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Letter

Galvanic Coupling Measurements Are a Predictive Tool for Cooperative Redox Enhancement (CORE) in Thermocatalytic Alcohol Oxidation

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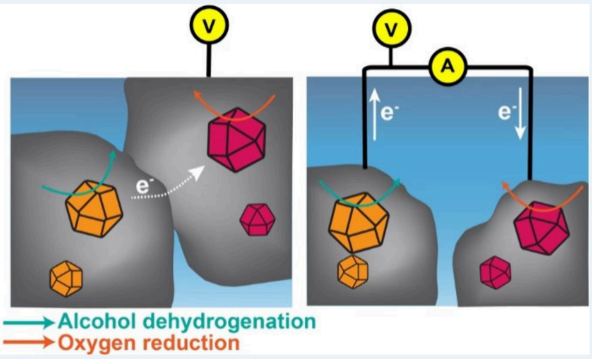
ABSTRACT: The Cooperative Redox Enhancement (CORE) mechanism, driven by electrochemical coupling between physically separated yet electrically connected catalytically active sites, underpins significant rate enhancements in liquid-phase thermocatalytic reactions. In this study, we use galvanic coupling measurements to accurately predict the magnitude of this rate enhancement in Au−Pd bimetallic systems using the conversion of 1,4-butanediol as a model system. This electrochemical method enables the determination of the optimal ratio of Au/C to Pd/C monometallic catalysts and serves as a predictive approach across a range of reaction conditions. These findings underscore the utility of electrochemical measurements to evaluate and optimize bimetallic thermocatalytic systems, advancing strategies for liquid-phase redox reaction design.



KEYWORDS: *Bimetallic Catalysis, Heterogeneous Catalysis, Mixed-Potential, Oxidative Dehydrogenation, Butanediol Oxidation*

INTRODUCTION

Multiple studies have recently demonstrated that an electrochemical mechanism underpins some liquid-phase reactions, which were previously only considered from a thermocatalytic viewpoint.[1−13] These insights provide new paradigms for understanding and designing the catalysts utilized in these types of reactions.[1−4,6,7] A primary example of this is the Cooperative Redox Enhancement (CORE) mechanism, which describes the operation of several reaction systems, including oxidative dehydrogenation (ODH) and hydrogenation.[1−7]

Detailed descriptions and derivation of the CORE mechanism have been published elsewhere.[2,3,5] Briefly, CORE occurs due to electrochemical coupling between disparate active catalytic sites. Due to differing reaction selectivity, distinct active sites catalyze the component half-reactions of a redox system; in the case of the ODH, these are dehydrogenation (DH) and the oxygen reduction reaction (ORR). When electrically connected via a conductive support and placed in an electrolytic solution, the catalysts operate akin to a nanoscale galvanic electrochemical cell. This mechanism is analogous to galvanic corrosion and other galvanic cells, such as fuel cells and batteries, where differences in half-reaction mixed potentials at physically separated active sites drive current flow.[14,15] In the CORE mechanism, the two half-reactions are the oxidation and reduction of chemical species present in the electrolyte solution, and the reaction sites are physically separated, with dissimilar catalysts on an electrically connected conductive support, yielding nanoscale galvanic cells that are constantly operating under effectively short-circuited conditions.

Herein, we show that this galvanic coupling between physically separated disparate catalysts can be demonstrated and evaluated by using short-circuit current measurements between macroscale electrodes of the same materials. Furthermore, we directly demonstrate that the driving force for this current flow is the difference in mixed potential between the catalysts and that the magnitude of this driving force correlates exceptionally well with the magnitude of the CORE phenomenon observed for the thermocatalytic rate. Finally, we determine the extent to which this electrocatalytic flow of current between particles impacts the overall observed conversion. Galvanic coupling measurements offer a facile and powerful tool to quickly determine the presence of CORE in bimetallic thermocatalytic systems and a straightforward route to further understanding the catalytic mechanism.

