Catalytic Synergies in Bimetallic Ru–Pt Single–Atom Catalysts via Speciation Control

Vera Giulimondi, Andrea Ruiz–Ferrando, Adam H. Clark, Selina K. Kaiser, Frank Krumeich, Antonio J. Martín, Núria López,* and Javier Pérez–Ramírez*

Bimetallic single–atom catalysts (b–SACs) have recently gained prominence by virtue of the unique catalytic cooperative interactions they can exhibit, intertwining electronic and geometric effects. To date, research efforts have exclusively focused on direct mechanisms such as electron density transfer or sequential reactivity. Herein, the first study on indirect, coordination–induced catalytic synergies in carbon-supported Ru–Pt SACs is conducted. To this end, a holistic approach is developed, combining i) precision synthesis, ii) advanced characterization, iii) exploration of single–site adsorption properties via the hydrogen evolution reaction, and iv) modeling through density functional theory. Despite the lack of both intermetallic coordination in the first or second shell and charge redistribution effects, the Ru–Pt SACs exhibit a H₂ formation rate enhanced up to 15–fold compared with their monometallic counterparts. To unfold the origin of the intermetallic cooperativity, modifications of the structural and catalytic properties induced by the integration of a second metal species are investigated. Thus, Pt atoms are found to selectively occupy the most energetically favorable cavities in the support, prompting Ru atoms to assume a distinct, more active, configuration. This contribution unveils a novel principle of bimetallic cooperativity, demonstrating the key role of integrative experimental and computational analyses in studying b–SACs.

1. Introduction

Carbon–supported single–atom catalysts (SACs) have attracted considerable attention in the field of catalysis owing to their maximized metal efficiency and unique reactivity in many applications.[1,2] Nevertheless, single–metal sites present intrinsic limitations in their catalytic properties originating from the finite variety of chemical states that they can assume through coordination with functionalities in the support. To overcome this, the integration of a second metal species in the host has emerged as a compelling strategy to further expand the spectrum of SAC catalytic properties.[1–6] By virtue of metal–metal interactions, this novel class of materials, herein defined as bimetallic SACs (b–SACs), has demonstrated enhanced activity, tunable product selectivity, and superior durability for a variety of applications, including thermocatalytic, electrocatalytic and photocatalytic ones.[4–8] However, the intrinsic complexity of these materials poses challenges to the resolution of both the metal–site architectures and the synergistic modes of action. Metal–metal interactions do not occur exclusively in the presence of intermetallic bonds (i.e., in dimers), but also in their absence.[6] The resolution of long–range metal–metal interactions requires advanced techniques, mainly relying on X–ray absorption spectroscopy (XAS) to assess the presence of bimetallic interactions up to the second coordination shell, and density functional theory (DFT) to resolve their impact on the catalytic fingerprints of b–SACs.[8] Pioneering studies combining in–depth spectroscopic and computational
analyses have reported \( M_1 \text{--} N/O \text{--} M_2 \) structures (where \( M_1 \) and \( M_2 \) are chemically different metal atoms) that exhibit direct cooperative effects stemming from \( i \) intermetallic electron density transfer, which tunes the binding energy of key intermediates, \( ii \) sequential participation of metal sites in cascade reactions, or \( iii \) unique reactant adsorption configurations adopted on the two metal sites that enhance the reaction kinetics.[9–11]

Nevertheless, the study of this promising class of SACs is still in its infancy. The varied and complex nature of catalytic synergies is largely unexplored and calls for a deeper understanding of the origin of the enhanced activity. Besides, atomically-precise synthesis of b-SACs remains a major challenge in this respect.[12,13] Owing to the broad distribution of compositions and anchoring sites in the carbon supports, unraveling underlying structure–property relationships is not straightforward. A reliable approach may consist in thoroughly investigating structural modifications induced by the integration of the second metal species in the synthetic strategy, affecting the coordination of the former one. Diverse metal–site configurations can exhibit both specific geometric and charge redistribution effects, which are convoluted and arduous to resolve.[14]

Specifically, disentangling indirect cooperativity mechanisms (i.e., coordination–induced effects) from direct ones (e.g., electron density transfer or sequential reactivity) remains a major challenge. To this end, the integration of secondary metal atoms in monometallic SACs that are completely isolated from each other (i.e., not bridged via N/O atoms) may offer an effective strategy to assess whether the presence of direct metal–metal interactions is necessary for intermetallic cooperativity. A suitable combination may be Ru and Pt, since the two metals have been studied for diverse applications as both monometallic single atoms and bimetallic dimers on carbon supports.[12,13,14]

Herein, we conduct the first study on indirect catalytic synergies in carbon–supported b–SACs. For this purpose, spatially– and electronically–isolated Ru and Pt atoms are generated on a N–doped carbon host, as \( i \) corroborated by the lack of intermetallic interactions in either the first or second coordination shell by in–depth XAS characterization, and \( ii \) confirmed by DFT analysis of possible charge redistribution effects. Despite the isolated nature of the metal atoms, the Ru–Pt SACs exhibit up to 15–fold enhanced activity compared with their monometallic counterparts for the hydrogen evolution reaction (HER), which serves here as a model probe for single–site H–adsorption properties.[15] To unravel the origin of the cooperativity, the b–SAC structure is thoroughly studied by integrative XAS and DFT analyses. The coordination configurations of each metal species are investigated by simulating the key steps in the synthetic process, while potential geometric and electronic synergistic effects are systematically probed. As a result, the enhanced activity of the Ru–Pt SACs is attributed to the stabilization of Ru atoms in distinct cavities in the presence of Pt atoms, resulting in a close–to–neutral H–adsorption strength (i.e., the metric for high HER activity). These results expand the scope of cooperativity effects in b–SACs, evidencing that indirect coordination–induced synergistic effects should not be overlooked when studying this novel class of catalytic materials.

2. Results and Discussion

2.1. Synthetic Strategy for Isolated Ru and Pt Atoms

Carbon–supported Pt single atoms (“SA” in the sample code) are derived by simple incipient wetness impregnation of a polyaniline–derived N–doped carbon (NC) with a solution of \( H_2PtCl_6 \) dissolved in water (w), followed by thermal activation in the range of 473–1073 K (Figure 1; Figures S1 and S2, Supporting Information).[16] Conventionally, the generation of Ru single atoms requires a strongly oxidizing agent, i.e., aqua regia (a), and mild activation temperatures (Ru SAC denoted as RuSA/NC–a–473, Figure 1; Figures S1 and S2, Supporting Information).[16] In aqueous solutions, the RuCl \(_3\) precursor undergoes hydrolysis, exchanging Cl\(^{-}\) ligands for H\(_2\)O molecules.[17] The resulting Ru species are then reduced by surface functional groups of the carbon support, yielding Ru nanoparticles.[38] Notably, this process is hindered by the addition of \( H_2PtCl_6 \) in the aqueous solution, generating a Ru–Pt SAC (Figure 1, denoted as [Ru–Pt]SA/NC–w–473), as visualized in HAADF–STEM and corroborated by X–ray diffraction (Figures S1 and S3, Supporting Information). This is explicable by the rapid and partial hydrolysis of \( H_2PtCl_6 \), which is capable of releasing Cl\(^{-}\) ions in water while maintaining from two to four Cl\(^{-}\) ligands depending on the solution pH,[19] and thus ii) of stabilizing the Ru species as single atoms on NC via a Cl–mediated oxidation mechanism.[14,16] In line with the affinity of both metal atoms for the N–functionalities in the support,[16] microscopy analysis evaluating the intensity profiles of Ru and Pt proximal atoms identifies interatomic distances of at least 4 Å (Figure S4, Supporting Information), suggesting full spatial isolation between the metal species.[39]

