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Time-dependent surface polarization breaks static scaling relationship for selective acetylene hydrogenation

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Abstract

Controlling the surface-adsorbates interactions is critical to advancing numerous chemical processes. Static scaling correlations between adsorption energies of chemically related surface species impose limits on selectivity in chemical processes, as exemplified by constraints in heterogeneous catalysis. Here, we demonstrate that dynamic surface polarization under oscillating electric potentials can overcome this limitation in Pd-catalyzed acetylene semi-hydrogenation. Unlike static polarization, which only imparts a minor improvement to ethylene selectivity, dynamic polarization drastically enhances selectivity without further sacrificing conversion, yielding a high ethylene productivity. Mechanistic insights from hydrogenation kinetics, in-situ DRIFTS, XAS, and DFT reveal that time-dependent polarization dynamically modulates the Pd's electronic structure and adsorption energetics. Alternating

between strong-binding states with positive polarization during acetylene hydrogenation and weak-binding states with negative polarization during ethylene formation effectively suppresses over-hydrogenation while maintaining semi-hydrogenation activity. This work establishes dynamic electric surface modulation as a powerful strategy for decoupling adsorption-energy correlations to improve heterogeneous catalysis and other adsorption-mediated processes.

Introduction

The chemical adsorption of atoms and molecules on solid surfaces underpins many physical chemical phenomena. Controlling the surface-adsorbates interactions is critical to advancing numerous chemical processes, including heterogenous catalysis[1], corrosion[2] and molecular separation[3]. A central challenge, particularly in catalysis, is achieving distinct adsorption energies for different species to control their individual reactivity[3]. However, on many materials, adsorption energies of chemically related species are often correlated due to shared properties and interactions with the same surface, as captured by linear scaling relationships[4]. While helpful for catalyst design, these correlations impose inherent limitations[5]. For instance, activity is typically bounded by the Sabatier principle, where optimal turnover occurs at moderate binding strength[6]. Likewise, selectivity, governed by the relative rates of competing pathways[7], is frequently compromised by coupled tuning of adsorption energies and activation barriers dictated by linear scaling and the Brønsted-Evans-Polanyi (BEP) principle. Consequently, lowering a desired step's barrier may hinder desorption or trigger further reactions, typically leading to a activity–selectivity trade-off[8].

To overcome the limitations from static scaling relationship, dynamic catalysis driven by external stimuli is emerging to modulate surface reactivity in real time[9]. Heterogeneous reactions generally involve adsorption, surface reaction, and desorption steps on different timescales. By synchronizing periodic changes in binding characteristics with these timescales, dynamic systems can surpass static performance limits. Along this line, oscillating electric potentials represent a promising tool, demonstrating the ability to enhance performances in electrocatalysis[10-13]. However, these promotions often stem from modulations in Faradaic charge transfer, local pH or ion transport, all tied to the liquid electrolyte environment[14]. In contrast, gas–solid thermocatalytic systems not only play a far more prominent role in current industrial processes but also offer a simpler platform for probing surface-specific effects of electric potentials. While non-Faradaic electrochemical modification of catalytic activity (NEMCA) or electrochemical promotion of catalysis (EPOC) under static potentials has been widely documented[15], dynamic potential effects in gas-solid systems remain largely unexplored. The few existing reports on gas-phase CO oxidation[16], ammonia synthesis[17] and ethylene hydrogenation[18] merely showed rate enhancements but lacked rigorous mechanistic insights. To date, experimental evidence for the utilization of dynamic stimuli to break conventional scaling relations limiting reaction selectivity has not yet emerged.

Acetylene semi-hydrogenation, a key ethylene purification step, illustrates the selectivity limits imposed by static scaling. The reaction involves two sequential steps: acetylene to ethylene (desired) and

ethylene to ethane (undesired). Pd-based catalysts, favored for their position near the volcano peak for acetylene hydrogenation[19], also promote ethylene over-hydrogenation due to similar binding characteristics. To address this, conventional strategies include catalyst modification through promoters[20,21], support interactions[21] or selective poisons[20] (**Figure 1 a**). Recent computational and machine-learning tools have expanded the catalyst design space[22,23]. Parallel to thermocatalytic approaches, electrocatalytic acetylene reduction has also emerged as a promising direction[24-26]. Nevertheless, the inherent kinetic overlap between the two hydrogenation steps, rooted in correlated adsorption energies, often persists. As a result, selectivity improvements frequently require trade-offs: reduced activity (e.g., site blocking, low H_2 pressure) or harsher conditions (e.g., elevated temperature/pressure). In contrast, time-dependent tuning of adsorption energetics provides a new paradigm to essentially break this static scaling relationship (**Figure 1 b**).

