

Beyond the Single-Atom Paradigm: Searching Metal Alloy Structure Space for Catalytic Synergies

A dissertation submitted by

Yicheng Wang

In partial fulfillment of requirements for the degree of

Doctor of Philosophy in Chemistry

Tufts University

August 2023

Advisor: Professor E. Charles. H. Sykes

Abstract

Single atom alloys (SAAs), composed of reactive metal alloyed in a more inert metal host, provide a reductionist approach to investigate the role of reactive dopants and the selectivity of the metal host. SAAs have proven to be promising catalysts for various industrially relevant reactions over the past decade. More recently, the theory-driven design of RhCu SAAs as highly efficient catalysts for propane dehydrogenation further demonstrates the strength of accurate modeling in the design of novel catalytic materials. The objective of this dissertation is to use the model catalysts approach to understand the activity trend of Cu-based SAAs ($X = \text{Pd}, \text{Pt}, \text{Ni}, \text{and Rh}$) in formic acid decomposition, another industrially relevant reaction. The characterization results demonstrated that these dopants form atomically dispersed sites in the Cu host, and isolated Rh sites exhibit the highest activity for C-H cleavage, which is the rate-limiting step in formic acid decomposition. This approach was also applied to other chemical processes, such as ethanol decomposition, methanol dehydrogenation, and iodomethane reaction. The obtained knowledge was further used to investigate the synergy between two different dopants in two-dopant single-atom alloys (TD-SAAs), and I demonstrated three synergistic effects using the aforementioned molecules.

Investigating the behavior of iodomethane on RhPdCu(100), I discovered the low-temperature formation of 1,3-butadiene using methyl and methylene groups as building blocks. The mechanism for this low-temperature 1,3-butadiene formation is that Rh facilitates methyl group C-H activation while Pd enables C-C coupling. Formic acid reaction on RhNiCu(100) TD-SAA shows that adding Ni/Pt as a second dopant can free up Rh sites and thus facilitate C-H activation at these Rh sites, potentially minimizing the usage of Rh. Ethanol experiments demonstrate that Rh pairs can perform C-H activation at a lower temperature compared to Ni sites

in the Cu host, which is currently the optimal SAA catalyst for dry ethanol dehydrogenation. Additionally, newly formed acetaldehyde molecules can move to Ni sites and desorb. Taken together, these results have shown that the model catalysts approach is a powerful tool to understand the role of different dopants in a well-defined single crystal and enables us to explore more complex materials for improved catalytic properties.

Acknowledgements

Back then you carried your ashes to the mountain:

would you now carry your fire into the valley

- Friedrich Nietzsche, Thus Spoke Zarathustra

A five-year graduate career is a long journey, and I am grateful for the support and guidance from numerous individuals. Firstly, I would like to thank my advisor, Prof. Charles Sykes, for sharing his passion for research with me, providing guidance in both academic and professional aspects, which made me a better scientist. I will never forget those precious moments when we were conducting LT experiments and debating for the underlying mechanism for the two-dopant single atom alloys. I feel extremely fortunate to have an advisor who placed immense trust in me, encouraged me during research setbacks, and created an open and collaborative environment that enabled my success both inside and outside the lab. Next, I would like to thank my committee members, Prof. Arthur Utz and Prof. Luke Davis. You both have always asked in-depth questions that helped me think critically about my results and motivated me to explore at a deeper level, for which I am deeply grateful. I would also like to thank my external committee member Professor Trenary.

Furthermore, I would like to thank my group members. Having a positive and collaborative environment is crucial to this journey. Firstly, I would like to thank the former Sykes lab members and postdocs for mentoring me at the beginning of my graduate school career: Dr. Amanda Larson, Dr. Dipna Patel, Dr. Alex Schilling, Dr. Laura Cramer, Dr. Tedros Balema, Dr. Paul Kress, and Dr. Ryan Hannagan. I appreciate Dipna, Tedros, and Laura for sharing their knowledge about STM, enabling me to have a quick start by standing on their shoulders. I am also grateful for the

experience of collaborating with Paul and Alex on their projects, which inspired my later projects. I want to especially thank Ryan for his patience and generosity in sharing his surface science knowledge and practical experimental skills, which set me on the right path. I also cherish the friendship with Paul, Alex, Ryan, Volkan, and Audrey. Being an international student is not easy, but your hospitality helped me fit into this group. More importantly, I want to thank Volkan and Audrey for their support during the most difficult times. Avery and Allison, I enjoyed the time discussing ideas and running experiments with you. And thanks to all the other members of the Sykes group.

Outside of the Sykes lab, I would like to thank all of my collaborators. In theory, Prof. Michail Stamatakis, Prof. Angelos Michaelides, and Prof. Philippe Sautet, as well as their students and postdocs: Konstantinos Papanikolaou, Romain Réocreux, Julia Schumann, Weitian Li, and Michael Ngan. In chemical engineering, I express my gratitude to Prof. Nathaniel Egan and Prof. Prashant Deshlahra, along with their student, Ho-Yi (Kenny) Lam. It has been an invaluable experience for me to discuss results together and has enabled me to develop an interdisciplinary mindset. I would also like to thank the members of the Utz lab (Eric High, Daniel Tinny, Laurin Joseph, and Molly Powers), as well as Larry Aulenback, for their constant readiness to help. Specifically, I appreciate Eric High for providing information about postdoc opportunities.

On a personal note, I am eternally grateful for my parents, who have always supported and loved me, enabling me to reach where I am today. I truly cherish the old times when we used to take our annual vacations in Thailand. The distance has made me realize how important family is. I also want to express my gratitude to my aunt, Wang, for her insights and encouragement that pushed me to pursue an overseas degree. Additionally, I consider myself lucky for the longstanding friendships in my life. Neng, Xu, and Jingbo, my best friends back in China, have constantly

encouraged each other throughout this journey. Jiaxing, the first friend I met abroad, I will always remember the old times when we struggled and prepared for our course finals together. Yu and Jing, I am forever grateful for your warm welcome during my first years and for introducing me to the Chinese community in our chemistry department. And Zhenyu, I have thoroughly enjoyed our inspiring, hard-core science discussions about photocatalysis.

Lastly, I want to thank my wife, Xiaoyuan, for her unconditional love, support, and understanding during this journey. Our relationship has been through tough times because of the distance and miscommunication. It is your bravery that broke down the walls and saved this relationship, for which I will always be thankful. You have helped me understand the profound meaning of *the will of the twain to create the one that is more than those who created it*. Meeting you and having you as my wife are blessings I cherish.

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Chapter 1: Introduction

1.1 Heterogeneous Catalysts

A typical chemical process involves energy transformation via breaking and/or forming new bonds. The reaction rate (probability) can be enhanced by increasing the temperature or lowering the activation barrier:

$$r = Ae^{-\frac{E_a}{kT}} \quad (1)$$

where r is the reaction rate, A is the preexponential factor, E_a is the activation barrier, k is the Boltzmann constant and T is the temperature.¹ Catalysts are materials that increase the reaction rate by lowering the height of the activation barrier (Fig.1A). Various catalytic systems are currently being investigated to meet diverse commercial demands. Catalysts are generally placed in three categories: heterogeneous catalysts, homogeneous catalysts and enzymatic catalysts. These catalysts are used for production of ~15 trillion dollars of goods annually.² Heterogeneous catalysts are often used in major industrial processes (such as the Haber-Bosch process,³ Fischer-Tropsch synthesis,⁴ and vegetable oil hardening⁵) since they are comprised of robust metal clusters or metal oxides, which can withstand a wide temperature window and are easily separated from the final products. Despite these advantages, the major downside for heterogeneous catalysts is often selectivity. Because of the coexistence of different active sites, multiple reaction pathways can result from a given chemical process.⁶ Moreover, multiple reaction pathways can produce both desired and undesired products and some of them even poison the surface and compromise catalytic performance.⁷ Thus, the major aim of catalyst research is to improve selectivity and long-term stability.^{8,9} Given the widespread nature of catalysts, even a small improvement in function can significantly benefit the economic and environmental aspects of the society.¹⁰

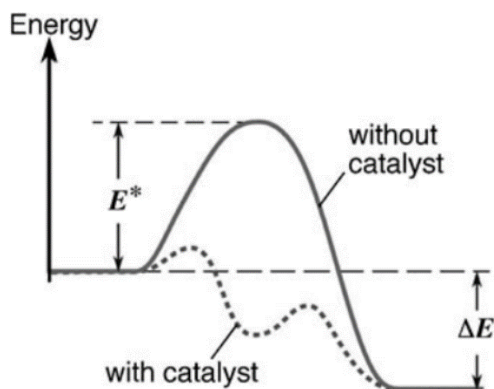


Fig 1. 1 Energy profile of a given chemical process with or without the presence of the catalyst. Adapted from Ertl.¹¹

The heart of heterogeneous catalysis studies is to reveal structure-activity relationships (also referred to as structure-dependent reaction rates).^{12,13} But structure-activity relationship assignments can be hindered by the non-uniformity of the active sites, such as different types of corners, edges and terraces that reactants or intermediates can interact with, and simultaneously by surface dynamics under reaction conditions, such as sintering and surface oxidation/reduction.^{14–18} Due to this complexity, precise characterization of active sites and their evolution under reaction conditions is still in its infancy.^{19–22} Thorough understanding of active sites both ex-situ and in-situ is therefore crucial to explore novel catalysts with high reactivity and selectivity for industrially relevant reactions.

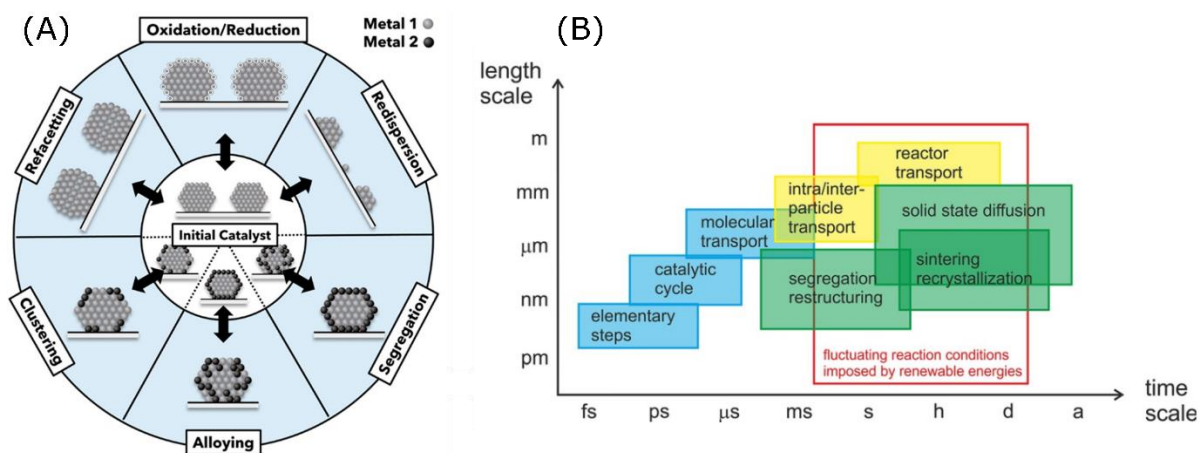


Fig 1. 2 Surface dynamics and the timescale for different chemical processes A) Possible surface restructuring pathways under reaction conditions. Adapted from Cargnello and coworkers.⁹ B) Typical time and length scales for surface dynamic processes. Adapted from Grunwaldt and coworkers.²³

1.2 Design Strategies for Heterogeneous Catalysts

Historically, the development of heterogeneous catalysts has mainly been through trial and error. A classic example is the story of establishing the Haber-Bosch process where industrialized iron catalyst was identified by vast material screening.²⁴ Current catalyst research, on the other hand, is moving toward developing methodology for rational catalyst design.^{25,26} This requires profound understanding of factors that determine the catalytic behavior of a given surface towards a chemical process. One of the key factor in understanding these processes to achieve rational catalyst design goal is the binding strength between investigated surfaces and surface species/transition states. The oldest catalyst design guideline is the Sabatier principle, which correlates thermodynamic descriptors (for instance, the binding strength of reactants and products) with the reaction rate.^{27,28} Sabatier plots normally form volcano shapes, and the ideal candidate for a given catalytic process falls at the top of the volcano (Fig. 1.3A). If a catalyst binds the reactant too weakly, the reactant will desorb before undergoing further activation steps (shown on the left of Sabatier optimum). If a catalyst binds the reactant too strongly, the reaction rate will be limited

by the surface preventing the desorption of the final products (shown on the right of the Sabatier optimum). As such, the best candidate materials are supposed to have intermediate binding strength (a classic example is the volcano plot for formic acid decomposition where Pd and Pt are considered to be ideal monometallic catalysts).^{29,30}

Another guiding principle is Brønsted-Evans-Polanyi (BEP) linear scaling.^{31,32} This principle reveals a linear relationship between the activation barrier of a given catalytic process and the surface-adsorbate bond strength (Fig.1.3 B).³³ Generally, strongly binding metal surfaces show low activation barriers while weakly binding metal surfaces show high activation barriers. Moving forward, considerable research has attempted to find effective ways of circumventing this traditional linear scaling relationship that limits further catalysts optimization.³⁴ The approach of using simple thermodynamic descriptors to understand and break the trends of catalytic material for industrially relevant reactions has been pioneered by Nørskov and coworkers.³⁵⁻³⁷ An ideal catalyst should exhibit both weak binding (the reaction rate will not be hindered by the desorption of the products) and low activation barrier. However, this is difficult to achieve as there is strong correlation between surface species binding and activation barrier.²⁶

A more recent guiding principle, the d-band model, has been proposed by Hammer and Nørskov to connect electronic structures to the binding strength between adsorbates and transition metal surfaces.^{38,39} A classic example is the electronic structure change when an H₂ molecule chemisorbs on transition metal and noble metal surfaces.³⁸ The hybridization interaction (the indicator of H-metal bond strength) between the H atom and a metal surface is determined by the d-band center of the metal surface relative to the Fermi level. The coupling of H s band and metal s/d band gives rise to bonding and antibonding states. d-bands closer to the Fermi level result in emptier antibonding states and subsequently stronger H-metal bonding. This model thus provides

further possibility towards DFT-guided catalyst screening (alloying, strain and defect engineering).^{40,41}

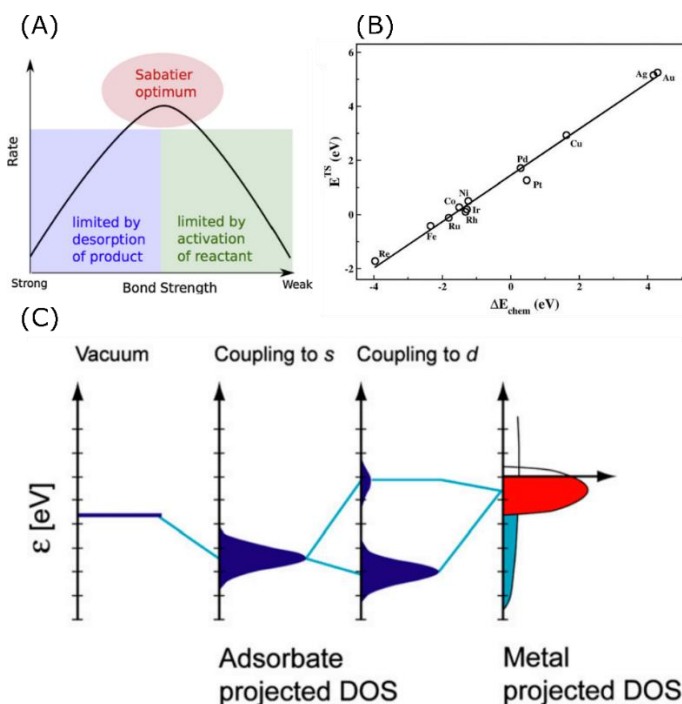


Fig 1. 3 Schematic illustration of catalysts design principles A) Sabatier volcano plot B) BEP linear scaling for CO dissociation on stepped transition metal surfaces C) A typical chemical bond formation between the valence level of the adsorbate and the s and d states of a transition metal surface. Adapted from Nørskov and coworkers.^{33,42}

1.3 A Model Catalysts Approach

As mentioned above, the key for catalytic research is to correlate atomic-scale geometric and electronic structures of the surface with the observed reactivity. However, the complex structures of nanoparticles (corners, edges and defects) obscure precise structure-activity relationship assignments.⁴³ Since the performance of heterogeneous catalysts mainly depends on reactant chemisorption on the surface, one solution is to use single crystals with well-defined facets to gain insights about the behavior of reactants and intermediates on the investigated surface.^{44–46} To minimize the impact of unwanted adsorbates, single crystal studies are mainly conducted under

ultra-high vacuum (UHV) conditions. Ultra-high vacuum is a vacuum regime wherein the chamber pressure is below 10^{-9} mbar, which enables the single crystal to remain free of impurities for an extended period of time.² This approach has provided insights in a variety of industrially relevant reactions, such as the Haber-Bosch process,⁴⁷ Fischer-Tropsch chemistry,⁴⁸ the three-way catalytic converter reaction,^{49,50} methanation,⁵¹ and methanol synthesis.⁵²

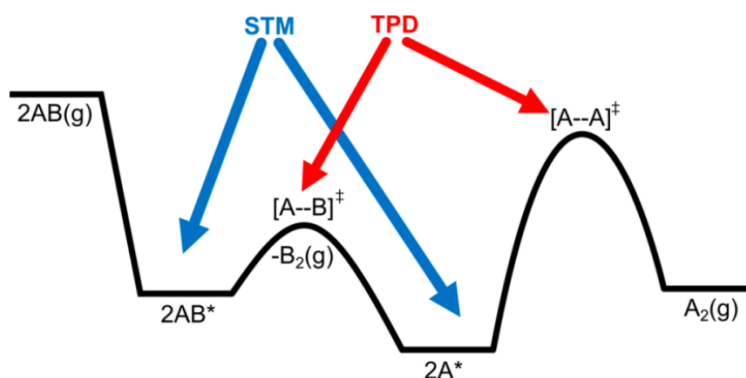


Fig 1. 4 Using the model catalyst approach to investigate a typical catalytic process which involves [A-B] bond cleavage, [A-A coupling]. STM visualizes surface bound species (AB^* and A^*) while TPD provides information about activation barrier for bond-cleavage steps (breaking A-B bond and A-A coupling). Adapted from Sykes and coworkers.⁵³

In this work, two main surface science techniques (STM and TPD) were used. For a given catalytic process, STM can be used to visualize the surface species while TPD measures the temperature (energy) required for the molecule to undergo chemical transformation (as shown in Fig. 1.4). Working in concert, STM and TPD results help to gain deeper understanding of structure-activity relationships and enable us to

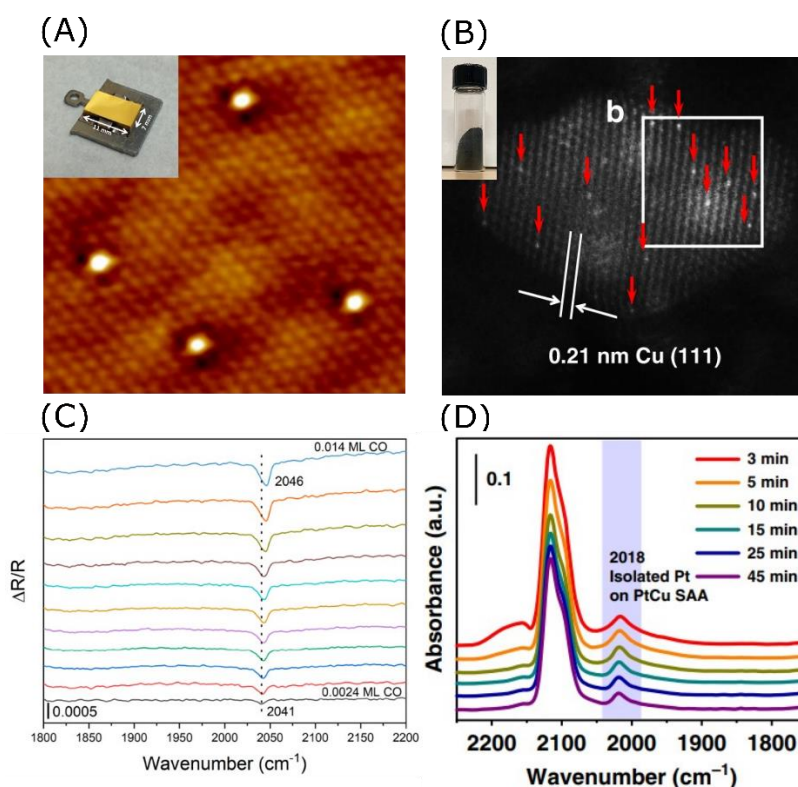


Fig 1. 5 PtCu SAA investigated under UHV and ambient pressure conditions. A) Scanning tunnelling microscopy (STM) images of PtCu (111) SAA wherein atomically dispersed Pt sites are observed. Adapted from Sykes and coworkers.⁵⁴ B) High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images of γ -Al₂O₃ supported PtCu SAA. Adapted from Gong and coworkers.⁵⁵ C) CO reflection absorption infrared spectra (RAIRS) on 0.027 ML of PtCu(111) SAA. Adapted from Trenary and coworkers.⁵⁶ D) CO diffusion reflectance infrared Fourier transform spectra (DRIFTS) on 0.1Pt10Cu/Al₂O₃. Adapted from Gong and coworkers.⁵⁵

explore novel catalysts for industrial relevant reactions. Moreover, investigating well-defined single crystals under UHV provides a reductionist approach to understand surface reaction mechanisms and sheds light on complicated nanoparticle studies under flow reactor conditions.⁵⁷ A good example is the structural investigation of PtCu SAA system. As shown in Fig. 1.4, atomically dispersed Pt sites in PtCu(111) SAA are visualized under UHV and this result is transferrable to nanoparticle studies.^{54–56} As STM and HAADF-STEM images merely provide localized images, the presence of atomically dispersed Pt in Cu host in both UHV and nanoparticle

studies were further validated by CO-RAIRS (CO atop Pt sites peak appears at $\sim 2048\text{ cm}^{-1}$) and CO-DRIFTS (linear CO at Pt single atom sites are observed at $\sim 2018\text{ cm}^{-1}$) data.

1.3 Single-Atom Alloys and Two-Dopant Single Atom Alloys

The ultimate goal for novel catalysts development is to simultaneously achieve high selectivity and activity (enable weaker binding of the surface species while maintaining low activation barrier for bond breaking).⁵⁸ Obviously, this is hard to achieve given the universal linear scaling relationship (surfaces with stronger binding are more likely to stabilize the transition states and thus give lower activation barrier). Reaching the activities that go beyond the traditional volcano limits requires increasing the complexity of catalysts (Such as strain engineering, tuning atomic structure, modifying active sites with ligands or introducing external forces).^{59–62} One effective strategy is investigating active dopants in single-atom limits that profoundly alters the activation barrier-binding strength relationship.⁶⁰ Such a strategy also suppress unwanted side reactions could poison the sites.^{63,64} Single-atom alloys (SAAs), a subclass of single atom catalysts (SACs), have been extensively studied in the past decade and show a great promise for a variety of industrially relevant reactions, such as semi-hydrogenation of acetylene, propane dehydrogenation and methanol reforming.^{55,65–72} For these materials, a trace amount of a reactive metal (such as Pd, Pt, Ni or Rh) is atomically dispersed in a more selective metal host (Cu, Ag and Au). SAAs exhibit unique properties such as high selectivity, sintering resistance, narrow d-states that resemble free-atom like states, deviation from traditional linear scaling relationships, and bifunctionally enabled by the spillover of surface species.^{66,69,73–75}

Industrially relevant reactions are generally comprised of multiple elementary steps and it is difficult to facilitate all the elementary steps using a single-atom site.^{76,77} This necessitates the investigation of strategies to further break the traditional linear scaling relationship and push the

catalysts performance beyond the top of the volcano plot.³⁴ One solution is to introduce a second dopant into SACs/SAAs to investigate the potential synergistic effects for a given reaction. Based on the distance between two different dopants, these novel systems can be categorized into dual-atom-site catalysts (DASCs, denoting two dopants that form touching dimers) or two-dopant single-atom alloys (TD-SAAs, denoting two dopants that form isolated sites).^{78,79} Specific to alloy-based catalysts, the tendency of two different dopants to form touching dimers can be predicted by theoretical calculations and their reactivity can be described by CO binding strength.⁸⁰ A previous study in our group has demonstrated a combined theoretical and model catalyst approach to identify PtCrAg(111) dual-atom alloys as a promising candidate for ethanol dehydrogenation and dehydration where PtAg(111) and CrAg(111) SAAs cannot activate ethanol molecules.⁷⁶ The observed performance of PtCrAg(111) towards ethanol decomposition can be rationalized by using two metals with vastly different behaviors (Pt is more carbophilic while Cr is more oxophilic and the PtCr heterodimers are more favorable binding sites compared to their single atom counterparts).⁸¹ However, catalysts with two different dopants forming isolated sites, which potentially exhibit different synergistic effects, have rarely been reported (Fig. 1.7). This poses the need for thorough understanding of the properties of different dopants towards multiple chemical reactions before finding a suitable probe molecule for synergistic effect investigation between two different dopant sites.

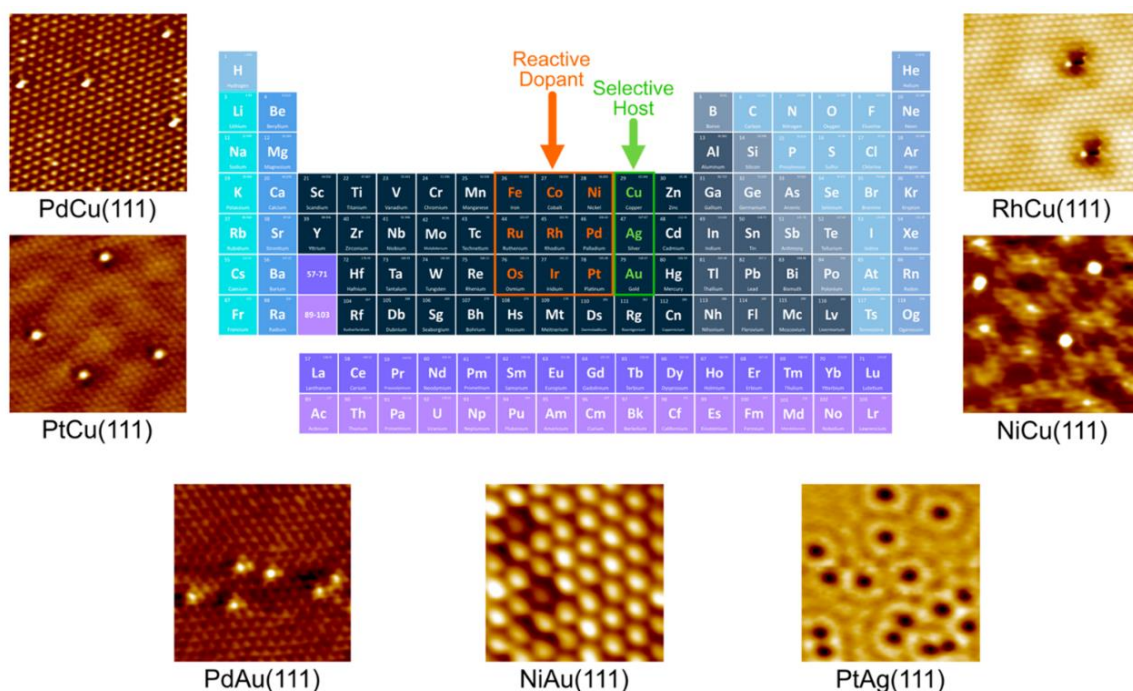


Fig 1. 6 Periodic table illustrating the concept of SAAs, wherein reactive metal sites are atomically dispersed in a more inert metal host. Isolated metal sites vary from depressions to protrusions based on the STM imaging conditions and tip states. Adapted from Sykes and coworkers.^{53,82}

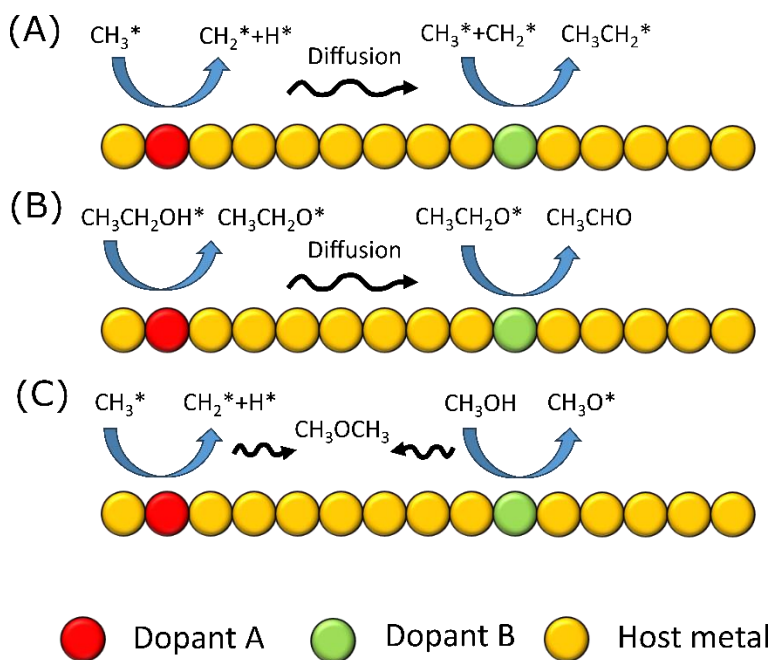


Fig 1. 7 Schematic illustration of potential synergistic effects for two isolated dopant sites which can be categorized into three general scenarios: A) dopant A catalyzes bond breaking and the surface species diffuse to dopant B to undergo coupling process. B) dopant A catalyzes O-H

activation and dopant B catalyzes C-H activation C) dopant A and B preferentially bind two different species and two intermediates diffuse to the metal host for final coupling.