Remarkably, the stabilizing effect of Pt atoms on their Ru counterparts is preserved upon thermal activation at high temperature (yielding a Ru–Pt SAC denoted as [Ru–Pt]SA/NC–w–1073, Figure 1; Figure S3, Supporting Information), leading to Cl\(^{-}\) ligand removal and subsequent Ru agglomeration in the monometallic case (Figure 1; Figure S2, Supporting Information).[16] The highly stable Pt single atoms likely block the diffusion paths of the Ru atoms that lead to the formation of Ru nanoparticles, simultaneously offering the possibility to lower the chlorination degree of Ru atoms until full depletion of Cl\(^{-}\) ligands (vide infra). These results demonstrate that the integration of stable metal atoms (e.g., Pt atoms) in SAC synthetic procedures is a valuable strategy to control the low nuclearity in sintering-prone metal atoms (e.g., Ru atoms) and attain distinct coordination properties compared to their monometallic counterparts.

2.2. Resolution of Metal Structure

2.2.1. Coordination Environment of Ru and Pt Atoms

The generation of isolated metal atoms in both [Ru–Pt]SA/NC–w–473 and [Ru–Pt]SA/NC–w–1073 is corroborated by the Fourier transform analysis of extended X–ray absorption fine structure (FT–EXAFS) spectra. No metal–metal bonds are identified, with the exception of minor Ru–Ru contributions.

© 2022 The Authors. Advanced Functional Materials published by Wiley-VCH GmbH
in [Ru–Pt]_{x,y}/NC–w–1073 (coordination number, CN = 0.5, Figures 2a; Figure S5 and Table S1, Supporting Information) that are assigned to few sporadic clusters observed in HAADF–STEM (Figure S3, Supporting Information). Interestingly, FT–EXAFS analysis of [Ru–Pt]_{x,y}/NC–w–473 suggests that the presence of RuCl$_3$ in the aqueous solution does

**Figure 1.** a) Schematic illustration of the role of synthetic parameters (i.e., solvent, presence of secondary metal precursor, and temperature of thermal activation, $T_a$) in controlling the nanostructure of NC–supported monometallic and bimetallic catalysts, as indicated by the structural representations. The simultaneous impregnation of NC with aqueous solutions of RuCl$_3$ and H$_2$PtCl$_6$ prevents the agglomeration of Ru single atoms into nanoparticles at both mild and high thermal activation conditions. b) HAADF–STEM images of monometallic and bimetallic SACs. The single metal atoms are highlighted by the white dotted circles.

**Figure 2.** a) Experimental and fitted FT–EXAFS spectra in the $R$-space of monometallic and bimetallic SACs along with reference materials. b) WT–EXAFS spectra at the Ru $K$ and Pt $L_3$ edges of the b–SACs. The absence of spectral features in the region of $R = 3–5$ Å and $k = 9–11$ Å$^{-1}$ corroborates the spatial isolation between the Ru and Pt atoms in both samples. The characteristic lobes are marked with the corresponding contributions (namely M–M, M–Cl, and M–O).
not affect the ability of the H₂PtCl₆ to preserve the necessary Cl⁻ ligands for the Pt complexes to form single atoms, as indicated by a similar chlorination degree of Pt atoms in [Ru−Pt]SA/NC−w−473 and the monometallic Pt SAC counterpart (Pt−Cl CN = 2.4 and 2.3 in [Ru−Pt]SA/NC−w−473 and PtSA/NC−w−473, respectively, Figure 2a; Figure S5 and Table S1, Supporting Information). Conversely, the chlorinated nature of the Ru atoms in [Ru−Pt]SA/NC−w−473 (Ru−Cl CN = 2.6, Figure 2a; Figure S5 and Table S1, Supporting Information) corroborates the Cl⁻–mediated nature of the dispersing effect of H₂PtCl₆ on Ru species. The latter ones need Cl⁻ ligands to stabilize as single atoms,[14] as indicated by the strongly chlorinated character of RuSA/NC−a−473 (Ru−Cl CN = 4.3, Figure 2a; Figure S5 and Table S1, Supporting Information), which is synthesized by using aqua regia as a solvent. Full depletion of the Cl⁻ ligands on both metal atoms is observed upon thermal activation at 1073 K (Ru−Cl CN = 0.0 and Pt−Cl CN = 0.0, Figure 2a; Figure S5 and Table S1, Supporting Information), reflecting a stronger interaction with the NC support (Ru−N/O/C CN = 1.7 and 2.3, and Pt−N/O/C CN = 1.8 and 4.0 in [Ru−Pt]SA/NC−w−473 and [Ru−Pt]SA/NC−w−1073, respectively, Figure 2a; Figure S5 and Table S1, Supporting Information).

To gain further insights into the structural and electronic features of the Ru−Pt SACs, the possible presence of intermetallic interactions in the first coordination shell is assessed. Similarly to analogous NC-supported Au–Ru SACs,[19] and in line with the affinity of both metal atoms for N–functionality,[14,19] no Ru−Pt bonds are detected in either [Ru−Pt]SA/ NC−w−473 or [Ru−Pt]SA/NC−w−1073. Therefore, the presence of Ru−Pt dimers, and thus of direct intermetallic electron density transfer, is excluded. Nevertheless, charge redistribution effects between two foreign metal atoms may also occur by bridging N− and O−functionalities in the carbon support (i.e., when the two metal atoms are in their mutual second coordination sphere).[19,21] To this end, the wavelet transform analysis of EXAFS spectra (WT−EXAFS) constitutes a highly suitable tool to probe the presence of N/O−bridged Ru−Pt species.[19,21] In their absence, longer-range electronic interactions between Ru and Pt atoms occurring via functionalities in the carbon support could be ruled out. By comparison to the metal chloride and metal oxide standards (Figure S6, Supporting Information), and in line with the Fourier transform analysis results, [Ru−Pt]SA/NC−w−473 presents i) M−Cl contributions, exemplified by the lobe centered at R = 1.8 Å and k = 1−10 Å⁻¹ at the Ru K edge and the one at R = 1.9 Å and k = 1−8 Å⁻¹ at the Pt L₁ edge, as well as ii) M−N/O/C contributions, exemplified by the lobe centered at R = 1.5 Å and k = 1−11 Å⁻¹ at the Ru K edge and the one at R = 1.7 Å and k = 1−11 Å⁻¹ at the Pt L₁ edge (Figure 2b). Additionally, a weak feature centered at R = 3.1 Å and k = 8−14 Å⁻¹ can be identified at the Ru K edge, which can be attributed to residual Ru−Cl=Ru species from the RuCl₃ precursor by comparison with the spectral fingerprint of the latter one (Figure S6, Supporting Information).