In this study, we explore whether time-dependent electric polarization can be used as a general strategy to overcome static constraints in thermocatalysis. Using Pd-catalyzed acetylene semi-hydrogenation as a model system with intrinsically coupled competing reaction pathways, we hypothesize that oscillating electric potentials can dynamically regulate surface states and energetics in a way that is inaccessible under static conditions. Specifically, we aim to determine whether this strategy can selectively favor acetylene hydrogenation while suppressing ethylene over-hydrogenation by decoupling adsorption scaling relationships at different stages of the reaction. By integrating kinetic measurements, in situ spectroscopy, and theoretical analysis, this work seeks to establish a mechanistic framework for dynamic polarization as a complementary strategy with material engineering to improve catalytic performance (**Figure 1 c** and **d**[27-38]).

Results and Discussion

Selectivity Promotion under Oscillating Potential

Hydrogenation tests were conducted in a two-electrode fuel-cell configuration under potentiostat control (**Figure 2 a**). After validation of the in-situ pseudo reversible hydrogen reference electrode (**Supplementary Figure 1**) and electrochemical characterization via cyclic voltammetry (**Supplementary Figure 2**), the influence of static potentials on reaction was first examined using a simulated front-end hydrogenation stream. Without applied potential, 10 mg 1% Pd on activated carbon (Pd/AC) catalyst exhibits 89.4% acetylene conversion, while the ethylene selectivity was only 35.1%, indicating over-hydrogenation dominated the reaction process. Such low selectivity at high conversion is common for Pd nanoparticle (NPs), such as Pd NPs/C[39] and Pd/MgO[40]. The carbon balance in all tests was around

99%, and the combined fraction (carbon basis) of non-C_2 species (mainly C_3 to C_6) accounted for less than 0.6% of the total carbon-containing species detected in the products (**Supplementary Table 2**). This indicates that side reactions such as oligomerization were negligible[41], likely suppressed by the high hydrogen partial pressure and low overall stream pressure[42]. Constant positive potentials enhanced selectivity but lowered conversion (**Figure 2 b**). For example, a 1.5 V potential increased selectivity by 12.6% but reduced conversion by 8.6%. In contrast, applying -0.5 V improved conversion by 2.2% but reduced selectivity by 4.7%. These trends reflect the expected scaling relationship: increasing the acetylene hydrogenation rate inevitably accelerates ethylene hydrogenation, and vice versa.

Square wave oscillating potentials, in contrast, significantly enhanced selectivity without further compromising conversion. To maximize the dynamic potential window while avoiding excessive electrochemical reactions, oscillation limits (-0.1 to 1.5 V) were selected based on electrochemical characterization (hydrogen evolution and oxidation current < 10 mA from **Supplementary Figure 2**; no hydrocarbon oxidation from **Supplementary Figure 3 to 6**). We employed a wide range of combinations of positive potential duration ($t_{1.5\ V}$) from 10^{-4} to 10 s and negative potential duration ($t_{-0.1\ V}$) from 10^{-3} to 10 s. Although high $t_{1.5\ V}$ ratios reduced conversion, selectivity improvements exceeded that under static 1.5 V conditions (**Figure 2 c** and **d**). Remarkably, a >45% increase in selectivity was achieved when $t_{1.5\ V}$ is approximately 1 to 10 s and $t_{-0.1\ V}$ ranges from 0.1 to 1 s. The highest 80.5% selectivity occurred with a 10 s 1.5 V + 0.1 s -0.1V oscillation, maintaining 81.0% conversion comparable to that under static 1.5 V (**Figure 2 c**) and with a <9% loss compared to the no-potential baseline. These results suggest two kinetically linked reactions, acetylene to ethylene and ethylene to ethane, respond differently to applied potentials. In particular, oscillating potentials appear to selectively slow the over-hydrogenation step while preserving acetylene conversion, enabling a decoupling of the reaction pathways and a substantial gain in selectivity.

Mechanistic Investigations

We conducted a series of mechanistic studies to better understand how electric polarization influences the reaction process. First, the role of electrochemical reactions (primarily hydrogen evolution and oxidation) was assessed. The current data recorded under varied conditions was used to calculate the maximum Faradaic ratios (FRs) under the assumption that all observed currents contribute to reaction variations, thereby representing the upper limit of Faradaic contributions.

$$Maximum\ Faradaic\ Ratio = \frac{Maximum\ reaction\ change\ by\ current}{Reaction\ change\ observed} \times 100\%$$

FRs remained below 10% in selectivity-enhancing conditions, including static positive potentials and oscillating potentials with dominant positive duration (4.7% at the optimal point). Such low Faradaic contributions are a hallmark of NEMCA-type non-Faradaic promotion[43], indicating that the observed selectivity improvements arise primarily from non-Faradaic effects (**Supplementary Figure 7**). Therefore, the promotion is non-Faradaic in nature and fundamentally differs from direct electrocatalytic acetylene reduction, where Faradaic electron transfer drives the hydrogenation chemistry[24-26].

To elucidate the effects of different polarization stages within each oscillation cycle, we conducted control experiments under the same conditions as **Figure 2** (**Figure 3 a**). Beginning from a repeating 1 s 0.25 V + 1 ms -0.25 V oscillation, we systematically increased the oscillation amplitudes while keeping durations fixed. The rate of acetylene hydrogenation remained largely unchanged, with only slight decreases at higher positive potentials. In contrast, ethylene hydrogenation declined apparently as the amplitude widened. Notably, lowering the negative potential was particularly effective in suppressing ethylene hydrogenation, underscoring the critical role of brief negative polarization pulses in enhancing selectivity during prolonged positive polarization periods.

