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Effectively Regulating Electrooxidation of Formic Acid over Bimetallic PtCo Alloys via the Integration of Theory and Experiment

Zhikeng Zheng, Bin Liu, Jiaxiang Qiu, Shaojun Xu, Yuchen Wang, Man Zhang, Ke Li, Zhongti Sun, Ziang Li, Yangyang Wan,* C. Richard A. Catlow,* and Kai Yan*

1. INTRODUCTION

Due to its exceptional qualities including high fuel safety, elevated theoretical open circuit potentials (1.48 V), substantial energy density (1740 W h kg^{-1}) and reduced

crossover flux through the Nafion membrane ($2.03 \times 10^{-8} \text{ mol}$

$\text{cm}^{-2} \text{ s}^{-1}$), direct formic acid fuel cells (DFAFCs) have emerged as a critical component in renewable energy.¹⁻⁶ At present, Pt catalysts continue to stand out as one of the most effective electrocatalysts for formic acid oxidation (FAO), playing a crucial role in the advancement of efficient and stable DFAFCs.^{7,8} The FAO process on Pt electrocatalysts is widely recognized to follow two distinct reaction pathways: the direct

pathway ($\text{HCOOH} \rightarrow \text{CO} + 2\text{H}^+ + 2\text{e}^-$) and the indirect

pathway ($\text{HCOOH} \xrightarrow{2} \text{CO}^* + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$).⁹⁻¹¹

In the indirect pathway, formic acid generates adsorbed CO intermediates through dehydration, necessitating further oxidation of these adsorbed CO species into CO_2 at a higher potential ($\sim 0.8 \text{ V}$ vs RHE).¹² These CO intermediates attach strongly to Pt sites at a lower potential ($\sim 0.4 \text{ V}$ vs RHE),

of CO_2 through the dehydrogenation step, bypassing the formation of CO intermediates. Despite their expense and susceptibility to catalyst poisoning, Pt catalysts remain essential due to their elevated catalytic activity and distinctive electronic

structure.¹⁵⁻¹⁷ As a result, researchers are actively exploring diverse strategies to develop Pt-based electrocatalysts that offer

high activity, durability, and cost-effectiveness for FAO.^{18,19}

The dehydration pathway requires neighboring Pt sites to proceed, and it motivates efforts to prevent excessive Pt site aggregation as an effective approach to enhance FAO performance and counteract CO intermediate formation.^{20,21} This end is often achieved through the incorporation of other

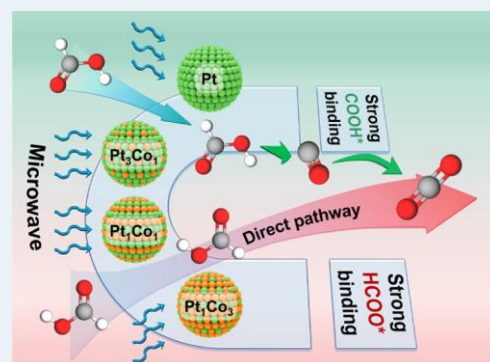
elements to create bimetallic or trimetallic catalysts.^{22,23} With

the support of various advanced catalyst synthesis strategies available today, it is feasible to construct Pt-based alloys with

leading to a reduction in active sites where Pt is functional and a notable suppression of FAO activity at lower potentials.^{13,14} In contrast, the direct pathway involves the direct production

ABSTRACT: Challenges in directly regulating the reaction pathways in the electrooxidation of formic acid have hindered widespread applications in direct formic acid fuel cells (DFAFCs). Hence, we report directly tuning the reaction pathway of formic acid oxidation (FAO) to avoid CO poisoning over the bimetallic PtCo alloys. The PtCo alloys are fabricated by using a facile one-step microwave method, avoiding the use of organic solvents and minimizing environmental pollution. The Pt₁Co₁ alloy displays a specific surface area of 17.58 m² g⁻¹ and exhibits a 121-fold increase in mass activity (1.18 A mg_{Pt}⁻¹) compared to its counterpart Pt (<0.01 A mg_{Pt}⁻¹). It also far outperforms Pt₃Co₁ (0.09 A mg_{Pt}⁻¹) and Pt₁Co₃ (0.95 A mg_{Pt}⁻¹) alloys. *In situ* attenuated total reflection infrared spectra further confirm that the bimetallic PtCo alloys catalyzed FAO through the direct pathway to CO₂ formation, suggesting that adding Co plays a crucial role in enhancing Pt's resistance to CO poisoning. Density functional theory calculations further indicate that the incorporation of Co into the Pt coordination environment is crucial for altering the formation of transition intermediates, which can form a more stable bond with the HCOO intermediate, which is formed by breaking the O-H bond. Specifically, on the Pt₁Co₁ alloy with 50% Co incorporation, the free energy for HCOO* formation is significantly lower (-0.296 eV) compared to that of COOH* (0.028 eV). This trend is reversed when compared with pure Pt (0.196 eV for HCOO* and -0.190 eV for COOH*), thereby promoting FAO via a direct pathway. This work provides a reference for the rational development of high-efficiency Pt-based alloy electrocatalysts.

KEYWORDS: formic acid oxidation, alloy, electrocatalysis, reaction pathway, density functional theory



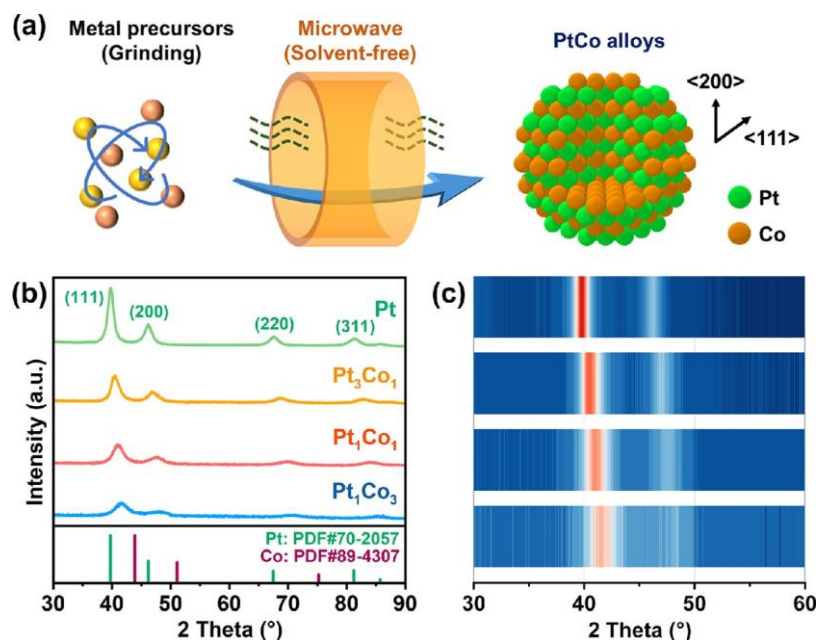


Figure 1. Materials synthesis and phase identification. (a) Synthesis of bimetallic PtCo alloys through the microwave strategy. (b) XRD patterns of Pt and PtCo alloys with different molar ratios. (c) Enlarged XRD patterns in the range of 30° to 60°.

stable structural and energetic characteristics, such as filling vacancies resulting from the removal of certain Pt atoms with Ni or Co atoms, which minimally disrupt the original Pt crystal structure.²⁴ Previous studies on FAO systems have demonstrated that the introduction of guest metals (e.g., Sn, Bi, Cu) into Pt-based alloys can optimize the Gibbs free energy change of the FAO process, promoting the selectivity of the direct pathway by favoring the initial dehydrogenation of HCOOH through O–H bond cleavage to form HCOO*.^{25,26} Therefore, to achieve stable adsorption of HCOO* species, Co, with its strong binding affinity to oxygen species, emerges as a potential target element to enhance the performance of Pt-based alloys.²⁷ In addition, incorporating Co into the Pt lattice will basically not destroy the stability of the original crystal structure, facilitating research into the regulatory effects of PtCo alloys on reaction pathways. Moreover, the introduction of Co, which is cost-effective and readily available, reduces the usage of precious metals, benefiting subsequent in-depth studies.²⁸ Thus, constructing a research system including PtCo alloys promises an accurate and efficient investigation of the regulation of the formic acid oxidation reaction pathways by bimetallic Pt-based catalysts.