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■ RESULTS AND DISCUSSION

Quantitative Analysis of the ODH of 1,4-Butanediol by Mixed Potential and Tafel Analysis. The selective oxidation of 1,4-butanediol (BD) is used as a model reaction as, under mild conditions (i.e., <60 °C, <2 bar O_2), it can yield valuable reaction products such as succinic acid (SA), a versatile precursor for many industrial chemicals.[16] In this work, SA is the only quantifiable reaction product. Therefore, as the focus here is on the use of galvanic coupling as a predictive tool for thermocatalytic activity, only BD conversion is considered. The overall BD ODH reaction occurs through two coupled half-reactions; 1,4-butanediol oxidation reaction (BDOR) and ORR. Au/C (1 wt %) and Pd/C (1 wt %) are exclusively used as heterogeneous thermo- and electrocatalysts throughout both monometallic and physical mixture scenarios. In line with previous reports, these are synthesized via sol immobilization, resulting in particle size distributions of 2.4 ± 1.0 nm and 3.0 ± 1.1 nm, respectively (Figure S1).[1−3,5] Terminology definitions can be found in Table S1.

We recently reported on the application of Tafel analysis as an appropriate approach to link the electrocatalytic activity of individual catalysts to their thermocatalytic activity, as both experiments can be conducted under identical conditions.[3] By sweeping the potential as a function of oxidative or reductive currents, we can extrapolate the current densities from the regions of potential where the ORR (i) and BDOR (iii) dominantly occur (Figure 1a). Their intersection determines the mixed potential (E^{M}_{Tafel}), defined as the potential at minimum current density where the ORR and BDOR occur at equal rates (yellow star). The associated mixed current density (J^{M}_{Tafel}) is the expected exchange current density and represents the rate of the balanced electrochemical half-reactions, which accurately reflects the catalytic turnover rate in thermocatalytic reactions.[3,12,14,17]

Tafel slopes of Au/C and Pd/C were measured to determine their activity toward the BD ODH half-reactions in the presence of BD, gaseous oxygen, and an alkaline electrolyte (Figure 1b). While the mixed current density, J^{M}_{Tafel}, derived for the monometallic electrocatalysts accurately predicts their thermocatalytic activity, the current density as a function of polarization provided by Tafel analysis is critical in understanding the bimetallic case, where spontaneous polarization occurs. Comparing the monometallic catalytic performance at an overpotential of +150 mV from their respective rest potentials (where the BDOR dominates the current) shows that Au/C and Pd/C generate 63.5 A $mmol^{-1}$ and 1.4 A $mmol^{-1}$ of current, respectively, confirming the higher activity of Au/C for this half-reaction. For ORR, Au/C and Pd/C both show similar activities at the −150 mV overpotential.[18−20]