Subsequently, we examined the hydrogenation of pure acetylene and pure ethylene under both static potentials (**Figure 3 b** and **c**) and oscillating potentials (**Supplementary Figure 8**) to investigate their individual kinetics. For both reactions, rates increased under negative potentials and decreased under positive potentials (**Figure 3 b** and **c**), confirming that static potentials can't decouple the two pathways. Consequently, ethylene selectivity in acetylene hydrogenation increased slightly under positive potential, but at the cost of reduced activity. Notably, oscillating potentials further enhanced selectivity (**Supplementary Figure 8**). Under the optimal condition (10 s 0.75 V + 1 ms -0.75 V), 70.8% selectivity was achieved, representing 23.9% improvement over the no-potential baseline while maintaining conversion similar to static 0.75 V (right side of **Figure 3 b**). These results align with those from the mixture hydrogenation tests, confirming that oscillating from a prolonged positive to a brief negative potential inhibits over-hydrogenation while preserving semi-hydrogenation.

Additionally, oscillating potential with a dominant negative duration led to extra rate accelerations compared to static negative potentials (left side of **Figure 3 b** and **c**). Though not the primary focus of

this study, these accelerations are discussed in **Supplementary Information** following **Supplementary Table 4** (key mechanism illustrated on the left half of **Figure 5 b**).

We further determined the reaction orders of the hydrocarbon and hydrogen in both hydrogenations. Without polarization, the reaction orders for acetylene and hydrogen were -0.15 and 0.9 in acetylene hydrogenation (**Figure 3 d**), consistent with literature[44] and suggesting a greater hydrogen dependence. Similarly, the original reaction orders for ethylene and hydrogen were approximately 0.2 and 0.9 (**Figure 3 e**), respectively, in agreement with typical values[45]. Negative polarization led to a gradual convergence of hydrocarbon and hydrogen orders, indicating a more balanced reactants availability. Positive polarization, in contrast, exacerbated disparities. Potential-induced reaction order variation has also been observed in ethylene oxidation on Pt[46]. Since both hydrogenation reactions in this study are believed to follow a Langmuir-Hinshelwood mechanism[47], these variations likely reflect shifts in reactants surface coverage under applied potentials.

To directly probe coverage, in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed on pure acetylene and ethylene using a custom-built cell (**Supplementary Figure 9**). In the acetylene adsorption spectra (**Figure 4 a**), six peaks were observed: the C═C vibration (1739 cm^{-1}) and C–H scissoring vibration (1376 cm^{-1}) for di-σ-adsorbed acetylene, the C–H wagging vibration (1716 cm^{-1}) and C═C vibration (1216 cm^{-1}) of vinylidene, and the C═C vibration (1646 cm^{-1}) and the C–H wagging vibration (1455 cm^{-1}) for vinyl groups[48]. For both di-σ-adsorbed acetylene and vinylidene, which are directly formed from adsorbed acetylene, their intensity increases under positive polarization, indicating enhanced acetylene adsorption. For ethylene spectra (**Figure 4 b**), peaks at 1585 cm^{-1} and 1654 cm^{-1} correspond to C═C vibrations in π-adsorbed ethylene and ethylidene[49]. Their intensities peaked at 0.75 V and decreased at lower potentials, consistent with reaction order trends. These potential-induced surface coverage changes explain conversion and selectivity trends under static potential tests: without applied potential, acetylene or ethylene coverage is much higher than hydrogen (as shown by reaction orders in **Figure 3 d** and **e**); negative potentials balance their coverage, accelerating reactions but reducing ethylene selectivity; positive potentials further enhance hydrocarbon adsorption over hydrogen, suppressing rates but boosting selectivity. Overall, these results demonstrate that applied potentials effectively tune the adsorption strength of chemisorbed intermediates and thereby modulate reaction pathways[50].

In-situ X-ray absorption spectroscopy (XAS) was conducted in a modified fuel cell (**Supplementary Figure 12**) to assess electric polarization effects on Pd catalysts. Difference X-ray absorption near-edge structure (XANES) spectra (spent catalyst vs. Pd foil) showed no Pd carbide formation after the reaction[51] **(Supplementary Figure 12)**. As potential increased, white line intensity rose (**Figure 4 c**), while extended X-ray absorption fine structure (EXAFS) regions remained unaffected (**Figure 4 d**). Linear combination fitting further revealed a gradual increase in Pd valence with potential (**Figure 4 e**), whereas EXAFS fitting confirmed stable Pd–Pd distance and coordination environment (**Figure 4 f**). Full fitting results are provided in **Supplementary Figure 13**. Transmission electron microscopy (TEM) also confirmed consistent Pd particle sizes (~3.4–3.8 nm) after reaction under various potentials (**Supplementary Figure 15**).