In this context, we have successfully synthesized PtCo alloys with adjustable proportions using a one-step microwave synthesis method, thereby enabling the efficient tuning of the direct FAO pathway. X-ray diffractometry (XRD), X-ray photoelectron spectroscopy (XPS), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and X-ray absorption fine structure (XAFS) confirmed the successful fabrication of bimetallic PtCo alloys with varying element ratios. Electrochemical investigations employing cyclic voltammetry (CV), linear sweep voltammetry (LSV), and chronoamperometry (CA) demonstrated the superior activity of Pt₁Co₁ alloy (with a 1:1 ratio) over that of Pt, and the catalyst's performance exhibited a volcanic trend. Furthermore, from the perspective of gas products and reaction intermediates, gas chromatography and *in situ* attenuated total reflection infrared spectroscopy (ATR-IR)

provided compelling evidence that the direct pathway facilitated FAO on the Pt₁Co₁ alloy. Density functional theory (DFT) calculations were then employed to simulate the free energy diagram of PtCo alloys with varying element ratios for FAO. The results indicated that the introduction of Co atoms into the Pt lattice directly alters the free energy of HCOO* and COOH* intermediates in the FAO process. The FAO performance exhibited a volcanic plot behavior with increasing Co content, confirming that the Pt₁Co₁ alloy possessed the optimal FAO activity. To the best of our knowledge, this has not been reported previously. This work provided valuable insights into the rational design of electrocatalysts and the effective regulation of FAO.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization. A series of PtCo alloys with varying ratios was systematically synthesized. An overview of the facile one-step microwave synthesis method employed for PtCo alloys fabrication is provided in Figure 1a. This technique offered the distinctive advantage of circumventing the need for organic solvents and eliminating secondary contamination. The synthesis process involved the initial grinding and subsequent transfer of platinum(II) acetylacetonate (Pt(acac)₂) and cobalt(II) acetylacetonate (Co(acac)₂) precursors with varying molar proportions to a microwave reactor. Through controlled microwave energy input, the precursors underwent decomposition and fusion, resulting in the creation of bimetallic PtCo alloys. Confirmation of the Pt and Co proportions in each sample was achieved via inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis, attesting to the precision of the synthesis method and its potential for diverse alloy synthesis (Figure S1). The structural assessment of the obtained PtCo alloys was conducted using XRD. The XRD patterns of the PtCo alloys are shown in Figure 1b. The diffraction peaks were situated between the characteristic peaks of standard Pt (No. 70-2057) and Co (No. 89-4307), signifying the successful integration of Co into the Pt face-

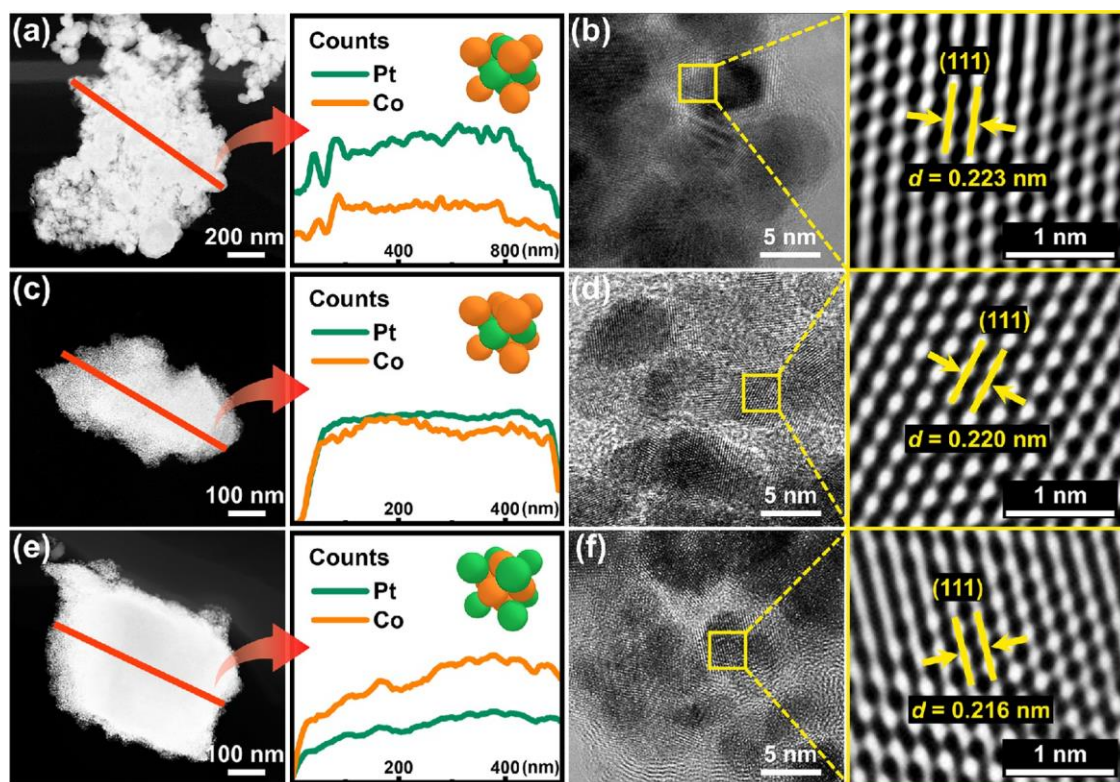


Figure 2. Morphology and microstructure characterization. (a) HAADF-STEM image and corresponding line scanning profiles and (b) HRTEM image and corresponding lattice view of Pt₃Co₁ alloy, along with (c) and (d) for Pt₁Co₁ alloy and (e) and (f) for Pt₁Co₃ alloy.