In contrast, [Ru−Pt]SA/NC−w−1073 shows only lobes associated to Ru−N/O/C and Pt−N/O/C contributions. Markedly, no prominent spectral features in the region of R = 3−5 Å and k = 9−11 Å⁻¹ can be identified in either the [Ru−Pt]SA/NC−w−473 and [Ru−Pt]SA/NC−w−1073. This indicates the lack of intermetallic interactions in both the first or second coordination shell, suggesting full spatial and electronic isolation between the Ru and Pt atoms.[9]

The lack of charge redistribution effects between Ru and Pt atoms is further corroborated by X−ray absorption near edge structure (XANES) analysis. In line with literature−reported studies,[3,9] intermetallic electron density transfer that may occur through the functionalities in the carbon support can be identified by comparing the white line intensity values of the bimetallic SACs to the monometallic ones. In the presence of intermetallic charge redistribution effects, i) the b−SAC spectrum of the electron−donating metal edge should present a more oxidized character than its monometallic counterpart, while ii) the b−SAC spectrum at the electron−accepting metal edge should exhibit a more reduced character than its monometallic analog.[10,22] In agreement with X−ray photoelectron spectroscopy (XPS) analysis (Figure 3a; Figure S7 and Tables S2−S4, Supporting Information), both metals in [Ru−Pt]SA/NC−w−473 and [Ru−Pt]SA/NC−w−1073 present a slightly higher white line intensity value than one of the monometallic SAC counterparts (Figure 3b). Not only does the more positively charged character of both metals in the b−SACs provide further evidence for the electronically−isolated nature of the Ru and Pt atoms, additionally corroborated by DFT analysis (vide infra), but it also suggests stronger metal−support interactions compared to the monometallic SACs. Specifically, the lesser chlorination degree of the Ru atoms in [Ru−Pt]SA/NC−w−473 compared to RuSA/ NC−a−473, reflects in the metal atom coordination sphere presenting fewer M−Cl bonds in favor of more M−N/C/O bonds (Table S1, Supporting Information). Unlike the Ru atoms, the Pt atoms in the bimetallic [Ru−Pt]SA/NC−w−473 and the monometallic PtSA/NC−w−473 present a similar chlorination degree. Nevertheless, the more oxidized character of the Pt species likely derives from the partial Cl⁻ ligand transfer mechanism to the Ru ones that occurs during the b−SAC synthesis, ultimately resulting in more prominent M−N/C/O interactions (Table S1, Supporting Information). Similarly, the complete removal of Cl⁻ ligands in [Ru−Pt]SA/NC−w−1073 by high thermal treatment results in a prominently stronger interaction of both metal atoms with the NC support compared to the monometallic SACs (Table S1, Supporting Information).

2.2.2. Role of Pt in Controlling Ru Speciation

The reactivity of SACs is usually rationalized by probing the catalytic properties of distinct metal−site configurations via DFT models, which are constructed on the basis of XAS analysis. Consequently, the study of b−SACs should not overlook the impact of the second metal species on the speciation of the former ones. A reliable approach consists of developing integrative theoretical models investigating i) potential intermetallic interaction occurring during the catalyst synthesis, ii) concerted adsorption of the metal species on the support, and iii) possible charge redistribution between metal centers. Accordingly, aiming to uncover the active−site structure of the Ru−Pt SACs, DFT models are developed to simulate their synthetic procedure by incipient wetness impregnation. Provided the tendency of H₂PtCl₆ to lose 2−4 Cl⁻ ligands in aqueous solutions, PtCl₄ and RuCl₃ species are employed as metal precursors in the DFT
calculations. Similarly to analogous Au–Pt SACs,[20] XAS characterization of the Ru–Pt SACs suggests a Cl–mediated dispersing action of the Pt precursor on Ru species (vide supra). This is corroborated by the exothermicity of the exchange of 1–4 Cl\(^{-}\) ligands from the PtCl\(_4\) precursor to Ru or RuCl\(_x\) species (\(x = 0–3\), Table S5, Supporting Information). To further demonstrate the key role of Cl\(^{-}\) ligands in preventing metal sintering, models simulating Ru complexes in aqueous solutions with varying chlorination degree, RuCl\(_x\)(OH)\(_{3−x}\) (\(x = 0–3\)), are constructed to predict their tendency to deliver nanoparticles over single atoms. OH\(^{-}\) ligands are selected as exemplary negatively charged ligands coming from the aqueous phase to ensure neutrality among the models and remove any differential charge effects to the sintering process. Provided the i) strong affinity of Ru toward oxygenated compounds,[16] and ii) the large cohesive energy of RuO\(_2\) (i.e., 5.0 eV per formula unit), the formation energy of RuO\(_2\) is calculated as a function of \(x\) and compared to the binding energy of the corresponding RuCl\(_x\)(OH)\(_{3−x}\) species to the NC scaffold in reference to their gas–phase species (Figure 4a). In line with the FT–EXAFS results, each Cl\(^{-}\) ligand is predicted to prevent the oxidation of Ru by at least 0.8 eV, thus hindering the formation of Ru clusters on the surface of NC. Therefore, while Ru species in an aqueous phase undergo prominent Cl\(^{-}\) ligand exchange for OH\(^{-}\) ones and are not able to preserve the necessary Cl\(^{-}\) ligands to form single atoms, the partial and rapid hydrolysis of H\(_2\)PtCl\(_6\) results in a higher concentration of Cl\(^{-}\) ions that ultimately thwarts the ligand exchange process and yields Ru single atoms.

Having resolved the dispersing effect of the chlorinated Pt species on the Ru ones (Figure 4b), the coordination configurations of the two metal atoms are unraveled. For this purpose, the energy paths for the adsorption and dechlorination of each metal species are calculated under different thermal conditions (i.e., 473 and 1073 K). In an effort to represent the wide range of possible chemical environments in NC (Figure 4c), the energy paths are computed over a number of potential cavities in the support (Figure 4d; Figure S8 and Tables S6–S8). Among them, the 3×N5 (t–pyrrolic) and 4×N6 (sq–tetrapyrridinic) cavities are selected as representatives of trigonal (t) and square–planar (sq) geometries, respectively, in agreement with literature–reported studies.[21] Owing to the out–of–plane configuration imposed by trigonal cavities, highly chlorinated species (i.e., RuCl\(_3\) and PtCl\(_4\)) tend to adsorb on 3×N5 cavities. At 473 K, in line with the FT–EXAFS results of [Ru–Pt]/SANC–w–473 (Figure 2a; Table S1, Supporting Information), the adsorbed species are unlikely to undergo full dechlorination, mainly resulting in RuCl\(_3\)* and PtCl\(_2\)* configurations (~4.1 and ~3.5 eV, respectively). At 1073 K, full depletion of Cl\(^{-}\) ligands of Pt species is hindered over trigonal cavities. This hints at the migration of PtCl\(_2\)* and Pt* species to 4×N6 cavities, where the full depletion of Cl\(^{-}\) is strongly exothermic (> 3.6 eV). Conversely, the formation of Cl–free Ru*
species is allowed with isoenergetic configurations over both 3xN5 and 4xN6 cavities (−3.2 eV).