1.4 Conclusion

In the work of this dissertation, I used surface science techniques to gain atomic-scale understanding of catalytic relevant SAA surfaces ($X=\text{Pd}$, Pt , Ni and Rh) and correlate the observed structures to reactivity in various probe reactions and apply this knowledge to investigate the potential synergistic effects in DAA systems. Chapter 2 provides details about experimental methodologies used to accomplish the aforementioned goal. Chapter 3 uses Rh dopants as an example to illustrate the different alloying mechanisms on low miller index Cu facets ($\text{Cu}(111)$, $\text{Cu}(100)$ and $\text{Cu}(110)$) and concludes that Rh sites are better dispersed in $\text{Cu}(100)$ and $\text{Cu}(110)$, which inspired further investigation of TD-SAAs containing Rh . Chapter 4 demonstrates a general characterization approach (using CO-TPD and CO-RAIRS) to investigate the active sites in $\text{RhCu}(100)$ SAAs. Chapter 5 and 6 introduce a combined theoretical and model catalysts approach to identify RhCu SAAs as promising formic acid dehydrogenation catalysts. Chapter 7 summarizes a general linear trend of Cu -based SAAs ($X=\text{Pd}$, Pt , Ni and Rh) towards several important model reactions (formic acid decomposition, C-H activation in iodomethane, methanol dehydrogenation and ethanol dehydrogenation). Chapter 8 uses iodomethane and toluene as probe molecules to illustrate the synergistic effect between Rh and Pd sites in $\text{RhPdCu}(100)$ DAA. Chapter 9 demonstrates transient CO movement between Rh and Ni sites that periodically opens up Rh sites and allows 0.3% $\text{RhNiCu}(100)$ DAA to exhibit similar activity as a 0.7% $\text{RhCu}(100)$ SAA. This result is exciting in that it may potentially minimize costly Rh usage in catalysts. Chapter 10 demonstrates how Rh non-touching dimers and Ni single atoms work in concert to facilitate ethanol dehydrogenation. Together, these chapters demonstrate that surface science techniques

enable us to gain deeper understanding about surface reactions on different SAA/DAA surfaces and subsequently shed light on nanoparticle studies.

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Chapter 2: Experimental Sections

2.1 Ultra-High Vacuum Chambers

Ultra-high vacuum (UHV) is defined as pressures below 10^{-9} mbar, which is important for maintaining a clean surface for model chemical process studying.¹ The work in this thesis makes use of two main chambers. The first one is the low-temperature scanning tunneling microscope (LT-STM) and the second one is the temperature programmed desorption (TPD) chamber which has a reflection absorption infrared spectroscopy (RAIRS) addition (Fig. 2.1). LT-STM and RAIRS are utilized for single-atom alloys (SAAs) and two-dopant single-atom alloys (TD-SAAs) structural characterization and intermediates for a given catalytic process visualization while TPD is utilized to study various catalytic processes to draw a complete diagram of structure-activity relationship of a given SAAs or TD-SAAs.

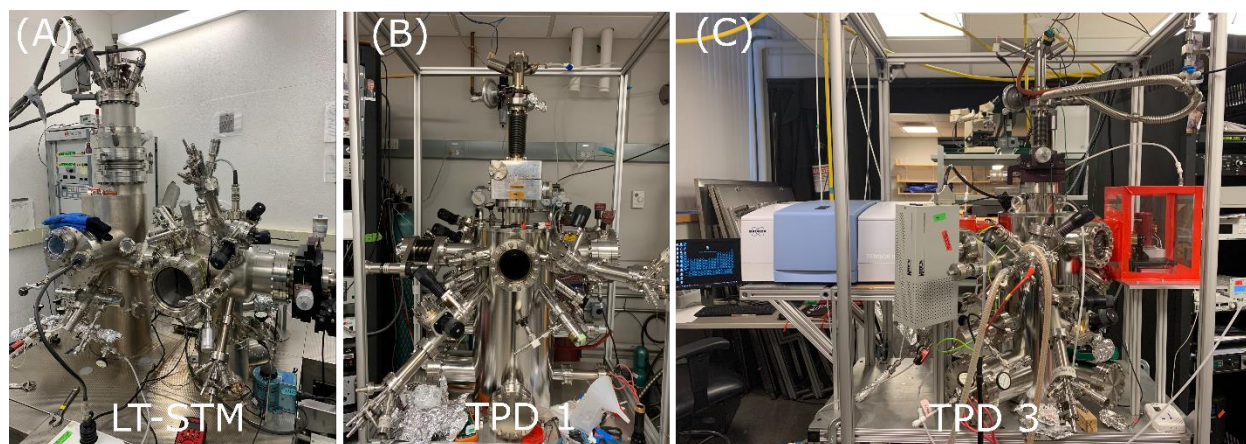


Fig 2. 1 Photos of ultra-high vacuum chamber on which experiments in this thesis were conducted. A) Low-temperature STM for SAAs and DAAs characterization and intermediates visualization. B) Temperature program desorption utilized for dry ethanol dehydrogenation on RhNiCu (111) project C) Temperature program desorption and reflection absorption infrared spectroscopy utilized for dicarbonyl observation on RhCu(100) and formic acid dehydrogenation on SAAs and TD-SAAs projects.

LT-STM is a commercial instrument from Scienta Omicron which comprised of a preparation chamber and a STM chamber. These two chambers are separated by a VAT gate valve. The preparation chamber is equipped with a hot filament gun (RBD, model 32-165) and a cold cathode gun (Scienta Omicron, ISE 5), which can perform noble gas sputtering for sample cleaning. The chamber is also

equipped with three electron bombardment evaporators (EFM 3, Scienta Omicron) for precise control of dopant metals deposition. Sample transfer is achieved by a linear motion manipulator equipped with a pyrolytic boron nitride (PBN) heater that can heat the sample from room temperature to over 1000 K. The STM chamber is equipped with a dual cryostat assembly that can be cooled to ~ 77 K or ~ 4.7 K by liquid nitrogen and liquid helium respectively. Both chambers are equipped with high precision leak valve (MDC and Lesker) for molecule dosing from their liquid or gaseous reservoir. In the STM chamber, the base pressure is below 1×10^{-11} mbar while in the preparation chamber, the base pressure is $\sim 2 \times 10^{-10}$ mbar. The low chamber pressure is maintained by a series of turbo pumps backed by rotary mechanical pumps, ion pump and titanium sublimation pump. The sample crystal is mounted on a tantalum plate by spot welding tantalum strips that hold the sample crystal.

The second chamber is the TPD and RAIRS chamber. The chamber is pumped by a turbo (HiPace 300) and titanium sublimation pump (Scienta Omicron) to maintain the chamber pressure at $\sim 5 \times 10^{-11}$ mbar. The sample is mounted onto a manipulator (PSP) with motion in the x (± 10 mm), y (± 10 mm), and z (± 50 mm) directions as well as rotation 360° (McAllister). Sample cleaning is achieved by RBD gun (model 32-165) and precise control of dopant metals deposition by three electron bombardment evaporators (EFM 3, Scienta Omicron). Sample heating is conducted by resistively heating of tantalum wire (Alfa Aesar, 0.25mm, 99.9+%) which holds the crystal in place through the four holes around the perimeter of the crystal. The Cu(100) crystal is suspended between two copper blocks that connect the cryostat that is capable of cooling to ~ 90 K. A K-type thermocouple is laser welded on the back of the crystal to allow accurate temperature reading by a process control unit (Eurotherm). The heating rate is 2 K/s. TPD measurements are made by bringing the quadrupole mass spectroscopy (Hidden Hal RC 201) within 1mm of the crystal face using a linear z-drive (MDC). The ionization energy is set at 70 eV, which is important for determining ionization cross sections used in calculations for subsequent data analysis. RAIRS experiments are made by using IR radiation generated by a Bruker Tensor II spectrometer and directed to the crystal with a grazing angle by a series of gold coated mirrors. The reflected beam is focused onto a

mercury cadmium tellurium (MCT) detector with another series of gold coated mirrors. ZnSe windows (MPF products) are used in the chamber to prevent the loss of IR signal and the external beam path is contained in a dry-air purge box (Parker, model 75-62) to prevent the water content fluctuation from external. Molecule doses are conducted by a combination of collimated and uncollimated leak valve (MDC and Lesker). All exposures are given in Langmuir ($1\text{Langmuir}=1\times 10^{-6}\text{ mbar/s}$) without further correction for ion gauge sensitivity.

2.2 Preparation of Model Surfaces

All the work in this dissertation was conducted on Cu(111), Cu(100) and Cu(110) (Princeton-Scientific, 99.999% purity, $<1^\circ$ polish). These surfaces were cleaned by repeat argon/helium bombardment and thermal annealing to a cleanliness of less than 1 defect or impurity out of 10,000 surface atoms.² Sputtering was conducted using RBD gun or cold cathode gun with a drain current of $\sim 1.5\ \mu\text{A}$ (RBD gun) or $\sim 20\ \mu\text{A}$ (cold cathode gun). For TPD experiments, the crystal was heated resistively using Ta wires and measured with k-type thermocouple welded on the back of the crystal. For STM experiments, the crystal was heated resistively by the PBN heater, and the temperature was calculated by the external temperature calibration curve. Dopant metals (Pd, Pt, Ni and Rh) were deposited by electron bombardment evaporation of a high purity Pd/Pt/Ni/Rh rod (Goodfellow, 99.9% purity) using an EFM 3 evaporator. Dopants coverage calibration was performed by counting the dopant atoms and divided by surface atoms (for Cu(111) $\sim 17.6\text{ atoms/nm}^2$, Cu(100) $\sim 15.2\text{ atoms/nm}^2$, Cu(110) $\sim 10.8\text{ atoms/nm}^2$) (STM case), or by integrating saturation CO TPD spectra (TPD case). Equation 1 gives the dopant coverage ($\theta_{\text{dopants}\%}$) by comparison of integrated CO TPD peak area from Cu ($A_{\text{CO, Cu}}$) and dopants ($A_{\text{CO, dopants}}$).

$$\theta_{\text{dopants}\%} = \frac{A_{\text{CO, dopants}}}{A_{\text{CO, dopants}} + \frac{A_{\text{CO, Cu}}}{\rho_{\text{CO, Cu}}}} \dots\dots\dots(2.1)$$

$\rho_{\text{CO, Cu}}$ is the packing density of CO on Cu surfaces. The packing density is 0.52 on Cu(111) and 0.57 on Cu(100).^{3,4}

2.3 Theory of Scanning Tunneling Microscopy

Invented in the early 1980s by Gerd Binnig and Heinrich Rohrer, STM imaging utilizes an atomic sharp tip, usually made of tungsten or Pt/Ir wire, to image a conductive surface to gain atomic-scale images of the surface.⁵ The tip is attached to a *piezodrive*, which expands or contracts under different voltage and allows the tip to move in *x*, *y*, and *z* direction. The tip can be brought within several angstroms of the sample via the coarse positioner and *z* piezo to allow wavefunction overlapping between the tip and the surface that generates tunneling current. Constant current mode is applied for the work presented in this dissertation. This mode is achieved by converting tunneling current to voltage via a current amplifier and compared to a reference value to adjust the *z* piezo. A two-dimensional array of equilibrium *z* position is obtained as the tip moves across the surface and presents an equal tunneling-current surface. The tunneling current, *I*, is proportional to the *z* position:

$$I \propto e^{-2\kappa z} \dots\dots\dots(2.2)$$

Where κ is defined as

$$\kappa^2 = \frac{2m}{\hbar^2} (eU_B - E) \dots\dots\dots(2.3)$$

Where *E* is energy of state from which tunneling occurs, $\hbar$ is the reduced Planck's constant and *eU_B* is barrier height. κ is on the order of 1Å⁻¹. In this case, even a change of 1Å leads to order of magnitude change in tunneling current. It is worth noting that STM only probes the local density of states between the tip and the surface, but the density of states is correlated with the position of atomic nucleus and therefore represents the atoms of the surface.¹ However, one of the drawback for this technique is to determine the identity of the features observed in the STM, which is a convolution of tip and surface electronic structure. In other words, the electronic state and geometry of the tip (referred to as “tip state”) can alter the way features appear on the surface. Scanning tunnelling spectroscopy can be used to deliver

more information than just topography, such as probing into vibrational states by using inelastic scanning tunneling spectroscopy.^{6,7}

2.4 Theory of Temperature Programmed Desorption

Temperature programmed desorption is a useful tool to probe the reactivity and binding strength of adsorbates on the surfaces.⁸ The surface is exposed to a certain coverage of adsorbates under cryogenic condition (normally ~85 K) and the temperature is ramped up linearly. Throughout this process, the adsorbates either desorb reversibly or undergo a chemical reaction to produce the products that will desorb. Desorbing species is measured with mass spectrometry. The desorption temperature of a certain product reveals the underlying catalytic behavior of the surface under investigation, which informs the reactivity and selectivity of the surface. The desorption rate can be described by the Polanyi-Wigner equation derived from the Arrhenius Equation and the rate of desorption as a result of linear heating:

$$R = -\frac{d\theta}{dT} = \frac{A}{\beta} \theta^n \exp\left(\frac{-E_d}{R_g T}\right) \dots\dots\dots(2.4)$$

Where R is the desorption rate, $-\frac{d\theta}{dT}$ the change of surface coverage with respect to surface temperature, θ the adsorbate coverage, n the reaction order, E_d the desorption energy, R_g the universal gas constant and T the surface temperature. By varying the coverage of the adsorbates, the information of reaction order can be obtained by analyzing the characteristic desorption peak.⁸ This is a critical method to interpret if reaction occurs consecutively on two different dopant sites for DAAs.

Besides qualitative information drawn from TPD, quantitative information can also be obtained from the TPD. For instance, the desorption energy can be extracted from the TPD data by several methods.⁸⁻¹⁰ Here, we only focus on the Redhead analysis.

The desorption energy correlates linearly with the desorption energy.⁹ For the first order desorption process, the Redhead equation is listed as follow:

$$E_d = RT_p \left(\ln \left(\frac{AT_p}{\beta} \right) - 3.46 \right) \dots\dots\dots(2.5)$$

Where E_d is the desorption energy, T_p the desorption temperature peak, A is the pre-exponential factor, β the heating rate. Typically, a value of 10^{13} Hz is assumed for the pre-exponential factor as it is the standard attempt rate for a reaction, but better estimates can be made by considering gas entropy and correlations presented by Campbell.¹¹ This method only gives an estimation of the binding energy given the presumption made by the Redhead analysis.¹²

In order to further investigate the product distribution of a given chemical reaction, various of correction factors needs to be applied.¹³ There are three major correction factors: quadrupole mass spectroscopy correction, fragmentation pattern correction and ionization cross section correction. To gain monolayer coverage from the TPD spectra, we need to integrate the raw area and divided by the product of aforementioned correction factors and compare the corrected area to a reference molecule with known packing density (CO molecules in this work). For the quadrupole correction, the mass spectroscopy sensitivity lowers with increasing m/z values. The calibration curve can be obtained by plotting a wide range of adsorbates' intensities against their respective m/z values and the absolute value of a monolayer (ML) can be acquired using this factor. For the fragmentation pattern correction, a typical TPD only tracks the most intense fragment for a given molecule, but the molecule can be ionized into multiple fragments. Correction can be conducted by finding the intensity of a given fragment (m/z) and divided by the total intensities of all fragments (m/z) that the molecules can be ionized (The fragmentation data can be found in NIST). For the ionization cross section correction, larger molecules are more likely to get ionized and for the TPD collected in this work, the incident electron energy has been set to 70 eV and the ionization cross section value for a certain molecule can be obtained in NIST.

2.5 Theory of Reflection Absorption Infrared Spectroscopy

Reflection absorption infrared spectroscopy (RAIRS) is a powerful technique for catalysts characterization and adsorbates behavior in surface science study.^{14,15} As mentioned in the experimental

part, beam is generated by a light source and splits into two beams that pass through two optical pathway and eventually reach the MCT detector. The entire beam path is enclosed in a dry-air box to prevent gas phase water level fluctuation. RAIRS measures the vibrational modes of the adsorbates as this technique is sensitive to the change of vibrational potential introduced by chemical bonding change, which enable us to use probing molecule for catalytic environment study. This can be achieved by evaluating the vibration transition probability by the following equation:

$$M_{vv'} = \int \psi(v)\mu\psi(v')d\tau \dots\dots\dots(2.6)$$

where $\psi(v)$ is the initial state vibrational wavefunction, $\psi(v')$ the final state wavefunction and μ is the dipole moment. Transition is allowed only if one of components (x, y, z) is nonzero, where z is considered to be perpendicular to the surface. Group theory and symmetry arguments can be used to determine if a given vibrational mode is IR active or no.¹⁶ Also, only the mode with a perpendicular component is visible since the parallel component is canceled by the image dipole in the metal surface.¹ Molecular adsorption orientation information can be drawn by analyzing the IR peak intensity.¹⁷ The absorption spectrum is expressed by comparing the relative change of reflectivity between clean surface and adsorbate coverage surface:

$$\frac{\Delta R(v)}{R_0(v)} = \frac{R_0(v)-R(v)}{R_0(v)} \dots\dots\dots(2.7)$$

Where $R_0(v)$ is the reflectivity of the clean surface, $R(v)$ is the reflectivity of adsorbate covered surface. And reflectivity difference can somehow reflect the adsorbates coverage ($\Delta R(v)$). However, strong interactions between adsorbates need to be considered since it may cause deviation of the linear proportion between IR peak and the coverage of adsorbates.¹⁴ The use of RAIRS enable us to study the surface intermediates in a given catalytic process and help us to understand the reaction mechanisms.¹⁵

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Chapter 3: Surface Facet Dependence of Competing Alloying Mechanisms

This chapter was modified from the following original publication: Wang, Y.; Papanikolaou, K. G.; Hannagan, R. T.; Patel, D. A.; Balema, T. A.; Cramer, L. A.; Kress, P. L.; Stamatakis, M.; Sykes, E. C. H. Surface Facet Dependence of Competing Alloying Mechanisms. *J. Chem. Phys.* **2020**, *153* (24).

3.1 Abstract

Metal alloys are ubiquitous in many branches of heterogeneous catalysis and it is now fairly well established that the local atomic structure of an alloy can have a profound influence on its chemical reactivity. While these effects can be difficult to probe in nanoparticle catalysts, model studies using well defined single crystal surfaces alloyed with dopants enable these structure-function correlations to be drawn. The first step in this approach involves understanding the alloying mechanism and the type of ensembles formed. In this study, we examined the atomic-structure of RhCu single-atom alloys formed in Cu(111), Cu(100) and Cu(110) surfaces. Our results show a striking difference between Rh atom alloying in Cu(111) versus the more open Cu(100) and Cu(110) surface facets. Unlike Cu(111) on which Rh atoms preferentially place-exchange with Cu atoms in the local regions above step edges leaving the majority of the Cu surface free of Rh, highly dispersed, homogeneous alloys are formed in the Cu(100) and (110) surfaces. These dramatically different alloying mechanisms are understood by quantifying the energetic barriers for atomic hopping, exchange, swapping and vacancy filling events for Rh atoms on different Cu surfaces through theoretical calculations. Density functional theory results indicate that the observed differences in alloying mechanism can be attributed to a faster hopping rate, relatively high atomic exchange barriers and stronger binding Rh atoms in the vicinity of step

edges on Cu(111) compared to Cu(110) and Cu(100). These model systems will serve as useful platforms for examining structure sensitive chemistry on single-atom alloys.

3.2 Introduction

Single-atom alloys (SAAs) are an emerging class of heterogeneous catalyst, in which trace amounts of a reactive metal dopant exists in the form of isolated atoms in a less reactive but more selective host metal.^{1–16} The unique electronic and geometric properties of these SAA catalysts give rise to enhanced selectivity and stability for many reactions, deviations from “traditional” transition metal scaling relationships that limit catalyst performance, free-atom like d-states, and resistance to common catalyst poisons.^{7,15,17,18} As such, there has been widespread interest in these new materials in both the surface science and heterogeneous catalysis communities. However, the vast majority of the model system research has been conducted on (111) terminated surfaces, as (111) is the most commonly exposed facet of face-centred cubic (fcc) metal nanoparticles. To date, PtCu(111), PdCu(111), PdAu(111), PtAg(111), NiCu(111), NiAu(111), RhCu(111) and PdAg(111) SAA model catalysts have been reported.^{1,19–25} Despite the thorough study of (111) terminated SAA surfaces, little research has been done on more under-coordinated (100) and (110) surfaces.

Structure sensitivity plays an important role in catalysis with the classic example of NH₃ synthesis on body-centred cubic (bcc) Fe(111), Fe(100) and Fe(110), where the more open/undercoordinated Fe(111) surface exhibits the highest dissociative N₂ sticking coefficient and is responsible for the overall activity of the industrial catalyst.^{13,14} In terms of hydrocarbon chemistry, Zaera and coworkers examined the behavior of iodomethane and iodoethane on Cu(111), Cu(100) and Cu(110) by using temperature-programmed desorption (TPD). Their results revealed that methylene coupling and β -hydride elimination are structure sensitive, while α -hydride elimination is not. At high methyl iodide coverage, ethane desorption was 40 K lower for

Cu(110) compared to Cu(100) and Cu(111), which represents approximately two orders of magnitude difference in the reaction rates.²⁸ Specific to SAA catalysts, Gao and coworkers investigated higher alcohol synthesis on RhCu(111) and RhCu(100) SAA surfaces using Density Functional Theory (DFT). The energetic landscapes indicated that methanol formation is favored on RhCu(111) while ethanol may be the preferred product on RhCu(100).²⁹ Jiang and coworkers experimentally studied the semi-hydrogenation of phenylacetylene on PdCu SAA nanosheets and nanocubes with predominantly (111) and (100) surfaces exposed, respectively.³⁰ The authors concluded that while hydrogen spillover from the isolated Pd atoms to Cu occurred on both Cu surface facets, the H atoms that had spilled over were only active for phenylacetylene semi-hydrogenation on Cu(100). The lower barrier for addition of the first H atom and the stronger phenylacetylene adsorption on Cu(100) vs. Cu(111) were proposed as the reasons for the higher observed activity of the PdCu(100) based catalyst. However, such nanoparticle studies cannot completely rule out the contribution from minor exposed facets or adsorbate-induced reconstructions. Examining single crystals under ultra-high vacuum (UHV), as we do in this paper, enables us to study the structure and alloying mechanism in well-defined facets with atomic-scale imaging resolution.

Theory work by Stamatakis and coworkers has shown that SAA preparation is thermodynamically feasible on the (100) surface, as isolated dopant atoms have a positive aggregation energy, thereby remaining dispersed as isolated sites rather than agglomerating into dopant clusters.³¹ They also reported that the binding of CO is similar on SAAs formed in the (111) and (100) facets of Cu. For instance, the CO binding energies for RhCu(111) and RhCu(100) are -1.71 eV and -1.75 eV, respectively. Therefore, we may expect similar reactivity on (100) and (111) surfaces, as the adsorption strength of small molecules often scales with reactivity.

Modelling of CO₂, N₂ and NO dissociation was conducted to probe the structure-sensitivity of SAAs in Cu(100) and Cu(111) using DFT. These reactions exhibit similar structure-sensitivity on SAA and coinage metal surfaces, which is considerably less than platinum group metals (PGM) surfaces. For example, the dissociation barrier for CO₂ on RhCu(100) and RhCu(111) are 0.74 eV and 0.63 eV, respectively. This small degree of structure sensitivity can be attributed to slight differences in the electronic state of the Rh atom which arises from the different coordination environments of Rh in the two surfaces.³² However, direct experimental evidence for SAA structure sensitivity on well-defined facets remains very limited. The first step towards elucidating the aforementioned effects involves the construction of SAA model catalysts on more open surfaces, and key to that is a thorough understanding of alloy mechanisms of dopant atoms on these surface facets.

In this paper, we present a combined scanning tunnelling microscopy (STM) and DFT study of the strikingly different alloying mechanisms of Rh in different facets of Cu. We find that Rh forms dense brims in the Cu(111) surface, whereas in the more open (110) and (100) surfaces Rh alloys uniformly across the terraces. Our calculations reveal that this occurs because of a delicate balance between diffusion and place exchange barriers at different surface sites on the different surface facets. Overall, this work highlights the importance of the surface structure of the host material on alloying behavior, and these systems serve as well-defined model catalyst surfaces with which to interrogate the effect of structure sensitivity on SAA reactivity.

3.3 Experimental Methods

LT-STM experiments were conducted in UHV with a base pressure of $\sim 1 \times 10^{-11}$ mbar using an Omicron LT-STM. Sample cleaning was performed in the adjacent preparation chamber with base pressure less than 2×10^{-10} mbar. Repeated cycles of Ar (Airgas 99.99%) ion

bombardment and thermal annealing to 750 K were used for cleaning the Cu(111), Cu(100) and Cu(110) single crystals. Rh deposition was performed with a Rh rod (Goodfellow 99.9%) in a flux monitored EFM 3 (Scienta Omicron) electron beam evaporator while the Cu sample temperature was held at 380 K during deposition of a constant flux of $\sim 0.01 \text{ ML} \cdot \text{min}^{-1}$. The STM images were acquired after cryogenically cooling the STM stage to 80 K.