Based on the well-known Dewar−Chatt−Duncanson mechanism, the metal's electronic structure strongly governs the binding of unsaturated hydrocarbon, which happens primarily via π-orbital donation from the adsorbate into empty metal states, and to a lesser extent, d→ π* back-donation from the metal[52]. In our system, applied potentials modulate Pd's electronic structure through electrochemical polarization, introducing surface charge (**Figure 4 c** and **Supplementary Figure 14**) accompanied by interfacial electric fields (**Supplementary Figure 10**). Under positive polarization, electron-deficient Pd exhibits an enhanced capacity to accept π-electrons from acetylene and ethylene, offsetting the modest decrease in d→π* back-donation, leading overall to stronger hydrocarbon adsorption (**Supplementary Figure 14**). Conversely, negative polarization diminishes the relative contribution of π-donation from hydrocarbons (**Supplementary Figure 14**). These observations directly parallel the well-established dependence of catalytic behavior on work function, an intrinsic descriptor of a metal's electronic structure, which underpins the mechanisms of NEMCA/EPOC effects[53].

Grand canonical density functional theory (DFT) calculations, by control the work function of the system as a fined number[54], quantitively elucidates the impact of polarization on the reaction energy landscape. Under positive polarization, adsorption energies of both ethylene and acetylene increased on Pd(111), whereas hydrogen adsorption weakened slightly (**Figure 5 a**), aligning with experimental findings. Reaction Gibbs free energy profiles for acetylene hydrogenation to ethylene and then to ethane show that rate-determining steps in both reactions is the first hydrogen addition (**Figure 5 b**), consistent with prior reports[52]. Positive polarization simultaneously stabilizes all reaction intermediates (lower energy), while negative polarization simultaneously destabilizes them (**Figure 5 b**). These uniform shifts follow the scaling relationship and, according to the BEP principle, result in minor changes to energy barriers due to minimal enthalpy differences, namely the differences in binding

energy between intermediates. Thus, static potentials modestly affect activity and selectivity—mainly through surface coverage, not intrinsic barriers.

However, this static correlation can be overcome by periodically switching between two polarization states. As demonstrated in our previous reaction tests (**Figure 2** and **3**), brief negative polarization periods have a distinct effect on selectivity enhancement, which can be attributed to dynamic modulation of binding energies. First, the brief negative polarization stage effectively reduced ethylene's binding energy, facilitating its desorption. In the meanwhile, the change of surface state significantly slows the reaction. During prolonged positive polarization, most of the intermediates remain in a relatively low-energy state. Such rapid switch to negative polarization then dramatically raises the energy barrier that these ground-state intermediates must overcome for the next hydrogenation step (illustrated in the right half of **Figure 5 b**). If this switch occurs precisely when acetylene is converted to ethylene, further hydrogenation of ethylene can be effectively suppressed without disrupting the earlier steps. This dual effects prevent over-hydrogenation to ethane. Upon the subsequent positive polarization, newly adsorbed acetylene occupies the vacant sites left by desorbed ethylene and undergoes hydrogenation, ensuring continuous and selective catalysis. Moreover, increasing the oscillation amplitude further raises the over-hydrogenation barrier, resulting in a more pronounced suppression of ethylene hydrogenation (**Figure 3 a)**. Notably, decreasing the negative potential is more effective than increasing the positive potential, as it simultaneously enhances ethylene desorption, leading to an asymmetric decreasing trend observed in **Figure 3 a**.

To ensure the effectiveness of this mechanism, oscillation timing must align with the kinetics of each reaction step. The positive duration should match the semi-hydrogenation timescale. Given the turnover frequency (TOF) of Pd-based catalysts for this reaction (0.32 to 0.70 s^{-1} between 298 to 328 K; **Supplementary Table 5**), each semi-hydrogenation cycle takes around 1-3 s, which remains largely unchanged under positive polarization due to minimal energy barrier changes. As a result, the observed optimal positive duration in both acetylene-ethylene mixture hydrogenation and pure acetylene hydrogenation is around 1-10 s, despite differences in positive potentials applied (1.5 V and 0.75 V). In contrast, negative polarization duration is governed by ethylene desorption, namely surface residence time, which can be theoretically estimated according to adsorption energies through the Frenkel equation[55]

$$\tau = \frac{1}{v}\exp\left(\frac{-\Delta H_{ads}}{k_B T}\right)$$

where v is the attempt frequency (10^{13} s^{-1} for both acetylene[56] and ethylene[57]), ΔH_{ads} is the adsorption energy and k_B is Boltzmann constant. Under vacuum, ethylene desorbs in ~10000 s at +0.75 V, ~5 s at -0.1 V and ~0.02 s at -0.75 V, while acetylene desorption is negligible under any potentials (~10^{23} s at +0.75 V and ~10^{18} s at -0.75 V). Under realistic hydrogenation conditions, the adsorption energy of ethylene is significantly reduced due to two main effects: (1) bonding competition, steric repulsion[58] and downshift of d-band center[59] under higher surface coverage and (2) competitive adsorption with the more strongly binding acetylene[60]. For example, if the adsorption energy decreases by ~0.05 eV, the corresponding desorption time is shortened by about one order of magnitude. This aligns with experimental observations: in acetylene–ethylene mixture hydrogenation at –0.1 V, the optimal negative potential duration is ~0.1 s, whereas in pure acetylene hydrogenation at –0.75 V, a high-selectivity regime appears at a much shorter negative potentials duration of ~1 ms.