Notably, these energy fingerprints point to an irreversible occupation of the 4xN6 cavities by Pt atoms (−6.0 eV), while Ru atoms can be reversibly adsorbed on both and 4xN6 cavities. This leads to the preferential stabilization of Ru atoms on the 3xN5 cavities in [Ru−Pt]/SANC−w−1073 as a result of the reduced availability of free 4xN6 ones (filled by Pt atoms). Additionally, the presence of Pt atoms firmly anchored to 4xN6 cavities hinders the diffusion and agglomeration of Ru species during thermal treatment under high temperature, leading to the stabilization of Ru as single atoms. The cavity control...
exerted by Pt atoms is further corroborated by the more negative adsorption energy values in reference to bulk metals for both i) Ru single atoms compared with their Pt analogs on 3×N5 cavities and ii) Pt single atoms compared with their Ru analogs on 4×N6 cavities (Figure 4e). This concerted adsorption of Ru and Pt is already expected to take place at mild activation temperatures, since a varied distribution of chlorinated and non–chlorinated Ru and Pt species is predicted to populate the surface of NC in [Ru–Pt]5A/NC–w–473. At 1073 K, this phenomenon is maximized as full depletion of Cl− ligands is achieved.

The DFT–predicted architectures for both the Pt and Ru atoms in [Ru–Pt]5A/NC–w–1073 are in line with the FT–EXAFS analysis results. Specifically, the square–planar coordination of the Pt atoms on 4×N6 sites in [Ru–Pt]5A/NC–w–1073 agrees well with the Pt–N/O/C coordination number of 4.0 identified by EXAFS analysis (Table S1, Supporting Information). For the Ru atoms, the DFT–predicted out–of–plane configuration on 3×N5 sites is corroborated by the Ru–N/O/C coordination number of 2.3 (Table S1, Supporting Information). The slightly lower value than the theoretical one of 3, can be explained by i) the averaging character of the EXAFS technique, and ii) inevitable contributions of low–coordinated metal species in edge defects or other nitrogenated sites that are also present in the NC support.[24] Furthermore, a small degree of heterogeneity in the metal species configurations, as mirrored by the presence of a short–bonding Ru–N/O/C contributions (CN = 0.4), will also contribute to minor deviations between the theoretical and experimental results. In the case of [Ru–Pt]5A/NC–w–473, the chlorinated character of the catalyst complicates an accurate evaluation of the metal atom interaction with the support, owing to prominent M–Cl spectral features that can mask weaker M–N/O/C contributions. Furthermore, both the Ru–N and Pt–N distances of the DFT–modeled structures increase by at least 0.1 Å when a Ru or Pt atom presents two Cl− ligands in its coordination environment (Table S9, Supporting Information). The metal atoms are vertically displaced due to the steric hindrance of the Cl− ligands, resulting in asymmetries in the metal atom position within the 3×N5 that can yield lower M–N/O/C coordination numbers for chlorinated structures.

Upon rationalization of the metal–specific architectures, the tendency of Ru and Pt atoms to stabilize in dimeric architectures is computationally explored (Table S10, Supporting Information). In line with the FT– and WT–EXAFS analyses, the formation of dimeric species is found to be thermodynamically improbable (>1.3 eV). Having excluded the presence of intermetallic bonds, DFT models featuring Ru and/or Pt species in adjacent 3×N5 and 4×N6 cavities are constructed to probe potential intermetallic charge redistribution effects. Metal–metal distances of 4.1 and 5.9 Å were selected as the minimal possible intermetallic distances, in agreement with both EXAFS analysis, showing lack of intermetallic interactions in either the first or second coordination shells (Figure 2; Table S1, Supporting Information), and microscopy analysis of the intensity profiles of Ru and Pt proximal atoms, indicating intermetallic distances of >4 Å (Figure S4, Supporting Information). In line with the spectroscopic analysis, differences up to 0.1–0.2 eV in core–level shifts between the configurations point to the exclusive presence of electronically–isolated Ru and Pt single atoms supported on NC (Table 1). This evidence lays the basis for the study of catalytic fingerprints in Ru–Pt SACs that stem exclusively from coordination–induced effects.

Table 1. Differences in simulated core–level shifts and H–adsorption free energies (∆CLS and ∆ΔGad, respectively, in eV) of Ru and Pt species on adjacent 3×N5 and 4×N6 cavities between monometallic and bimetallic systems.

| M–M distance / Å | Configuration | ∆CLS eV−1 | ∆ΔGad eV−1 |
|------------------|---------------|-----------|-------------|
| 4.1              | Ru/3×N5       | 0.05      | 0.03        |
|                  | Pt/3×N5       | 0.06      | 0.08        |
|                  | Ru/4×N6       | 0.15      | 0.06        |
|                  | Pt/4×N6       | 0.24      | 0.09        |
| 5.9              | Ru/3×N5       | 0.00      | 0.06        |
|                  | Pt/3×N5       | 0.01      | 0.04        |
|                  | Ru/4×N6       | 0.00      | 0.07        |
|                  | Pt/4×N6       | 0.06      | 0.03        |

2.3. Catalytic Synergies Between Isolated Ru and Pt Atoms

2.3.1. Evaluation of Single–Site H–Adsorption Properties

Following the structural identification of the Ru–Pt SACs, their catalytic fingerprints can be explored by means of hydrogen evolution reaction (HER). The single–site nature of this reaction offers a platform for the exploration of intermetallic cooperativity mechanisms between isolated metal sites. Specifically, the HER constitutes a unique probe for H–adsorption properties owing to i) the high sensitivity of the reaction kinetics to the coordination environment of the active site, together with the ii) well–established two–step mechanism and kinetic features, mirroring the catalyst H–adsorption strength.[14,15] A recent pioneering study reported outstanding catalytic synergies for the HER in carbon–supported Ru–Pt dimers, enhancing H–adsorption properties via direct electron density modulation between Ru and Pt atoms.[13] In our study, by spatially and electronically isolating the Ru and Pt atoms, we probe potential indirect modes of synergistic action. Remarkably, the Ru–Pt SACs are found to magnify the activity for the HER of their monometallic counterparts, which present similar catalytic performances, by ∼5 times in [Ru–Pt]5A/NC–w–473 and by ∼15 times in [Ru–Pt]5A/NC–w–1073 (Figure 5a; Figure S9 and Table S11, Supporting Information).