DFT calculations were performed using the Vienna *ab initio* simulation package (VASP).^{33,34} The electron-ion interactions were treated by the projector augmented method (PAW),³⁵ and the wave functions of the valence electrons were expanded by plane waves with a kinetic energy cutoff of 400 eV. To describe the exchange and correlation effects, we employed the Perdew-Burke-Ernzerhof (PBE) functional.³⁶ Using this functional, we computed a lattice constant for Cu of 3.63 Å, which is in excellent agreement with previous works and in reasonable agreement with the experimental value of 3.59 Å.³⁷ The electronic wave function was converged to 10^{-7} eV and the Hellman–Feynman forces were relaxed to less than $10^{-2} \text{ eV } \text{\AA}^{-1}$. The low-index SAA Rh/Cu(111), Rh/Cu(100), Rh/Cu(110) and Rh/Cu(211) surfaces were modeled by a 4-layer $p(4 \times 4)$, 4-layer $p(4 \times 4)$, 8-layer $p(4 \times 4)$ and a 4-layer $p(4 \times 1)$ cell, respectively (see Appendix). Some (110) surfaces, like Au(110) and Pt(110), undergo a transition towards the energetically favored (1×2) missing row reconstruction geometry.^{38–40} Cu(110), however, is not known to be prone to such a reconstruction, and therefore our DFT calculations focus on an ideal (1×1) geometry.⁴¹ The bottom two layers of the (111), (100) and (211) surfaces were fixed at the PBE-computed Cu lattice constant, while the top two layers and any Rh or Cu adatom thereon, were allowed to relax during geometry optimization. For the (110) surface, the bottom four layers were fixed at the Cu lattice constant and the top four ones were allowed to relax. The following Monkhorst–Pack k-point meshes were used to sample the Brillouin zones of the considered

surfaces: $4 \times 4 \times 1$ k-point mesh for the (111) surface, $4 \times 4 \times 1$ for (100), $3 \times 4 \times 1$ for (110) and $5 \times 4 \times 1$ for the (211) surface.⁴² Finally, transition states were identified with the dimer method,⁴³ and vibrational analyses were performed in order to verify that each of the located transition states was a 1st order saddle point in the potential energy surface (PES). The adsorption energy of an Rh atom on a Cu surface and the reported activation barriers were calculated by eqns (1) and (2), respectively.

$$E_{ads}(\text{Rh}) = E_{tot}^{Rh+Slab} - E_{tot}^{Slab} - E_{tot}^{Rh(g)}, \quad (1)$$

$$E_a = E_{TS} - E_{IS}, \quad (2)$$

where $E_{tot}^{Rh+Slab}$, E_{tot}^{Slab} and $E_{tot}^{Rh(g)}$ are the total DFT energies for a Cu slab with a Rh adatom thereon, for a clean Cu slab, and for a Rh atom in the gas phase, respectively. E_{TS} and E_{IS} are the DFT-computed energies for the transition and initial states, respectively.

3.4 Results and Discussions

The RhCu alloys were prepared by depositing 0.01 monolayers (MLs) of Rh on Cu(111), Cu(100) and Cu(110) single crystals at a substrate temperature of 380 K. As shown in Fig. 1A, the isolated Rh atoms appear as depressions in the Cu(111) surface. These Rh atoms are densely packed into the regions above step edges, suggesting a preferred alloying mechanism of Rh diffusion to step edges where place exchange with Cu atoms in the upper terraces occurs, leading to the formation of an alloy brim above the step edges. This alloying mechanism has been observed for many other alloys formed by depositing dopant metals onto (111) surfaces.^{19,23,44} In sharp

contrast to the (111) facet, our results on the Cu(110) and (100) facets (Fig 3.1B and 3.1D respectively) reveal that under identical alloying conditions, unlike the (111) surface, Rh atoms are dispersed homogeneously in the Cu(100) and (110) terraces. Importantly, we did not observe any of the dense alloy brims in the regions above step edges for the RhCu alloys in the more open (100) and (110) surfaces. These results indicate that Rh can form SAAs in all three facets of Cu, in agreement with previous DFT studies which have revealed an enthalpic preference of Rh atoms to exist as isolated species in Cu(111) and Cu(100) surfaces.^{17,31}

The distribution of Rh atoms in the different Cu surface facets suggests that different alloying mechanisms are at play on Cu(111) vs. Cu(100) and (110). Place exchange at step edges appears to be favored for RhCu(111) vs. exchange directly into the terraces for RhCu(100) and RhCu(110). While this agrees with the mechanisms previously discussed in the literature, there has never been a direct comparison of alloying the same element into different surface facets under identical alloying conditions.

In order to elucidate the disparate alloying behavior exhibited by RhCu(111) and the other two low-index facets investigated (Fig 3.1), we performed periodic DFT calculations. These calculations were aimed at elucidating the mechanism by which Rh is incorporated into the Cu host metal, and also the mechanism by which Rh adatoms diffuse over the Cu(111), Cu(100) and Cu(110) surfaces. In terms of the diffusion of Rh adatoms, one may simply assume that this process occurs *via* site-to-site hops, with the Rh adatom sliding over a corrugated plane. Indeed, this is the simplest and most intuitive diffusion mechanism. However, surface science and theoretical studies have demonstrated that adatom diffusion over single crystals can be far more complex than that, thereby highlighting that other types of diffusion, besides *hopping*, merit consideration.^{45–47} For example, using an atom probe, Wrigley and Ehrlich argued that the diffusion of a W adatom across

the rows of Ir(110) occurs *via* a concerted *atomic exchange* mechanism.⁴⁸ Under these circumstances, the W adatom, which is initially adsorbed on a hollow site, displaces a neighboring

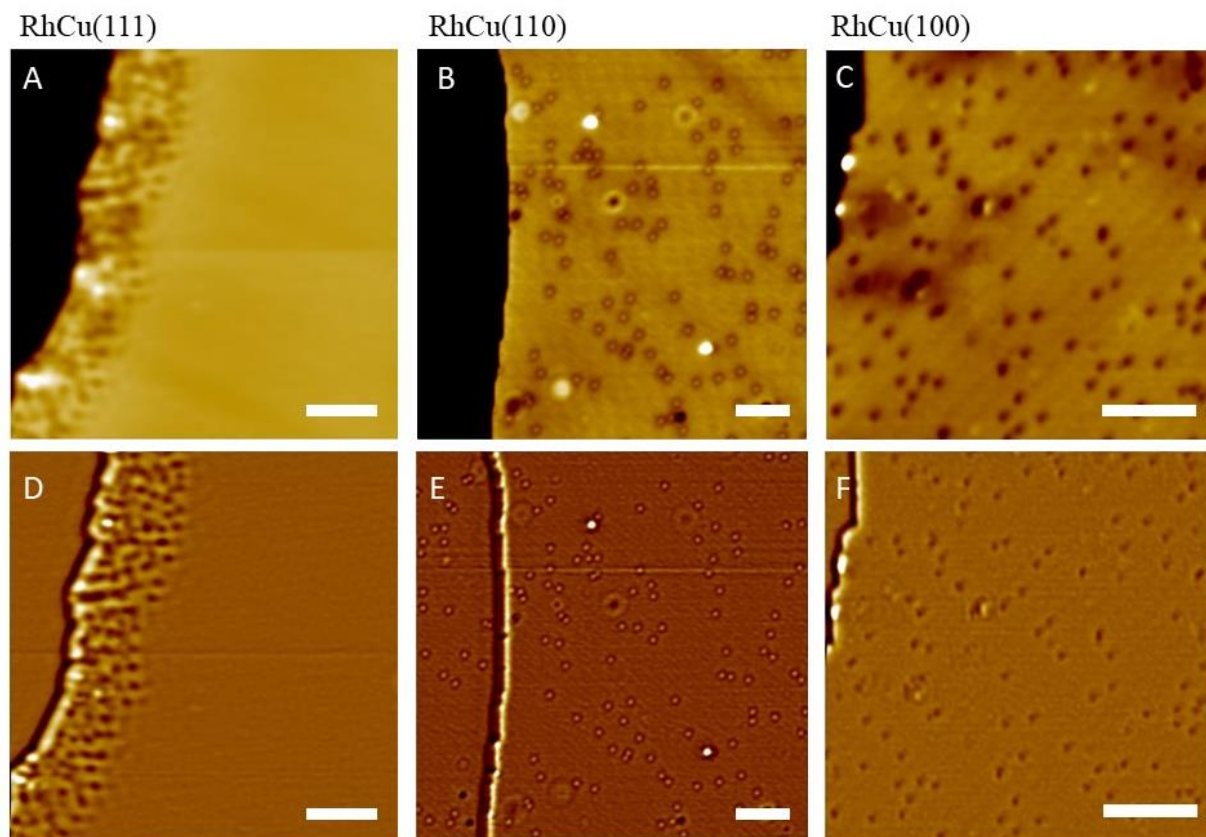


Fig 3. 1 STM images of 0.01 ML RhCu SAs prepared in the (111), (110) and (100) facets of Cu. (A) RhCu (111) in which dense brims of Rh appear in the regions above step edges and the Rh atoms appear as depressions. (B) RhCu (100) in which isolated Rh atoms can be seen alloyed throughout the terrace with no dense brims at the step edges. (C) RhCu(110) in which isolated Rh atoms are also seen alloyed throughout the terraces. (D-F) Derivative STM images corresponding to images (A-C) that highlight the Rh alloying sites in the different Cu facets. Typical imaging conditions: 300 mV and 300 pA. The scale bars are 5 nm. All SAA surfaces were prepared via Rh deposition on Cu held at 380 K followed by cooling to 80 K for STM imaging.

Ir atom from a row of the (110) surface, and the latter becomes the “new adatom”. This atomic exchange mechanism has been observed and, often, corroborated as the dominant adatom diffusion mechanism in a number of field-ion microscopy and theoretical studies, which focus on low-index facets with an open structure (e.g. (110), (100) and (001)).^{49–54} Another possible diffusion mechanism is diffusion *via* an existing vacancy in the host material. This is the so-called *vacancy-*

mediated exchange diffusion,⁵⁵ which has been shown to be pronounced on more densely packed surfaces like Cu(111).⁵⁵

With this in mind, we used DFT to study the following surface processes on Cu(111), Cu(100) and Cu(110) surface facets: (i) hopping of a Rh adatom from site-to-site on the surface; (ii) atomic exchange between a Rh adatom and a Cu surface atom; (iii) integration of a Rh adatom into the Cu surface *via* a vacancy; and (iv) atomic swapping between Rh and Cu surface atoms (Fig 3.2). Rh diffusion *via* hopping involves “jumps” of a Rh adatom from a hollow site to another hollow site *via* a twofold bridge site, which is the 1st order saddle point in the PES (Fig 3.2A). The hollow sites correspond to fourfold sites on Cu(110) and Cu(100), and threefold sites (either fcc or hcp) on Cu(111) – (Fig. 2A). Our results suggest that simple Rh adatom hopping is significantly more facile on the Cu(111) surface ($E_{a,\text{fcc} \rightarrow \text{hcp}} = 0.23$ eV or $E_{a,\text{hcp} \rightarrow \text{fcc}} = 0.06$ eV) surface than on Cu(100) – ($E_{a,(100)} = 0.90$ eV) and Cu(110) – ($E_{a,(110)} = 0.37$ eV). The same trend has been reported for the self-diffusion of Cu over these three low-index surfaces by Nørskov and co-workers,⁵⁶ and the fast adatom hopping over Cu(111) is in line with the work of Anderson et al. on a PbCu(111) system.⁵⁵ Importantly, we note that the reported hopping barrier for Cu(110) in Fig 3.2A involves Rh hopping along the rows of the Cu(110) surface. We have also computed the corresponding barrier for Rh hopping across these rows, and we have found a large kinetic barrier of 1.82 eV (see Appendix). This high value implies that diffusion across the rows will be highly unlikely *via* hopping, in qualitative agreement with previous works.^{48,54,56}

Atomic diffusion on either pure metal or alloy surfaces often takes place *via* a concerted mechanism, in which more than one atom participates in the diffusion event.^{47,57–59} To this end, we continue our investigations by computing the energy barriers for a concerted atomic exchange between a Rh adatom and a Cu atom (Fig 3.2B). The atomic exchange proceeds in a similar manner

on the three Cu surfaces: the Rh adatom is initially adsorbed on a hollow site; in the transition state a Cu atom is “lifted-up” by the adatom and a “Rh-Cu dimer” is formed above a surface vacancy; in the final state Rh is integrated into the Cu host surface, while the lifted-up Cu atom ends up as an adatom over a mixed hollow site (Fig 3.2B). Contrary to the previously discussed hop diffusion (Fig 3.2A), we find that atomic exchange events are much more easily activated on the open Cu(100) – ($E_{a,(100)} = 0.71$ eV) and Cu(110) – ($E_{a,(110)} = 0.27$ eV) surfaces as compared to Cu(111), where $E_{a,(111)} = 1.04$ eV. Consequently, the computed barriers in Fig 3.2A and Fig 3.2B indicate that the predominant alloying mechanism toward the SAA phase will be different among the three low-index surfaces, and begins to explain the observed disparate distribution of Rh atoms over these three surfaces (Fig. 1). In particular, our results in Fig 3.2A and 3.2B demonstrate that Rh atoms which land on Cu(111) will be able to diffuse *via* hopping across the surface before they experience the appropriate alloying sites (e.g. step edges) that enables them to integrate into the Cu host surface. By contrast, Rh integration *via* direct atomic exchange into the terraces of the Cu host will be more favorable on Cu(100) and Cu(110) than hopping. This allows Rh adatoms to incorporate easily and directly in the terraces, and therefore form a uniform and well-dispersed SAA phase over the whole single crystal surface (Fig 3.1).

Another mechanism by which Rh can be incorporated in the host material is *via* an existing vacancy on the Cu host surface (Fig 3.2C). To investigate this type of mechanism, we first computed the energy cost for the creation of a vacancy on the Cu crystal (Fig 3.2C and Fig 3.3A), and then the energy cost for the filling of this vacancy by a Rh adatom. The computed vacancy formation barriers are 1.83 eV for Cu(111), 1.31 eV for Cu(100) and 1.10 eV for Cu(110) – (Fig 3.2C). According to this result, the more open a surface is, the higher its tendency to form a vacancy. Moreover, we calculated the vacancy formation barrier on the edge of a (211) step (see

Fig 3.3A), which serves as a model of the region around step edges of the Cu crystals seen in Fig 3. 1. The computed vacancy formation barrier at this site, for a clean Cu(211) surface without the presence of a Rh adatom, is 1.36 eV.

It is noteworthy that the kinetic barrier for vacancy filling (i.e. the 2nd barrier from left to right in the PES of Fig. 2C) is 1.10 eV for Cu(100) and 0.46 eV for Cu(110). These values are ca. 0.40 eV and 0.20 eV larger than the corresponding atomic exchange barriers, respectively, and merely reflect the difficulty of Rh hop diffusion over these Cu surface facets (Fig 3.2A). Consequently, the incorporation of Rh on these surfaces will be more probable *via* an atomic exchange mechanism even in the presence of vacancies on the host material. In contrast, the vacancy filling barrier on Cu(111) – ($E_{a,(111)} = 0.55$ eV) is almost half of the corresponding atomic exchange barrier ($E_{a,(111)} = 1.04$ eV). Therefore, we conjecture that the high concentration of Rh atoms in the vicinity of step edges of Cu(111) – (see Fig. 1) may be explained by the following four factors: (i) the fast Rh adatom hopping on Cu(111) – (Fig 3.2A); (ii) the higher susceptibility of the region near the step towards the formation of vacancies as compared to the densely packed (111) plane (Fig 3.3A); (iii) the relatively easy integration of a Rh adatom into an existing vacancy on the Cu(111) surface (Fig 3.2C) and (iv) the high stability of a Rh atom embedded in the Cu(111) host surface (see the first inset in Fig 3.2B and 3.2C).

Furthermore, the significantly stronger binding of Rh in the vicinity of step edges as compared to the threefold sites of Cu(111) – ($E(\text{Rh})_{\text{ads,(211)}} - E(\text{Rh})_{\text{ads,(111)}} = -0.96$ eV) will be the driving force for Rh migration to the step edges of Cu(111) after deposition (Fig 3.3A). This migration is expected to occur through simple and fast hop diffusion. Accordingly, the incorporation of Rh adatoms on Cu(111) will probably occur *via* existing or created vacancies, which are more likely to occur in the vicinity of the step edges (Fig 3.3A). This will lead to a

kinetically trapped state, whereby the majority of Rh atoms are incorporated in the region above the step edge (Fig 3.1).^{19,23,24,44} Depending on the conditions, the system could remain trapped in this metastable state for a considerable amount of time,⁵⁵ before reaching equilibrium—namely a state where entropy will be the driving force towards a well-dispersed SAA phase.^{16–18,23,24,31,44,60} In contrast, on Cu(100), the atomic exchange events exhibit a relatively small barrier of 0.71 eV and given the fact that an embedded Rh atom in the Cu host surface exhibits high stability (see Fig 3.2B), we speculate that the integration of Rh adatoms into the Cu(100) surface will occur at or near their “point of landing”, thereby leading to the formation of a uniformly dispersed SAA surface as seen in Fig. 3.1.

The last type of surface event we studied involves the atomic swapping of an embedded Rh atom and a Cu surface atom (Fig 3.2D) that leads to the diffusion of the Rh atom in the Cu surface. We find that atomic swapping is not a concerted event (i.e. the initial and final states are not separated by just one transition state) but rather occurs in two steps. The first step involves the displacement of a Cu atom out of the Cu host surface by a neighboring Rh atom; in the second step the displaced Cu “diffuses back” and fills the created vacancy (Fig 3.2D). Our calculations reveal a very large barrier for the first step on RhCu(111) – ($E_{a,(111)} = 2.20$ eV), while the corresponding kinetic barriers for the first step on RhCu(100) and RhCu(110) surfaces are moderate ($E_{a,(100)} = 1.41$ eV and $E_{a,(110)} = 1.32$ eV) – (Fig 3.2D). In this way, atomic swapping and atomic exchange between an embedded Rh atom and a Cu adatom will be equally likely events on RhCu(100), but they will be activated at relatively high temperatures ($E_a > 1.40$ eV for both events) – (see Fig 3.2B and 3.2D). In contrast, our results predict that the dominant diffusion event for RhCu(110) will be the atomic exchange (Fig 3.2B and 3.2D).

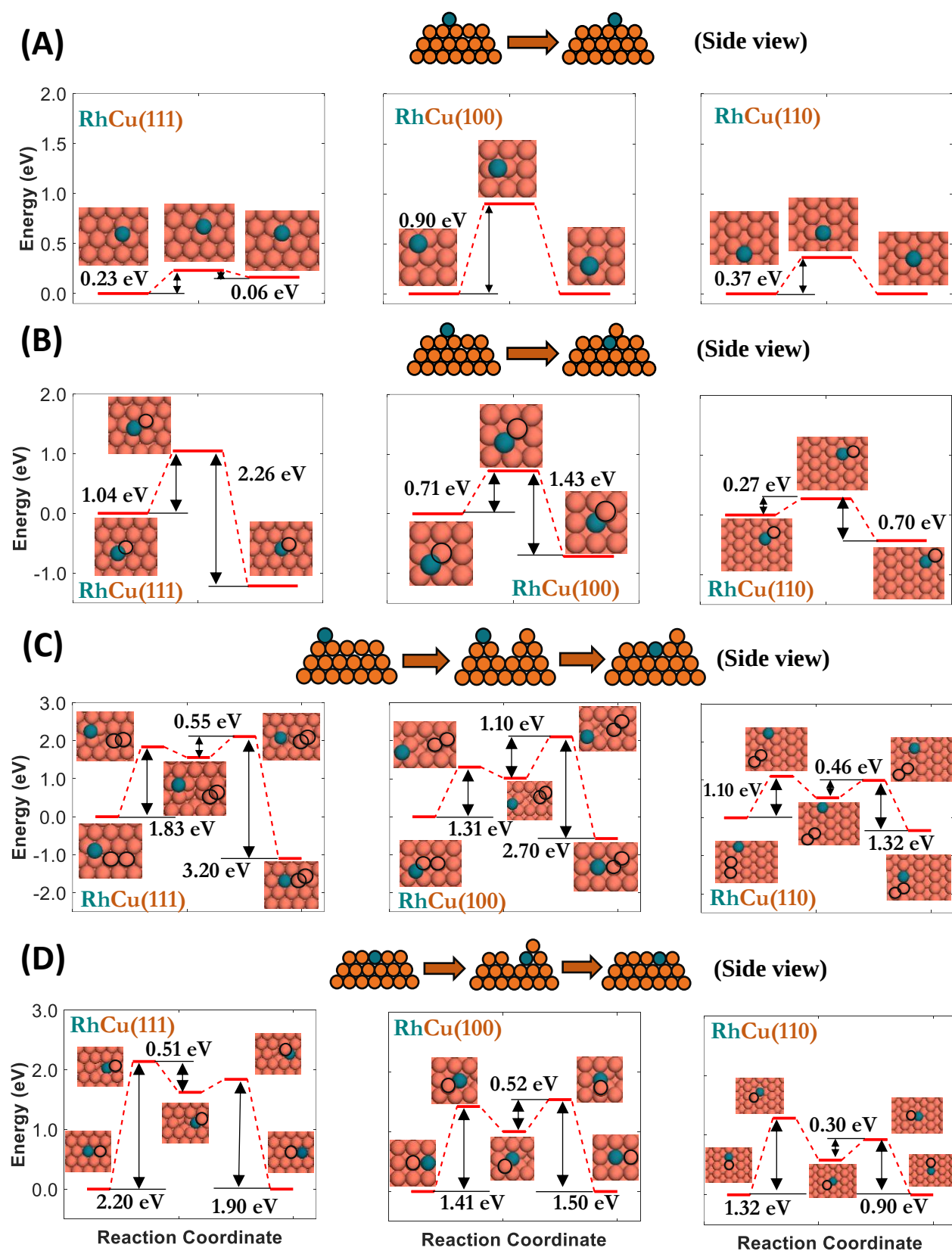


Fig 3. 2 DFT-computed kinetic barriers for (A) Rh hop diffusion; (B) atomic exchange; (C) Rh integration via a vacancy and (D) atomic swapping for the 3 investigated low-index surfaces. A side view representation of the different alloying steps is given above each panel, where we only show states that correspond to a minimum in the PES. Cu and Rh atoms are shown in orange and teal, respectively. Cu atoms that participate in an event are annotated by black circles.

Finally, we elucidated the distinctive alloying behavior of the three surfaces further by calculating the approximate rates of the different surface processes. According to the computed kinetic barriers, and by using the Eyring equation⁶¹ with a prefactor of $k_B T/h$ (k_B and h are Boltzmann's and Planck's constants, respectively), we computed the approximate rates for the investigated processes within the temperature range: 50°C – 250°C (Fig 3.3C-F). Since Rh incorporation and atomic swapping are not elementary processes, the reported rates are those for their first steps, which exhibit the largest kinetic barriers. Our principal observation is that atomic exchange, vacancy formation and atomic swapping are faster on Cu(100) and Cu(110) than on Cu(111) by at least five orders of magnitude at 110°C (Fig 3.3C-F), while the opposite holds true for hop based diffusion. This observation further clarifies the disparate behavior of the three facets in relation to the diffusion and incorporation of Rh atoms, and suggests that indeed the integration of Rh will occur *via* different mechanisms on the three surface facets.

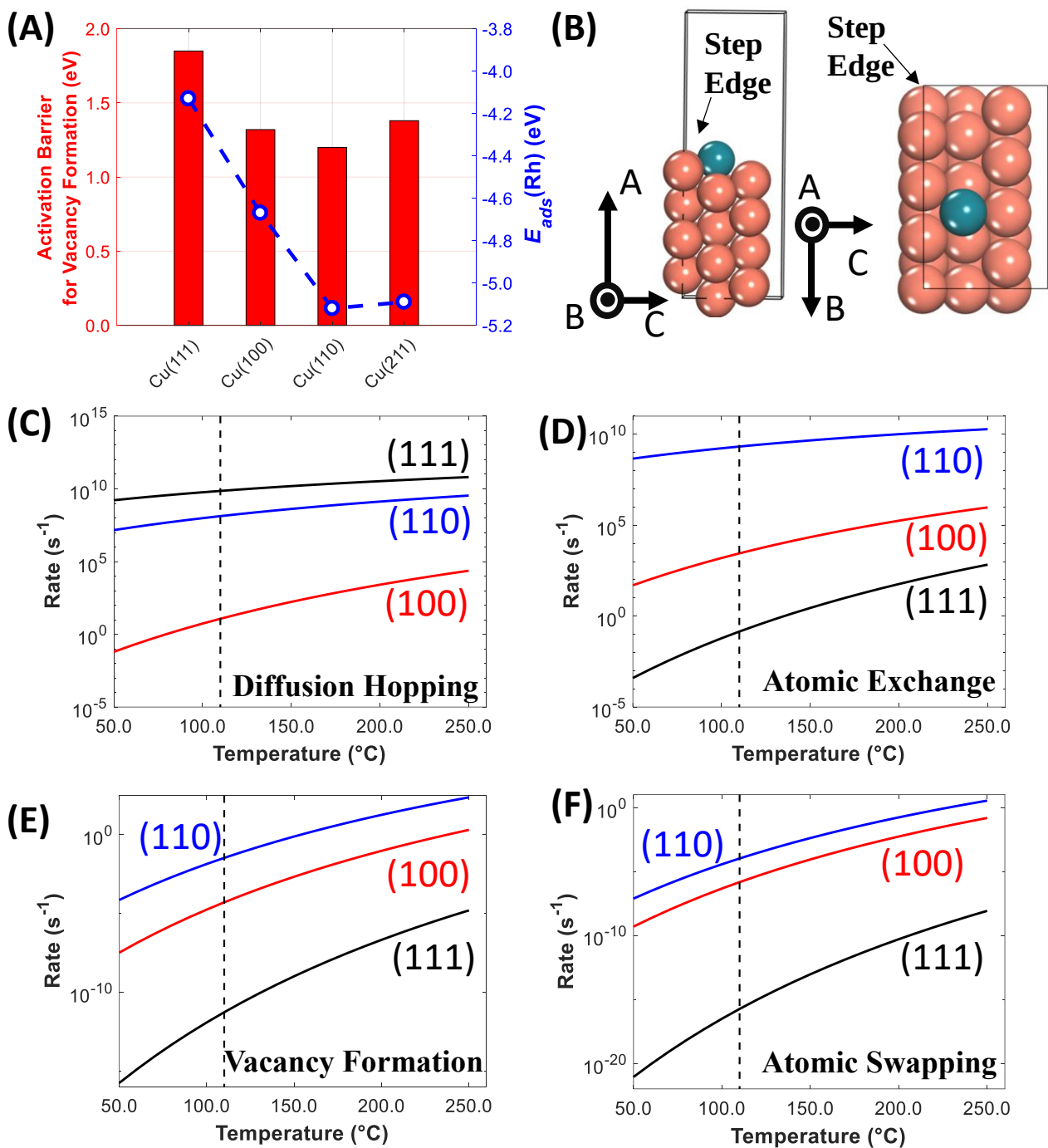


Fig 3. 3 Energy cost for vacancy formation on pure Cu surfaces and adsorption energies of a Rh adatom on the most stable adsorption site of the same surfaces. The reported barriers in panel (A) refer to clean Cu surfaces without the presence of a Rh adatom. The most stable adsorption site for Rh is a fcc site for Cu(111), and a fourfold site for Cu(100) or Cu(110). (B): the most stable adsorption site for a Rh adatom (shown in teal) on the (211) surface. (C), (D), (E) and (F): computed rates for Rh hop diffusion, atomic exchange, vacancy formation (in the presence of a Rh adatom in the close vicinity to the vacancy) and atomic swapping, respectively. The dashed

line is always at 110°C, which is the temperature at which alloying was performed in our experiments.