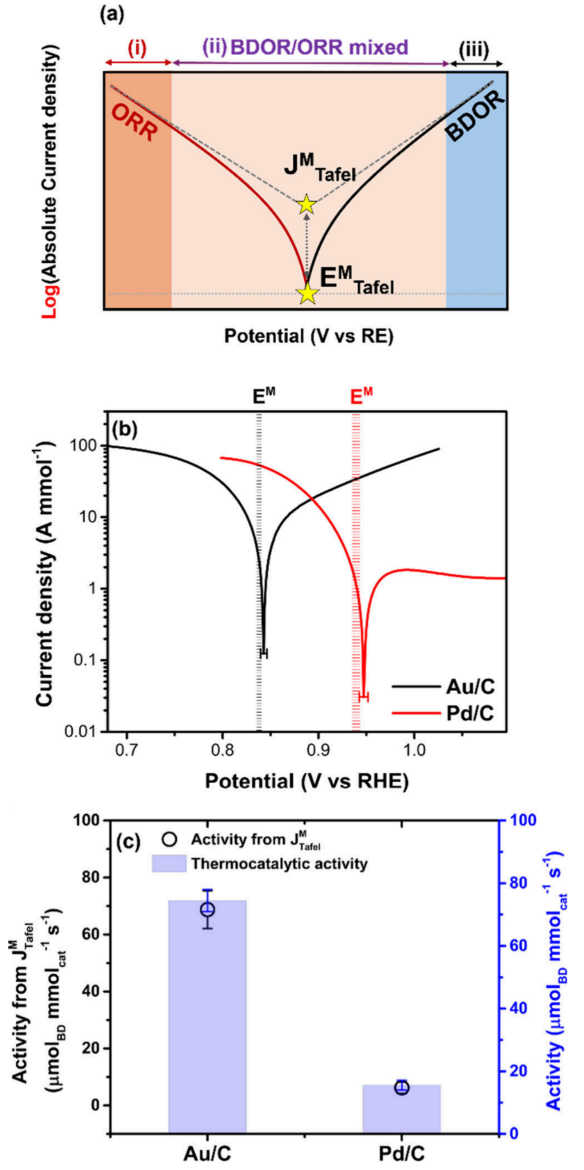

Figure 1. (a) Exemplary Tafel slope that explains how mixed current density (J^{M}_{Tafel}) and mixed potential (E^{M}_{Tafel}) are measured during the overall BD ODH reaction. (b) Tafel slopes of Au/C and Pd/C. The E^{M}s and sketched areas indicate E^{M} of Au/C (black) and Pd/C (red), determined by open-circuit potential, with their standard deviation. (c) Comparison of faradaic activity from J^{M}_{Tafel} of Au/C and Pd/C and thermocatalytic activity. Conditions for thermocatalytic reaction: 400:1 = substrate: total metal (mol/mol), 50 °C, 0.1 M NaOH, 0.1 M butanediol, 1 bar O_2, 2 h. Conditions for electrocatalytic reaction: mmol of Au (6.46×10^{-6}) and Pd (1.2×10^{-5}), 50 °C, 0.1 M NaOH, 0.1 M BD, 1 bar O_2, 1500 rpm. Error bars show the standard deviation from at least three repeat measurements. Rotating disk electrodes were employed to minimize diffusion limitations.

The mixed potentials (E^M) of the catalysts were determined by measuring their open-circuit potential (OCP) in the presence of oxygen and BD. The excellent agreement between the measured E^M (dashed line in Figure 1b) and E^{M}_{Tafel} values determined from the Tafel plots confirms that the Tafel analysis was conducted without diffusion limitations. Moreover, the mixed potential difference between Au/C and Pd/C indicates the possibility for active site polarization when utilized concurrently, which allows Au/C and Pd/C to offer even higher BDOR and ORR activity, improving the catalytic performance relative to the monometallic systems through CORE. Thermocatalytic ODH reactions of BD with Au/C and Pd/C were conducted under the same reaction conditions using powder catalysts. Figure 1c shows the excellent agreement in thermo- and electrocatalytic activities, clearly displaying the ability of Tafel analysis to predict thermocatalytic performance.

Quantifying CORE in Physically Mixed Bimetallic Thermocatalytic Systems Via Galvanic Coupling. When two catalysts are electronically connected, their E^M values polarize into a new median value termed the CORE potential, E^{CORE} (Table S1). This shift in potential leads to negative polarization of Pd/C, driving the ORR reaction on the more

Table 1. Comparison of Measured Electrode Potentials (E^M and E^{CORE}), Short-Circuit Potentials, BD Conversion (15 min), and Short-Circuit Current (10 min)[a]

Catalysts	E^{CORE} (V)	E^M (V)	Short-circuit potential (V)	Conversion (%)	Short-circuit current (μA)
Au/C	N.A.	0.836 ± 0.002	0.844 ± 0.006	11.2 ± 0.6	0.3 ± 0.6
(8:2) Au/C + Pd/C	0.839 ± 0.001	N.A.	0.856 ± 0.003	16.1 ± 1.2	26.2 ± 1.4
(6:4) Au/C + Pd/C	0.868 ± 0.002	N.A.	0.858 ± 0.005	18.5 ± 1.8	33.6 ± 6.1
(5:5) Au/C + Pd/C	0.872 ± 0.003	N.A.	0.865 ± 0.001	21.5 ± 1.0	42.2 ± 2.5
(4:6) Au/C + Pd/C	0.878 ± 0.002	N.A.	0.866 ± 0.003	17.9 ± 1.4	37.5 ± 6.9
(2:8) Au/C + Pd/C	0.888 ± 0.008	N.A.	0.886 ± 0.001	13.2 ± 3.2	23.8 ± 2.6
Pd/C	N.A.	0.938 ± 0.007	0.922 ± 0.006	2.3 ± 0.3	0.2 ± 0.3