The influence of applied potential on acetylene and ethylene desorption kinetics was further validated using time-resolved in-situ DRIFTS (the signal variation is confirmed to only result from desorption according to **Supplementary Figure 11**). Pd foil was adopted instead of Pd/AC to eliminate interference from physisorption in the porous carbon support. Although Pd foil is significantly harder to polarize due to its larger size, it qualitatively reflects the same trends as Pd nanoparticles. IR spectra of adsorbed acetylene on Pd foil exhibited four characteristic adsorption peaks similar to Pd/AC, including the C═C vibration (1739 cm^{-1}) and C–H stretching (1376 cm^{-1}) in di-σ-adsorbed acetylene, the C═C vibration (1716 cm^{-1}) and C–H stretching (1216 cm^{-1}) in the vinylidene group[48] (**Supplementary Figure 9**). In contrast, ethylene displayed only weak peaks in the 2800 to 3000 cm^{-1} range, corresponding to the –CH_2 stretching of di-σ-adsorbed ethylene[49].

Time-resolved DRIFTS by introducing acetylene on Pd foil with preadsorbed hydrogen atoms offers insights into the surface residence times of intermediates under different conditions. Under +1.5 V (**Figure 6 a**), di-σ-adsorbed acetylene and vinylidene peaks were already weak at the beginning of scan, while strong signals at 1484 cm^{-1}, 1118 cm^{-1}, and in the 2800-3000 cm^{-1} region emerged, indicating the hydrogenation of di-σ-adsorbed acetylene and vinylidene into vinyl and ethylidyne, and their subsequent conversion into di-σ-adsorbed ethylene. These peaks remained unchanged in 1120 s, indicating sustained adsorption. At -0.75 V (**Figure 6 b)**, similar intermediates formed initially, but di-σ-adsorbed ethylene peaks decayed rapidly within 300 s, while vinyl and ethylidyne signals persisted. This indicates negative polarization significantly shortens ethylene residence time while preserving strong adsorption of acetylene-derived species. Under -0.75 V in 0.25% acetylene atmosphere (**Figure 6 c**), spectra were obtained by subtracting the blank 0.25% acetylene background from raw spectra

(**Supplementary Figure 9**). Except for the vinyl, ethylidyne and di-σ-adsorbed ethylene, the di-σ-adsorbed acetylene peaks reappeared due to newly introduced gas-phase acetylene. The di-σ-adsorbed ethylene signals disappeared in around 40 s, 10 times faster than in the absence of acetylene, supporting our theoretical prediction that acetylene accelerates ethylene desorption under realistic conditions. Furthermore, acetylene adsorption spectra were recorded under oscillating potentials consisting of 400 s at 1.5 V and 400 s at –0.75 V on a clean Pd foil in a 0.25% acetylene atmosphere (**Figure 6 d**). Under 1.5 V, the intensities of the di-σ–adsorbed acetylene, vinyl and vinylidene species remained stable. Upon switching to –0.75 V, all signals gradually decreased, consistent with weakened adsorption. In contrast, re-adsorption upon returning to 1.5 V was rapid, reaching equilibrium within a single collection period (14 s). During three oscillation cycles, the spectra clearly displayed a reversible "breathing" pattern of adsorption and desorption.

Based on these insights, we propose a selectivity enhancement mechanism under oscillating polarization (**Figure 6 e**). During positive polarization, limited surface hydrogen reacts preferentially with adsorbed acetylene to produce ethylene. However, due to the scaling relationship and BEP principle, ethylene remains strongly adsorbed and readily undergoes further hydrogenation if the positive potential is maintained. Introducing a brief negative pulse raises the energy barrier for over-hydrogenation and weakens ethylene binding, promoting its desorption rather than further hydrogenation. Importantly, to maximize the selective suppression effect while minimizing the slowdown of acetylene hydrogenation, the surface state transition must be synchronized with reaction and desorption kinetics.

In preliminary tests, this oscillating polarization approach has been successfully extended to other transition metals including Pt and Rh (**Supplementary Figure 16** to **17**). Also, similar mechanisms may be generalized to other multistep reactions, such as methane oxidation to methanol (minimizing CO_2)[61] or CO_2 hydrogenation to alcohol (preventing methane)[62]. Oscillatory switching between strong- and weak-binding states raises the barrier for over-conversion while enabling selective desorption of intermediates. Beyond catalysis, temporal control of adsorption energetics could benefit gas separation, storage, and sensing: facilitating low-energy gas release without heating or depressurization steps, faster sensor recovery, and stepwise adsorption/desorption in complex mixtures for selective separation and controlled delivery.