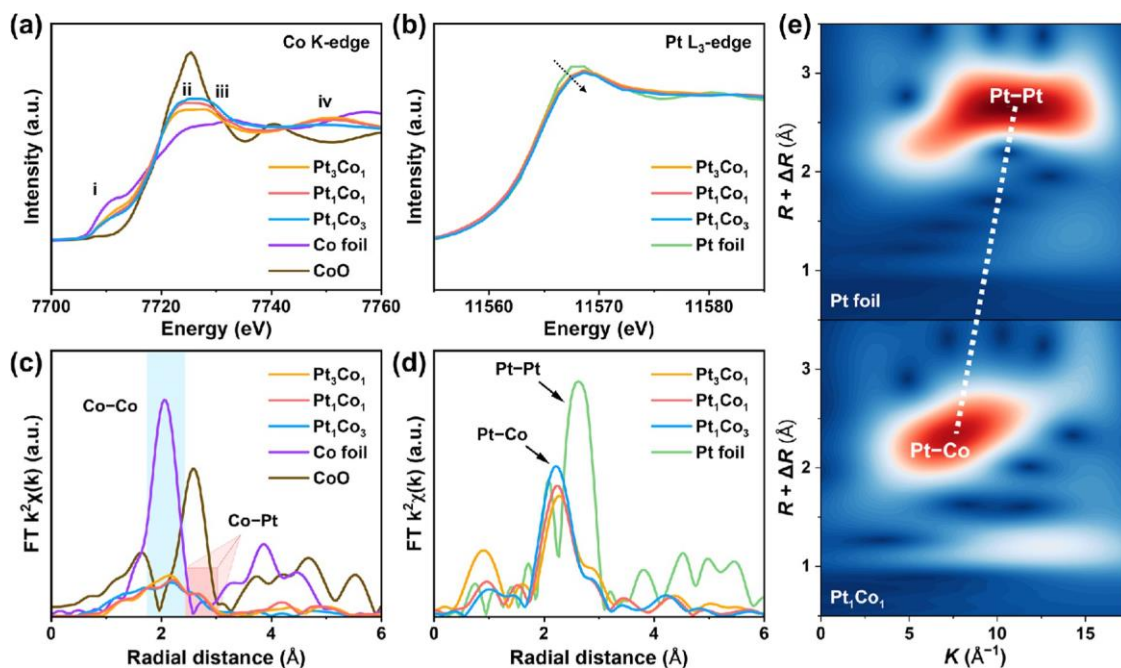


Figure 3. XAFS characterization results. XANES spectra of the normalized (a) Co K-edge and (b) Pt L₃-edge. (c) Fourier transforms of the k^2 -weighted Co K-edge of the extended X-ray absorption fine structure (EXAFS) spectra of PtCo alloys, Co foil, and CoO. (d) Fourier transforms of the Pt L₃-edge of the EXAFS spectra of PtCo alloys and Pt foil. (e) WT EXAFS plots of the Pt₁Co₁ alloy and Pt foil.

centered cubic (FCC) lattice. This observation confirmed the effective synthesis of PtCo alloys.^{29,30} Notably, as the Co content gradually increased, deviations in peak positions and reduced peak intensities were evident. These findings indicated a decreased crystallinity and a reduction in particle size.

Particularly, by evaluating the (111) plane peak position from the magnified XRD patterns (Figure 1c), the interplanar spacing d value of the (111) plane for Pt, Pt₃Co₁, Pt₁Co₁, and Pt₁Co₃ alloys were determined as 0.226, 0.223, 0.220, and 0.216 nm, respectively. The elemental chemical states of the

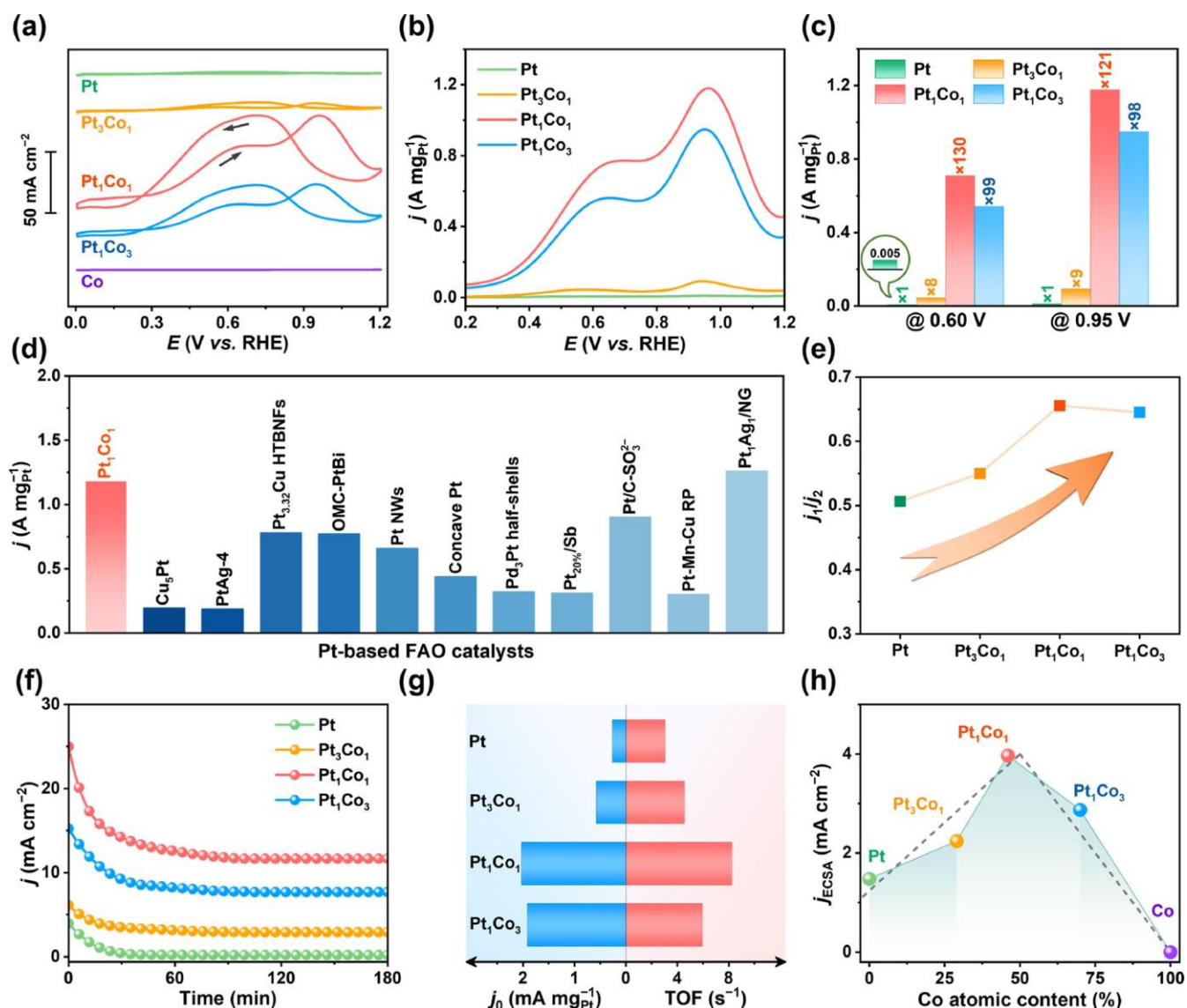


Figure 4. Electrocatalytic performance for FAO. (a) CV tests of FAO on Pt, Pt₃Co₁, Pt₁Co₁, Pt₁Co₃ and Co in Ar-saturated 0.5 M H₂SO₄ + 0.5 M formic acid at a scanning rate of 50 mV s⁻¹. (b) Pt mass-normalized curves of LSV toward FAO of catalysts with different Pt/Co proportions. (c) Pt mass-normalized activity of catalysts calculated at 0.60 and 0.95 V vs RHE. (d) Comparison of mass activity for Pt₁Co₁ alloy with those reported FAO catalysts. (e) Ratio of the current densities of the j₁ and j₂ peaks during the forward scan obtained from (a). (f) CA curves evaluated at 0.60 V vs RHE for 180 min. (g) Diagram comparison of the exchange electrical current density (j₀) and the turnover frequency (TOF). (h) Volcanic trend of FAO activities plotted as a function of the Co atomic content.

catalysts were then characterized by using XPS. Figure S2 shows the high-resolution XPS spectra of the Pt 4f for Pt₁Co₁ alloy and Pt, and Co 2p for Pt₁Co₁ alloy. Clearly, the peak areas corresponding to the zerovalent states of Pt and Co were significantly larger, indicating that both elements predominantly existed in the metallic state (Pt⁰ and Co⁰). This observation was consistent with the alloy phase identified by XRD. Compared to the binding energy of Pt⁰ 4f_{7/2} in pure Pt (71.36 eV), the binding energy of Pt⁰ 4f_{7/2} in the Pt₁Co₁ alloy (71.15 eV) shifted to a lower value by 0.21 eV, indicating significant electronic interactions between Pt and Co due to the formation of the PtCo alloy structure, which resulted in changes in the electronic configuration.