3.5 Conclusions

We have examined and directly compared the alloying behavior of small amounts of Rh with Cu(111), Cu(100) and Cu(110) surface facets using STM. In agreement with previously published results on Cu(111), we observed that most of the Rh atoms are found in dense brims of isolated sites above step edges. In stark contrast, on the Cu(100) and (110) surfaces we found that Rh atoms alloy directly into the terrace of Cu(100) and Cu(110) surfaces. This result suggested that the direct exchange of Rh with Cu atoms in terraces is favored on more open surfaces. DFT calculations were used to quantify the relevant energetics behind these striking differences in alloying behavior. We found that the lowest hopping diffusion barrier for Rh atoms occurs on the Cu(111) facet while atomic exchange is favored over diffusion on Cu(100) and Cu(110) facets. The vacancy filling mechanism was then investigated by examining the activation barrier for vacancy formation and vacancy filling. Vacancy formation on Cu(211) was studied as well to simulate the step edges on Cu(111) where alloying occurs. These results indicated that the vacancy formation barrier is comparable among the Cu(211) and Cu(100) and Cu(110) surfaces, and much lower than the corresponding barrier on Cu(111). Furthermore, the stronger binding of Rh atoms to Cu sites in the vicinity of step edges acts as a driving force for Rh migration to these sites on Cu(111). Furthermore, approximate rates for the aforementioned processes were computed in the temperature range 50°C – 250°C. The results indicate that atomic exchange, vacancy formation and atomic swapping occur much faster on Cu(100) and Cu(110), while atomic hopping is much faster on Cu(111). These predictions that Rh atoms tend to become kinetically trapped in the regions above step edges on Cu(111), while atomic exchange and swapping tend to occur on

Cu(100) and Cu(110) rationalize our experimental STM results which show a high dispersion of Rh in Cu(100) and (110) versus a preference for formation of dense alloy regions above step edges on Cu(111). Together, our synergistic experimental-theoretical approach demonstrates and explains the different alloying mechanisms in the three most common facets of Cu and paves the way for direct cross-comparison of reactivity and the elucidation of structure sensitivity in SAA catalysis.

3.6 References

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Chapter 4: Observation and Characterization of Dicarbonyls on a RhCu Single-Atom Alloy

This chapter was modified from the following original publication: Wang, Y.; Schumann, J.; Happel, E. E.; Volkan, C.; Sykes, E. C. H.; Stamatakis, M.; Michaelides, A.; Hannagan, R. T. Observation and Characterization of Dicarbonyls on a RhCu Single- Atom Alloy. *J. Phys. Chem. Lett.* **2022**, *13*, 6316–6322.

4.1. Abstract

Dicarbonyl species are ubiquitous on finely dispersed Rh/oxide catalysts and are known to form on Rh^+ centers. However, dicarbonyl species have never been directly observed on single-atom alloys (SAAs) where the active site is metallic. Herein, using a combined surface science and theoretical approach, we provide clear evidence of dicarbonyl species at isolated Rh sites on a RhCu(100) SAA. This surface science approach not only enables us to directly visualize dicarbonyl species at Rh sites, but also demonstrates that the transition between the mono and dicarbonyl at Rh sites can be achieved by changing surface temperature and CO pressure. Density functional theory calculations further support the mono and dicarbonyl assignments and provide evidence that these species should be stable on other SAA combinations. Together, these results provide a picture of the structure and energetics of both the mono and dicarbonyl configurations on the RhCu(100) SAA surface and should aid with IR assignments on SAA nanoparticle catalysts. Furthermore, these dicarbonyls may serve as intermediates for C-C coupling in CO_2 electroreduction.

4.2. Introduction

CO infrared spectroscopy is a ubiquitous tool used in catalyst characterization due to the sensitivity of the C-O stretch frequency to different surfaces and binding sites.^{2,3} This technique

has been widely applied to study CO oxidation on supported metal nanoparticles, as well as used in the characterization of active sites in single-atom catalysts.⁴⁻⁸ However, definitive peak assignments on complex catalysts samples is challenging. While the fast growing field of single-atom catalysis has produced many promising catalysts for a variety of reactions, definitively attributing catalytic activity to single atom or cluster sites can be difficult and controversies exist in the literature over the assignment of IR spectra.^{4,7}

Single-atom alloys (SAAs) are a type of single-atom catalyst consisting of a somewhat inert host metal doped with single atoms of a more reactive metal.⁹⁻¹⁷ Unlike most catalysts, single-atom alloys were discovered using fundamental microscopy and desorption measurements on single crystals under model-system Ultra-High Vacuum (UHV) conditions before making the transition to nanoparticle analogs. Since these initial studies, close synergy between model-system work under UHV and nanoparticle studies under industrially relevant conditions has enabled the design and understanding of these materials. Several nanoparticle catalysts have been developed using this combined methodology, and some examples include: RhCu SAAs for propane dehydrogenation,¹⁰ PdCu SAAs for acetylene semi-hydrogenation to ethylene,¹⁵ and NiAu SAAs for the dehydrogenation of ethanol.¹²

While dicarbonyl species have been observed on single-atom catalysts consisting of metal atoms supported on oxides, these species have not been reported on SAAs.^{18,19} Furthermore, it would not be expected that dicarbonyls would be stable on SAAs considering that they normally form on Rh⁺ species according to the 18 electron rule.²⁰⁻²³ It is well known that atomically dispersed Rh atoms on oxide supports exhibit two characteristic CO IR peaks which correspond to the asymmetric and symmetric stretch of the dicarbonyl at isolated Rh sites.^{20,24-28} In fact, the appearance of these spectral features (and the absence of linear and bridge bound CO,

characteristic of CO adsorption on nanoparticles) is often considered as strong evidence of active site dispersion on oxides.^{26,29}

Herein, we examine a well-defined RhCu(100) SAA surface to understand CO adsorption at the active site. Using a combination of Temperature Programmed Desorption (TPD) and Reflection Absorption Infrared Spectroscopy (RAIRS), we find two unique features in the spectra: a weakly bound dicarbonyl feature at 1926 cm^{-1} (stable below $\sim 265\text{ K}$), and a strongly bound monocarbonyl feature at 1978 cm^{-1} (stable below $\sim 440\text{ K}$). Due to the surface selection rules on metallic samples, we only observe the symmetric feature, unlike dicarbonyls on metal oxides where both symmetric and asymmetric bands are observed. To confirm our assignments, we exposed the surface to an isotopic mixture of CO which led to the band associated with the symmetric dicarbonyl stretch splitting into three features, while the band associated with the monocarbonyl stretch split into two, consistent with the expected isotopic scrambling. Interestingly, we found that even modest pressures of CO ($\sim 1 \times 10^{-6}\text{ mbar}$) can cause the conversion of the monocarbonyl feature to the dicarbonyl at room temperature. This is the first observation of dicarbonyls on SAAs and is important in terms of catalyst characterization, but may also have broader implications, since the dicarbonyl structure may act as a reaction intermediate for C-C coupling in CO₂ reduction.

4.3. Results and Discussion

Previous results have shown that low coverages of Rh in Cu exist as isolated sites forming a SAA.^{18,30} This is in agreement with theoretical studies which show that the formation of small Rh ensembles (such as dimers and trimers) is endothermic in Cu.^{31,32} Interestingly, due to the kinetics of alloy formation under model system conditions, we have previously found that the host

metal facet (111 vs 100) impacts the dispersion of the active sites.^{18,30} On RhCu(100), single Rh atoms are finely dispersed across the entire surface, while on RhCu(111) most of the isolated Rh atoms are located in dense brims in the regions above the step edges. Density Functional Theory (DFT) calculations demonstrated that these observed Rh distribution differences between RhCu(100) and RhCu(111) were due to different alloying mechanisms on the two different surface facets.³⁰ Specifically, the diffusion barrier for Rh atoms on Cu(100) is higher than that on Cu(111) and therefore direct atomic exchange of Rh into the terraces is favored on Cu(100). This results in the observed well dispersed Rh atoms in Cu(100) while dense alloyed brims are formed in the regions above the step edges on Cu(111) due to the higher diffusion rate on Cu(111) that enabled the Rh atoms to reach step edges and place exchange into the surface at those sites.³⁰

In order to further study the properties of isolated Rh sites in Cu(100), 0.7% of a monolayer of Rh was deposited on Cu(100) at 300 K, the surface was cooled, and CO TPD and IR spectroscopy were conducted. As shown by the TPD results in Fig 4.1A, we observe the desorption of CO from the c(2×2) phase on Cu(100) <180 K.³³ These results are consistent with previous reports as well as our controls on Rh-free Cu(100) presented in Fig 4.1A (black trace).^{33,34} At higher temperatures, two features, which are found only in the presence of Rh, are observed at ~265 K and ~440 K. The high temperature feature at ~440 K corresponds to CO bound in a monodentate configuration to the isolated Rh atoms.¹⁸ However, the feature at ~265 K has never been observed before. To rule out the possibility that defect sites such as steps and kinks on the Cu(100) surface could be responsible for this desorption feature, we intentionally increased the step edge density of the crystal via argon ion bombardment at 300 K.³⁵ This led to the appearance of an additional CO desorption feature at 200 K (grey trace),³³ indicating that the desorption peak at ~265 K is associated with the Rh atoms not Cu defect sites. The ratio of the area of the low

temperature Rh feature to the high temperature feature is $\sim 1:1$ which is consistent with adsorption of two CO molecules at each Rh site in a dicarbonyl configuration.

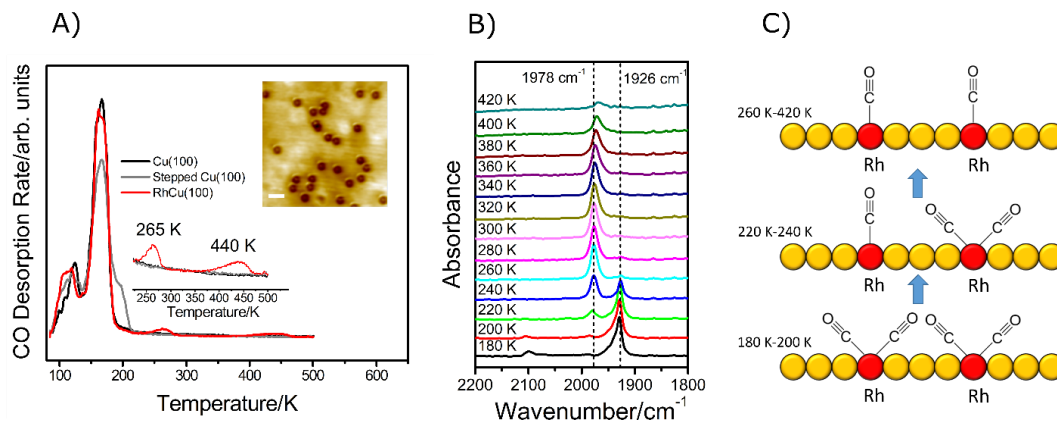


Fig 4. 1 TPD and RAIRS results showing two distinct binding sites for CO on isolated Rh atoms in Cu (100). A) TPD spectra of saturation CO exposures on Cu (100), roughened “stepped” Cu (100), and a 0.7% RhCu (100) SAA. A magnified view of the high temperature desorption features is shown above the TPD traces. The inset shows an STM image of a RhCu (100) SAA in which the Rh sites appear as depressions. Image conditions: 300 mV, 300 pA, scale bar is 2 nm. B) RAIRS spectra of saturation CO on RhCu (100) SAA as a function of temperature. C) Schematic illustration of the proposed structure of the low and high temperature carbonyls.

To aid assignment of these features, we computed the stability of CO bound to Rh in the mono and dicarbonyl configurations using DFT as shown in Appendix. These results demonstrate the formation of a dicarbonyl at the Rh dopant atom is more stable (-2.90 eV, with the particular exchange-correlation functional used, see Supporting Information) compared to a situation where there is only one CO molecule adsorbed on Rh and the other CO is adsorbed on the Cu host (-2.40 eV). This result is initially very surprising, given there is usually a strong steric and electronic CO-CO repulsion on metal surfaces that prevents CO from aggregating at low and intermediate coverages.^{36,37} However, dicarbonyl formation on SAAs can be rationalized by the strong adsorption energy of CO on the Rh dopant and the associated energy gain ΔE from moving the CO from the weakly binding Cu host to the dopant, that outweighs the steric and dipole repulsion upon bringing two CO molecules close together. The calculations show that the desorption energy

of CO from the dicarbonyl configuration is lower (1.09 eV) than the monocarbonyl (1.81 eV), but still stronger than on the Cu host (0.59 eV), in agreement with the experimental values derived from Redhead analysis with an assumed pre-factor of 10^{15} (0.8 eV for the peak at ~ 265 K and 1.3 eV for the peak at ~ 440 K). The reason we used a pre-factor of 10^{15} here is because we assume a late 2D-gas-like transition state between a temperature range of 200-440 K.

In order to better understand the behavior of the carbonyls as a function of temperature and pressure, CO RAIRS experiments were conducted by exposing the as-prepared RhCu(100) SAA to a saturation coverage of CO at 180 K and collecting IR spectra at increasing surface temperature. As shown in Fig. 1B, two peaks at 2099 cm^{-1} and 1926 cm^{-1} were observed. The peak at 2099 cm^{-1} originates from CO on Cu and disappears by 220 K, consistent with our TPD data.³³ Upon further increasing the temperature such that CO is only bound to Rh sites, the feature at 1926 cm^{-1} shrinks and a peak at 1978 cm^{-1} appears. According to our theoretical modeling, the monocarbonyl and symmetric dicarbonyl stretches should appear at 1934 cm^{-1} and 1891 cm^{-1} with a 43 cm^{-1} interval. This 43 cm^{-1} difference is in good agreement with the 52 cm^{-1} interval in the experimental results (1978 cm^{-1} for monocarbonyl vs 1926 cm^{-1} for dicarbonyl).^{18,31,38} The $\sim 40\text{ cm}^{-1}$ offset between the experiment and theory is typical of similar studies.^{38,39}

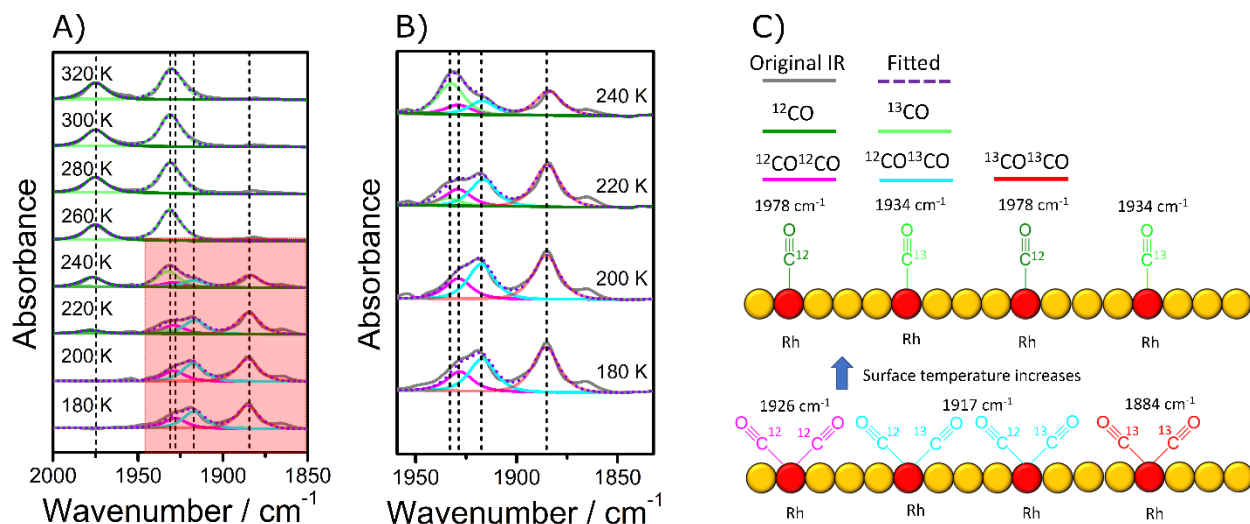


Fig 4. 2 Isotopic evidence of mono and dicarbonyl assignments. A) RAIRS spectra after exposing saturation coverage of a 2:3 ratio ¹³C¹⁶O:¹²C¹⁶O mixture to 0.7% RhCu (100) and taking the IR spectra over the temperature range 180 K to 320 K with peak fitting. B) Expanded view of red highlighted region in panel A. C) Schematic illustration of the three isotopically labelled dicarbonyl species observed between 180 K and 320 K.

While dicarbonyls are typically identified by their characteristic symmetric and asymmetric stretches, due to the surface selection rules on metals, only the symmetric stretch is observed (see Appendix).⁴⁰ In order to further support our mono and dicarbonyl assignments, we exposed the RhCu SAA surface to a mixture of ¹³C¹⁶O and ¹²C¹⁶O (the ¹³C¹⁶O:¹²C¹⁶O ratio was 2:3 as measured by mass spectroscopy). This is a well-known approach for the identification of dicarbonyl species when only symmetric modes can be observed.⁴⁰ Specifically for this case, the monocarbonyl should exhibit two peaks arising from the (¹³CO)-Rh and (¹²CO)-Rh stretches. In contrast, the dicarbonyl should exhibit three peaks due to the symmetric stretches of the (¹³CO)-Rh-(¹³CO), (¹³CO)-Rh-(¹²CO), and (¹²CO)-Rh-(¹²CO) dicarbonyls.

Consecutive IR spectra were then taken at 20 K intervals starting from 180 K. As shown in Fig. 2A, when the surface temperature is 180 K, three peaks (1926 cm⁻¹, 1917 cm⁻¹ and 1884 cm⁻¹) are observed which correspond to (¹²CO)-Rh-(¹²CO), (¹²CO)-Rh-(¹³CO) and (¹³CO)-Rh-(¹³CO) symmetric stretching modes, respectively. The intensity of these initial features starts to

diminish as the surface temperature increases. At 220 K, IR peaks at 1978 cm^{-1} and 1934 cm^{-1} are observed. These two peaks can be assigned to monocarbonyl species at isolated Rh sites (1978 cm^{-1} and 1934 cm^{-1} peaks corresponding to $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}$, respectively). This observation agrees with the IR data in Fig 4.1B where dicarbonyl species begin to convert into monocarbonyl species at $\sim 220\text{ K}$. Importantly, in our TPD experiments, we observe a desorption maximum for half of the CO adsorbed at Rh sites at $\sim 265\text{ K}$, which is consistent with the temperature at which we observe the complete conversion of dicarbonyl features to monocarbonyls in the RAIRS measurements. This provides further support for our IR assignments of a lower temperature dicarbonyl state and a high temperature monocarbonyl species.

As we have described, the relative populations of the mono and dicarbonyls can be controlled by surface temperature, and we now discuss how these species are affected by CO pressure (Fig 4.3). Exposure of the surface to saturation CO at 250 K followed by pumping down to UHV results in a mixture of dicarbonyl and monocarbonyl species as evidenced by the peaks at 1978 cm^{-1} and 1926 cm^{-1} . Heating to 300 K converts the dicarbonyl species at 1926 cm^{-1} to the monocarbonyl species at 1978 cm^{-1} . However, when we backfill the chamber and conduct the RAIRS experiments in-situ, we see a steady increase in the dicarbonyl configuration with increasing pressure. At 300 K and $1 \times 10^{-6}\text{ mbar CO}$, nearly all of the Rh exists in the dicarbonyl configuration. Further evacuation of the CO leads to the disappearance of dicarbonyl peak and again the monocarbonyl species becomes dominant. The result indicates that we can reversibly transition between monocarbonyl and dicarbonyl species at the Rh sites by changing the CO partial pressure in the chamber. Fig 4.3C shows a phase diagram based on DFT energies and harmonic approximations for free energy corrections for gas-phase, mono-, and dicarbonyl species. The shaded areas correspond to regions of coexistence of several phases. We can see that the

observations made under the conditions used in the RAIRS experiment, indicated by black crosses in the phase diagram, are in good agreement with the theoretical predictions of the observable species.

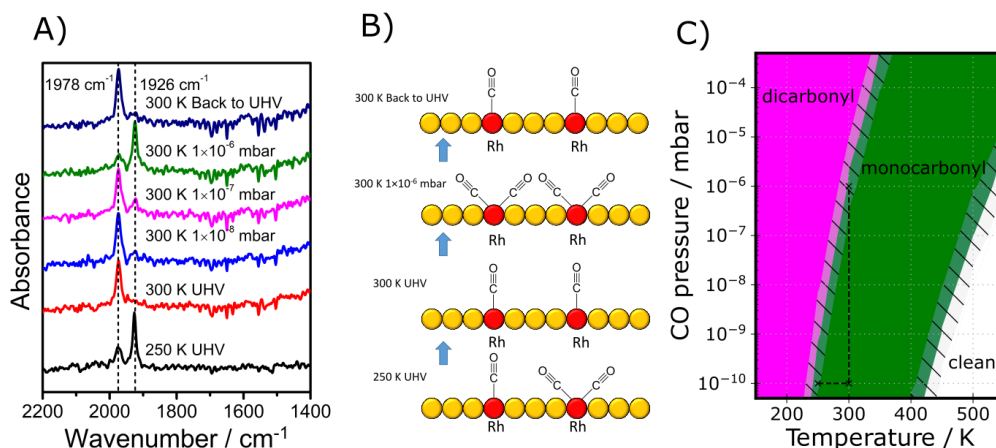


Fig 4. 3 In-situ RAIRS experiments showing pressure induced conversion of mono to dicarbonyl species. A) RAIRS spectra as a function of CO pressure on 0.7% RhCu (100) SAA. B) Schematic illustration of the process. C) Calculated phase diagram for the CO/RhCu (100) system. The most stable configurations for different conditions are indicated. Shaded areas correspond to regions of coexistence of both phases. Black crosses indicate experimental conditions.

Using LT-STM, we are also able to directly visualize the dicarbonyl species observed in the TPD and IR experiments. As shown in Fig 4.4, dicarbonyl species (red arrows) appear as dark linear three-lobed depressions while the CO-free Rh atoms appear as bright protrusions (green arrows). These dicarbonyl features are similar in appearance to those previously observed via STM for Fe atoms deposited on top of a Ag(110) surface, in which the dicarbonyl appears as a linear depression feature.⁴¹ It is important to note that the dicarbonyl species we observe in Fig. 4.4A aligned with both high symmetry directions of the Cu(100) lattice, which enabled us to rule out the possibility that their shape was an artifact of the STM tip. By conducting localized STM tip pulses on each of the dicarbonyl features,⁴² we were able to remove the adsorbed CO and reveal the Rh atoms underneath the dicarbonyl features as shown in panel b. It can be seen that there is a

Rh atom at the center of where each dicarbonyl feature had been observed, thereby confirming the adsorption site of the dicarbonyls as a single Rh atom site.

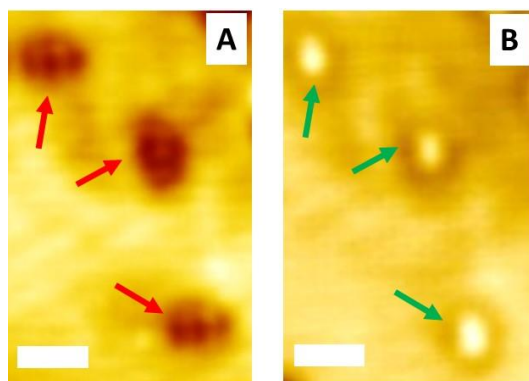


Fig 4. 4.5 K STM images after CO adsorption on RhCu(100) SAA. A) STM image after adsorption of CO followed by ~ 220 K anneal to populate Rh sites, but not Cu. Red arrows highlight three dicarbonyl features, two oriented horizontally and one vertically. B) STM image of the same area after -3 V STM tip pulses were used to remove the CO from the Rh sites. Green arrows correspond to the CO-free Rh atom sites on which the dicarbonyl species were adsorbed. Imaging conditions in both cases: 12 mV, 500 pA. The scale bar is 1 nm in both images.

Based on this unexpected observation of the dicarbonyl species on a metallic Rh center, we assessed the possibility of dicarbonyl formation on other SAA surfaces with late transition metal dopants. Fig 4.5A shows the spillover energies (ΔE) of dicarbonyls on 5 different SAAs in both the 100 and 111 facet of Cu. This ΔE corresponds to the energy necessary to move the 2nd CO from the host metal to a dopant bound to a single CO. Negative values of ΔE in this case mean a favorable dicarbonyl formation. It can be seen that, (i) RhCu(100) has the highest preference for the formation of the dicarbonyl species; (ii) the more open (100) surface has a higher stability of the dicarbonyl species than the close-packed (111) surface; and (iii) the stability trends of the dicarbonyl do not follow the stability of the monocarbonyl adsorbates as compared with literature values.^{31,32} For example, the IrCu(111) SAA binds one CO in a monocarbonyl configuration stronger than RhCu(111), however, RhCu(111) binds the second CO in a dicarbonyl configuration

stronger than IrCu(111). Importantly, these results indicate that other SAAs, beyond what was studied experimentally in this paper, should form dicarbonyls.

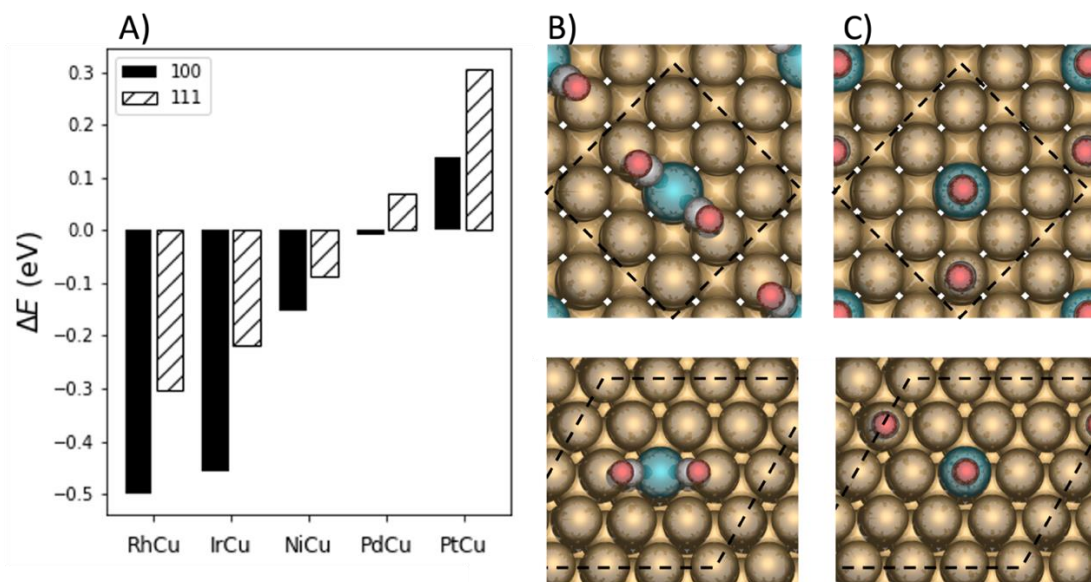


Fig 4. 5 DFT calculated stability of the dicarbonyl adsorbate configuration relative to separated monocarbonyl species on dopant and host. A) Dicarbonyl spillover energies of 5 different SAAs with different surface terminations: (100) and (111). B) Structure of the dicarbonyl adsorbate on RhCu(100) (top) and RhCu(111) (bottom). C) Structure of the separated monocarbonyl species on dopant and Cu host surfaces. Carbon atoms are colored in grey, oxygen atoms in red, Rh atoms in blue, and Cu atoms in brown.