Conclusion

Using selective acetylene hydrogenation on Pd as a model system, in this study we demonstrated that dynamic surface polarization enables precise, time-resolved control over binding energies within the

catalytic cycle. This decouples the static scaling relationship of chemically related species, allowing independent tuning of specific steps in complex pathways. Leveraging this strategy, we achieved one of the best performances in acetylene semi-hydrogenation using a simple Pd/C catalyst. Given its ability to break static adsorption correlations, this approach offers broad potential to enhance reaction selectivity not only in catalytic systems but also in adsorption-driven applications such as gas separation and chemical sensing.

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Author Contribution Statement

N.Y conceived and supervised the project. D. X. conducted the experiment and wrote the paper. C.C. helped to build the in-situ DRIFTS cell and conduct NMR analysis. D.X., M.J.H., C.W.L. and N.Y. analyzed the data. Z.L. helped to build the fuel-cell reactor. H.C. and G.S. performed the DFT calculations. N.Y., P.S. and M.J.H. revised the paper.

Competing Interests Statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Figure Legends/Captions

Figure 1. **Selective acetylene hydrogenation on Pd-based catalyst.** (a) Approaches for improving selectivity. (b) Time-dependent surface polarization to break static scaling relationship. (c) Activity-selectivity comparison and (d) productivity-temperature comparison with reported high-selectivity Pd-based nanoparticle (detailed references available in **Supplementary Table 1**).

Figure 2. **Selective acetylene hydrogenation in excess ethylene stream under electric potential.** (a) Fuel cell setup for reaction testing. (b) Acetylene conversion and ethylene selectivity under static potential. (c) Acetylene conversion and (d) ethylene selectivity under oscillating potential (10 mg 1% Pd/AC, Nafion 117 PEM, 298.15 K, 1 atm, 0.5 mL/min acetylene, 10 mL/min ethylene, 30 mL/min hydrogen and 9.5 mL/min nitrogen, conversion and selectivity definition are provided in **Methods** section). The “zig-zag” features in (c) and (d)

stem from the discrete, logarithmic sampling of oscillation time ($t_{-0.1\ V}$ and $t_{1.5\ V}$), which creates stepwise boundaries in the contour plots between regions dominated by negative or positive duration.

Figure 3. **Investigation of acetylene and ethylene hydrogenation variation under applied potential.** (a) Rate decrease ratios for acetylene-to-ethylene and ethylene-to-ethane in acetylene-ethylene mixture hydrogenation under oscillating potentials with varying positive (+*E*) and negative (-*E*) potential values (same test conditions as **Figure 2**). (b) Acetylene conversion and ethylene selectivity, as well as (d) reaction orders for pure acetylene hydrogenation. (c) Ethylene conversion and (e) reaction orders for pure ethylene hydrogenation (10 mg and 1mg 5% Pd/AC for acetylene and ethylene hydrogenation, respectively, Nafion 117 PEM, 298.15 K, 1 atm, 10 mL/min hydrogen and 10 mL/min hydrocarbon).

Figure 4. **In-situ spectroscopy analysis under different potentials.** IR spectra of (a) adsorbed acetylene and (b) adsorbed ethylene on Pd/AC catalysts. (c) XANES spectra, (d) k^2-weighted FT-EXAFS spectra, (e) linear combination fitting results and (f) EXAFS fitting results of Pd/AC catalysts.

Figure 5. **Influence of electric polarization to energy landscape.** (a) Adsorption energies of hydrogen, acetylene and ethylene under different potentials. (b) Gibbs free energy profile for acetylene hydrogenation to ethane on Pd(111) under +0.75 V and -0.75 V.

Figure 6. **Desorption kinetics investigation by time-resolved in-situ DRIFTS on Pd foil and proposed mechanism.** Variation of intermediates' adsorption peaks under different conditions (testing procedure illustrated in **Supplementary Figure 9 b**): (a) +1.5 V on Pd foil with H_{ads}, (b) -0.75 V on Pd foil with H_{ads}, (c) -0.75 V on Pd foil with H_{ads} in 0.25% acetylene atmosphere and (d) oscillating potentials consisting of 400 s at 1.5 V and 400 s at –0.75 V on clean Pd foil in 0.25% acetylene atmosphere. (e) Proposed mechanism for selectivity enhancement using oscillating electric polarizations.

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Methods

Electrode fabrication and membrane pretreatment.

The major catalyst used in this work is commercial 1% and 5% Pd on activated carbon (Pd/AC) purchased from Sigma-Aldrich. To adapt the catalysts for use in a fuel cell, an electrode was fabricated following a method from Liu[63]. In a typical procedure, the catalyst powder was homogenously dispersed in absolute ethanol (Vwr AnalaR NORMAPUR®, 99.8%) and subjected to sonication for 2 h. Subsequently, the resulting ink mixture was carefully drop-coated onto carbon paper with a gas diffusion layer (AvCarbGDS3250, BALLARD), then dried in a 90℃ oven.