Subsequently, the morphological and microstructural characteristics of the PtCo alloys were scrutinized through HAADF-STEM and high-resolution TEM (HRTEM). In Figure 2a,c,e, images of three PtCo alloys with distinct

proportions reveal irregular bulk morphologies possessing particle sizes of approximately 1 μm. Select positions (indicated by red lines) were chosen for Pt and Co line intensity distribution analysis. For instance, in the case of Pt₃Co₁ (Figure 2a), the positions of Pt's valleys and peaks closely aligned with those of Co, exhibiting nearly identical trends in their variations. The metal contents were found to be highly consistent with the feed ratio, corroborating the results obtained from ICP-OES analysis and effectively showcasing the composition of the Pt₃Co₁ alloy. Similar confirmations were also observed for Pt₁Co₁ and Pt₁Co₃ alloys. Moreover, EDS images (Figure S3a,c) showcased uniform distributions of both Pt and Co elements across PtCo alloys with differing metal ratios. The microstructural insight into PtCo alloys was further gleaned from HRTEM and selected area electron diffraction (SAED) images. From Figure 2b,d,f, the *d* value of the (111) plane decreased (0.223, 0.220, and 0.216 nm) with

ascending Co content, corroborating the XRD findings. Notably, the brighter diffraction rings in Figure S3d–f corresponded to the crystal planes of (111) and (200), aligned with the two highest-intensity characteristic peaks in the XRD pattern. These observations collectively validated the successful synthesis of PtCo alloys with distinct ratios using the one-step microwave technique.

To further understand the structure and coordination information on PtCo alloys, XAFS tests were conducted. The Co K-edge X-ray absorption near edge structure (XANES) spectra of PtCo alloys with different proportions and Co-based species as references are shown in Figure 3a. Three different PtCo alloys displayed the absorption edge position and white line peak intensity between those of standard Co foil and CoO, especially the white line peak positions were closer to that of Co foil. Specifically, the formation of alloy structure can be identified from four different features, denoted as i, ii, iii and iv.^{31,32} Compared with the Co foil, features iii and iv exhibited lower energy shifts, attributed to the expansion of unit cell parameters, indicating the participation of Co in a bimetallic phase, alloying with Pt possessing a larger atomic radius. Moreover, features i and ii corresponded to the transitions from 1s orbital to 3d, 4s, and 4p hybridized orbitals. Consequently, the observed decrease in feature i and increase in feature ii indicated a reorganization in hybridization, a process heavily influenced by the presence of

alloying. XANES spectra of PtCo alloys at the Pt L₃-edge are presented in Figure 3b, alongside the Pt foil for comparison.

Notably, the white lines of the catalysts displayed a rightward shift compared to the Pt foil, indicating that the Pt species no longer existed as separate Pt metal but some alloy species. Additionally, the slightly decreased white line intensity suggested that the average electron density of the Pt atoms in PtCo alloys was higher than that in Pt foil. Therefore, it can be inferred that Pt bonds with Co, which is relatively less electronegative. Combined with the fact shown in Figure 3a that the white line intensity of the bimetallic catalysts at Co K-edge was slightly higher than that of Co foil, which indicates an electron deficiency, it is evident that Pt has been alloyed with Co and a significant electron transfer occurred.

The bonding of Pt and Co atoms in alloy samples can be more directly demonstrated by extended X-ray absorption fine structure (EXAFS) spectroscopy. The corresponding *R*-space curve of the Fourier-transformed *k*²-weighted Co K-edge EXAFS spectrum of three experimental samples in Figure 3c provided strong evidence for alloying between Co and Pt that Co–Co coordination was presented with peaks at 2.1 Å and shoulder peaks attributed to the Co–Pt path were detected at a longer radial distance of 2.7 Å.^{33,34} In addition, the Pt L₃-edge EXAFS spectrum of PtCo alloys (Figure 3d) revealed a lower peak position (Pt–Co at 2.3 Å) shifting to a shorter radial distance by ~0.3 Å compared with that in Pt foil (Pt–Pt at 2.6 Å), which was related to the formation of a bimetallic bond. To investigate the coordination conditions of Pt centers, wavelet transform (WT) analysis providing radial distance and *K*-space resolution was performed. As shown in Figure 3e (Pt₁Co₁ alloy as an example), the maximum intensity position of Pt₁Co₁ alloy (7.4 Å⁻¹) was significantly different from that caused by the Pt–Pt coordination in Pt foil (10.8 Å⁻¹), which corresponded directly to the Pt–Co coordination in Pt₁Co₁ alloy, since the value in *K*-space is positively correlated with the weight of the atomic pair.³⁵ Similarly, the Co WT contour plot

agreement with the EXAFS spectrum. The valence state of the Co atom was close to 0, and the peak intensity distribution showed a tendency to extend to the larger *K* value (~10.5 Å⁻¹), corresponding to the Co–Pt coordination. Based on the above XAFS analysis results, it was concluded that Pt–Co direct coordination was formed in the prepared PtCo samples of different proportions, which further proved the typical alloy structure.

2.2. Electrochemical Evaluation for FAO. A preliminary assessment of the FAO activities across a series of PtCo alloys with varying ratios, along with pure Pt and Co, was conducted through CV measurements in an Ar-saturated 0.5 M H₂SO₄ solution containing 0.5 M formic acid (Figures 4a and S5a). The catalytic activities were notably influenced by the introduction of Co. Unlike the PtCo alloys and Pt, no FAO activity was observed on Co, underscoring the indispensability of Pt for the FAO process in this system (Figure S5b). Calculation of the Coulombic charge encompassing hydrogen desorption and adsorption regions (Figure S6) enabled determination of the electrochemical active surface area (ECSA). Specifically, the Pt₁Co₁ alloy exhibited an ECSA of 17.58 m² g⁻¹, surpassing Pt (0.62 m² g⁻¹), Pt₃Co₁ (2.74 m² g⁻¹), and Pt₁Co₃ (13.64 m² g⁻¹), which indicated that the Pt₁Co₁ alloy possessed a greater number of reactive sites. In the mass-normalized LSV curves (Figure 4b,c), it was observed

that the Pt₁Co₁ alloy exhibited a mass activity of 1.18 A mg⁻¹_{Pt} at 0.95 V vs reversible hydrogen electrode (RHE), representing a 121-fold increase compared to Pt (<0.01 A mg⁻¹). This of the Pt₁Co₁ alloy (Figure S4) also displayed a high

trend was also evident at lower potentials (0.60 V vs RHE), indicating that the introduction of Co indeed enhanced FAO activity. This modification not only significantly improved the catalytic performance but also effectively reduced the usage of the precious metal. Noteworthy, the FAO activity of Pt₁Co₃ alloy exhibited a slight decline in contrast to Pt₁Co₁ alloy, indicating that an excess of Co content instead led to a decrease in catalytic performance. Importantly, the Pt₁Co₁ alloy, which possessed FAO performance matching the current mainstream research, was synthesized using a one-step microwave method (Figure 4d).^{6,36-45} Compared with the complex methods reported for synthesizing various Pt-based catalysts suitable for FAO, the facile one-step microwave method avoided the use of organic solvents, minimizing environmental pollution.