Further insights into the distinct catalytic features of the Ru–Pt SACs can be gained by analysis of the reaction kinetics. Under acidic conditions, the HER mechanism consists of an initial adsorption step of H+ (coupled to electron transfer) onto the active site, followed by a H2 formation step (Figure 5b).[25] According to classical electro–kinetics, under potentiostatic sweep tests (i.e., linear sweep voltammetry, LSV) the response of the reaction rate to changes in potential (i.e., Tafel analysis) can provide an indication of the rate–determining step. To this end, the evaluation of the reaction rate–potential slopes at potentials close to equilibrium (i.e., Tafel slopes) can identify the initial adsorption or the H2 formation as the rate–determining step (corresponding to slopes of ∼120 and ∼40 mV dec−1, respectively).
respectively.\textsuperscript{[26]} While the HER over both monometallic SACs is limited by the adsorption step, the b–SACs feature the second step as the rate–determining one (Figure 5a; Figure S10 and Table S11, Supporting Information), reflecting the enhanced H–adsorption properties. However, the similar reaction rate–potential slopes exhibited by [Ru\textsuperscript{I}-Pt\textsuperscript{II}]SA/NC–w–473 and [Ru\textsuperscript{I}-Pt\textsuperscript{II}]SA/NC–w–1073 may apparently contradict the significantly more prominent catalytic synergy exhibited by the latter one. This is explicable by the poisoning effect of Cl\textsuperscript{−} ligands in [Ru\textsuperscript{I}-Pt\textsuperscript{II}]SA/NC–w–473, which results in a shift of the onset potential to more negative potentials. In line with the high chlorination degree and limited interaction with the support, [Ru\textsuperscript{I}-Pt\textsuperscript{II}]SA/NC–w–473 and Ru\textsubscript{SA}/NC–a–473 show pronounced deactivation already during a second LSV (\textapprox{}38.0 \pm 9.0% compared to the activity in the first LSV, Figure S9 and Table S11, Supporting Information). Conversely, the Cl–free and well–anchored metal atoms in [Ru\textsuperscript{I}-Pt\textsuperscript{II}]SA/NC–w–1073 show minor deactivation (\textapprox{}11.1 \pm 2.6% compared to the activity in the first LSV, Figure S9 and Table S11, Supporting Information). HAADF–STEM analysis of the used catalysts (including “–u” in the sample code) shows metal–atom agglomeration into nanoparticles (average size: 3.3 nm, Figure 5c) in the former and only minor cluster formation in the latter (average size: 1.4 nm, Figure 5c). Consequently, catalyst deactivation of both [Ru–Pt\textsubscript{II}]SA/NC–w–473 and Ru\textsubscript{SA}/NC–a–473 is imputed to Ru single–atom agglomeration induced by Cl\textsuperscript{−} ligand stripping upon applying a sufficiently high cathodic current density.

Figure 5. a) HER activity plot representing H\textsubscript{2} evolution rates (i.e., cathodic current densities) and Tafel slopes at –0.2 V versus RHE in 0.5 m H\textsubscript{2}SO\textsubscript{4} for the monometallic and bimetallic SACs. Data presented as mean \pm SD (n = 3). b) Schematic representations of the rate–determining steps in the HER mechanism of monometallic and bimetallic SACs (upper row) and together with schematic representations of the single–atom agglomeration mechanism via Cl\textsuperscript{−} ligand stripping in [Ru–Pt\textsubscript{II}]SA/NC–w–473 (lower row), which is hindered in [Ru–Pt\textsubscript{II}]SA/NC–w–1073. c) HAADF–STEM of used monometallic and bimetallic SACs at –0.2 V versus RHE in 0.5 m H\textsubscript{2}SO\textsubscript{4}, together with average particle sizes (d\textsubscript{p}). d) Radar plot of H–adsorption Gibbs free energy (\Delta G\textsubscript{H}) of RuCl, Ru, and Pt species on both 3\times N5 cavities (upper purple region) and 4\times N6 cavities (lower blue region), accompanied by their structural representations. Cl–free Ru species on 3\times N5 cavities are identified as the most active species for the HER, owing to their neutral \Delta G\textsubscript{H} value (0.09 eV).
reducing potential (Figure 5b). Hence, by displacing Ru atoms in distinct cavities (vide supra) and allowing for complete depletion of their Cl⁻ ligands at thermal activation conditions (i.e., 1073 K) by blocking the sintering paths of Ru atoms, the Pt species are found to exert coordination–induced promotional effect on their Ru counterparts that reflects not only in the catalytic activity for the HER but also in its stability.

2.3.2. Origin of Intermetallic Cooperativity

When two distinct single-metal atoms are present on the same support, they can either catalyze the reaction in parallel or cooperate with each other. The H–adsorption free energy (ΔG_{H^*}) is commonly employed as a descriptor of catalytic activities for the HER, as it follows a volcano trend where ΔG_{H^*} = 0 corresponds to the highest hydrogen evolution rates. Recently, this model was improved by linking microkinetics to the thermodynamic diagrams for the HER, showing that slightly more positive values (ΔG_{H^*} = 0.2 eV at U = 0 V) would be responsible for the current densities observed in the kinetically active region. Therefore, DFT is employed to systematically evaluate the ΔG_{H^*} of all potential active site architectures (i.e., MCl₂, MCl, and M species stabilized on both trigonal and square–planar cavities, as summarized in Figure S11 and Table S12, Supporting Information).

In stark contrast with carbon–supported Pt nanoparticles, which are the state–of–the–art commercial catalysts for the HER, experimental catalytic tests of Pt SACs show modest activity. This can be assigned to the DFT–predicted square–planar geometry of Pt species (vide supra). Owing to their weak H–adsorption strength (ΔG_{H^*} = 1.37 and >2.00 eV for Pt⁴⁺ and PtCl⁺, respectively, Figure 5d; Figure S11 and Table S12, Supporting Information), the reaction kinetics of the Pt SACs is limited by the H–adsorption step (Figure 5a; Figure S10, Supporting Information). Similarly, in line with the Tafel analysis (Figure 5a; Figure S10, Supporting Information), chlorinated Ru species stabilized on trigonal cavities that likely populate the monometallic Ru SAC (vide supra) also exhibit weak H–adsorption strength (ΔG_{H^*} = 0.7 eV for both RuCl⁶⁻ and RuCl⁸⁻). Consequently, the enhanced activity of the Ru–Pt SACs cannot be attributed to either Pt species or chlorinated Ru ones. Nevertheless, the b–SACs present a lower chlorination degree of the Ru sites, the Pt loading is varied while the Ru loading is kept constant (i.e., 0.5 wt.%). Nevertheless, the prerequisite for the stabilization of Ru single atoms over 3xN5 sites is the prevention of the metal sintering, which is achieved by virtue of the Cl⁻–mediated dispersing effect exerted by the Pt species during the catalyst synthetic process (vide supra). In line with this, the synthesis of a Ru–Pt catalyst featuring a lower Pt loading (i.e., 0.25 wt.% sample code: [Ru₅.5–Pt₀.25]₅S₅/NC–w–1073) results in atomic dispersion for both metals (Figure S12, Supporting Information). While the [Ru₅.5–Pt₀.75]₅S₅/NC–w–1073 exhibit similar synergistic effects to [Ru₅–Pt₁]₅S₅/NC–w–1073 (12–fold and 15–fold enhancement in the activity with respect to the monometallic SAC counterparts, respectively), a slight reduction in prominence of the cooperativity mechanism is observed (Figure S9, Supporting Information).