Nafion 117 proton exchange membrane (PEM), as solid electrolytes in the PEM fuel cell, were pretreated to enhance conductivity before their use. The pretreatment involved sequential boiling in H_2O_2 (2 h), deionized water (2 h) and 0.5 M H_2SO_4 at 90 ℃ (1 h). Before cold pressing with electrodes into a membrane-electrode assembly (MEA), the membrane was wiped carefully to remove all the attached liquid, which would ensure a gas-phase environment during reaction testing.

Hydrogenation reaction tests.

The hydrogenation reactions were performed in a commercial fuel cell reactor (FUEL CELL TECHNOLOGIES, INC), composed of end plates, current collectors, graphite plates with a single serpentine flow channel, gaskets with a 5 cm^2 reacting area in the core, gas diffusion electrodes (GDE) coated with catalysts, and a PEM from outside to inside, as illustrated in **Figure 2 a**. The fuel cell is connected to the electrochemical working station (Gamry Reference 3000 Potentiostat) for various electrochemical tests.

All the reactions were conducted at ambient temperature and pressure. The substrate gases, ethylene (Air Liquide, 99.9%) or acetylene (Air Liquide, 99.8%), were mixed with hydrogen (Air Liquide, 99.9995%), while nitrogen (Air Liquide, 99.9995%) serving as an inert gas to control partial pressures. The reactant stream was introduced into the chamber on the right side of the cell, where reactions occurred on the working electrode. Meanwhile, the left side of the cell functioned as both counter electrode and reference electrode, which was established by flowing 1 atm of pure hydrogen over the Pd electrode interfaced with Nafion 117 saturated by 0.5 M H_2SO_4 ($[H^+]$=1 M). Under these conditions, the left electrode can be regarded as a reversible hydrogen electrode (RHE) considering the negligible overpotential for hydrogen oxidation on Pd, which is a commonly used method to construct in-situ pseudo-reference electrode in fuel cell[64,65]. The quasi-equilibrium RHE was validated to work stably

under all tested conditions as shown in **Supplementary Figure 1**. Cyclic voltammetry (CV) under different atmospheres (**Supplementary Figure 2**) indicated that the major electrochemical processes were hydrogen evolution reaction (HER) under negative potentials and hydrogen oxidation reaction (HOR) under positive potentials.

Consequently, various potentials can be applied to the working electrode according to this quasi-equilibrium reference electrode and the influence of applied potentials on both selectivity and conversion was explored while maintaining low HER and HOR rates (within potential ranges where current<10mA). Product mixtures under different potential conditions were analyzed using a gas chromatography (GC8890, Agilent) equipped with a flame ionization detector (FID) and GS-Al/KCl column to determine conversion (representing reaction rate) and selectivity. Catalyst loading was adjusted based on the specific objectives of each hydrogenation test. For the hydrogenation of an acetylene/ethylene mixture, 1% Pd/AC was used to prioritize high selectivity. In contrast, for pure acetylene hydrogenation, a higher loading (10 mg of 5% Pd/AC) was applied to compensate for the sluggish reaction kinetics under low hydrogen partial pressures, while remaining within the geometric constraints of the 5 cm^2 electrode. For pure ethylene hydrogenation, a lower loading (1 mg of 5% Pd/AC) was selected to match the Pd loading used in the acetylene hydrogenation test for trend comparison and to maintain low conversion levels, thus avoiding external mass transfer limitations.

For hydrogenation reaction, the conversion is conventionally defined as

$$Conversion = \frac{c_{feed} - c_{effluent}}{c_{feed}} \times 100\%$$

where c_{feed} and $c_{effluent}$ represent substrate concentrations in the feed and effluent. In the selective hydrogenation of acetylene, which can yield ethylene and ethane, the selectivity for ethylene is defined as

$$Selectivity = \frac{C_2H_{2\,feed} - C_2H_{2\,effluent}}{C_2H_{2\,feed} - C_2H_{2\,effluent} + C_2H_{6\,effluent} - C_2H_{6\,feed}} \times 100\%$$

Before applying polarizations, the catalyst was stabilized under reaction conditions for 8 h. For the static polarization test, a constant potential remaining unchanged over time was applied, while a square wave potential oscillating between low potential (-*E*) and high potential (+*E*) with certain duration t_{low} and t_{high} is imposed in the oscillating polarization test, which can be realized via configuring the corresponding parameters in the electrochemical working station:

$$Frequency(Hz) = \frac{1}{t_{low} + t_{high}} \times 100\%$$

630 $$Duty\ cycle = \frac{t_{high}}{t_{low}+t_{high}} \times 100\%$$

631

632 In-situ DRFITS.

633 In-situ DRIFTS was conducted in a dedicated in-situ chamber utilizing Thermo Scientific Nicolet™
634 iS50 FTIR Spectrometer. The chamber (**Supplementary Figure 5**) was modified from a Praying Man-
635 tis™ commercial reaction chamber consisting of a shell, a cylindrical hollow sample holder and a
636 dome with one glass observation window and two infrared transparent windows. During the test, the
637 MEA was positioned on the holder, with the tightly pressed membrane effectively segregating the two
638 chambers below and above the sample holder. The working electrode faced upward, while the refer-
639 ence/counter electrode faced downward, both connected to the electrochemical working station via
640 thin aluminum foil. Substrate gases, ethylene or acetylene, were introduced into the upper chamber
641 while hydrogen flows through the lower chamber, just like the fuel-cell reactor. A 6-mm-diameter
642 hole was drilled through Al foil and carbon paper on the working electrode to allow the IR beam to
643 directly interact with Pd/AC catalyst layer.