As mentioned previously, FAO commonly followed two oxidation pathways, closely tied to characteristic features in the CV curve (Figure S7, taking Pt₁Co₁ alloy as an example).^{38,46,47} The current densities corresponding to the shoulder (j_1) and top (j_2) peaks during the forward scan and the reverse peak (j_3) are tabulated in Table S1. The direct pathway involved the cleavage of C-H and O-H bonds, leading to the direct oxidation of formic acid to CO₂, whose process occurred efficiently throughout the forward scan stage (0.5–1.0 V vs RHE), contributing to j_1 and j_2 . The indirect pathway involved the dehydration step stemming from the breaking of C-O and C-H bonds, which also contributed to j_1 and j_2 . More specifically, the formation of adsorbed CO* intermediates in the indirect pathway occurred at a lower potential (0.5–0.7 V vs RHE), and these intermediates were further oxidized to CO₂ at higher potentials (0.9–1.0 V vs RHE) by hydroxyl groups formed on the catalyst surface, only corresponding to j_2 . Therefore, the ratio of j_1 to j_2 can indirectly reflect the contribution rate of the indirect pathway in the FAO process. In Figure 4e, an increase in turn in the $j_1/$

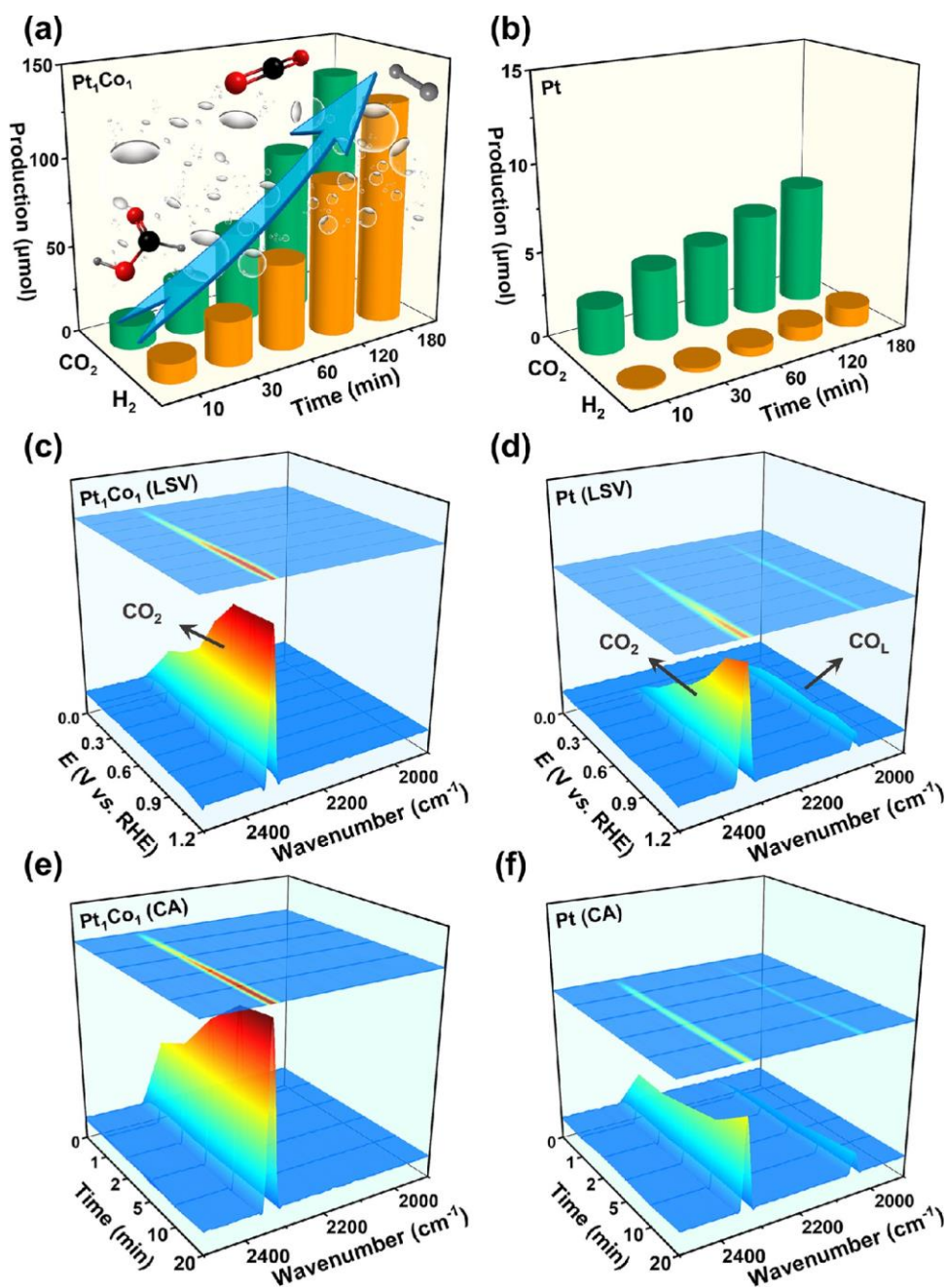


Figure 5. Reaction pathway studies. Production of H_2 and CO_2 during FAO at 0.60 V vs RHE on (a) Pt_1Co_1 alloy and (b) Pt measured by gas chromatography. Potential-resolved *in situ* ATR-IR spectra for FAO on the (c) Pt_1Co_1 alloy and (d) Pt. Time-resolved *in situ* ATR-IR spectra for FAO on (e) Pt_1Co_1 alloy and (f) Pt during the CA test at 0.60 V vs RHE.

j_2 ratio for Pt (0.51), Pt_3Co_1 (0.55), and Pt_1Co_1 (0.66) was illustrated, indicating that with the gradual introduction of Co, the indirect pathway gradually lost its dominance, suggesting the progressive shift toward the direct pathway. However, the j_1/j_2 ratio of Pt_1Co_3 (0.65), demonstrating minimal change in comparison to Pt_1Co_1 , indicated that introducing Co in a 1:1 ratio can enhance FAO through the direct pathway. Since the tightly adsorbed CO^* on the catalyst surface was oxidized at high potentials, releasing the active sites, j_3 was mainly influenced by the direct pathway process. Therefore, the j_1/j_3 ratio denoted resistance to CO^* poisoning at low potentials. A substantial rise in the j_1/j_3 ratio for Pt (0.31), Pt_3Co_1 (0.49), and Pt_1Co_1 (0.65) suggested that the FAO process on Pt_1Co_1 alloy faced less inhibition from CO^* , enabling continued

utilization of surface-active sites (Table S1). The j_1/j_3 ratio of Pt_1Co_3 (0.65) did not significantly increase, indicating that the resistance to CO^* poisoning for both Pt_1Co_1 and Pt_1Co_3 was essentially similar, implying that introducing more Co no longer contributed to an increased resistance to CO^* poisoning. CO -stripping was further employed to forcefully evaluate the anti- CO properties of the PtCo alloys (Figure S8). Compared with Pt, the oxidation peak potential of Pt_3Co_1 , Pt_1Co_1 , and Pt_1Co_3 alloys with preadsorbed CO had a negative shift of about 12, 40, and 40 mV, respectively, which implied a better CO -resistance of Pt_1Co_1 and Pt_1Co_3 alloys during FAO, indicating excellent durability. Durability measured by the CA technique was evaluated at 0.60 V vs RHE (Figure 4f). The Pt_1Co_1 alloy exhibited a current density significantly higher