4.4. Conclusion

Using a combination of CO TPD, RAIRS, and STM we were able to characterize and directly visualize the binding of CO to isolated Rh atoms in the surface of Cu(100). We find that Rh atoms in these SAAs are able to coordinate two CO molecules in a dicarbonyl configuration at low temperature (<260 K) under UHV conditions, in agreement with theoretical modelling. However, at room temperature the dicarbonyl state can also be populated with modest standing pressures of CO ($\sim 1 \times 10^{-6}$ mbar). Importantly, due to the surface selection rules of adsorbate vibrations on metal surfaces, even when a dicarbonyl is present only one symmetric vibrational mode is observed due to screening of the asymmetric stretch by the electrons of the underlying

metal. The use of isotopically labeled CO enables us to demonstrate that this IR signature was indeed due to a dicarbonyl as opposed to monocarbonyl species. This contrasts with Rh dicarbonyl species on oxide supports which exhibit both antisymmetric and symmetric CO stretching modes. While the RhCu system reported here is the first example of a dicarbonyl being directly observed on a SAA, we speculate that such species may be quite common for other SAAs that bind CO strongly. Indeed, our DFT calculations have identified two other SAA systems where dicarbonyls are predicted to be stable. Understanding the molecular structures associated with IR signatures is important in the characterization of the active sites of high surface area catalysts and may also open up avenues of catalyst design. In particular, it may enable the discovery of SAAs on which two species can bind to the same active site, which is important, for example, in the context of coupling reactions.

4.5 References

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Chapter 5: Reactivity Trends in Copper-Based Single-Atom Alloys for Formic Acid Decomposition

5.1 Abstract

The complexity of heterogeneous catalysts makes cross comparison of the reactivity of different metal catalysts difficult. However, single-atom alloys, with their atomically dispersed active sites in the inert host metal surface, make this problem tractable. Herein, we compare the structure and reactivity of four different single-atom alloys in a Cu host using well-defined surface science experiments. Formic acid decomposition, an important reaction for on-site hydrogen production, exhibits a reactivity trend for SAAs (RhCu>NiCu>PtCu>PdCu) that is distinctly different to that of the pure metals Pt>Pd>Rh>Ni. Isotope labeling studies are used to demonstrate that formic acid decomposition proceeds on all four SAA surfaces via the formate pathway, which informs our theoretical calculations that explain this unique reactivity trend. These results, accompanied with nanoparticle studies uncover metals, that are not considered to be optimum catalysts in their bulk phase, could be promising catalysts in the single atom alloy regime.

Cross comparison of the reactivity of heterogeneous catalysts can be challenging since this process is hindered by their ambiguity of active sites nature.¹⁻³ One approach to simplify this complexity is comparing active sites in single atom limits.⁴ Herein, we compared and contrasted the reactivity of four different Cu-based SAAs for formic acid decomposition, an important industrial process for on-site hydrogen production.⁵ According to previous model catalyst studies, a general trend in the decomposition rate for monometallic surfaces has been established (Pt(111) > Pd(111) > Rh(111) > Ni(111)).^{6,7} The trend could be understood by carefully investigating the

reaction pathway, which the formic acid decomposition proceeds stepwise via either the dehydration ($\text{HCOOH} \rightarrow \text{CO} + \text{H}_2\text{O}$) or dehydrogenation pathway ($\text{HCOOH} \rightarrow \text{CO}_2 + \text{H}_2$). The formate pathway is generally most common given the high activation barrier to break a C-H bond as compared to an O-H bond.⁸ And the reason that Pt and Pd are considered to be optimal candidates for this reaction is that they have intermediate binding strength for the formate so that the subsequent C-H activation would not be required to surpass a high activation barrier. Selectivity is another important aspect to consider as model catalysts studies show that the dehydration pathway, which produces CO to poison the active sites and leads to significant performance loss, can occur on Pt(111), Pd(111) and Pd(100) surfaces.^{9,10} Binary alloy systems have been introduced to achieve CO-free H_2 production from formic acid decomposition. PdAg is by far the optimum catalyst for selective formic acid decomposition.^{11–13} And Nørskov and coworkers have rationalized the high performance of PdAg using an interpolation concept. However, the wide application of PdAg could be hindered by the cost and necessitates the exploration of Cu-based binary systems (Cu_3Pt for instance).¹⁴

SAAs, a subclass of SAC with maximized utilization of precious metal, could further enhance the cost-efficiency.^{15,16} Initial attempt has been demonstrated by the PtCu SAA in our group. However, PtCu shows marginal improvement for this reaction as Pt single atoms sites are not capable of facilitating the C-H activation step.¹⁷ The follow-up NiCu SAA tried to provide guidance for the design of formic acid decomposition catalysts. Herein, we provided a more systematic investigation of the reactivity of Cu-based SAAs (SAA=Pd, Pt, Ni and Rh) towards formic acid decomposition using a combined simulations and surface science approach. We have found that the reactivity trend of these SAAs is: $\text{RhCu}(100) > \text{NiCu}(100) > \text{PtCu}(100) > \text{PdCu}(100)$, which is distinctly different from the aforementioned trend on monometallic surfaces.

Crucially, monometallic Rh and Ni are not generally considered good candidates for formic acid decomposition as they bind carboxyl or formate intermediates too strongly, which hinders further reaction steps.^{8,18} On the other hand, our data shows that in the single atom regime, RhCu shows the highest reactivity towards this reaction. Our DFT results reveal that the isolated dopant metal sites bind adsorbates more weakly than their monometallic surface counterpart, thereby destabilizing formate and lowering the activation barrier of the subsequent C-H activation step. Moreover, these RhCu alloy nanoparticle catalysts show significant reactivity increase over other counterparts and high stability under 20-hour-stream. Overall, our study shows that candidates which are not considered to be optimum catalysts in their bulk phase may show promising catalytic behavior in the single-atom regime.

5.2 Methods

Low-Temperature Scanning Tunnelling Microscopy (LT-STM). LT-STM experiments were conducted in an UHV chamber with a base pressure of $\sim 1 \times 10^{-11}$ mbar using an Omicron LT-STM. Sample cleaning was performed in an adjacent preparation chamber with a base pressure less than 2×10^{-10} mbar. Repeated cycles of Ar (Airgas 99.99%) ion bombardment (1 keV, 10-20 μA) and thermal annealing to 750 K were used for cleaning the Cu(100) single crystal. Rh/Ni/Pt/Pd deposition was performed from Rh/Ni/Pt/Pd rods (Goodfellow 99.9%) using a flux monitored EFM 3 electron beam evaporators (Scienta Omicron), while the Cu(100) sample temperature was held at 300 K during deposition of a constant Rh/Ni/Pt/Pd flux of $\sim 0.01 \text{ ML} \cdot \text{min}^{-1}$. The STM images were acquired after cryogenically cooling the STM stage to 80 K.

Temperature-programmed Desorption (TPD). TPD experiments were performed in a separate UHV chamber with a base pressure of $< 1 \times 10^{-10}$ mbar equipped with a quadrupole mass

spectrometer (Hidden HAL/3F 301) capable of being advanced to less than 1 mm in front of the crystal. The Cu(100) crystal was cleaned by repeated cycles of Ar ion sputtering (0.5 keV, $1.5\mu\text{A}$) and annealed to 750 K. The RhCu(100)/NiCu(100)/PtCu(100)/PdCu(100) SAAs were prepared by a flux monitored EFM 3 (Scienta Omicron) electron beam evaporators at a surface temperature of 300 K. For dopant metals coverage quantification, the as-prepared surfaces were cooled to 90 K via a liquid nitrogen cryostat and exposed to CO (99.99% Airgas) through a high-precision leak valve. For formic acid reactivity and reaction mechanism studies, the as-prepared surfaces were cooled to 90 K via the liquid nitrogen cryostat and exposed to HCOOH (99.0% Fisher Scientific) or DCOOH (95 wt. % in H_2O) through a high-precision leak valve. Annealing was done by resistively heating Ta wires that support the Cu(100) crystal, and temperatures were measured via a thermocouple spot welded to the back of the crystal. All TPD measurements were run with a heating rate of 2 K/s. Reactivity of the SAA surfaces was examined by dosing 0.1 Langmuir [$1\text{ Langmuir (L)} = 10^{-6}\text{ torr}\cdot\text{s}$] HCOOH (0.06 equivalent monolayers). HCOOH was tracked using $m/z = 46$. Products, CO_2 and H_2 were tracked using $m/z = 44$ and 2, respectively, and CO and H_2O were tracked using $m/z = 28$ and 18 respectively. For isotopic experiments, DCOOH was tracked using $m/z = 47$. D_2 and HD were tracked using $m/z = 4$ and 3 respectively.

Reflection Absorption Infrared Spectroscopy (RAIRS). RAIRS experiments were performed in the same chamber as the TPD experiments using a Bruker Tensor II spectrometer. The grazing-incidence IR beam was directed from the spectrometer onto the crystal and out of the chamber to a mercury-cadmium-tellurium (MCT) detector using a series of gold-coated mirrors. The external part of the IR spectrometer was encased with a dry air purge box and the UHV chamber was equipped with ZnSe windows to prevent IR radiation loss. RAIRS spectra were taken at the indicated temperatures and referenced to a background collected at 180 K. Spectra were

averaged over 2000 scans with 4 cm⁻¹ resolution. Manual background subtractions that accounted for slight background drift over time were applied to all the IR spectra.

Density Functional Theory (DFT). In this project, DFT calculations were performed using the Vienna *Ab initio* Simulation Package (VASP) 5.4.1.^{19–21} The van der Waals exchange-correlation functional, optB86b-vdW, was chosen to calculate formation energies of adsorbates in heterogeneous systems accurately.^{22–25} Project Augmented Wave (PAW) potentials were used to alleviate computational efficiency challenges caused by core electrons.^{26,27} For valence electron expansion, the cutoff energy was set to 400 eV. When optimizing surface configurations, the convergence criterion of the ionic step was set at 10⁻⁵ eV, and the Hellmann–Feynmann forces on all free atoms were required to be lower than 0.02 eV/Å. The Brillouin zone was sampled with a 3 × 3 × 1 Monkhorst-Pack k-point grid. Stable structures were identified by the Conjugate Gradient method. Transition states were searched by the dimer method before refining with the quasi-Newton method. Frequency tests were then performed to validate these states by ensuring each transition state only had one ideal imaginary frequency.^{28,29} Simulation of STM images was performed according to the Tersoff-Hamann method.³⁰ Partial charge density files calculated in VASP were visualized by the HIVE-STM program.³¹

5.3 Results and discussion

Model Catalysts Studies. We began the study by making and characterizing the SAA surfaces with low-temperature STM. Representative STM images of as-prepared PdCu(100), PtCu(100), NiCu(100) and RhCu(100) SAA surfaces are shown in Fig 5.1A-D. It can be seen that all the dopant sites are dispersed from each other in the Cu(100) terraces. These STM results are consistent with the previous DFT calculations predicting positive aggregation energies of Pd, Pt, Ni and Rh in Cu(100), meaning that it is energetically preferred for the dopant atoms to be

surrounded by host metal atoms.³² DFT simulated STM images of the aforementioned SAAs are shown in the inset of Fig 5.1E-H to compare with the experimental STM data. Isolated Pt and Pd atoms appear as protrusions which agrees well with simulated DFT data. However, Fig 5.1 panels C and D reveal that isolated Ni and Rh atoms appear as depressions instead of protrusions as DFT predicted due to adsorption of CO from the chamber background.^{33,34} Furthermore, previous theoretical calculations demonstrate that the CO binding strength follows the trend RhCu > NiCu > PtCu > PdCu.³² This rationalizes why adsorption of background CO is only an issue for NiCu and RhCu SAAs. However, to achieve atomic resolution of the Ni and Rh atoms, the STM tip needs to be placed very close and can induce CO desorption or relocation to reveal CO-free Ni or Rh atoms underneath.^{35,36} As shown in Fig 5.1G, these CO-free Ni atoms appear as protrusions, in agreement with the DFT simulation. This also applies to isolated Rh atoms, which bind CO even stronger than Ni.³⁷

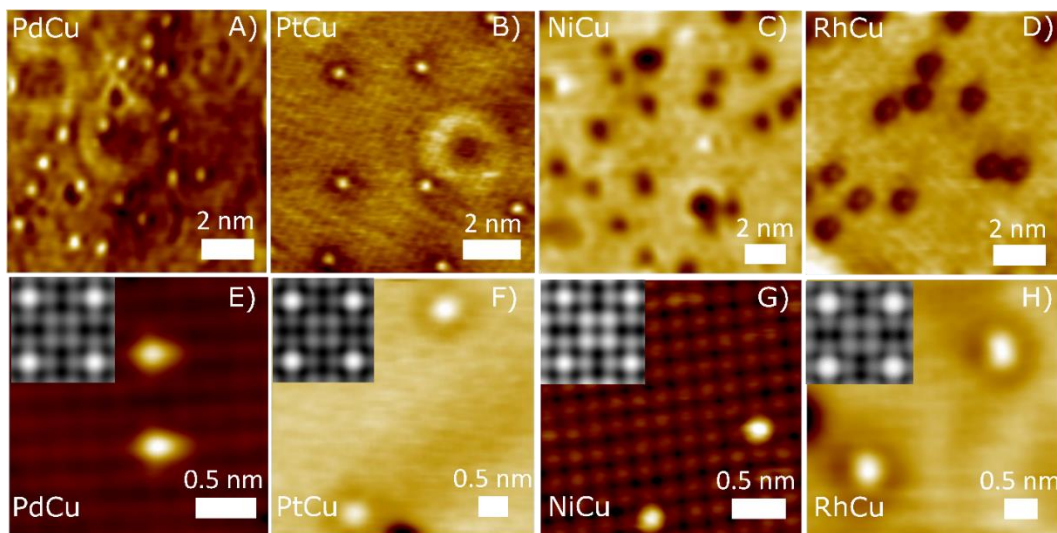


Fig 5. 1 Experimental and DFT-simulated STM images of highly dispersed single-atom alloys. A) PdCu (100) SAAB) PtCu (100) SAA. C) NiCu (100) SAA. D) RhCu (100) SAA; High resolution image of individual E) Pd atoms in Cu (100) host. F) Pt atoms in Cu (100) host. G) Ni atoms in Cu (100) host. H) Rh atoms in Cu (100) host. Inset shows DFT simulated STM images of single atoms in Cu (100). In these images, Pd and Pt atoms appear as protrusions, while Ni and Rh appear as depressions. Imaging conditions can be found in the Appendix.

To compare the reactivity of these four different SAAs, we performed formic acid dehydrogenation. Figure 5.2A shows TPD profiles of H_2 ($m/z = 2$) and CO_2 ($m/z = 44$) evolution after exposing 0.1 L formic acid to Cu(100), PdCu(100), PtCu(100), NiCu(100) and RhCu(100) SAA surfaces. Specifically, 0.7% of a monolayer of the dopant metal was deposited on the Cu(100) surface at 300 K, the surface was then cooled and exposed to formic acid, and TPD was conducted. For hydrogen desorption traces, two peaks were observed for Cu(100), PdCu(100), PtCu(100), NiCu(100) while three peaks were observed on RhCu(100). Our previous study of PtCu(111) indicates that there are two elementary steps in formic acid dehydrogenation process.¹⁷ O-H activation occurs first and is followed by C-H activation which results in two H_2 peaks observed. The first hydrogen peak originates from H atom recombination after O-H activation and the second peak from H atom recombination after C-H activation, which is known as the formate pathway. CO_2 starts to desorb after the rate limiting C-H activation step and this process is reaction-limited given that molecular CO_2 desorbs at ~ 90 K on Cu(100).³⁸ In this way we can compare the capability of C-H activation on different dopant metals based on the CO_2 desorption temperature. The trend for the C-H activation capability is as follows: RhCu(100) > NiCu(100) > PtCu(100) > PdCu(100) > Cu(100), with CO_2 desorption peak at 282 K, 376 K, 380 K, 405 K and 410 K, respectively. Surprisingly, the trend for single-atoms in Cu host does not follow the trend of monometallic single crystals (CO_2 desorption temperature: Pt(111) < Pd(111) < Rh(111) < Ni(111)) or that of monometallic nanoparticles (CO_2 desorption temperature: Pt < Pd < Ni < Rh) where Pt and Pd are the best candidates in both cases.^{6,39} As further proof that formic acid dehydrogenation on these SAAs proceeds via the formate pathway (i.e. O-H cleavage followed by C-H scission), DCOOH experiments were performed. As shown in Figure 5.5.2B, H_2 ($m/z = 2$) (black) and D_2 ($m/z = 4$) (Red) traces were tracked by exposing 0.1 L of DCOOH to Cu(100) and SAA surfaces

with 0.7% of a monolayer dopant coverage. These results show that H_2 ($m/z = 2$) always desorbs before D_2 ($m/z = 4$) on all investigated surfaces, illustrating that the first step is O-H activation followed by C-D activation thus confirming that the formate reaction pathway is predominant on these surfaces.

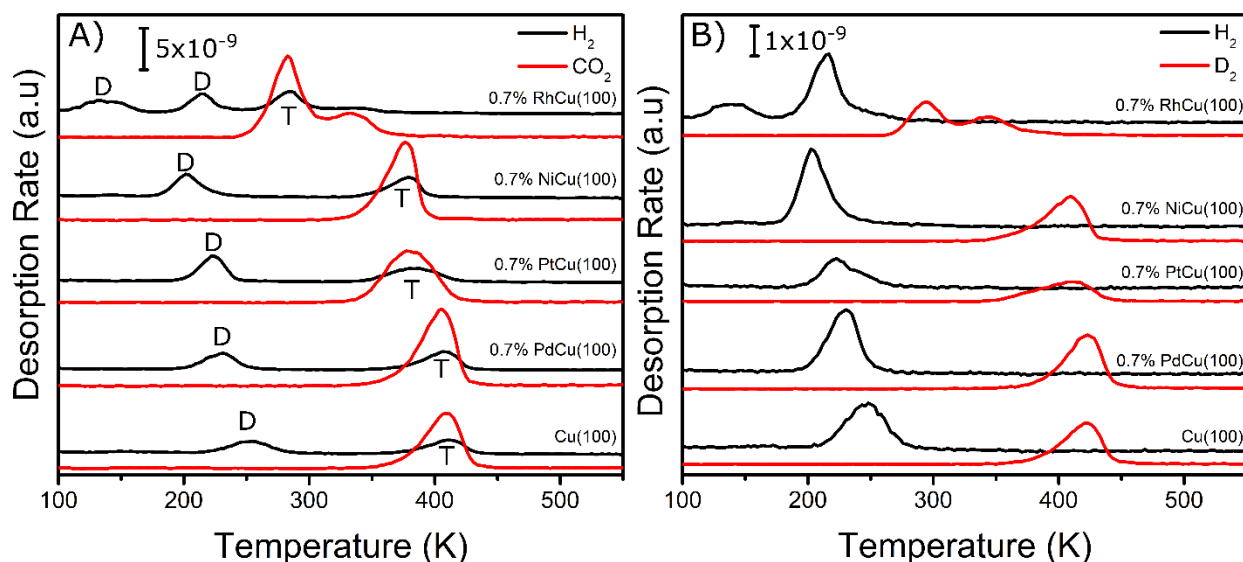


Fig 5. 2 HCOOH dehydrogenation on different SAAs compared with DCOOH dehydrogenation to reveal the reaction pathway on those surfaces. A) TPD spectra showing H_2 (black) and CO_2 (red) desorption from formic acid reaction on the different surfaces. Each surface was exposed to 0.1 Langmuir [1 Langmuir (L) = 10^{-6} torr·s] of HCOOH at 90 K. The coverage of all dopants is 0.7% of a monolayer. D peaks result from H that is formed during O-H activation (formic to formate) while T peaks result from H that is formed during C-H activation (formate to CO_2 and H_2). B) TPD spectra showing H_2 (black) and D_2 (red) desorption from DCOOH dehydrogenation on different surfaces. Each surface was exposed to 0.1 Langmuir [1 Langmuir (L) = 10^{-6} torr·s] of DCOOH at 90 K. The coverage of all dopants is 0.7% of a monolayer.

Linear scaling relationships in catalysis make a molecule's adsorption energy a good proxy for the magnitude of subsequent activation barriers, and hence reactivity.^{40–42} To further investigate the observed reactivity trend on these SAAs, CO TPD and IR were conducted on these surfaces to compare the relative CO binding strength of the active sites. SAA surfaces with 0.7% of a monolayer of the dopant metal were prepared at 300 K, the surface was cooled, and CO TPD and IR spectroscopy were conducted. Previous work on CO adsorption on Cu(100) indicated that

the $c(2 \times 2)$ CO phase desorbs from Cu(100) terraces below 180 K, and from Cu steps below 200 K.^{37,43} Therefore, CO desorption above 200 K gives a measure of its binding strength to the different dopant metal atom sites. As shown in Figure 5.3A, one peak is seen for PdCu(100) (~258 K), PtCu(100) (~358 K) and NiCu(100) (~374 K), while two CO desorption peaks are observed for RhCu(100) (~250 K and 449 K). The peak observed on PdCu(100), PtCu(100) and NiCu(100) is attributed to monocarbonyl desorption from the dopant metal sites. On RhCu(100) on the other hand, the 2 peaks can be attributed to the desorption of a dicarbonyl species: at 250 K the more weakly bound dicarbonyl desorbs while the 449 K peak corresponds to the desorption of the remaining monocarbonyl, which is in agreement with our previous CO TPD and IR experiments on RhCu(100) SAA.³⁷ The monocarbonyl desorption energy has been derived from Redhead analysis using a prefactor of 10^{15} s^{-1} .^{37,44} The desorption energies for monocarbonyl on PdCu(100), PtCu(100), NiCu(100) and RhCu(100) are 0.8 eV, 1.1 eV, 1.2 eV and 1.4 eV, respectively. These trends compare well with the DFT calculated CO adsorption energies: -0.93 eV, -1.30 eV, -1.46 eV, -1.79 eV for PdCu(100), PtCu(100), NiCu(100) and RhCu(100) respectively. IR spectroscopy was further conducted to confirm that the active sites were well dispersed and to investigate the CO binding strength on the different SAAs. Specifically, the full width at half maximum (FWHM) of the C-O stretching peak is a good indicator of the uniformity of the dopant metal sites to which CO binds,^{37,44} with narrower FWHM values indicating better dispersion. For the spectra shown in Figure 3B, the FWHM for PdCu(100), PtCu(100), NiCu(100) and RhCu(100) are 11.4 cm^{-1} , 8.8 cm^{-1} , 16.7 cm^{-1} and 14.0 cm^{-1} , respectively. Narrow FWHM for those SAAs ($< 17 \text{ cm}^{-1}$) indicate uniform distribution of active sites, which agrees with the STM results that all dopant metal sites are highly dispersed in the Cu(100) terrace. We then correlated the C-O stretching frequency to the observed CO desorption temperature on the range of SAAs investigated. Figure 3C shows the

CO desorption peak temperature and C-O stretching ($\nu(\text{CO})$) frequency trend of the SAAs investigated. The TPD spectra show that the relative CO binding strength trend for those SAAs is: PdCu(100) SAA < PtCu(100) SAA < NiCu(100) SAA < RhCu(100) SAA since lower CO desorption peak temperature results in lower CO desorption energy according to the Redhead analysis. Note also that weaker CO binding strength results in higher $\nu(\text{CO})$. The $\nu(\text{CO})$ red shift from PdCu(100) to RhCu(100) can be understood via π back-donation to the antibonding molecular orbitals which weakens the C-O bond while strengthening the C-metal bond, thereby making the CO bind to the dopant more strongly.^{45,46} Comparison of the red shift of $\nu(\text{CO})$ with the trend in CO binding strength and the SAA performance for formic acid decomposition indicates that the C-H activation capability (as quantified by the respective activation energy: RhCu (0.68 eV) < NiCu (0.91 eV) < PtCu(0.92 eV) ~ PdCu (0.99 eV)) on the investigated dopant metals sites follows the same trend as CO adsorption energy on these dopant metal sites.

DFT calculations were further conducted to study the reaction pathway of formic acid dehydrogenation on these SAA surfaces. To understand the properties and reactivity of formate dissociation, many key configurations (including formate bound to dopant-host and host-host bidentate sites, transition state for C-H cleavage, $\text{H}^* + \text{CO}_2$ coadsorbed in chemisorbed and physisorbed geometries, and $\text{CO}_2(\text{g}) + \text{H}^*$), along the pathways of C-H activation on Cu and Cu-based SAAs were systematically examined. The reaction profile was then built to compare the potential energies of the C-H activation on these catalysts.

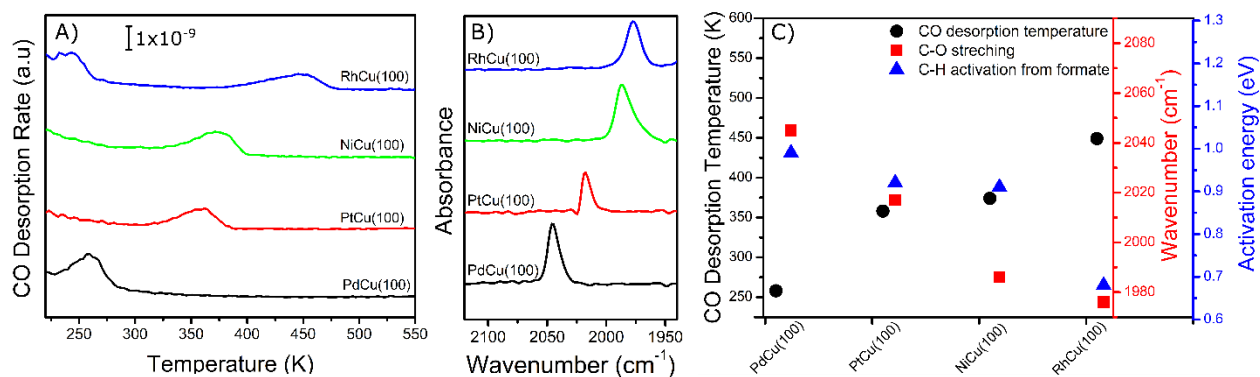


Fig 5. 3 CO TPD and RAIRS of CO binding at the active sites in the different SAA systems. A) TPD spectra of saturation CO exposures on 0.7% PdCu (100), 0.7% PtCu(100), 0.7% NiCu(100) and 0.7% RhCu(100) SAAs. The monocarbonyl desorption temperature reflects the relative CO binding strength at the single atom sites where CO binding strength trend follows Pd sites < Pt sites < Ni sites < Rh sites. B) RAIRS of saturation CO exposures on 0.7% PdCu (100), 0.7% PtCu (100), 0.7% NiCu(100) and 0.7% RhCu(100). All spectra were obtained at 240 K. C) The trend of monocarbonyl desorption temperature (Black) versus C-O stretching frequency (red) versus C-H activation energy of HCOOH for different SAAs. The C-H activation energy was derived for each surface from Redhead analysis assuming a preexponential factor of 10^{12} s^{-1} . Higher monocarbonyl desorption temperature from active sites trends correlates with lower C-O stretching frequency and lower C-H activation energy.