Upon resolving how the integration of Pt atoms affects the configuration and H–adsorption properties of Ru atoms, diverse cooperativity mechanisms are systematically studied. First, possible direct synergistic actions are explored, including potential intermetallic charge redistribution effects. In line with the XAS analysis, differences up to 0.1 eV in the ΔG_{H^*} between models featuring Ru and/or Pt species in adjacent 3xN5 and 4xN6 cavities corroborate the lack of electron transfer between the metal atoms (Table 1, Supporting Information). Furthermore, a direct cascade mechanism is investigated. The process can be described as consisting of two consecutive steps: i) a water dissociation in one site, leading to the adsorption of H⁺ and a free OH⁻ and ii) the transfer of a proton from a second water molecule to the free OH⁻ species with the subsequent adsorption of the remaining OH⁻ on the other metal site. Driven by the dissociative adsorption of water on Ru atoms stabilized on 3xN5 cavities (~0.7 eV, Table S13, Supporting Information), which leads to the formation of H⁺–Ru–OH⁻ centers, proton shuttle effects are probed over neighboring Pt atoms (Figure 6a). However, the endothermicity of water adsorption (0.8 eV) and dissociation (>2.0 eV) over square–planar Pt excludes this kind of cooperativity interactions between the Ru and Pt atoms (Table S13, Supporting Information).

Henceforth, indirect synergistic effects are explored. Seeking for large–scale configurational effects at the water–catalyst
interface, the interaction of a layer of water molecules with the surface of monometallic Ru and bimetallic SACs is analyzed. Nevertheless, despite the distinct configuration that water molecules adopt over Ru and Pt atoms (O– and H–oriented, respectively), no differences are observed between the monometallic Ru SAC, no improvement of the configurational disorder is identified upon integration of the Pt atoms. These results evidence the cavity control exerted by Pt atoms over Ru ones as the only effect leading to catalytic synergies.

3. Conclusion

In summary, we explored indirect catalytic synergies in bimetallic b–SACs, stemming exclusively from metal–site configurations. To avoid direct intermetallic charge transfer or sequential participation in cascade mechanisms, isolated Ru and Pt atoms (with intermetallic distance > 4 Å) were generated on N–doped carbon by a simple dry impregnation synthetic strategy, where the formation of Ru nanoparticles was hindered by a remarkable dispersing effect of Pt species on the Ru ones. The lack of intermetallic coordination, as well as electron density redistribution, was confirmed by microscopic, spectroscopic, and DFT analyses. By investigating the catalytic fingerprints via the HER, employed as probe for H-adsorption properties of single–metal sites, cooperativity effects in the Ru–Pt SACs were unveiled, leading up to 15–fold enhanced activity. The development of an integrative approach combining spectroscopic and computational techniques proved key to unfold the role of the b–SAC synthetic strategy in controlling the metal–site configurations and exclude different potential geometric and electronic synergistic effects for the HER. Thereby, a novel principle of intermetallic cooperativity action was unraveled. Owing to the occupation of the most energetically–favorable cavities in the support by the Pt atoms, the Ru ones are induced to adopt distinct and more active configurations. Finally, our contribution shows that metal–metal interactions are not necessary for intermetallic cooperativity mechanisms to occur. As a result, prior investigating catalytic properties, the study of b–SACs should encompass a thorough analysis of the metal–coordination environment that is determined in the synthetic process. Only in this way potential coordination–induced synergistic effects can be assessed, an undertaking that is pivotal for a clear mechanistic understanding of complex metal–metal and metal–host interactions in b–SACs.