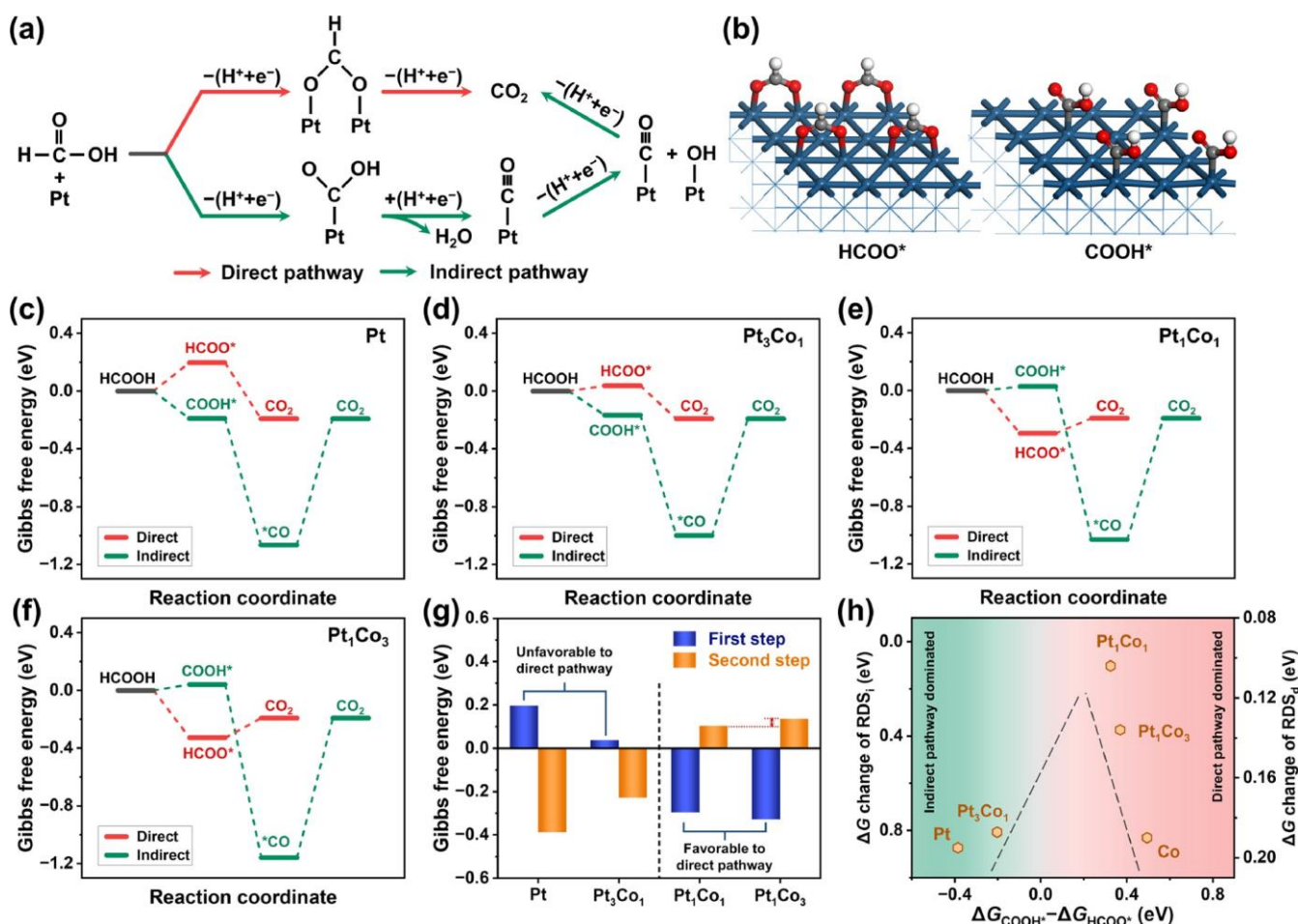


Figure 6. Calculation results for constructing the theoretical structure. (a) Schematic diagram of electrochemical FAO via direct (red line) and indirect pathways (green line) on Pt(111) surface. (b) Most stable adsorption structures of HCOO* (HCOO*) and COOH* (COOH*) on Pt(111) surface. Blue, red, gray, and white balls represent Pt, O, C, and H atoms, respectively. Gibbs free energy diagrams of the direct and indirect pathways on the surfaces of (c) Pt, (d) Pt₃Co₁, (e) Pt₁Co₁, and (f) Pt₁Co₃, respectively. (g) Magnitudes of Gibbs free energy of the two sequential dehydrogenation steps during the direct pathway on Pt(111) surfaces of Pt, Pt₃Co₁, Pt₁Co₁, and Pt₁Co₃, respectively. (h) Trend of Gibbs free energy change values for the rate-determining step (RDS) in indirect and direct pathways. The vertical axis represents the change values that need to be overcome in the RDS. ($\Delta G_{\text{COOH}^*} - \Delta G_{\text{HCOO}^*}$) indicates the energy difference between adsorbed COOH* and HCOO*. Positive (negative) values indicate the preferential stabilization of HCOO* (COOH*).

than that of other materials throughout the process and achieved a very stable value after 100 min, further revealing its

potential for high long-term stability toward FAO. Moreover, Pt₃Co₁ and Pt₁Co₃ alloys also showed a relatively stable current density after 60 min, indicating that Co introduction in alloy structures effectively promoted durable FAO. To further demonstrate the long-term stability and durability advantages of the optimal Pt₁Co₁ alloy under continuous operation, we performed 5 CA cycle tests and extended the constant potential reaction time (Figure S9). The results showed that in each 2 h cycle, the current density stabilized within the first 30 min. In the 10 h long-term test, the current density consistently remained around 17 mA cm⁻², further proving the stability and durability of the alloy structure.

Tafel slopes derived from LSV are depicted in Figure S10. All four catalysts maintained a strong linearity within the lower potential range. Notably, the slope values of the Pt₁Co₁ and Pt₁Co₃ alloys (277 and 278 mV dec⁻¹, respectively) were significantly lower than those of the other two samples, associated with their higher activity resulting from better resistance to poisoning. Furthermore, the Pt₁Co₁ alloy

demonstrated a mass-normalized exchange electrical current density (j_0) of 2.03 mA mg_{Pt}⁻¹ (blue bar chart in Figure 4g),

approximately 8 times more pronounced than that of Pt (0.26 mA mg_{Pt}⁻¹). The turnover frequency (TOF), a crucial parameter for electrocatalytic efficiency, revealed that Pt₁Co₁ alloy outperformed the other samples with a TOF value of 8.26 s⁻¹ (red bar chart in Figure 4g), signifying superior FAO performance.⁴⁸ The specific activity for each catalyst, determined through ECSA, was presented in Figure 4h. Notably, the ECSA-normalized FAO activity of Pt₁Co₁ stood at 3.97 mA cm⁻² at 0.95 V vs RHE, surpassing Pt (1.48 mA cm⁻²). Moreover, a conspicuous volcano trend in experimental FAO activity was evident with an increase in Co content.