To calculate the apparent activation energies of the dehydrogenation, the most stable initial states on each SAAs were first located by comparing related potential energies. Although formate molecules are di- σ bonded on all the studied catalysts,⁴⁷ the results demonstrate that their geometries vary slightly on different Cu-based SAAs (Fig 5.4A). For example, formate prefers to bind to host-host sites on PdCu(100) and PtCu(100) in a bidentate geometry, as the formation energies of formate on these sites are 0.22 eV and 0.21 eV lower than that on dopant-host site on PdCu(100) and PtCu(100) (Fig 5.4B). In addition, for the PdCu(100) and PtCu(100) the formation energy of formate can be further reduced (up to 0.03 eV for PdCu(100) and 0.06 eV for PtCu(100)) if the formate molecules are pushed far away from the dopant atom towards the Cu(100) sites. On the other hand, the most stable site for formate on RhCu(100) and NiCu(100) are dopant-host sites. Formate fragments trapped in these sites require relatively large amounts of energies of 0.32 and 0.17 eV, respectively, to diffuse to the nearest host-host site where C-H activation occurs.

RhCu(100) is slightly different from other SAAs, as the two O atoms bind on the dopant-host bridge site and the host-host bridge site respectively (Fig 5.4B).

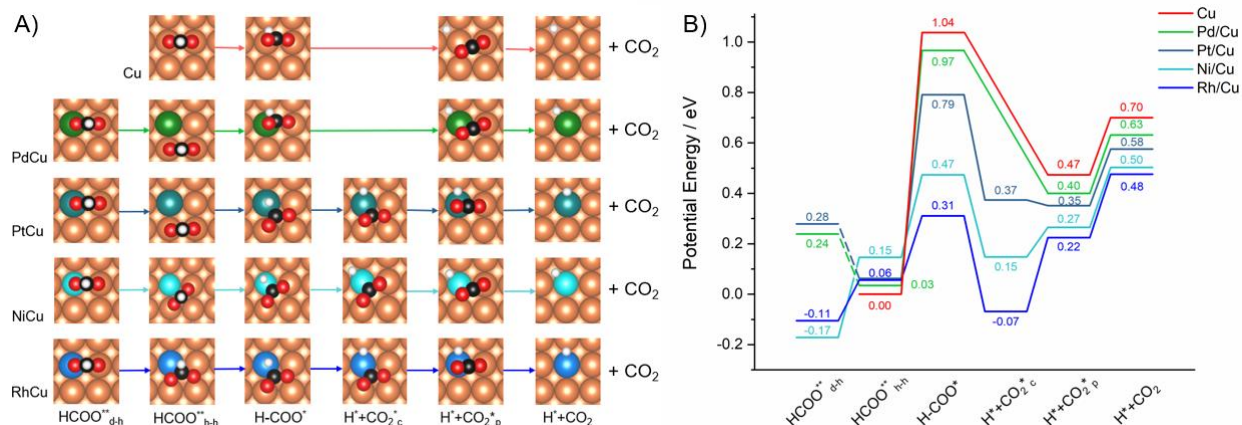


Fig 5. 4 The geometries and the respective formation energies for formate dissociation on different systems. A) The following geometries of formate are shown from left to right: bound to the dopant-host di- σ site, bound to the host-host di- σ site, transition state for C-H scission, final state with chemisorbed CO₂ (CO₂^{*}_c), final state with physisorbed CO₂ (CO₂^{*}_p), and state after CO₂ desorption. A five-layer slab was used in these calculations along with a p (4 × 4) unit cell. Only a portion of the cell is shown for clarity. B) Reaction profiles with zero-point energy corrections for the C-H activation reaction on Cu and Cu-based SAAs. Only the minimum energy paths are considered in each particular case.

During the activation process, the molecular plane of formate rotates to orient the molecule parallel to the catalyst surface, causing the C-H bond to move close to the dopant atom where the scission then occurs. If the most stable state on each catalyst is considered as the initial state of the C-H activation, their apparent activation energies exhibit a following trend: Cu (1.04 eV) > PdCu (0.97 eV) > PtCu (0.79 eV) > NiCu (0.64 eV) > RhCu (0.42 eV) (Fig 5.4B). The energy trend is similar to that of the experimental results, while the actual barriers calculated from DFT are 0.41 eV less for NiCu and 0.25 eV less for other SAAs than the experimental results. One possible reason may be that the desorption of CO₂ has the potential to become rate limiting for formate dissociation instead of the C-H elementary step. In addition, formate adsorbing on Cu sites on PtCu

and PdCu introduce an entropic penalty that amounts to about 0.1 eV. Also, DFT activation energies tend to be underestimated because of the delocalization error from GGA functionals.^{48,49}

After the C-H activation, the H adatom moves to the dopant-host bridge site on PtCu(100) and RhCu(100), whereas it adsorbs on the four-fold hollow site on the other catalysts. Besides, CO₂ adsorbs only weakly on Cu(100) and PdCu(100) with almost no deformation mainly through van der Waals forces, while bent CO₂ fragments adsorb on PtCu(100), RhCu(100), and NiCu(100) surfaces with a 125-135° angle between the two C-O bonds before changing to physisorbed CO₂ (Figure 4A), which is in line with our previous results on (111) surfaces.^{50,51} The reaction energy on each catalyst, defined as the energy of H*+CO₂, with the latter in the physisorbed state, minus the energy of the most stable initial state, can then be calculated and follows the trend: Cu (0.47 eV) > NiCu (0.44 eV) > PdCu (0.37 eV) > RhCu (0.33 eV) > PtCu (0.29 eV) (Fig 5.4B). Except for NiCu(100) and RhCu(100) where formate binds to dopant-host sites towards more stable initial states, the trend of the reaction energy on the other surfaces follows the same trend as the apparent activation energies. After that, the physisorbed CO₂ desorbs from the surface. The desorption energies of these processes are similar on Cu and Cu-based SAAs (0.23 eV on Cu(100), PtCu(100), NiCu(100), and PdCu(100), with a slightly higher desorption energy of 0.26 eV on RhCu(100) (Fig 5.4B).

5.4 Conclusion

Using a combined theoretical-surface science-catalysis approach, this work aimed to understand the observed activity trend of Cu-based SAAs (X=Pd, Pt, Ni and Rh) towards formic acid decomposition. We find that the activity trend for these SAAs is: RhCu(100)>NiCu(100)>PtCu(100)>PdCu(100), which is distinctly different from the trend for the monometallic surfaces (Pt(111)>Pd(111)>Rh(111)>Ni(111)). Furthermore, isotopic experimental

results show that these SAAs do not change the reaction pathway (formate pathway) of the Cu surface and the rate limiting step (RLS) is the C-H activation step. CO TPD and RAIRS results enable us to correlate this observed activity trend to the CO binding strength: the stronger the CO binding, the lower the C-H activation barrier. Further theoretical calculation results confirm that RhCu(100) SAA has the lowest C-H activation barrier among other investigated SAAs. While model catalysts study and theoretical modeling provide insights into fundamental chemistry on these surfaces, ongoing catalysis study will investigate the reactivity of these SAAs under flow reactor condition and thus complete this theoretical-surface science-catalysis loop.

5.5 Reference

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Chapter 6: Elucidating Synergistic Effects between Isolated Rh and Pd Sites using Iodomethane and Toluene

6.1 Introduction

Single Atom Alloys (SAAs) are a subclass of single atom catalysts (SAC) where active metal dopants are atomically dispersed in an inert metal host, and have shown their potential for industrially relevant reactions in the past decade.^{1–7} For example, PtCu and RhCu SAAs have shown high activity and selectivity for propane dehydrogenation;^{1,6} PdAg SAA exhibits high conversion rate and selectivity towards ethylene in acetylene hydrogenation;⁸ NiAu SAA has shown 100% selectivity for dry ethanol dehydrogenation to acetaldehyde;⁹ RuCo SAA can enhance Fischer-Tropsch activity and C₅ hydrocarbon selectivity.¹⁰ However, it is difficult for one single-atom site to perform all reaction steps with high efficiency, which necessitates the design of multiple different dopant sites and the need to thoroughly understand the role of each site.^{11,12}

Recently, dual-atom site catalysts with two isolated or adjacent dopant sites have attracted widespread interest in heterogeneous catalysts.¹³ Specific to thermal catalysis, Christopher and coworkers reported Rh-WO_x pair site bifunctional catalysts to be highly selective and active for propanal production via hydroformylation, a reaction typically performed homogeneously.¹⁴ Huang and coworkers reported synergistic effects for 4-nitrostyrene hydrogenation using Ir₁Mo₁/TiO₂ catalysts where Ir sites catalyze H₂ activation and Mo sites are responsible for 4-nitrostyrene adsorption.¹⁵ Li and coworkers reported a Ru₁Zr₁/Co dual-atom-site catalyst that exhibits higher reactivity and selectivity to the production of C₅ products towards the Fischer-Tropsch reaction compared to its Ru/Co and Zr/Co SAA counterparts.¹² However, characterizing two different dopants present in nanoparticles at low concentrations remains a challenge.

Surface science techniques and single crystal studies enabled us to visualize metal dopants in the surface of a metal host using scanning tunneling microscopy (STM).¹⁶ Previous studies on PtCu SAA have shown that well defined Pt sites obtained under STM studies can be correlated to their analogous nanoparticle studies using high-angle annular dark field scanning transmission electron microscopy.^{1,17} The initial attempt to investigate two different dopant sites using surface science techniques has been reported in our group. Ethanol was used as a probe molecule to investigate the PtCrAg dual-atom alloy sites catalyst. These adjacent Pt-Cr dimer sites help stabilize ethanol and can break the O-H bond, unlike their CrAg and PtAg SAA counterparts, enabling the dehydrogenation of ethanol.⁹ However, reports on using this method to characterize two different non-adjacent single atom sites, which belong to another important two-dopant system with promising synergy, are still rare.

In this work, we extended this model catalyst approach to investigate the synergistic effect between isolated Rh and Pd atom sites in RhPdCu(100), denoted as two-dopant single-atom alloy (TD-SAA), by tracking 1,3-butadiene formation from methyl iodide (CH_3I). Using a combined STM and CO reflection absorption infrared spectroscopy (RAIRS) characterization approach, we visualized isolated Rh and Pd atoms in Cu(100) and observed two distinct monocarbonyl peaks on Pd and Rh sites respectively, which confirmed the structure of the TD-SAA. TPD spectra show that 1,3-butadiene evolves ~ 70 K lower from the 0.2% Rh PdCu TD-SAA surface (0.2% RhPdCu(100) refers to 0.2% of a monolayer of Pd and Rh in the Cu(100) host) compared to 0.4% PdCu(100) SAA surface, while no 1,3-butadiene desorption was observed for 0.4% RhCu(100). The formation of 1,3-butadiene involves C-H activation and C-C coupling, therefore, we can understand the role of Rh and Pd sites by examining methane (C-H activation capability) and ethane formation (C-C coupling capability) on RhCu SAA and PdCu SAA. The Methane and

ethane traces indicate that the synergistic effect in the RhPdCu TD-SAA originate from Rh atom sites enabling the C-H activation step while Pd sites facilitate the C-C coupling step. Moving forward, we investigated the decomposition of toluene on these surfaces. The results reveal that only Rh sites are capable of C-C bond cleavage, leading to the formation of phenyl groups from toluene. Additionally, we examined the production of biphenyl from the reaction of iodobenzene, and the PD profiles indicate that Pd sites facilitate phenyl-phenyl coupling. These findings suggest that RhPdCu TD-SAA has the potential to generate biphenyl through toluene reactions, with Rh sites assisting in C-C bond cleavage to form phenyl groups, while Pd sites enable phenyl-phenyl. Together, this work indicates that the surface science approach is a powerful tool to visualize two isolated dopant sites and it enables us to correlate the obtained atomic-scale understanding of surface structure to the observed activity, which can be generalized to rationally design TD-SAA catalysts for industrial relevant reactions.

6.2 Results and discussion

We began our study by making and characterizing the RhPdCu(100) TD-SAA with low-temperature STM. Fig. 6.1A and 6.1B show STM images of the same area in RhPdCu(100) TD-SAA before and after acquiring atomic resolution. It can be seen from Figure. 1A that Rh atoms appear as bright protrusions (~20 pm) while Pd atoms appear as shallow protrusions (~4 pm). However, after acquiring atomic resolution at the same area, the Rh atoms appear as sombrero shapes while Pd atoms appear as protrusions (Fig 6.1B). The Pd features, upon acquiring atomic resolution, are consistent with previous work reported by Besenbacher and coworkers. The Pd atoms alloy into the Cu host through place exchange and appear as protrusions.¹⁸

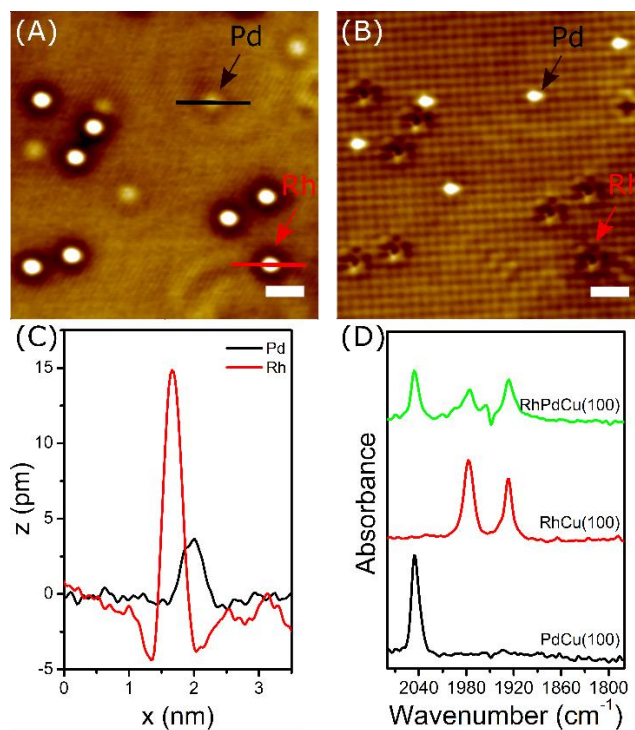


Fig 6. 1 Characterization of the RhPdCu (100) TD-SAA using STM and RAIRS. A) STM image of RhPdCu (100) before acquiring atomic resolution where Rh atoms appear as bright protrusions and Pd atoms appear as shallow protrusions. B) STM image of the same region seen in panel (A) after acquiring atomic resolution where Rh atoms appear as sombrero shaped features and Pd atoms appear as protrusions. C) Apparent height profile of Pd and Rh atom acquired from Fig.1A. D) RAIRS of saturation CO exposures on PdCu (100), RhCu (100) and RhPdCu (100). All spectra were obtained at 240 K. Imaging condition: A) 300 mV, 0.3 nA B) – 3 mV, 9 nA. The scale bar is 1 nm in both images.

While STM provides valuable information, it is important to also examine the surface under more catalytically relevant conditions. Therefore, we need to correlate UHV and ambient pressure information using one technique (in our case, infrared spectroscopy, denoted as IR).^{19,20} CO as a probing molecule has been widely used for catalyst characterization since the C-O stretch frequency is sensitive to different metals and different binding sites.²¹ This approach has also been applied for the active site characterization (as the CO stretch frequency also provides information about the adsorption configuration of CO, whether it is bridge-bound or atop-bound. This information assists us in deciphering the dispersion of metal dopants) of a variety of SAAs under UHV conditions (such as PdCu(111), PdAg(111), PtCu(111), NiCu(111), RhCu(111) and

RhCu(100) SAAs).^{19,20,22–25} Thus, we conducted CO RAIRS to further characterize the active sites in the RhPdCu(100) TD-SAA. 0.2% of a monolayer of Pd was deposited on Cu(100) followed by 0.2% of Rh deposited on the same surface (the surface temperature was held at 300 K). The as-prepared surface was then cooled to 90 K and exposed to a saturated amount of CO before CO-TPD and CO-IR spectroscopy were performed. As shown in Fig 6.1 D, CO-IR was acquired by holding the surface at 240 K where CO occupies primarily dopant sites (Rh and Pd). It can be seen that three distinct peaks (2045 cm^{-1} , 1976 cm^{-1} and 1926 cm^{-1}) were observed for 0.2% RhPdCu(100). By comparing with CO RAIRS on 0.4% PdCu(100) SAA (2046 cm^{-1}) and 0.4% RhCu(100) SAA (1977 cm^{-1} and 1927 cm^{-1}), we can correlate the 2045 cm^{-1} peak to CO atop Pd atom sites, the 1975 cm^{-1} peak to CO atop Rh atom sites, and 1925 cm^{-1} to the dicarbonyl at Rh atom sites, which is consistent with our previous study.²⁵ The fact that the wavenumber for 0.2% RhPdCu(100) showed minimal shift compared to 0.4% PdCu(100) and 0.4% RhCu(100) SAAs indicates dipole-dipole interactions are minimized and Rh and Pd sites are separate from each other.^{19,26,27} Moreover, no Bridge bond CO was observed in RhPdCu(100) spectra which further confirms Rh and Pd form isolated sites (the wavenumber of bridge bond CO on Pd(100) and Rh(100) are 1895 cm^{-1} and 1881 cm^{-1} , respectively).^{26–28} However, it is hard to differentiate the two different sites from CO TPD since the dicarbonyl desorption peak from Rh sites overlaps with the monocarbonyl desorption peak from Pd sites (See Appendix). Together, STM and RAIRS results show that Rh and Pd form isolated sites.

To further investigate the synergistic effect between Rh and Pd sites, we used methyl iodide (CH_3I) as a probe molecule to examine C-H activation and C-C coupling. Specifically, C-I bond cleavage is facile on Cu surfaces yielding methyl groups (CH_3) and I atoms on the surface as it heated.²⁹ Then, C-H activation is the rate determine step (RDS) which yields surface adsorbed H

and CH₂. Surface H atoms typically react spontaneously with CH₃ groups to form methane.²⁹ Subsequently, longer chain hydrocarbon products (C₃ and C₄ products) can be formed by the methylene (CH₂) insertion process.³⁰ Therefore, methane desorption temperature can be used as a probe for C-H activation capability and the formation of C₃-C₄ products involve C-H activation to form methylene and subsequently C-C coupling. Therefore, 1,3-butadiene traces (m/z=54) on different surfaces were used to illustrate the synergistic effect. In Fig 6.2, it can be seen that 1,3-butadiene evolves from Cu(100) and 0.4% PdCu(100) at 429 K and 413 K, respectively. No 1,3-butadiene formation was observed on the 0.4% RhCu(100) surface. For the 0.2% RhPdCu(100) TD-SAA surface, on the other hand, 1,3-butadiene is seen evolving at ~342 K, ~ 70 K lower than either SAA surface, indicating a potential synergistic effect between Rh and Pd sites (Fig 6.2A).

The role of Rh and Pd sites can be further understood by tracking methane desorption (C-H activation capability) and ethane desorption (C-C coupling capability) on the RhCu and PdCu SAAs.^{3,6} It can be seen that methane evolves at ~430 K on the Cu(100) surface, which indicates that C-H activation occurs at this temperature and is consistent with previous reports.³⁰ C-H activation occurs at 413 K and 274 K on the 0.4% PdCu(100) and 0.4% RhCu(100) SAAs, respectively (Fig 6.2B). This result is also consistent with previous studies in our group which showed that RhCu SAA exhibits facile C-H activation.^{6,31} The evolution of ethane (m/z=30) is indicative of C-C coupling events.³² Fig 6.2C shows that C-C coupling occurs at 412 K on Cu(100) and 399 K on 0.4% PdCu(100), respectively. However, no ethane desorption was observed for the RhCu(100) surface. Together, these methane and ethane traces indicate that Rh sites exhibit high activity towards C-H activation while Pd sites enhance C-C coupling, which leads to the low temperature desorption (~342 K) of 1,3-butadiene on 0.2% RhPdCu(100).

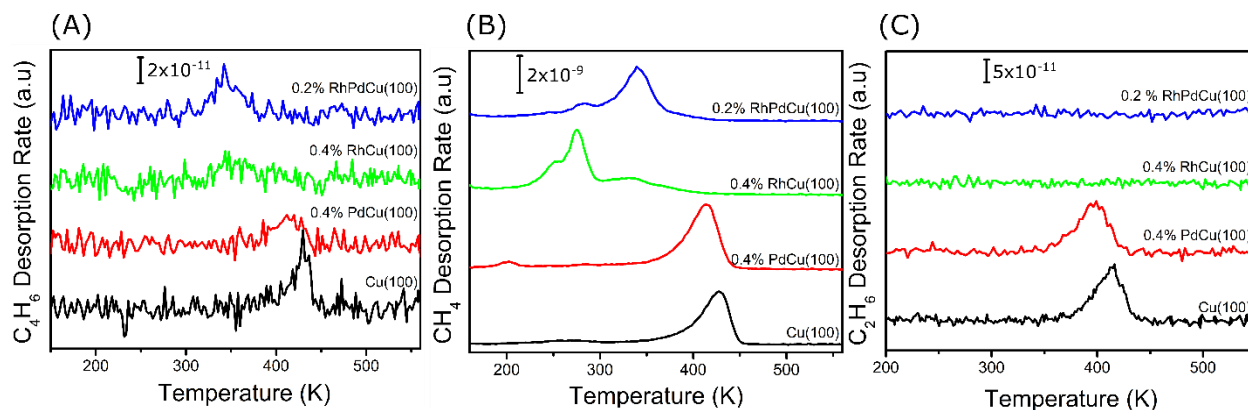


Fig 6. 2 TPD spectra of exposing 4 Langmuir [1 Langmuir (L)= 10^{-6} torr·s] of CH_3I at 90 K to different surfaces (Cu(100)-black, PdCu(100) SAA-red, RhCu(100) SAA-green, RhPdCu(100) SAA-blue. A) Butadiene desorption ($m/z=54$) evolution from the different surfaces. B) Methane desorption ($m/z=16$) from the different surfaces. The lower the methane desorption temperature, the lower the C-H activation barrier.^{3,6} C) Ethane desorption ($m/z=30$) from the different surfaces. This is the indicator of the capability of methyl-methyl coupling on different surfaces.³⁰

In order to translate the observed synergistic effect between Rh and Pd sites to a more realistic system, we used toluene as a probe molecule with which we could apply the UHV knowledge to more realistic nanoparticle studies. Our assumption here is that Rh sites would break the C-C bonds and make benzene when exposed to toluene while Pd sites would facilitate C-C coupling between phenyl groups to produce biphenyl. The first step is to investigate the behavior of toluene on Cu(100), PdCu(100) SAA, RhCu(100) SAA and RhPdCu(100) TD-SAA surfaces. Fig 6.3A, B and C show the TPD profiles of C_7H_8 ($m/z=91$), H_2 ($m/z=2$) and C_6H_6 ($m/z=78$) on the aforementioned surfaces after exposure to 1 L of C_7H_8 at 90 K. For the toluene TPD trace, the peak at ~ 246 K corresponds to intact molecular toluene desorption. For RhCu(100) and RhPdCu(100), on the other hand, a second peak at ~ 381 K can be observed, which must correspond to recombinative desorption of toluene.

Further information can be obtained by examining the H_2 TPD desorption trace as shown in Fig 6.3B, as the H_2 TPD trace can be used to monitor the toluene thermal decomposition

process.^{33,34} No H₂ desorption was observed on Cu(100) and PdCu(100) surfaces while two hydrogen peaks (260 K and 410 K) can be observed when there are Rh sites present. Previous studies for toluene decomposition on Ni(111) and Pt(111) showed that aliphatic C-H activation occurs before aromatic C-H activation (H₂ TPD trace from aromatic C-H evolves ~433 K on Ni(111) while ~493 K on Pt(111)).^{33,34} The benzene evolution peak (414 K) is observed on RhCu(100) and RhPdCu(100) surfaces while no benzene peak is seen on Cu(100) and PdCu(100). Moreover, molecular benzene desorbs from the Cu(111) surface below 250 K thus indicating the benzene formed at 414 K is reaction limited.³⁵ Based on these TPD profiles (H₂ TPD traces are flat on Cu(100) and PdCu(100), and no benzene evolution is observed on these surfaces), we can conclude that PdCu(100) and Cu(100) surfaces are not capable of activating toluene. For toluene on RhCu(100) SAA, C-H activation at the methyl group occurs first (as the first H₂ peak is ~260 K which is similar to the C-H activation temperature (274 K) for the iodomethane experiment) to produce benzyl groups (CH₂C₆H₅) and H atoms.⁶ We further hypothesize that these newly formed adsorbed H atoms can recombine and form H₂ to desorb (H₂ peak observed at 260 K). As for the produced benzyl groups, these surface species which are near Rh sites undergo further C-H activation to produce CH-C₆H₅ groups and H atoms. These adsorbed H atoms can then recombine with the remaining CH₂-C₆H₅ groups to produce toluene which desorbs at ~381 K. To further testify this hypothesis, benzene formation from toluene decomposition was tracked at a range of Rh coverages and toluene exposures, respectively. As shown in Fig 6.4, the benzene yield at constant toluene coverage (0.5 L) scales linearly with Rh coverage while the benzene yields barely change as a function of toluene coverage with constant Rh coverage (3%). This means that the formed benzyl groups are not capable of spillover and only benzyl groups close to Rh sites undergo further C-H activation and C-C bond cleavage process. The remaining CHC₆H₅ groups undergo

C-C bond cleavage to produce CH and C₆H₅ groups. The CH groups then undergo further C-H bond scission, producing adsorbed H atoms that can recombine with C₆H₅ groups to form benzene at 414 K. The absence of observed methane evolution in RhCu(100) and RhPdCu(100) further suggests that C-H activation primarily occurs at the methyl group and undergoes deep dehydrogenation before C-C bond cleavage, which is consistent with previous studies of the toluene reaction on Pt(111) and Ni(111) that also showed C-H activation indicate that Rh sites are crucial for C-C bond cleavage to produce phenyl is first centered at methyl groups.^{33,34} However, no biphenyl formation was observed. These results and the phenyl group will quickly recombine with

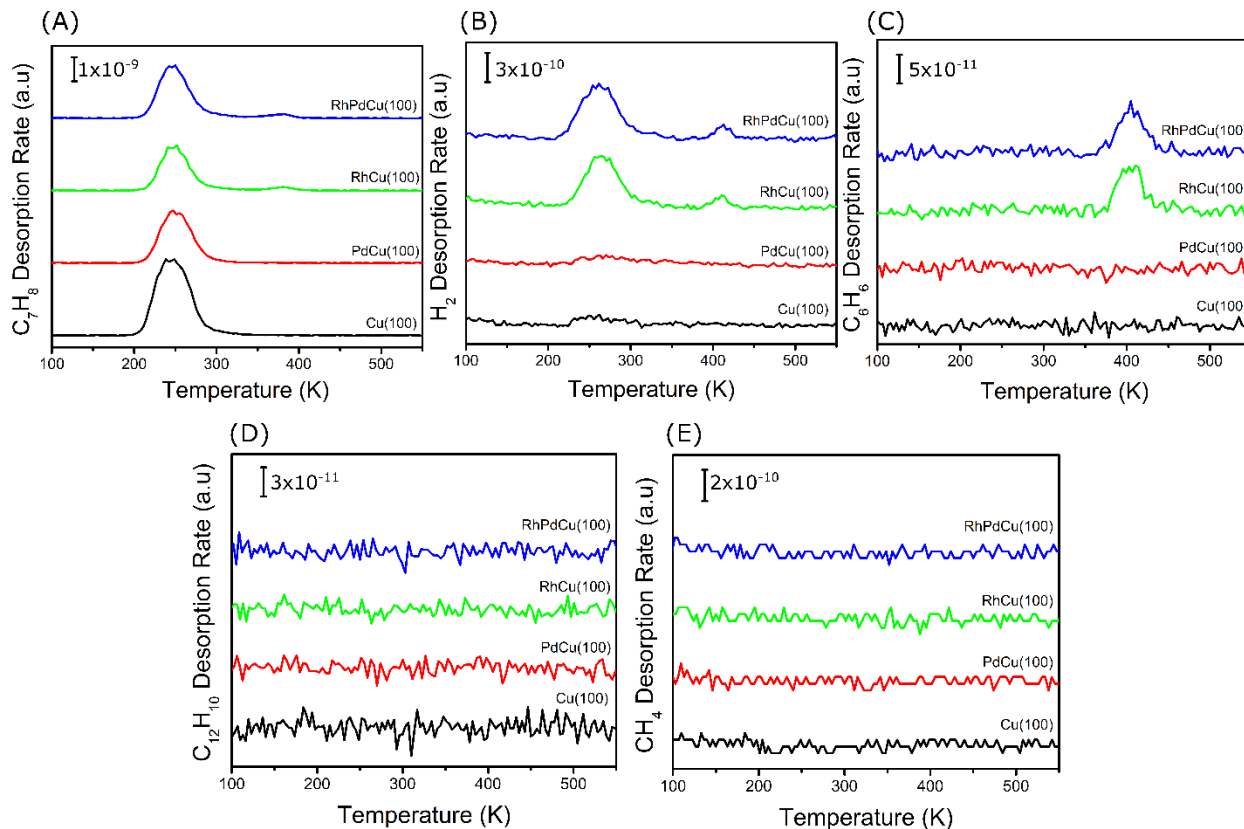


Fig 6. 3 TPD traces after exposing 1 Langmuir [1 Langmuir (L)= 10^{-6} torr·s] of C₇H₈ at 90 K to different surfaces (Cu(100)-black, PdCu(100) SAA-red, RhCu(100) SAA-green, RhPdCu(100) TD-SAA-blue). Products evolution of toluene reaction on different surfaces A) toluene (m/z=91), B) hydrogen (m/z=2), C) benzene (m/z=78), D) biphenyl (m/z=154) E) methane (m/z=16).

surface bound H atoms to produce benzene instead of phenyl groups combining with each other to produce biphenyl. Bent and coworkers have investigated phenyl-phenyl coupling on a Cu(111) surface using iodobenzene and showed that there are two reaction mechanisms for biphenyl formation.³⁶ At low iodobenzene coverage, biphenyls evolve at ~ 370 K as iodobenzene molecules undergo C-I bond cleavage to form phenyl groups which subsequently couple (phenyl-phenyl coupling is the RLS as molecular biphenyl desorbs 30-50 K lower).³⁷ At high iodobenzene coverage, adsorbed phenyl groups can couple with intact iodobenzene and form biphenyls at ~270 K. Also, the biphenyl yield of the 370 K pathway decreases while the 270 K pathway increases when the iodobenzene dosage is above 5 L. Together, these results indicate that a higher coverage of phenyl groups is required for us to observe phenyl groups coupling to produce biphenyls.