[a] Definitions of these terms can be found in Table S1. The reaction conditions are equivalent to those given in Figure 1, with more detail found in the experimental section of the Supplementary Materials. N.A. indicates "Not Applicable".

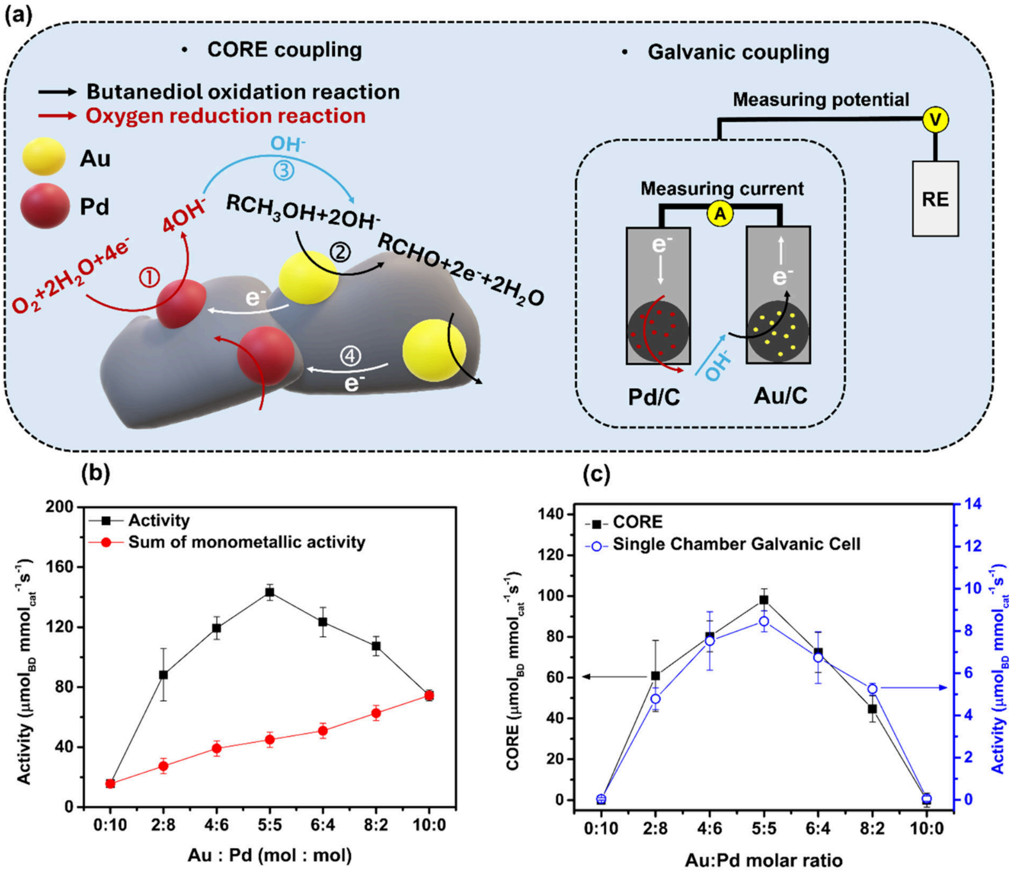

Figure 2. (a) Schematic illustrating the CORE mechanism and galvanic coupling, where the CORE mechanism is simulated by short-circuiting macroscale Au/C and Pd/C electrodes in a single-chambered electrochemical cell. The spontaneous current flow between the electrodes describes the magnitude of the CORE phenomenon. (b) Thermochemical conversion of BD; the expected sum of monometallic conversions of BD at that molar ratio of Au:Pd (red circles) and actual conversion observed (black squares), with the difference between the two (blue arrow) being the magnitude of the CORE phenomenon. SA was analyzed as the only quantifiable product in Figure S2. (c) Alignment between the magnitudes of CORE in thermochemical testing (black squares) and the short-circuit currents observed in electrochemical testing (blue circles). Thermochemical conditions: 50 °C, 0.1 M NaOH, 0.1 M BD, 1 bar O_2, 400:1 = substrate: metal (mol/mol), 15 min. Electrochemical conditions: Total mmol of metals (2.59×10^{-5} mmol), 50 °C, 0.1 M NaOH, 0.1 M BD, 1 bar O_2, 10 min. Error bars show the standard deviations from at least three repeated experiments.

