circuit measurements and product analysis to calculate the fraction of total catalytic turnovers that occur from faradaic CORE electrocatalysis *versus* non-faradaic purely thermal catalytic steps. We demonstrated that $43.3 \pm 10.3\%$ of catalytic turnovers were due to the CORE mechanism for ODH of hydroxymethylfurfural.⁶

The spontaneous separation of the two half reactions in a single-chamber electrochemical cell points towards an opportunity to build upon current CORE observations and design efficient electrochemical cells for chemical production. A single-chamber system greatly simplifies the design and implementation of such a system. There are clear opportunities to improve the design of the electrodes to optimize performance beyond the relatively rudimentary electrode structures utilized in this and our previous studies. Furthermore, there are opportunities to expand beyond oxidative dehydrogenation reactions towards other catalytic mechanisms as the fundamental principles of the CORE mechanism are not unique to any given reaction. It is only necessary to provide an environment where the electrochemical circuits may be established, and the two catalysts have sufficient overlap in activity as demonstrated in Fig. 4.

Conclusions

CORE plays a key role in ODH catalysis of benzyl alcohol to benzaldehyde and benzoic acid utilizing Au/C and Pd/C catalysts. Spontaneous electrochemical polarization occurs when the two catalysts are physically mixed in solution due to the differing mixed potentials of the individual catalysts. Aggregation of the particles enables electrical contact between the two support materials to establish nanoscale electrochemical cells operating as closed circuits in solution. This leads to separation of the two ODH half reactions between the catalysts with the anodic Au/C performing substrate oxidation and the cathode Pd/C performing the ORR. The underlying CORE mechanism can be demonstrated through Tafel analysis. Closed circuit macroscale electrode experiments suggest a route towards CORE-enabled electrocatalytic e-chemical production.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data that support the findings of this study are included in the article and its supplementary information (SI) or from the corresponding authors upon request followed by standard practice of our schools. Supplementary information is available. See DOI: <https://doi.org/10.1039/d6fd00091f>.

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