Moving forward, we examined the phenyl-phenyl coupling on RhCu(100) and PdCu(100) by tracking biphenyl evolution from the C_6H_5I reaction. For Cu(100), a single biphenyl peak appears at 377 K, similar to the biphenyl evolution at 370 K on Cu(111) reported by Bent and coworkers.³⁶ The biphenyl peak shifts to 367 K and 360 K for PdCu(100) and RhCu(100), respectively. As mentioned above, phenyl-phenyl coupling is the RLS and thus we conclude that adding Pd or Rh in Cu(100) lowers the coupling barrier.³⁶ Biphenyl yield, another important factor to evaluate coupling capability, was further investigated by integrating the biphenyl evolution peak of the investigated surfaces. As shown in Fig 6.5B, RhCu(100) shows similar biphenyl yield as Cu(100) while PdCu(100) exhibits 5-fold biphenyl yield compared to Cu(100). Overall, these results indicate that Pd sites are better at facilitating phenyl coupling. Ongoing flow reactor from Professor Nathaniel Eagan will further validify the proposed synergistic effect between Rh and Pd sites.

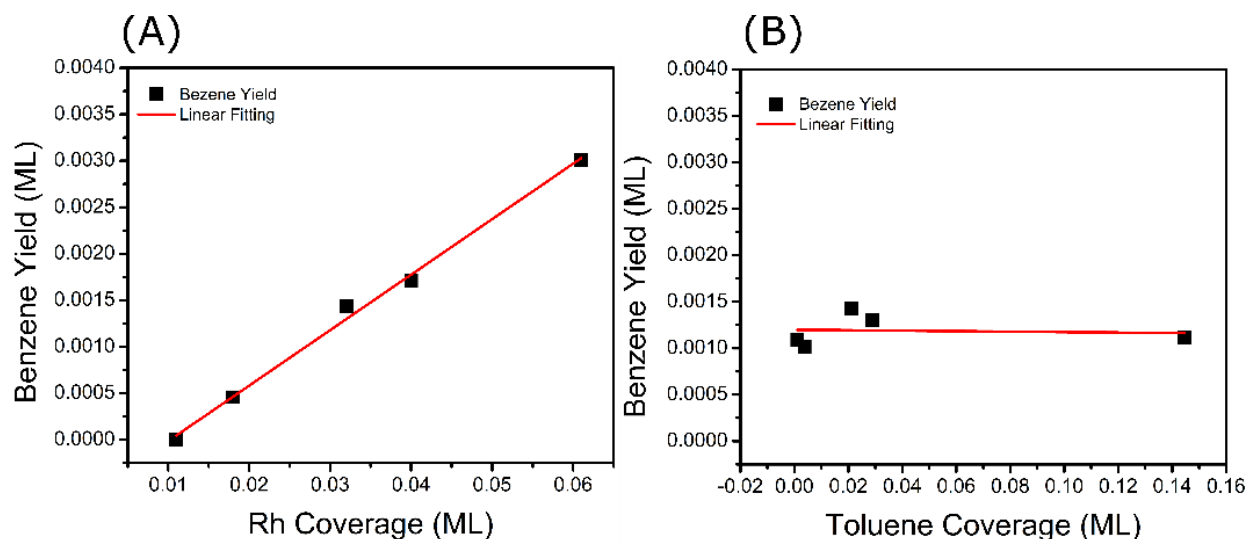


Fig 6. 4 A) Benzene yield after exposing 0.5 L of toluene to Cu surfaces with different Rh coverages (0.01-0.06 ML) B) Benzene yield after exposing different amounts of toluene to 0.03 ML RhCu (100) SAA surface.

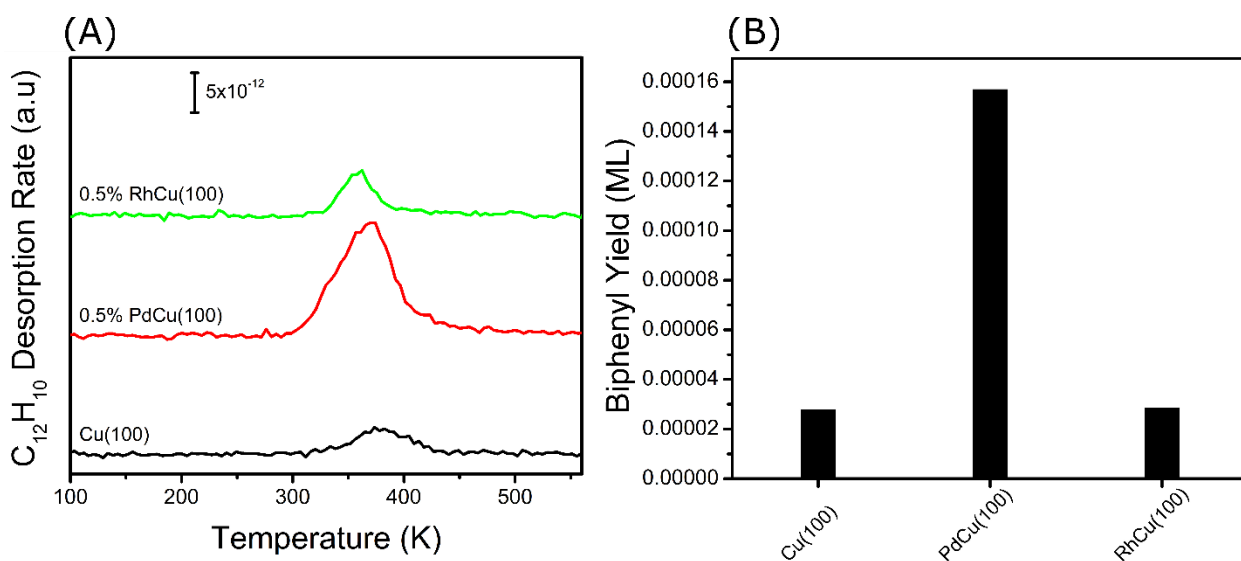


Fig 6. 5 A) TPD traces after exposing 5 Langmuir [1 Langmuir (L)= 10^{-6} torr·s] of C_6H_5I at 90 K to different surfaces (Cu (100)-black, PdCu (100) SAA-red, RhCu (100) SAA-green) B) Quantifying biphenyl yield from C_6H_5I reaction.

6.3 Conclusion

In summary, we have prepared a RhPdCu(100) TD-SAA under UHV conditions and characterized the active sites in this system. Combined STM, CO RAIRS, and TPD results show

that Rh and Pd form isolated sites. The synergy between Rh and Pd sites was further examined with iodomethane, toluene and iodobenzene. Iodomethane experiments indicated that Rh sites facilitate C-H activation while Pd sites enable methylene insertion (C-C coupling). In order to transfer this knowledge to a more relevant reaction, we further investigated the toluene reaction, and the results implied Rh is capable of breaking the C-C bond while Pd is not. Limited by the amount of phenyl groups generated from toluene experiments, we tracked biphenyl yield from an iodobenzene reaction to evaluate the coupling capability of Rh and Pd sites. The results show that Pd sites are better at phenyl-phenyl group coupling. Our collaborators will perform flow reactor experiments to provide a complete picture.

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Chapter 7: Transient CO Movement between Rh and Ni Minimizing Rh Usage for Formic Acid Dehydrogenation

7.1 Introduction

H₂ is a promising clean energy source that attracts widespread interests.^{1,2} However, safe and efficient H₂ storage and distribution from large-scale centralized centers remains a challenge.³ An alternative to centralized hydrogen production involves on-site hydrogen generation *via* steam reforming of organic fuels or hydrogen storage materials.^{4,5} Among which, formic acid is a promising H₂ carrier owing to its low toxicity, high abundance (produced by CO₂ hydrogenation) and H₂ storage value (4.4 wt% H₂).⁶ Increasing attention has been paid to catalytic hydrogen generation *via* heterogeneous catalysts owing to the ease of product separation and catalyst recycling.⁷ For monometallic candidates, Pt and Pd exhibit the optimal surface-reactant binding strength and therefore are among the top of the volcano plot.^{8–10} Selectivity to produce CO-free H₂ is another important aspect since formic acid can be decomposed through a dehydrogenation pathway (producing H₂+CO₂) or a dehydration pathway (producing H₂O+CO).^{9,11} Previous model catalyst studies have observed the dehydration pathway on Pt(111), Pd(111) and Pd(100) surfaces.^{12–14} One strategy to enhance selectivity for CO-free H₂ is through alloying.^{15,16} Over the past decade, Pd-based alloys (for instance, PdAg and PdAu) have shown great promise owing to their high selectivity and reactivity.^{17–20} Moving beyond the known limitations depicted by the volcano plot for monometallic catalysts, one solution is to increase the complexity of the current catalysts.²¹ For instance, Jiang and coworkers reported Co_{0.30}Au_{0.35}Pd_{0.35}/C trimetallic alloys that show better reactivity than Co_{0.30}Pd_{0.70}/C, Au_{0.50}Pd_{0.50}/C and physically mixed Co/C, Pd/C and Au/C.²² Furthermore, they proposed surface energy (γ) as a descriptor to screen third metal candidates to further improve the reactivity of the AuPd bimetallic system.^{23,24} Au_{0.35}Pd_{0.5}Ir_{0.15}

shows 3-fold H₂ TOF compared to Au_{0.5}Pd_{0.5}. Together, these results support that carefully-tuned alloy composition is critical to achieve the observed high reactivity. However, fundamental understanding of ternary alloy systems enhancing formic acid dehydrogenation reactivity is hindered by the compositional and structural complexity.^{16,25}

Single-atom alloys (SAAs), composed of an atomically dispersed metal stabilized in the surface of another metal host, provides a reductionist approach to investigate the role of reactive dopant and more selective host.^{26,27} For instance, Sykes and coworkers proposed a bifunctional PtCu SAA catalyst for highly selective 1,3-butadiene semi-hydrogenation.²⁸ Their results show that atomically dispersed Pt sites enable H₂ dissociation and spillover to Cu sites, which perform further hydrogenation. However, industrially relevant reactions normally involve multiple elementary steps, and it is difficult for a single site to perform high activity towards each step.²⁹ One option is to introduce a second dopant metal to the SAAs.³⁰ Recently, Sykes and coworkers proposed that Pt-Cr adjacent sites in a Ag(111) host are active for ethanol dehydrogenation, while the individual component PtAg and CrAg are not.³¹ Further theoretical calculations show that Pt-Cr adjacent sites are needed for the critical O-H bond breaking step. This research has enabled expansion beyond SAAs to gain fundamental understanding of the role of two dopants in a host.^{15,32}

Herein, we used formic acid as a probe molecule to understand the synergy between two non-adjacent dopant metal sites, in a catalytic system referred to as two-dopant single-atom alloys (TD-SAA). Chapter 5 showed that RhCu SAAs exhibit the highest reactivity towards formic acid dehydrogenation among other Cu-based SAAs (X= Pd, Pt, Ni and Rh). However, the industrial application of RhCu SAAs is still hindered by the cost of Rh. To mitigate this cost, a second dopant to reduce Rh loading would be ideal. Our surface science results show that formic acid

decomposition is a coverage-dependent reaction and introducing Ni as second dopant facilitates 0.3% RhCu SAA reactivity and resembles the performance of 0.7% RhCu SAA. This reactivity enhancement via introducing Ni as second dopant has been further investigated by ongoing KMC simulations (Prof. Michail Stamatakis), which show there is transient CO movement between Rh and Ni sites that periodically free up Rh sites and enhance the overall Rh reactivity. This has been further validated by the fact that Pt (which binds CO equally as strongly as Ni sites) also exhibits similar enhancement while no enhancement was observed when the second dopant was changed to Pd (which binds CO weakly). This study provides fundamental insights into how the addition of a second dopant atom can affect reactivity, and the results may be generalizable for the design of industrially relevant catalysts.

7.2 Experimental

Low-Temperature Scanning Tunnelling Microscopy (LT-STM). LT-STM experiments were conducted in an UHV chamber with a base pressure of $\sim 1 \times 10^{-11}$ mbar using an Omicron LT-STM. Sample cleaning was performed in an adjacent preparation chamber with a base pressure less than 2×10^{-10} mbar. Repeated cycles of Ar (Airgas 99.99%) ion bombardment (1 keV, 10-20 μ A) and thermal annealing to 750 K were used for cleaning the Cu(100) single crystal. Rh/Ni deposition was performed from Rh/Ni rods (Goodfellow 99.9%) using flux monitored EFM 3 electron beam evaporators (Scienta Omicron), while the Cu(100) sample temperature was held at 300 K during deposition of a constant Rh /Ni flux of ~ 0.01 ML $\cdot$ min $^{-1}$. For RhNiCu TD-SAA, Ni was deposited first followed by Rh deposition. The STM images were acquired after cryogenically cooling the STM stage to 77 K.

Temperature-programmed Desorption (TPD). TPD experiments were performed in a separate UHV chamber with a base pressure of $< 1 \times 10^{-10}$ mbar equipped with a quadrupole mass

spectrometer (Hiden HAL/3F 301) capable of being advanced to less than 1 mm from the front of the crystal. The Cu(100) crystal was cleaned by repeated cycles of Ar ion sputtering (0.5 keV, 1.5 μ A) and annealed to 750 K. The NiCu(100)/ RhCu(100) SAAs were prepared by a flux monitored EFM 3 (Scienta Omicron) electron beam evaporators at a surface temperature of 300 K. For dopant metal coverage quantification, the as-prepared surfaces were cooled to 90 K via a liquid nitrogen cryostat and exposed to CO (99.99% Airgas) through a high-precision leak valve. For formic acid reactivity and reaction mechanism studies, the as-prepared surfaces were cooled to 90 K via the liquid nitrogen cryostat and exposed to HCOOH (99.0% Fisher Scientific) through a high-precision leak valve. Annealing was performed by resistively heating Ta wires that support the Cu(100) crystal, and temperatures were measured via a thermocouple spot welded to the back of the crystal. All TPD measurements were run with a heating rate of 2 K/s. Reactivity of the SAA and TD-SAA surfaces were examined by dosing 0.1 Langmuir [1 Langmuir (L) = 10^{-6} torr·s] HCOOH (0.06 equivalent monolayers). HCOOH was tracked using $m/z = 46$. Products, CO₂ and H₂ were tracked using $m/z = 44$ and 2, respectively, and CO and H₂O were tracked using $m/z = 28$ and 18, respectively.

Reflection Absorption Infrared Spectroscopy (RAIRS). RAIRS experiments were performed in the same chamber as the TPD experiments using a Bruker Tensor II spectrometer. The grazing-incidence IR beam was directed from the spectrometer onto the crystal and out of the chamber to a mercury-cadmium-tellurium (MCT) detector using a series of gold-coated mirrors. The external part of the IR spectrometer was encased with a dry air purge box and the UHV chamber was equipped with ZnSe windows to prevent IR radiation loss. RAIRS spectra were taken at the indicated temperatures and referenced to a background collected at 90 K. Spectra were averaged over 2000 scans with 4 cm^{-1} resolution. Manual background subtractions that accounted

for slight background drift over time were applied to all the IR spectra. Multi-peak fitting with a mixed Gaussian/Lorentzian (25%/75%) line shape was performed with the CO IR spectra on RhNiCu(100) using CasaXPS.

7.3 Results and discussion

We began our study by making and characterizing a RhNiCu(100) two dopant single-atom alloy (TD-SAA) with low-temperature STM. To make the RhNiCu(100) TD-SAA surface, Ni was deposited first followed by Rh deposition while holding the surface at 300 K. Then the surface was cooled to 77 K for imaging. RhCu(100) and NiCu(100) SAA surfaces were prepared by following procedures published in previous studies from our group. The Rh atoms (Fig 7.1A) appear as protrusions while Ni atoms (Fig 7.1B) appear as depressions. It can be seen that Rh and Ni atoms form isolated sites in RhNiCu(100) TD-SAA system. To atomically dispersed Rh in Cu(100) has been reported in the previous studies from our group.³³ Similarly, CO desorption from isolated Ni sites (~ 374 K) in Cu(100) is similar to those Ni sites (~ 394 K) in Cu(111).³⁴ CO RAIRS experiments were then conducted by exposing the as-prepared RhCu(100) SAA, NiCu(100) SAA and RhNiCu(100) TD-SAA to a saturation coverage of CO at 90 K and then collecting IR spectra after heating the as-prepared surface to 240 K, where CO occupies primarily Rh and Ni sites, as CO molecules desorb from Cu(100) surface < 200 K.³⁵ Two distinct peaks can be observed in RhNiCu(100) TD-SAAs: the 1925 cm^{-1} peak corresponds to dicarbonyls at Rh sites and the broad peak at 1982 cm^{-1} corresponds to the monocarbonyls at Ni and Rh sites. Peak fitting was further conducted on the broad peak, which can be deconvoluted to a 1987 cm^{-1} and a 1975 cm^{-1} peak. These two peaks match well with the monocarbonyls at Ni sites and Rh sites by comparing with CO RAIRS spectra of RhCu(100) SAA and NiCu(100) SAA. Moreover, the lack of bridge-bound CO as reported by previous studies for Rh(100) ($2005\text{-}2016\text{ cm}^{-1}$ when the CO coverage is below

0.16 ML) and Ni(100) (1896-1909 cm^{-1} when the CO coverage is below 0.14 ML) indicates that Rh and Ni sites are separate from each other.^{36,37} Together, these results show that Rh and Ni atoms form isolated sites in Cu(100).

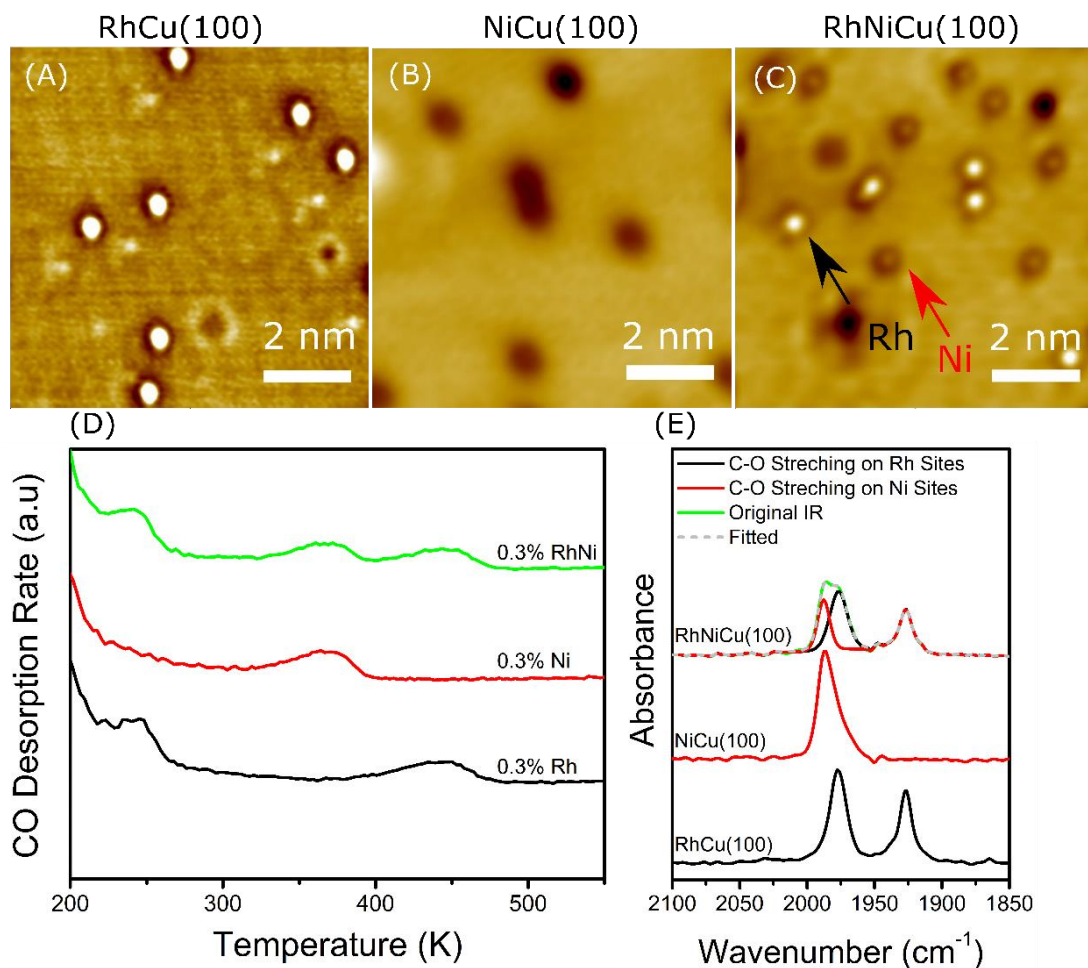


Fig 7. 1 Characterizing RhNiCu (100) TD-SAA using STM, TPD and RAIRS. STM images of as-prepared A) RhCu (100) SAA, B) NiCu (100) SAA and C) RhNiCu (100) TD-SAA. D) TPD spectra of saturation CO exposures on 0.7% RhCu (100), 0.7% NiCu (100) and 0.3% Rh 0.3% NiCu (100). E) RAIRS spectra of saturation CO on 0.7% RhCu (100), 0.7% NiCu(100) and 0.3% Rh 0.3% NiCu(100). All RAIRS spectra were obtained at 240 K.

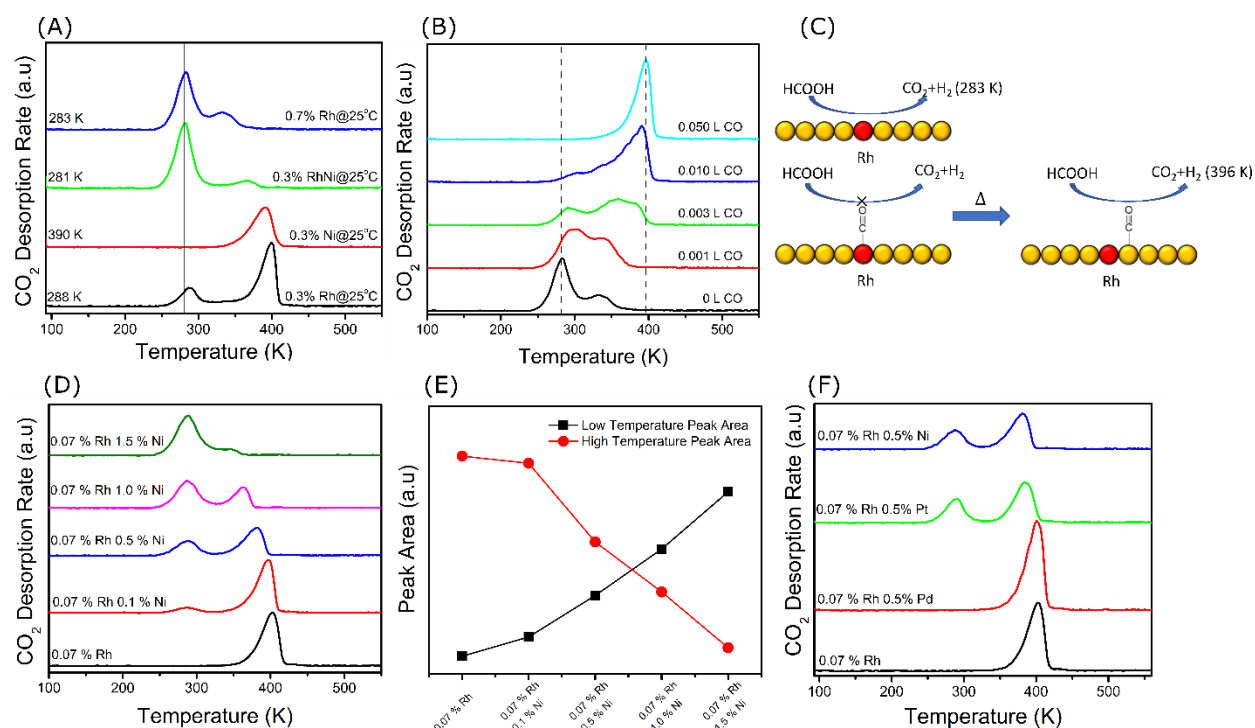


Fig 7. 2 Model systems demonstrate that adding Ni as second dopant promotes C-H activation in low coverage RhCu SAA for formic acid dehydrogenation. A) TPD spectra showing CO_2 desorption from formic acid reaction on the different surfaces. Each surface was exposed to 0.1 Langmuir [1 Langmuir (L)= 10^{-6} torr·s] of HCOOH at 90 K. B) TPD spectra of CO_2 desorption from formic acid reaction on RhCu SAA by varying pre-dose CO coverage. CO was dosed at 250 K and the surface was cooled down to 90 K before formic acid was deposited. C) Schematic illustration of formic acid dehydrogenation at Rh sites (C-H activation occurs at 283 K) vs CO covered Rh sites (C-H activation occurs at 399 K). D) TPD spectra showing growing intensity of the low temperature CO_2 peak by increasing Ni coverage at a constant Rh coverage. E) Low/High temperature CO_2 desorption peak area changes as a function of Ni coverage at a constant Rh coverage. F) CO_2 desorption from formic acid decomposition as a function of second dopant (X= Pd, Pt and Ni). Each surface was exposed to 0.1 Langmuir [1 Langmuir (L)= 10^{-6} torr·s] of HCOOH at 90 K.