active ORR catalyst, and positive polarization of the Au/C catalyst, driving the BDOR on the more active BDOR catalyst.[2] Thus, this polarization and separation of the half-reactions on different catalytic sites drives the overall reaction to occur at an accelerated rate and has been defined as the origin of CORE.[2] In this case, the mixed potentials of Au/C and Pd/C are 0.836 ± 0.002 V and 0.938 ± 0.007 V, respectively, and the CORE potential of an equimolar Au/C and Pd/C (Au/C + Pd/C, 5:5 molar ratio) is 0.872 ± 0.003 V, Table 1. Note that when the individual catalysts or a mixture of catalysts are placed on an electrode in the solution without an externally applied potential, they act as they would under thermocatalytic conditions.

While it is not possible to directly observe the CORE coupling that occurs on a nanoscale in our current setup, we can utilize two electrodes at the macro scale and operate under identical conditions to the thermocatalytic system (Figure 2a).[13] As in all such studies, we note that this approach

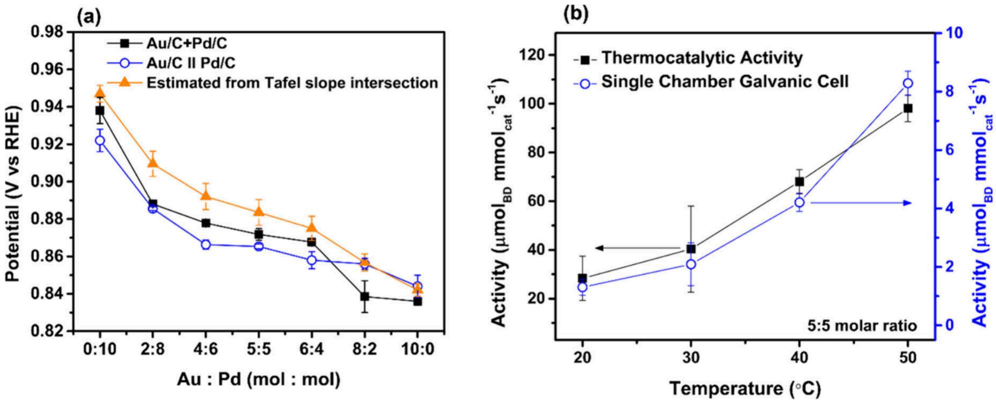

Figure 3. (a) Comparison between E^{CORE} from OCP measurements of physically mixed catalysts on a single electrode (Au/C + Pd/C), the short-circuit potential measured from the galvanic coupling with various molar ratios of Au:Pd (Au/C ‖ Pd/C) and, intersection potentials from Tafel slopes of Au/C and Pd/C with varying molar ratios. (b) Comparison of BD ODH activity from thermocatalytic reaction and short-circuit current with temperature variation when using 5:5 molar ratio of Au/C and Pd/C. Thermochemical conditions: 400:1 = substrate: metal (mol/mol), 0.1 M NaOH, 0.1 M BD, 1 bar O_2, 2 h. Electrochemical conditions: Total mmol of metals (2.59×10^{-5} mmol), 0.1 M NaOH, 0.1 M BD, 1 bar O_2. Error bars show the standard deviation from at least three repeat measurements.