4. Experimental Section

Catalyst Preparation: The N–doped carbon support (NC) was prepared in a two–step synthesis, consisting of an oxidative polymerization of aniline and a subsequent carbonization step.24 Aniline (50 mmol, Acros, 99.5%) was dissolved in deionized water (40 cm³, pH 0.4; adjusted by hydrochloric acid, 1.25 M, Sigma–Aldrich, > 99%) at room temperature, cooled to 277 K, and subsequently added to a precooled solution (277 K) of ammonium persulfate (50 mmol, Acros, 98%) in deionized water (20 cm³). After 5 min of vigorous manual stirring, the mixture was kept at room temperature for 24 h to complete the polymerization process. The formed polyaniline was thoroughly washed with deionized water for neutralization, dried in vacuum at 393 K for 12 h, and afterward treated at 1073 K (heating rate 5 K min⁻¹, hold time 1 h, static N₂). The obtained N–doped carbon, having a N–content of 9.7 wt.% and a total surface area of 517 m² g⁻¹, was ground and sieved (particle size 0.4–0.6 mm). All metal–based catalysts were prepared via an incipient wetness impregnation method with a nominal metal loading of 1 wt.%. The metal precursors, RuCl₃·H₂O (ABCR, 99.9%, 40.0 wt.% Ru) and H₂PtCl₆·H₂O (ABCR, 99.9%, 40.0 wt.% Pt), were dissolved in water or aqua regia (1.5 cm³ g⁻¹, hold time 1 h, static air) to yield the respective monometallic single–atom catalysts, denoted as Ru₅₀/NC–a–473 and Pt₅₀/NC–a–473, if aqua regia was used as the solvent, or Ru nanoparticle and Pt single–atom catalysts, denoted as Ru₅₀/NC–w–473, Ru₅₀/NC–w–1073 and Pt₅₀/NC–w–473, Pt₅₀/NC–w–1073, respectively, if water was used as the solvent. The bimetallic catalysts, denoted as [Ru–Pt₅₀] SA /NC–w–473 and [Ru–Pt₅₀] SA /NC–w–1073, were obtained by impregnation of the NC support with an aqueous solution containing both metal precursors with a 1:1 Ru:Pt weight ratio, keeping the total metal loading at 1 wt.% The metal loading was varied (i.e., 0.25 and 1 wt.%) while keeping the Ru metal loading constant (i.e., 0.5 wt.%). The data was recorded in the
10–20°/29 range with an angular step size of 0.07° and a counting time of 0.26 s per step. Scanning transmission electron microscopy (STEM) images with a high-angle annular dark-field (HAADF) detector were acquired on an aberration-corrected HD2700CS (Hitachi) microscope operated at 200 kV. Samples were prepared by dipping the copper grid supporting a holey carbon foil in a suspension of the solid in ethanol and subsequent drying in air. X-ray fluorescence (XRF) spectroscopy, was conducted using an Ornis Micro–EDXRF spectrometer equipped with a silicon drift detector and a Rh source operated at 35 kV and 800 µA. The weight percentage of impurities (Mg, Ca, P, Mn, Fe, Ni, and Cu) was found to be at least 20 times lower than the concentration of Ru or Pt. X-ray photoelectron spectroscopy (XPS) spectra were acquired on a Physical Electronics Quantera SXm instrument using monochromatic Al–Kα radiation, generated from an electron beam operated at 15 kV, and equipped with a hemispherical capacitor electron–energy analyzer. The samples were analyzed at an electron take-off angle of 45° and a constant analyzer pass energy of 55 eV for the fresh samples, and a constant analyzer pass energy of 69 eV for the used catalysts. The detection of the metal signals in the used catalysts required a higher pass energy to increase the intensity of the signal, since the signal intensity was reduced by the presence of fluorine in the Nafion–based ink in which catalysts were embedded (vide infra). The Ru 3p and Pt 4f spectra were fitted by mixed Gaussian–Lorentzian component profiles after Shirley background subtraction. The selected peak positions are based on literature-reported data and fixed with an error of ±0.2 eV. The detailed fitting parameters are given in Tables S3 and S4 (Supporting Information). X–ray absorption fine structure (XAFS) measurements were carried out at the SuperXAS beamline of the Swiss Light Source.[32] The incident photon beam was provided by a 2.9 T super magnet and subsequently collimated using a Pt–coating (for the Ru K edge) and a Rh–coating (for the Pt L3 edge). The X–ray beam is then energy selected by a liquid nitrogen–cooled Si (111) channel–cut Quick–EXAFS monochromator.[33] The rejection of higher harmonics and focusing was achieved with a Pt–coating (for the Ru K edge) and a Rh–coating (for the Pt L3 edge), respectively, at 2.5 mrad. The beamline was calibrated using the respective metal foils. The area of sample illuminated by the X–ray beam was 1.0 mm×0.2 mm. All spectra were recorded in transmission mode at room temperature. The extended X–ray absorption fine structure (EXAFS) spectra were acquired with a 1 Hz frequency (0.5 s per spectrum) and then averaged over 5 min. The resulting raw data were processed using the ProEXAFS software,[34] and the EXAFS spectra were analyzed using the Demeter software.[34] Catalytic Evaluation: The electrocatalytic hydrogen evolution reaction (HER) measurements were performed using a three–electrode cell. A glassy carbon rotating–disk electrode (0.1956 cm2) was used as the working electrode (Pine Instruments), a standard single junction silver/silver chloride electrode as the reference electrode (3 M, Pine Instruments), and a graphite electrode as the counter electrode. An ink made of 5 mg of the catalysts, 1.6 cm3 of ultrapure water, 0.4 cm3 of isopropanol, and 0.04 cm3 Nafion (5% solution, Sigma–Aldrich), sonicated for 10 min, was prepared, and 0.015 cm3 of the ink was cast–dropped onto the RDE. The linear sweep voltammeteries (LSVs) were recorded in a N2–saturated 0.5 M H2SO4 electrolyte by sweeping the applied potential between 0.4 and −0.2 V versus RHE at a scan rate of 0.05 V s−1, while rotating the working electrode at 1800 rpm to favor the removal of H2 gas bubbles. The catalyst sample size (n) and the catalyst activity parameters, together with their standard deviation (SD) values, are reported in the Table S11, Supporting Information. Computational Methods: Density functional theory (DFT) on models of the Ru and Pt single atoms representing the different monometallic and bimetallic SACs was employed as implemented in the Vienna ab initio Simulation Package (VASP 5.44).[35] The generalized gradient approximation of the Perdew–Burke–Emzerhof functional (GGA–PBE)[36] was used to obtain the exchange-correlation energies with dispersion contributions introduced via Grimme’s DFT–D3 approach,[37] Projector augmented wave (PAW)[38] and plane waves with a cut–off energy of 450 eV, with spin polarization allowed when needed, were chosen to represent the inner electrons and the valence monoelectronic states, respectively. For the simulation of the NC support, a two–layer (6+6) slab of graphitic carbon separated by 15 Å of vacuum was used and sampled through a gamma–centered grid of 3×3×1 of k–points. The arising dipole was corrected in all slab models.[39] To represent the wide range of possible chemical environments in NC,[30] a set of seven cavities was constructed, comprising trigonal (t) and square–planar (sq) configurations with pyridinic and/or pyrrolic nitrogens: i) 3N6 (t–tripyridinic), ii) 3N5 (t–tripyridinic), iii) 4N6 (t–tetrapyrrolic), iv) 3N6+1C (t–tripyridinic), v) 2N6 + 2C (sq–bipyridinic), vi) 1N6+3C (sq–monopyridinic), and vii) 2N5+2 N6 (sq–tetrapyridinic/ pyridinic). Single–atom catalysts were modeled by placing PtCl4 and RuCl3 at the center of the distinct NC cavities, with subsequent removal of chlorine to the solvent or gas–phase reservoir. The corresponding dechlorination paths were explored at 473 and 1073 K, and the core–level shifts of the resulting species were calculated. To predict the formation of Ru single atoms based on the ligands of the Ru species in the solvent (i.e., water or aqua regia), RuCl4(OH)3−x, x (x = 0–3) species were placed at the center of the 3×5 cavity, and the subsequent adsorption energy was calculated versus the reaction energy associated to sintering, modeled as the formation of RuO2. Gas–phase molecules were optimized in a box of 14.0×14.5×15.0 Å3. For all investigated systems, structures were relaxed using convergence criteria of 10−4 and 10−5 eV for the ionic and electronic steps, respectively. For the Gibbs free energy on the dechlorination paths, entropic contributions from molecules were considered, while for the calculation of the hydrogen Gibbs free adsorption energies at overpotential U = 0 V, entropic contributions from both molecules and slabs were accounted. The experimental and computational datasets are made available through Zenodo at https://doi.org/10.5281/zenodo.6929058 and ioChem–BD at https://doi.org/10.19061/iochem-bd-1-247, respectively. Statistical Analysis: The data analysis for all techniques that are presented and discussed in this article is reported in the Supporting Information (Table S14, Supporting Information). Supporting Information: Supporting Information is available from the Wiley Online Library or from the author. Acknowledgements: V.G. and A.R.–F. contributed equally to this work. This publication was created as part of NCCR Catalysis (180544), a National Centre of Competence in Research funded by the Swiss National Science Foundation. A.R.–F. acknowledges funding from the Generalitat de Catalunya and the European Union under Grant 2021FI_B 00109. The authors thank the Scientific Centre for Optical and Electron Microscopy at the ETH Zürich, ScopeM, and the SuperXAS beamline at PSI, for access to their facilities. The Spanish Ministry of Science and Innovation is acknowledged for financial support (RTI2018–103944–B–100 and Severo Ochoa Grant MCIN/AEI/10.13039/50110011033 CEX2019–000925–S) and the Barcelona Supercomputing Center–Mare Nostrum (BSC–RES) for providing generous computer resources. Open access funding provided by Eidgenössische Technische Hochschule Zürich. Conflict of Interest: The authors declare no conflict of interest. Data Availability Statement: The data that support the findings of this study are openly available in Zenodo at https://doi.org/10.5281/zenodo.6929058 and ioChem BD at https://doi.org/10.19061/iochem-bd-1-247, reference number 41.
Keywords
active site coordination, bimetallic systems, cooperativity effects, single-atom catalysts

Received: June 8, 2022
Revised: August 13, 2022
Published online: September 14, 2022