2.3. Electrocatalytic FAO Pathway Discussion. In order to elucidate the reaction pathway of the FAO process on the Pt₁Co₁ alloy, gas products of FAO were analyzed using gas chromatography during the CA process illustrated in Figure 4f (characteristic product peaks shown in Figure S11). In the direct pathway, a formic acid molecule was stripped of two protons and two electrons near the working electrode, resulting in the conversion of formic acid to CO₂ which then evolved

from the acidic solution, while the protons in solution and the electrons transferred through the external circuit combine near the counter-electrode to evolve as H₂. Therefore, at lower potentials, the equimolar production of H₂ and CO₂ indicated dominance of the direct pathway, realizing the direct conversion of formic acid to CO₂ in the contribution of Faraday current, accompanied by the generation of H₂.^{49–51} As depicted in Figure 5a, after substituting the test results of gas samples into the standard curve (Figure S12), the calculated gas production of H₂ and CO₂ at 0.60 V vs RHE on Pt₁Co₁ alloy remained almost equal over reaction time of 10, 30, 60, 120, and 180 min, respectively. For instance, after 10 min, the yields of H₂ and CO₂ were 11.21 and 13.64 μ mol, respectively. The consistent production of H₂ and CO₂ continued as the reaction time was extended to 180 min, reaching approximately 130 μ mol for both gases. The calculation results of the Faradaic efficiency (Figure S13) demonstrated that the contribution of the reaction current for simultaneously generating CO₂ and H₂ consistently exceeded 80% and then stabilized at ~90%. These findings confirmed that the FAO process on the Pt₁Co₁ alloy occurred predominantly through the direct pathway of the dehydrogenation at a low potential. On the contrary, as demonstrated in Figure 5b, the H₂ and CO₂ yields on pure Pt varied significantly. H₂ was virtually absent within the first 10 min of FAO on Pt, and after 180 min, only 1.13 μ mol of H₂ and 7.02 μ mol of CO₂ were generated. This substantial discrepancy confirmed that Pt catalysts were significantly inhibited by CO*, leading to a suppressed dehydrogenation and reduced FAO activity. Notably, the total gas yield of Pt₁Co₁ alloy is 259.41 μ mol, which is much higher than that of pure Pt (8.16 μ mol). This reinforced the notion that the Pt₁Co₁ alloy effectively enhanced the FAO process, in agreement with the results of electrochemical tests. The introduction of Co augmented the active area of the Pt₁Co₁ alloy, resulting in improved FAO activity primarily through the direct pathway.

To further validate the reaction pathway at the molecular level during FAO, *in situ* ATR-IR measurements were performed via electrochemical and spectroscopic methods. Typically, during the FAO process on Pt surfaces, the presence of linearly adsorbed CO intermediates (CO_L) is easily observed, indicating that the process proceeds via an indirect oxidation pathway.^{52,53} In contrast, the Pt₁Co₁ alloy exhibited no distinct peak associated with CO_L. In Figure 5c, a peak at ~2340 cm⁻¹ on Pt₁Co₁ alloy corresponded to the adsorption of CO₂ at a potential of 0.15 V vs RHE. As the potential increased to 1.2 V vs RHE, spectra collected at 0.15 V intervals revealed the exclusive production of CO₂ on Pt₁Co₁ alloy. Conversely, the Pt surface, used as a control, clearly exhibited CO_L (~2050 cm⁻¹) at 0.15 V vs RHE, originating from the breaking of C–O and C–H bonds in the indirect pathway (Figure 5d). Additionally, the intensity of the CO₂ peak on Pt₁Co₁ alloy was markedly higher than that on Pt within the 0–1.2 V vs RHE potential range, underscoring the robust activity of Pt₁Co₁ alloy. Correspondingly, time-resolved spectra collected at 0.60 V vs RHE in Figure 5e,f affirmed an upward trend in CO₂ production over time on Pt₁Co₁ alloy. In contrast, FAO on Pt occurred via the indirect path involving CO intermediates, a behavior not observed on the Pt₁Co₁ alloy. Through the introduction of Co, the successful synthesis of PtCo alloys facilitated the direct oxidation of formic acid to CO₂, effectively mitigating the CO intermediate poisoning effect on the catalyst surface during FAO.

To gain deeper insights into the catalytic activity of PtCo alloys, DFT calculations were conducted to investigate the reaction energetics of FAO via both direct and indirect pathways. We initiated our investigation by conducting theoretical computations of electrochemical FAO on a pure Pt surface. As noted, prior studies have delineated two distinct pathways for FAO: the direct and indirect pathways, illustrated in Figure 6a.^{26,54,55} In the direct pathway, the O–H bond was activated, and the reaction proceeded via the intermediate HCOO*. Conversely, the indirect pathway involved a CO* intermediate formed via formic acid dehydration, with the pivotal intermediate being the adsorbed carboxylate (COOH*) species. The most stable configurations of adsorbed HCOO* and COOH* on the Pt(111) surface are illustrated in Figure 6b, while Figure 6c presented the calculated free energy (ΔG) of FAO on the Pt(111) surface via both pathways (see Table S2 for specific values). Our calculations revealed that the dehydrogenation of formic acid to yield COOH* was energetically more favorable than the formation of HCOO*. Specifically, the ΔG values for generating HCOO* and COOH* were 0.196 and -0.190 eV, respectively. Furthermore, the formation of CO* from COOH* dehydration was exothermic, with an ΔG variation of -0.875 eV. Consequently, electrochemical FAO on a pure Pt surface was poised due to CO adsorption, potentially leading to Pt poisoning due to the high additional energy required for further oxidation of CO (0.873 eV). These results are well matched with the experimental findings.

To circumvent CO formation during FAO, it was necessary to modulate the HCOO* and COOH* intermediates. Our study extended to FAO on PtCo surfaces with varying Co concentrations (25, 50, and 75%), as detailed in Figures S14 and S15 (termed Pt₃Co₁, Pt₁Co₁, and Pt₁Co₃ based on the atomic proportion of elements). As shown in Figure 6d, introducing 25% Co resulted in a decrease in the formation energy of HCOO*, with a ΔG of 0.037 eV. Although the ΔG for HCOO* formation was higher than that of COOH*, the direct pathway was bolstered, in contrast to the pure Pt surface. With the Co concentration escalating to 50 and 75% (Figure 6e,f), the free energy levels of HCOO* and COOH* were reversed. Specifically, the formation of HCOO* became more energetically favorable than that of COOH*, indicating that the direct pathway dominated the FAO process, and the formation of CO* was significantly suppressed on the two surfaces. This demonstrated that the first dehydrogenation step was critical, determining whether the reaction proceeded via a direct or indirect pathway. When the FAO process on the catalyst surface followed the direct pathway, the reaction performance was significantly enhanced. Furthermore, when the direct pathway was dominant (e.g., in Pt₁Co₁ and Pt₁Co₃), the second dehydrogenation step, converting HCOO* to CO₂, influenced the performance (Figure 6g). Our findings indicated that the ΔG for the release of CO₂ from HCOO* increased from 0.104 eV (Pt₁Co₁) to 0.136 eV (Pt₁Co₃), suggesting that excessive Co concentrations may impede FAO efficiency through the second dehydrogenation step. Therefore, we found that the introduction of Co was able to modulate the intermediates. Table S2 gives the ΔG values for different species on the surfaces involved in the DFT calculation. The results for Co correspond to Figure S16, indicating that the further increase in the Co content made the direct pathway associated with HCOO* more favorable. However, it also displayed that the energy barrier for

converting HCOO^* to CO_2 via the direct pathway will increase to 0.190 eV, further limiting FAO performance.