prevents a direct 1:1 correspondence between thermocatalytic and electrocatalytic rates, even for the same weight loading of catalyst, as the manufacture of a macroscale electrode will lead to a number of buried catalytic interfaces and a possibility that mass transfer limitations can influence the observed rate. Additionally, the distance of the catalysts in the physical mixture can impact the magnitude of the CORE phenomenon, though controlling the distance remains challenging in our system.[1] Nevertheless, by using the same reaction conditions, the measured potentials in the electrochemical system are those present in the thermocatalytic reaction, often termed E_{CAT}.[21] While we cannot exactly match turnover per particle in the system, we can demonstrate a very strong correlation between electrocatalytic and thermocatalytic activity over a wide range of conditions that is repeatable over all prepared electrodes when determined both from direct measurements of substrate conversion and when derived by analysis of Tafel plots.

The spontaneous short-circuit current flowing between the electrodes is generated by the potential difference between the polarized catalysts in thermocatalytically active conditions. The magnitude of this current flow gives a direct indication of CORE coupling, while the direction of electron flow specifies the role of each catalyst. To confirm this hypothesis, galvanic coupling and corresponding thermocatalytic tests are performed using various molar ratios of Au and Pd (Figure 2b,c). In both thermocatalytic and electrocatalytic testing, the different molar ratios of Au:Pd were achieved by varying the mass of each 1 wt % catalyst used, keeping the total moles of metal constant.

When Au/C and Pd/C are physically mixed in the thermocatalytic reaction vessel, the observed activity far exceeds the expected activity from the sum of the monometallic conversion values (Figure 2b). This CORE effect is observed at multiple pH values, temperatures, and oxygen pressures (Figures S3, S4). The most active molar ratio (Au mol: Pd mol = 5:5) resulted in a conversion that was 3.2 times higher than the sum of the two monometallic conversions. This result aligns with previous studies into CORE using Au/C and Pd/C for the ODH of 5-hydroxymethylfurfural (HMF) and ethanol, where we observed a 5.35 times increase in ODH rate with an equivalent catalytic system.[3] No evidence of alloying was observed from postreaction X-ray photoelectron spectroscopy (Figure S5). This is further supported by postreaction TEM analysis from our previous study using equivalent catalysts and similar conditions (80 °C and 3 bar O_2).[2] No Au leaching (0%) and minimal leaching of Pd (<5%) were observed for all molar ratios of catalysts from inductively coupled plasma analysis (Table S2).

The differences between the expected sum of individual catalyst activity and the actual activity for each molar ratio of Au:Pd were calculated and plotted alongside the spontaneous short-circuit current measured under analogous electrochemical conditions. Figure 2c reveals exceptional alignment between the magnitude of increased thermochemical activity through CORE coupling and the short-circuit activity, calculated from observed short-circuit current across all analyzed molar ratios. Note that the observed current was confirmed to flow from Au sites to Pd sites, verifying the role of Au as the BDOR catalyst, generating electrons, and Pd as the ORR catalyst, consuming electrons (Figure 2a). The absence of current flow for monometallic catalysts (the 0:10 and 10:0 cases, where only Au or Pd was applied for both of the electrodes) correlates with the lack of observed thermocatalytic CORE in these cases, as one may anticipate, given that polarization requires differences in catalytic selectivity for the two-half reaction between catalysts within the same electrolytic solution. The measurement of E^{CORE} and the presence of spontaneous short-circuit current are thus strong descriptors for the presence and extent of thermochemical CORE.[2] These results demonstrate that the approach presented herein is a facile electrochemical technique that we envision to be a capable tool for designing heterogeneous catalytic systems.