644

645 During DRIFTS testing on Pd/AC, the background spectrum was first collected by flowing 40 mL/min
646 argon through the upper chamber and 20 mL/min hydrogen through the lower chamber for 60 mins.
647 Then the argon was replaced with 40 mL/min substrate gas for 5 mins to enable sufficient adsorption,
648 during which various potentials were applied. Finally, 40 mL/min Argon was reintroduced to purge
649 the gas-phase substrate, after which the spectrum of adsorbed species was acquired. Each spectrum
650 was obtained with 64 scans at a resolution of 4 cm^{-1}.

651

652 During the time-resolved DRFITS on Pd foil, the Pd foil was first pretreated in 20 mL/min hydrogen
653 in the in-situ cell for 30 min to saturate its surface with adsorbed hydrogen atoms. Subsequently, 20
654 mL/min acetylene was introduced for approximately 5 minutes to form hydrogenation intermediates,
655 followed by argon purging. IR spectra were recorded under different conditions every 14 seconds (20
656 scans) once the gas-phase acetylene peak disappeared.

657

658 In-situ XAS.

659 The fuel cell setup was modified in order to ensure reliable XAS signals (**Supplementary Figure 6**).
660 Modifications included perforating the end plates and current collectors with a 3 cm × 3 cm hole to
661 allow X-ray transmission. Additionally, a 1-cm-diameter hole was drilled into the counter electrode to

prevent X-ray absorption by Pd in the counter electrode. The graphite plate and PEM were left unaltered due to their low X-ray absorption properties. To meet the minimum sample loading density required for transmission mode XAS, each electrode was coated with 40 mg of 10% Pd/C, and five electrodes were stacked together during testing, achieving a 5 mg/cm^2 Pd density.

Due to restrictions on the use of pure ethylene and acetylene at the SPring-8 facility, catalyst stabilization was conducted in-house by exposing the catalyst to reaction conditions for 8 h. Subsequently, the stabilized catalyst inside the reactor was hermetically sealed in an argon-filled bag to preserve their integrity during transportation to SPring-8. During the XAS testing, hydrogen flow was introduced and various electric potentials were applied to capture XAS data under different polarizations.

DFT calculations.

All density functional theory (DFT) calculations were performed using the Vienna Ab Initio Simulation Package (VASP, version 6.3)[66]. The exchange-correlation functional was treated within the generalized gradient approximation (GGA) framework, using the Perdew-Burke-Ernzerhof (PBE) formulation[67,68]. The effective potential of nuclei and core electrons were described by the projector augmented wave (PAW) method, while valence electrons were expanded in a plane-wave basis set with an energy cutoff of 400 eV[69]. The calculations utilized a Pd(111) slab model constructed with a 3×3 periodic supercell and four atomic layers. To mimic the bulk environment, the bottom two layers were fixed during the simulations. A 4×4×1 Gamma-centered k-point mesh was adopted for Brillouin zone sampling, and the total electronic energies were converged to a tolerance of 10^{-5} eV per unit cell[70]. A vacuum layer of 15 Å was introduced perpendicular to the slab model to eliminate interactions between periodic images. Transition states were identified using a combination of the climbing image nudged elastic band (CI-NEB) method and the DIMER approach[71,72]. Geometry optimizations were carried out using the BFGS algorithm, as implemented in the Atomic Simulation Environment (ASE) package until the forces on all atoms were below 0.03 eV/Angstrom[73,74].

Furthermore, grand canonical density functional theory (GC-DFT) calculations were conducted using the VASPsol++ package, incorporating an implicit water model to account for solvation effects[75,76]. The key aspects of this GC-DFT approach include: (a) The number of electrons in the system is dynamically adjusted during self-consistent field (SCF) iterations to achieve the target Fermi energy (ε_F), and the Fermi energy of the electrode (Pd slab) ε_F is defined relative to the energy level of the bulk electrolyte, and (b) finally the applied electrode potential U_{SHE} is related to the Fermi energies of the considered system and standard hydrogen electrode through:

$$U_{SHE} = \frac{\varepsilon_F - \varepsilon_F^{SHE}}{e}$$

In our calculations, the fermi energy of the standard hydrogen electrode is chosen as $\varepsilon_F^{SHE} = -4.57\ eV$, following the recommendation in the software manual.

Data availability

All data supporting the findings of this study are available within the paper and its Supplementary Information files. Source data are provided with this paper.

Methods-only reference

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Supplementary information reference

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