The trend elucidated above was effectively encapsulated by a volcano curve, where the transformation pathway of formic acid was governed by the competition between HCOO and the COOH intermediate adsorption. This competition was quantified by the free energy difference ($\Delta G_{\text{COOH}^*} - \Delta G_{\text{HCOO}^*}$) between these species. As depicted in Figure 6h, the change in ΔG of the rate-determining step correlated closely with ($\Delta G_{\text{COOH}^*} - \Delta G_{\text{HCOO}^*}$): a negative value indicated the dominance of the indirect pathway, potentially leading to CO^* -induced catalyst poisoning, with the further oxidation of CO^* acting as the rate-determining step; a positive value signified the prevalence of the direct pathway, which can easily circumvent catalyst deactivation caused by the indirect pathway, making the second dehydrogenation step of FAO become the rate-determining step. Therefore, considering the trends within the two regions dominated by the indirect and direct pathways, the optimal Co concentration can be found between 25 and 75%, potentially around 50%, which would be beneficial for achieving better FAO activity. These findings were consistent with the electrochemical test results, further confirming that PtCo alloys exhibited excellent resistance to CO poisoning and effectively regulated FAO to achieve high performance.

3. CONCLUSIONS

This study rationally designed and constructed a bimetallic PtCo alloy capable of effectively modulating the reaction pathways of FAO. A facile green microwave synthesis strategy was employed to synthesize tunable bimetallic PtCo alloys. Pt_1Co_1 alloy, with a 1:1 ratio, exhibited the superior catalytic activity (0.71 A mg^{-1} at 0.60 V vs RHE and 1.18 A mg^{-1} at 0.95 V vs RHE), outperforming counterpart Pt by over a hundredfold and exceeding Pt_3Co_1 and Pt_1Co_3 , while also demonstrating excellent kinetic properties and stability over a 3 h period. Importantly, this performance enhancement was attributed to the heightened selectivity of the direct pathway for FAO on the PtCo alloy, effectively mitigating CO intermediate poisoning on the catalyst surface. The results validated by gas chromatography and *in situ* ATR-IR spectroscopy provided strong evidence that formic acid was oxidized to CO_2 via the breaking of the O–H and C–H bonds at lower potentials on Pt_1Co_1 alloy catalyst. DFT calculations showed that introducing a Co content of 50% to form the Pt_1Co_1 alloy resulted in an enhanced preference for FAO through the direct pathway, avoiding the formation of CO poisoning. The two dehydrogenation steps in the system, characterized by ΔG changes of -0.296 and 0.104 eV, respectively, positioned the activity of the Pt_1Co_1 alloy near the top of the volcano plot behavior for FAO, further underscoring the crucial role of Co in promoting the preferred reaction mechanism. This study provides valuable insights into the rational design of bimetallic Pt-based alloys, showcasing the potential for effectively regulating the FAO reaction process.

4. METHODS

4.1. Preparation of Catalysts. Given the simplicity of the one-step microwave method and the tendency of metal compounds with organic ligands to lose their ligands during the heating process, this procedure, conducted under a reducing atmosphere, allows different metals to mix in various

proportions to form an alloy. Therefore, five different samples (Pt , Pt_3Co_1 , Pt_1Co_1 , Pt_1Co_3 , and Co) with different proportion of elements were synthesized through a one-step microwave-assisted process using only $\text{Pt}(\text{acac})_2$ and $\text{Co}(\text{acac})_2$ as precursors, blended in specific proportions. The quantity of $\text{Pt}(\text{acac})_2$ used for each sample was as follows: 243.3, 182.5, 121.6, 60.8, and 0 mg, respectively. Correspondingly, the amount of $\text{Co}(\text{acac})_2$ employed was 0, 39.8, 79.5, 119.3, and 159.1 mg. In the preparation of the catalyst, the corresponding amounts of $\text{Pt}(\text{acac})_2$ and $\text{Co}(\text{acac})_2$ were thoroughly mixed in a mortar. The resultant mixture was transferred to a porcelain boat and subjected to microwave heating in a quartz tube under a H_2/Ar atmosphere. The microwave power was controlled at 280 W, and the powder mixture was heated to 200°C over approximately 15 min, followed by a holding time of 1 h. Subsequently, the microwave power was adjusted to 1300 W for a rapid heating process to reach 400°C in 2 min, and retention at this temperature for 0.5 h. After the holding period, the sample was cooled to room temperature over 9 h. The primary component of the resulting products was PtCo alloys (or pure Pt and Co) with varying Pt and Co contents.

4.2. Electrochemical Measurements. Electrochemical experiments were conducted using a three-electrode electrochemical cell. Working electrodes were prepared by dropping 5 μL of catalyst-containing inks onto 5 mm diameter glassy carbon electrodes. The catalyst inks were formulated by mixing the catalysts with 0.05 wt % Nafion dissolved in isopropanol (4 mg of catalyst per mL). The glassy carbon electrode (0.196 cm^2) works as the working electrode, while Pt-wire as counter-electrode and saturated calomel electrode (SCE) as the reference electrode. In a typical working electrode preparation process, an ink containing 0.02 mg of the sample is dropped and dried on a glassy carbon electrode. All electrochemical experiments were performed at room temperature in an Ar-saturated 0.5 M H_2SO_4 solution (with or without 0.5 M formic acid). More details are provided in the Supporting Information.

■ ASSOCIATED CONTENT

★ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscatal.4c06198>.

Experimental details including chemicals, characterizations, electrochemical measurements and computational methods, and additional graphs of results (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Yangyang Wan – School of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013, China;
Email: yangyang.wan@ujs.edu.cn

C. Richard A. Catlow – School of Chemistry, Cardiff University, Cardiff CF10 3AT, U.K.; UK Catalysis Hub, Research Complex at Harwell, Rutherford Appleton Laboratory, Oxfordshire OX11 0FA, U.K.; Department of Chemistry, University College London, London WC1H 0AJ, U.K.; orcid.org/0000-0002-1341-1541;
Email: c.r.a.catlow@ucl.ac.uk

Kai Yan – Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation Technology, School of Environmental Science and Engineering, Sun Yat-sen University, Guangzhou 510275,

Authors

Zhikeng Zheng – Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation Technology, School of Environmental Science and Engineering, Sun Yat-sen University, Guangzhou 510275, China

Bin Liu – Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation Technology, School of Environmental Science and Engineering, Sun Yat-sen University, Guangzhou 510275, China

Jiaxiang Qiu – School of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013, China

Shaojun Xu – Department of Chemical Engineering, University of Manchester, Manchester M13 9PL, U.K.; School of Chemistry, Cardiff University, Cardiff CF10 3AT, U.K.; UK Catalysis Hub, Research Complex at Harwell, Rutherford Appleton Laboratory, Oxfordshire OX11 0FA, U.K.; orcid.org/0000-0002-8026-8714

Yuchen Wang – Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation Technology, School of Environmental Science and Engineering, Sun Yat-sen University, Guangzhou 510275, China

Man Zhang – Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation Technology, School of Environmental Science and Engineering, Sun Yat-sen University, Guangzhou 510275, China

Ke Li – Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation Technology, School of Environmental Science and Engineering, Sun Yat-sen University, Guangzhou 510275, China

Zhongti Sun – School of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013, China; orcid.org/0000-0002-4754-6583

Ziang Li – Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation Technology, School of Environmental Science and Engineering, Sun Yat-sen University, Guangzhou 510275, China

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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