[1] a) A. Wang, J. Li, T. Zhang, Nat. Rev. Chem. 2018, 2, 160; b) B. Bayatsarmadi, Y. Zheng, A. Vasiliev, S. Z. Qiao, Small 2017, 13, 1700191; c) M. B. Gawande, P. Fornasiero, R. Zbořil, ACS Catal. 2020, 10, 2231.
[2] X. Li, L. Liu, X. Ren, J. Gao, Y. Huang, B. Liu, Sci. Adv. 2020, 6, eabb6833.
[3] J. Shan, C. Ye, Y. Jiang, M. Jaroniec, Y. Zheng, S. Z. Qiao, Sci. Adv. 2022, 8, eabo0762.
[4] Y. Ying, X. Luo, J. Qiao, H. Huang, Adv. Funct. Mater. 2020, 31, 2007423.
[5] B. Singh, V. Sharma, R. P. Gaikwad, P. Fornasiero, R. Zbořil, M. B. Gawande, Small 2021, 17, 2006473.
[6] A. Pedersen, J. Barrio, A. Li, R. Jervis, D. J. L. Brett, M. M. Titirici, I. E. L. Stephens, Adv. Energy Mater. 2021, 12, 2102715.
[7] X. Zhong, B. Li, Q. Wang, D. Wang, Y. Li, Nano Res. 2022, 15, 7806.
[8] Z. Liang, L. Song, M. Sun, B. Huang, Y. Du, Sci. Adv. 2021, 7, eabl4915.
[9] Y. Yang, Y. Qian, H. Li, Z. Zhang, Y. Mu, D. Mo, B. Zhou, J. Dong, W. Yan, Y. Qin, L. Fang, R. Feng, J. Zhou, P. Zhang, J. Dong, G. Yu, Y. Liu, X. Zhang, X. Fan, Sci. Adv. 2020, 6, eaba6586.
[10] J. Fu, J. Dong, R. Si, K. Sun, J. Zhang, M. Li, N. Yu, B. Zhang, M. G. Humphrey, Q. Fu, J. Huang, ACS Catal. 2021, 11, 1952.
[11] T. Cui, Y. P. Wang, T. Ye, J. Wu, Z. Chen, J. Li, Y. Lei, D. Wang, Y. Li, Angew. Chem. 2022, 61, e202115219.
[12] a) X. Liu, Y. jiao, Y. Zheng, K. Davey, S. Z. Qiao, J. Mater. Chem. A 2019, 7, 3648; b) X. Li, Y. Yang, Y. Huang, T. Zhang, B. Liu, Adv. Mater. 2019, 31, 1902031.
[13] L. Zhang, R. Si, H. Liu, N. Chen, Q. Wang, K. Adair, Z. Wang, J. Chen, Z. Song, J. Li, M. N. Banis, R. Li, T. K. Sham, M. Gu, L. M. Liu, G. A. Botton, X. Sun, Nat. Commun. 2019, 10, 4936.
[14] V. Giulimondi, S. K. Kaiser, A. J. Martin, S. Büchele, F. Krumeich, A. H. Clark, J. PérezRamírez, Small 2022, 18, 2200224.
[15] F. C. Östgaard, A. Bagger, J. Rossmeisl, Curr. Opin. Electrochem. 2022, 35, 101037.
[16] S. K. Kaiser, E. Fako, I. Surin, F. Krumeich, V. A. Kondratenko, E. V. Kondratenko, A. H. Clark, N. López, J. PérezRamírez, Nat. Nanotechnol. 2017, 16, 606.
[17] a) M. J. Richardson, J. H. Johnston, T. Borrman, Eur. J. Inorg. Chem. 2006, 2006, 2618; b) I. Povar, O. Spinu, J. Electrochem. Sci. Eng. 2016, 6, 145.
[18] X. Sun, S. R. Dawson, T. E. Parmentier, G. Malta, T. E. Davie, Q. He, L. Lu, D. J. Morgan, R. Carpey, R. Johnston, S. A. Kordant, S. J. Freckly, C. J. Kiely, G. J. Hutchings, Nat. Chem. 2020, 12, 560.
[19] W. A. Spieker, J. Liu, J. T. Miller, A. Kropf, J. R. Regalbuto, Appl. Catal. A 2002, 232, 219.
[20] S. K. Kaiser, A. H. Clark, L. Cartocci, F. Krumeich, J. PérezRamírez, Small 2021, 17, 2004599.
[21] Y. Zhou, W. Yang, W. Uteiwiabo, Y. M. Lian, X. Yin, L. Zhou, P. Yu, R. Chen, S. Sun, J. Phys. Chem. Lett. 2020, 11, 1404.
[22] E. Bus, J. A. van Bokhoven, J. Phys. Chem. C 2011, 117, 7961.
[23] A. J. Saadun, A. RuizFerrando, S. Büchele, D. Faust Akl, N. López, J. PérezRamírez, J. Catal. 2021, 404, 291.
[24] R. Lin, S. K. Kaiser, R. Hauert, J. PérezRamírez, ACS Catal. 2018, 8, 1114.
[25] a) A. Lasia, Int. J. Hydrog. Energy 2019, 44, 19484; b) B. E. Conway, L. Bai, J. Electroanal. Chem. Int. J. Electrochem. 1986, 198, 149.
[26] T. Shimagawa, A. T. GarciaEsparras, K. Takehata, Sci. Rep. 2015, 5, 13801.
[27] P. Serp, Nanoscale 2021, 13, 5985.
[28] E. Skalason, V. Tripkovic, M. E. Björketun, G. Karlberg, J. Rossmeisl, T. Bligaard, H. Jónsson, J. K. Nørskov, J. Phys. Chem. A 2010, 114, 18312.
[29] P. Lindgren, G. Kastlunger, A. A. Peterson, ACS Catal. 2019, 10, 121.
[30] N. Cheng, S. Stambula, D. Wang, M. N. Banis, J. Liu, A. Riese, B. Xiao, R. Li, T. K. Sham, L. M. Liu, G. A. Botton, X. Sun, Nat. Commun. 2016, 7, 13638.
[31] O. Muller, M. Nachttegaal, J. Just, D. LutzenkirchenHecht, R. Frahm, J. Synchrotron Radiat. 2016, 23, 260.
[32] P. M. Abdala, O. V. Safonova, G. Wiker, W. van Beek, H. Emerich, J. A. van Bokhoven, J. A. Szlachetko, M. Nachttegaal, Chimia 2012, 66, 699.
[33] A. H. Clark, J. Imbao, R. Frahm, M. Nachttegaal, J. Synchrotron Radiat. 2020, 27, 551.
[34] M. Newville, J. Synchrotron Radiat. 2001, 8, 322.
[35] a) G. Kresse, J. Furthmüller, Phys. Rev. B: Condens. Matter Mater. Phys. 1996, 54, 11169; b) G. Kresse, J. Furthmüller, Comput. Mater. Sci. 1996, 6, 15.
[36] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 1996, 77, 3865.
[37] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. 2010, 132, 154104.
[38] P. E. Blöchl, Phys. Rev. B: Condens. Matter Mater. Phys. 1994, 50, 17953.
[39] G. Makov, M. C. Payne, Phys. Rev. B: Condens. Matter Mater. Phys. 1995, 51, 4014.
[40] M. ÁlvarezMoreno, C. de Graaf, N. López, F. Maseras, J. M. Poblet, C. Bo, J. Chem. Inf. Model 2015, 55, 95.
[41] V. Giulimondi, A. RuizFerrando, A. H. Clark, S. K. Kaiser, F. Krumeich, A. J. Martin, N. López, J. PérezRamírez, Catalytic Syn- ergies in Bimetallic RuPt Single-Atom Catalysts via Speciation Control, Zenodo 2022, https://doi.org/10.5281/zenodo.6929058.
[42] Lópe Research Group, Synergistic bimetallic PtRu NC, ioChem BD, https://iochem-bd.iciq.es/browse/handle/100/39934.