There is excellent agreement between the operating potential of the two monometallic Au/C and Pd/C electrodes during the galvanic coupling experiments (Au/C II Pd/C, short-circuit potential) and the potential of a physically mixed Pd/C + Au/C catalyst on a single electrode (Au/C + Pd/C, E^{CORE}, Figure 3a). This further confirms that E^{CORE} of the bimetallic catalysts is determined by the polarization between the two separate catalytic metals. In addition to these direct measurements, we can perform an analysis of the Tafel plots analogous to that discussed in reference to Figure 1, but now using the independently measured BDOR Tafel curve for Au and the ORR Tafel curve for Pd, to predict the operating potential and current density for the mixed metal system. By weighting the current density for each half reaction based on the molar metal ratio, we derive potentials that match extremely well with those measured by other methods across the range of Au:Pd molar ratio (Figure 3a). As we have discussed above, directly matching current densities between various electrodes is challenging due to the electrode preparation process; the shape of the derived catalytic activity versus molar ratio trend derived from this analysis (Figure S6) again directly matches the thermocatalytic and short-circuit current measurements. We note that the relative plateau in activity with a molar ratio between 4:6 and 6:4 Au:Pd ratio is related to the relative plateau in potential in this range, with the absolute activity determined by the complex interplay between potential and activity for each catalyst and their relative positions and activities when coupled.

Further validation of the galvanic coupling was conducted with temperature variations using the optimal molar ratios of Au/C and Pd/C in Figure 3b. The BD conversion is decreased significantly when close to room temperature; however, thermochemical and short-circuit activities still exhibit excellent alignment for all temperatures.

To quantify the impact of CORE on the measured thermocatalytic rate, we can measure the total charge transferred between the electrodes over a period and utilize Faraday's law to calculate the number of electrocatalytic ODH reactions that have occurred. This can then be compared to the total number of thermocatalytic and electrocatalytic ODH reactions determined by product analysis of the solution after the reaction. Unfortunately, the full range of reaction products from the BD ODH reaction presents an analytical challenge that is further complicated by low reactant conversion at short times in the electrocatalytic system. However, by changing the reaction to the ODH of 5-hydroxymethylfurfural (HMF) and extending the duration of the galvanic coupling experiment, we can directly ascertain the fraction of the total observed catalytic turnover that is directly attributable to electron transfer between the Au and Pd particles. Note that both electrodes were placed in the same electrolyte solution rather than using an H-cell apparatus to more accurately reflect the thermocatalytic system. After 10 h of short-circuit operation and subsequent reaction product analysis, 43.3 ± 10.3% of ODH reactions of the initial HMF and subsequent reaction intermediates were accounted for as Faradaic current between the electrodes (Figure S7). The remaining ODH reactions are attributed to the turnover of both half reactions on the same electrode, either Au/C or Pd/C, yielding no net current between electrodes. While this value will vary across reactions and experimental systems, CORE clearly plays a major role in determining the activity of physically separated bimetallic catalytic systems.

CONCLUSION

Electrochemical analysis via galvanic coupling measurements is shown to be an accurate and facile screening method for determining the presence of CORE in a bimetallic catalytic system through the measurement of spontaneous electron flow between physically separated but electrically connected catalysts. Furthermore, this method can predict the optimal molar ratio of a bimetallic physical mixture for maximum activity enhancement, which occurs at the point of maximum current, and the extent to which this CORE mechanism contributes to the total catalytic turnover. This electrochemical technique provides further evidence that the electrochemically based CORE mechanism is operative during thermochemical ODH. Thus, galvanic coupling is a highly useful electrochemical tool for designing heterogeneous catalytic systems.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.5c04484.

Thermochemical, electrochemical, and catalyst analysis materials and methods. XPS spectra for used catalyst samples, thermochemical activity, and selectivity data. Electrochemical activity data. ICP-MS results of post-reaction samples. Supplementary references (PDF)

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Author Contributions

BK, JS, ITD, SP, RJL, GJH, and SM^2 conceived and conceptualized the project. BK, SM^1, and JS conducted experimental investigations. BK and JS performed the data analysis. ITD, SP, RJL, GJH, and SM provided project supervision. GJH and SM 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. SM^1: Sameul Miller, SM^2: Steven McIntosh.

Author Contributions

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Notes

The authors declare no competing financial interest.

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