Formic acid was used as a probe molecule to further investigate the synergy between Rh and Ni sites in the RhNiCu(100) TD-SAA. As previously described in Chapter 5, formic acid dehydrogenation on Cu-based SAAs follows the formate pathway and the CO_2 desorption temperature is an indicator of C-H activation as molecular CO_2 desorbs from Cu(100) ~ 90 K.³⁸ The formic acid dehydrogenation pathway was investigated by dosing an isotopically labelled equivalent molecule (DCOOH in this instance), a widely used method for reaction pathway studies,³⁹ on the as-prepared SAAs (X= Pd, Pt, Ni and Rh). H_2 ($m/z=2$) desorbs first followed by

D₂ (m/z=4) desorption on all investigated surfaces. The results indicate O-H activation step occurs first followed by C-D activation (formate pathway) where C-H activation is the rate-limiting step.^{9,11,40,41} Also, formic acid dehydrogenation appears to be sensitive to the dopant coverage where C-H activation is more facile at higher dopant coverage SAAs (See Appendix). To better visualize this dopant coverage effect towards C-H activation in the formic acid dehydrogenation process, the CO₂ desorption peak temperature was plotted against dopant coverage. CO₂ desorption peak temperature varies <20 K for dopant coverage ranging from 0.3% to 1.2% for Rh and from 0.3% to 1.8% for Ni (See Appendix). Additionally, the lack of slope change (CO₂ desorption peak vs dopant coverage) suggests that dopant coverage ranging from 0.3% to 1.8% for Ni while 0.3% to 1.2% for Rh forms similar active sites (in single atom regime). Similar dopant coverage effects have been reported for formic acid dehydrogenation on PtCu(111) SAA and ethanol dehydrogenation/dehydration on PtCrAg(111) dual-atom alloy.^{31,41} Further evidence is shown in Appendix, where Rh sites are separate from each other as evidenced by atomic resolution of 5% Rh in Cu(100) host and the lack of dipole-dipole interactions for Rh coverage ranging from 0.3% to 5.2 % in a Cu(100) surface (a similar case has been reported by Trenary and coworkers for varying Pd coverage in a Cu(111) surface and they found that the peak shows less than 8 cm⁻¹ shift for Pd coverage ranging from 0.4% to 2.3%).⁴² Furthermore, the FWHM for 5.2% RhCu(100) and 8.9% NiCu(100) are 21.2 cm⁻¹ and 23.0 cm⁻¹, respectively (previous studies on RhCu(111) and NiCu(111) showed that the FWHM for 0.2% RhCu(111) and 0.2% NiCu(111) are 24.0 cm⁻¹ and 24.3 cm⁻¹, respectively).^{34,43} Noted that the FWHM is an important indicator for the uniformity of the active sites. The fact that FWHM values of higher coverage Rh and Ni sites in Cu(100) are lower than those of 0.2% RhCu(111) and 0.2% NiCu(111) further validates that the Rh and Ni sites stay in single atom regime at the investigated coverages (Rh coverage maximum is 1.2 %

while Ni coverage maximum is 1.8 %). This is supported by previous studies that show Rh and Ni form isolated sites at 0.2% dopant coverage in Cu(111) metal host.⁴⁴

The next step was to compare the activity of the RhNiCu(100) TD-SAA to the SAAs counterparts. The as-prepared 0.3% RhNiCu(100), 0.3% RhCu(100), 0.3% NiCu(100) and 0.7% RhCu(100) surfaces were exposed to 0.1 L formic acid at 90 K and CO₂ (m/z=44) evolution was tracked. It can be seen that 0.3% RhNiCu(100) shows similar CO₂ desorption peak temperature as 0.7% RhCu(100) (Fig 7.2A). Moreover, the CO₂ trace in 0.3% RhCu(100) and 0.3% NiCu(100) are presented for further comparison. Two CO₂ desorption peaks (288 K and 396 K) can be observed on 0.3% RhCu(100) while one peak (390 K) observed on 0.3% NiCu(100), indicating their inferior C-H activation capability compared to 0.3% RhNiCu(100) TD-SAA. The identity of the 396 K CO₂ desorption peak was further investigated by keeping Rh coverage constant (0.7% of a monolayer) and introducing a trace amount of CO at 250 K before exposing the surface to 0.1 L formic acid. The CO₂ desorption peak gradually shifts from lower temperature (~283 K) to higher temperature (~396 K) as the amount of pre-dosed CO increases from 0 L to 0.05 L. These results reveal that the 396 K peak originates from C-H activation of formate on CO-corked Rh sites (Fig. 2B). Similar effect has been observed in corking Rh single atom sites in RhCu(111) SAA as a function of CO coverage and tracking ethene evolution from iodoethane.⁴⁵ The ethene desorption peak temperature (an indicator of the capability of β -hydride elimination) shifts to higher temperature as the CO coverage increases, which tells us the β -hydride elimination capability is dictated by the ratio of CO-corked Rh sites versus CO-free Rh sites.

In order to investigate the mechanism of the synergistic effect between Rh and Ni atom dopants, we prepared RhNiCu(100) surfaces by keeping the Rh coverage constant (0.07% of a monolayer) and varying the Ni coverage (between 0.1 % and 1.5 %) and exposing these as-

prepared surfaces to 0.1 L formic acid and tracking CO₂ (m/z=44) as a product to evaluate the C-H activation capability. Only a high temperature CO₂ desorption peak (~402 K) can be observed for 0.07% RhCu(100) surface (Fig 7.2D). When Ni is introduced as the second dopant, a low temperature peak (~288 K) appears, and the area of this low temperature peak grows while the high temperature peak (~402 K) shrinks as the Ni coverage increases in the RhNiCu(100) TD-SAA system. To better visualize this trend, the low temperature CO₂ peak (~288 K) and high temperature CO₂ peak (~402 K) area at different Rh/Ni ratios are shown in Fig 7.2E. Our previous study of DCOOH on NiCu(100) surfaces showed that the rate limiting step is C-H activation and the CO₂ desorption temperature is the indicator of C-H activation capability (Chapter 5). Again, specific to the NiCu(100) SAAs, the CO₂ desorption peak temperature decreases as the Ni coverage increases, which indicates the system is in the single atom regime; the higher the Ni coverage, the lower the C-H activation barrier (See Appendix). At 1.8% Ni coverage, the CO₂ desorption temperature peak is 370 K, and the investigated Ni coverage is 0.1%-1.5%, which tells us the observed 288 K peak does not come from C-H activation at Ni sites. Therefore, we conclude that the low temperature CO₂ peak (~288 K) is attributed to C-H activation that occurs at Rh sites. Also, the fact that the area of this peak increases with increasing Ni coverage indicates that increasing Ni sites facilitates C-H activation at Rh sites. To further investigate the observed enhancement of C-H activation capability in 0.07% RhCu(100) by introducing Ni as second dopant, we prepared analogous TD-SAA surfaces for comparison with Pt and Pd as the second dopants. We kept the coverage of the second dopant X (X=Pd, Pt and Ni) constant at 0.5% and tracked CO₂ desorption after exposing 0.1 L formic acid to these as-prepared surfaces (Fig 7.2F). It can be seen that the low temperature CO₂ desorption peak (~288 K) can be observed in RhNiCu(100) and RhPtCu(100) TD-SAAs while not been observed in RhPdCu(100) TD-SAA. This can be

understood by the CO desorption temperature, which reflects the relative CO binding strength, on isolated Pd (~258 K), Pt (~358 K) and Ni (~374 K) sites in Cu(100) host.^{34,43} We thus hypothesized that there are transient CO movement between Rh and Ni/Pt sites that can periodically free up the Rh sites for increased C-H activation and we further elaborate upon this effect using Kinetic Monte Carlo (KMC) simulations.

7.4 Conclusion

Using a combination of surface science techniques, this work used formic acid as a probe molecule to demonstrate the synergy between atomically dispersed Rh and Ni sites. Combined STM, CO TPD and CO RAIRS characterization results show that Rh and Ni form isolated sites in the Cu(100) host. Further activity studies show that formic acid dehydrogenation is a dopant coverage sensitive reaction, and when in the single atom regime, higher dopant coverages result in more facile C-H activation to produce CO₂. The 0.3% RhNiCu TD-SAA exhibits similar activity to the 0.7% RhCu(100) SAA. We also find that CO₂ desorption peak temperature under constant formic acid dosage and Rh coverage is dictated by the amount of CO coked Rh sites. Moreover, we kept Rh coverage constant and investigated the activity of the RhNiCu(100) TD-SAA surface as a function of Ni coverage. We find that introducing Ni sites facilitates C-H activation at the Rh sites and this is attributed to transient CO movements between Rh and Ni that periodically free up Rh sites for highly efficient C-H activation. Ongoing KMC simulations from Prof. Michail Stamatakis' group will further elucidate this effect and provide a more complete picture of the reaction mechanism.

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Chapter 8: RhNiCu Facilitates Ethanol Dehydrogenation

8.1 Introduction

The production of acetaldehyde *via* non-oxidative ethanol dehydrogenation (EDH) has been extensively studied,^{1–5} as acetaldehyde is a key precursor for many industrial chemicals. The EDH approach leads to much easier product separation as EDH produces H₂ instead of H₂O.⁶ However, current monometallic Cu catalysts suffer from low conversion and deactivation caused by sintering.^{7–9} Moreover, model catalyst studies of ethanol reactions on Cu(110) and Cu(111) further support the highly selective but less active nature of Cu surfaces in terms of producing acetaldehyde and H₂.¹⁰ Therefore, developing highly efficient catalytic materials for EDH attracts considerable interest. One strategy to improve catalytic activity without compromising selectivity is to introduce trace amount of reactive metal (such as Pd, Pt, Ni and Rh) to a more selective metal host (such as Ag, Au and Cu) to form single-atom alloys (SAAs).¹¹ Specific to EDH nanoparticle studies, Flytzani-Stephanopoulos and coworkers reported a silica-supported NiCu SAA with improved catalytic reactivity and long-term stability compared to silica-supported monometallic Cu nanoparticles.¹² They further compared the apparent activation barrier of silica-supported PdCu SAA (47 kJ/mol, which is 23 kJ/mol lower than Cu), PtCu SAA (63 kJ/mol) and NiCu SAA (69 kJ/mol) and to show that for Cu-based SAAs, Ni in Cu is the most promising SAA for EDH.¹³

However, industrial reactions generally involve multiple elementary steps and it is unlikely for a single site to perform all reaction steps with high efficiency, which thus necessitates multiple site design.^{14,15} Specific to thermal catalysis, Hu and coworkers investigated the synergistic effect between Ru and Ni single-atom sites on a CeO₂ support for dry CH₄ reforming. Theoretical computation results show that Ru dissociates CO₂ to CO while Ni activates CH₄. As another recent example, Huang and coworkers reported a dual-single-atom catalyst (Ir₁Mo₁/TiO₂) with enhanced

selectivity for the hydrogenation of 4-nitrostyrene (4-NS) to 4-vinylaniline (4-VA) compared to its single-atom catalyst counterparts (Ir/TiO₂ and Mo/TiO₂).¹⁶ According to Density Functional Theory (DFT) results, the observed reactivity enhancement in this dual-single-atom catalyst can be explained that Ir sites facilitate H₂ dissociation while Mo sites enable 4-NS adsorption. For trimetallic catalysts, Li and coworkers demonstrated a MOF-derived RuZr/Co catalyst for high C₅ product selectivity in the Fischer-Tropsch reaction.¹⁴ DFT computation results show that CO prefers to stay in between Ru and Zr (C and O interact strongly with Ru and Zr sites, respectively) and thus lowers the C-O activation barrier. Furthermore, the presence of both Ru and Zr sites also lowers the barrier of C-C coupling. However, investigation of the synergistic effect between two separate sites in a metal host is still in its infancy. Surface science techniques utilizing well-defined single crystals has provided valuable insights of correlating atomically-resolved SAA surface structures (PdCu(111), PtCu(111), NiCu(111) and RhCu(111)) with their observed activities towards many industrial relevant reactions, such as acetylene semi-hydrogenation, propane dehydrogenation and ethanol dehydrogenation.¹⁷⁻¹⁹ Moving forward, we attempted to use this SAA knowledge acquired in the past decade to construct more complicated two-dopant single-atom alloys (TD-SAAs) and investigate the potential synergy between two different dopants.

Herein, we propose a combined theoretical simulation and surface science approach to investigate the synergistic effect between two dopants in TD-SAAs. Surface science studies enable us to directly image Rh and Ni sites in the Cu(111) host and the coexistence of these sites was further validated by CO temperature programmed desorption (TPD) experiments. The activity of Rh and Ni sites in Cu(111) was further demonstrated by the ethanol decomposition reaction. TPD results show that a 0.5% Rh 0.2%NiCu(111) TD-SAA has a lower activation temperature required for transforming ethanol to acetaldehyde than its SAA counterparts (0.7% NiCu(111) and 0.7%

RhCu(111)). The desorption temperatures of the ethanol decomposition products were further plotted against dopant coverage to understand the individual role of Rh and Ni sites. Specific to Rh sites, ethanol TPD profiles indicate that the ethanol decomposition pathway is sensitive to dopant coverage and Rh adjacent/non-adjacent sites are capable of breaking the C-C bond (Rh adjacent/ non-adjacent sites start forming at 0.4% Rh coverage). No C-C bond cleavage was observed in NiCu(111) system. We thus hypothesize that Rh adjacent/non-adjacent sites enable low temperature C-H activation, and the newly formed acetaldehyde can either diffuse to Ni sites and desorb or stay at Rh sites to undergo further C-C bond cleavage. Ongoing theoretical computations from Professor Philippe Sautet and Michael Ngan will calculate the reaction pathway of ethanol decomposition on Rh adjacent/non-adjacent sites and Ni single atom sites to provide more insights about the observed activity enhancement on RhNiCu TD-SAA.

8.2 Experimental

Low-Temperature Scanning Tunnelling Microscopy (LT-STM). LT-STM experiments were conducted in an UHV chamber with a base pressure of $\sim 1 \times 10^{-11}$ mbar using an Omicron LT-STM. Sample cleaning was performed in an adjacent preparation chamber with a base pressure less than 2×10^{-10} mbar. Repeated cycles of Ar (Airgas 99.99%) ion bombardment (1 keV, 10-20 μ A) and thermal annealing to 750 K were used for cleaning the Cu(111) single crystal. Rh/Ni deposition was performed from Rh/Ni rods (Goodfellow 99.9%) using a flux monitored EFM 3 electron beam evaporators (Scienta Omicron), while the Cu(111) sample temperature was held at 380 K during deposition of a constant Rh /Ni flux of ~ 0.01 ML $\cdot$ min $^{-1}$. For RhNiCu DAA, Rh was deposited first followed by Ni deposition. The STM images were acquired after cryogenically cooling the STM stage to 77 K.

Temperature-programmed Desorption (TPD). TPD experiments were performed in a separate UHV chamber with a base pressure of $<1 \times 10^{-10}$ mbar equipped with a quadrupole mass spectrometer (Hidden HAL/3F 301) capable of being advanced to less than 1 mm in front of the crystal. The Cu(111) crystal was cleaned by repeated cycles of Ar ion sputtering (0.5 keV, 1.5 μ A) and annealed to 750 K. The NiCu(111)/ RhCu(111) SAAs were prepared by a flux monitored EFM 3 (Scienta Omicron) electron beam evaporators at a surface temperature of 380 K. For dopant metals coverage quantification, the as-prepared surfaces were cooled to 90 K via a liquid nitrogen cryostat and exposed to CO (99.99% Airgas) through a high-precision leak valve. For ethanol dehydrogenation studies, the as-prepared surfaces were cooled to 90 K via the liquid nitrogen cryostat and exposed to CH₃CH₂OH (99.0% Fisher Scientific) through a high-precision leak valve. Annealing was done by resistively heating Ta wires that support the Cu(111) crystal, and temperatures were measured via a thermocouple spot welded to the back of the crystal. All TPD measurements were run with a heating rate of 1 K/s. Reactivity of the SAA surfaces was examined by dosing 20 Langmuir [1 Langmuir (L) = 10^{-6} torr·s] CH₃CH₂OH (0.05 equivalent monolayers). CH₃CH₂OH was tracked using $m/z = 46$. Products, CH₃CHO and CH₄ were tracked using $m/z = 29$ and 16, respectively, and CO and H₂O were tracked using $m/z = 28$ and 18 respectively.

8.3 Results and discussion

We began our study by making and characterizing RhNiCu TD-SAAs with low temperature STM. Specifically, to the RhNiCu(100) TD-SAA surface, Ni was deposited first followed by Rh deposition while holding the surface at 380 K and then the surface was cooled to 77 K for imaging. NiCu(111) and RhCu(111) SAAs were prepared by this method and imaged as reference for the RhNiCu(111) TD-SAA. Rh atoms (Fig 8.1A) appear as protrusions while Ni atoms (Fig. 1B) appear as depressions, which is consistent with previous results.^{18–22} These STM

images of RhCu(111) SAA and NiCu(111) SAA enable us to differentiate Rh and Ni sites in the RhNiCu(111) TD-SAA. To further confirm the active site distribution in the RhNiCu(111) TD-SAA, Rh and Ni were deposited on Cu(111) at 380 K, the surface was cooled, and CO TPD was conducted. CO TPD spectra of RhCu(111) SAA and NiCu(111) SAA were used as reference. As shown by the TPD results in Fig 8.1, two distinct peaks are observed for the RhNiCu(111) TD-SAA at 374 K and 475 K, which correspond to monocarbonyls at Ni sites and monocarbonyls at Rh sites, respectively (as indicated by the CO desorption trace for RhCu(111) SAA and NiCu(111) SAA counterparts). Moreover, the temperatures of CO desorption from Ni sites in NiCu(111) and Rh sites in RhCu(111) are consistent with previous studies in our group.^{20,26} Also, the fact that the two peaks (374 K and 475 K) observed in RhNiCu(111) TD-SAA matches individual CO desorption peak from RhCu(111) and NiCu(111) SAAs indicates the co-existence of Rh and Ni sites in this TD-SAA surface.

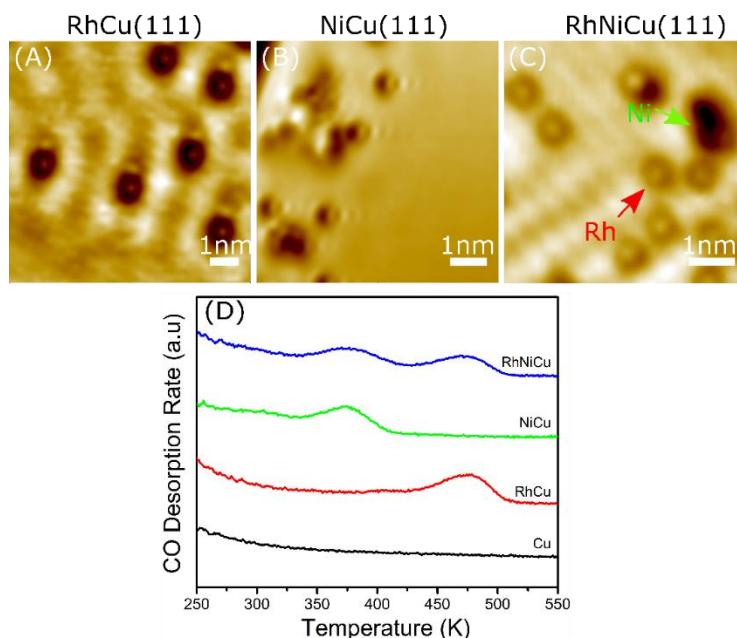


Fig 8. 1 Characterizing RhNiCu(111) TD-SAA using STM and TPD. STM images of as-prepared A) RhCu(111) SAA, B) NiCu(111) SAA and C) RhNiCu(111) TD-SAA. D) TPD spectra of saturation CO exposures on Cu(111), RhCu(111), NiCu(111) and RhNiCu(111) at 90 K.

Moving forward, we used ethanol as a probe molecule to further investigate the activity of Rh and Ni sites in RhNiCu(111) TD-SAA. Previous studies have shown that NiCu SAA exhibit promising ethanol dehydrogenation reactivity compared to PdCu and PtCu SAAs.¹³ To compare the activity of the RhNiCu(111) TD-SAA to their SAA counterparts, the as-prepared 0.5% Rh 0.2% NiCu(111), 0.7% RhCu(111) and 0.7% NiCu(111) surfaces were exposed to 20 L ethanol at 160 K (to avoid water affecting the alcohol dehydrogenation rate) and CH₃CHO (*m/z*=29) was tracked.²⁷ Ethanol dehydrogenation to form acetaldehyde proceeds step-wise and C-H activation is the rate limiting step (RLS) on Cu-based SAA catalysts (PdCu, PtCu and NiCu).^{3,5,13,19} Moreover, while chemisorbed molecular CH₃CHO desorbs from Cu(111) below 220 K, the CH₃CHO desorption peak on investigated surfaces ranges from 275 to 338 K indicates that the formation of CH₃CHO is a reaction limited process on Cu-based SAAs and TD-SAAs.^{10,19} Therefore, CH₃CHO desorption temperature can be used as indicator for C-H activation capability. In Fig 8.2, it can be seen that CH₃CHO desorbs from Cu(111), 0.7% RhCu(111), 0.7% NiCu(111) and 0.5% Rh 0.2% NiCu(111) at 337 K, 296 K, 295 K and 275 K, respectively. It is worth noting that CH₃CHO desorbs ~ 20 K lower than both 0.7% RhCu(111) and 0.7% NiCu(111), which indicates that 0.5% Rh 0.2% NiCu(111) exhibits better ethanol dehydrogenation activity.

To further investigate the observed ethanol dehydrogenation activity enhancement on RhNiCu(111) TD-SAA, we varied the coverage of dopant metals (Ni, Rh or RhNi) and exposed these surfaces to 20 L ethanol at 180 K and tracked CH₃CHO (*m/z*=29) desorption (See the Appendix). To better visualize the trend, we plotted CH₃CHO desorption peak temperature with respect to the total coverage of the dopants (Fig 8.2B). This shows that ethanol dehydrogenation is sensitive to dopant coverage, the higher dopant coverage the lower CH₃CHO evolution

temperature, that is, higher ethanol dehydrogenation activity. Specific to the NiCu(111) system, the drastic slope change between 0.007 ML and 0.01 ML Ni coverage is attributed to active site change. According to the previous studies, active site change (evolution from isolated sites to ensemble sites) modifies the observed reaction products.^{28,29} Specific to ethanol decomposition, the formation of CH₄ is a good indicator of C-C bond cleavage (C-C bond breaking produces methyl groups and aldehyde groups and subsequently the methyl group recombines with surface hydrogen to form methane). Therefore, quantifying CH₄ formation as a function of dopant coverages provide a precise way to probe ensemble sites.^{2-4,29}

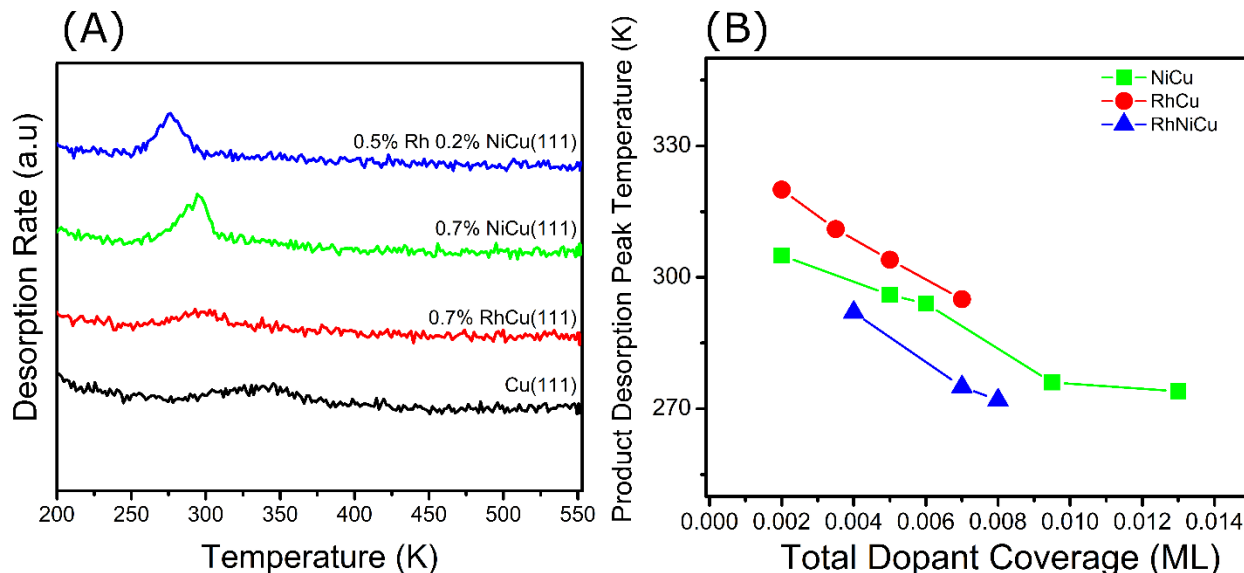


Fig 8. 2 Model catalyst studies for ethanol dehydrogenation on different surfaces. A) Acetaldehyde ($m/z=44$) yield from ethanol dehydrogenation on NiCu (111) SAA, RhCu (111) SAA and RhNiCu (111) TD-SAA. B) Acetaldehyde desorption peak temperatures versus the dopant coverages plotted as an indicator of C-H activation.

To gain a better understanding of the active sites evolution and investigate the potential synergy between Rh and Ni sites, H₂ ($m/z=2$) and CH₄ ($m/z=16$) from ethanol reactions on different surfaces was plotted over a range of dopant coverages (Fig 8.3 A-F). Cross comparison of the 177 K H₂ peak, which corresponds to H₂ formed from O-H activation step in NiCu(111), RhCu(111) and RhNiCu(111), that appears in the TPD spectra shows that this peak does not shift

with respect to the surface composition (varying dopant or dopant coverage). This indicates that the O-H activation barriers at Rh and Ni sites are similar and O-H activation is not the rate-limiting step on these surfaces, which is consistent with previous results.¹³ Moving forward, a second hydrogen peak appears in NiCu(111) system and this peak shifts to lower temperature as Ni coverage increases. It is worth noting that the observed second H₂ peak temperature (282 K at higher coverage) coincides with the acetaldehyde evolution temperature on NiCu(111), which tells us this peak originates from H₂ produced in C-H activation step. Furthermore, no CH₄ was observed in the scope of investigated Ni coverage, indicating Ni sites (single atom sites or potentially non-adjacent/adjacent pair sites are incapable of C-C bond cleavage). Rh sites, on the other hand, show a broadened H₂ peak starting at 0.5% Rh coverage and CH₄ peak appears at ~280 K when Rh coverage reaches 0.4% (Fig 8.3 G). These results indicate that the evolution of Rh sites (from single atom sites to adjacent/non-adjacent pair sites) and pair sites are capable of breaking the C-C bond to produce CH₄. Similar C-C bond cleavage has been observed on Rh(111) surface.² There are two H₂ peaks lying within the broadened hydrogen peak (~255 K and 297 K peaks correspond to C-H activation of the ethoxy group and subsequently the CHO group when Rh coverage reaches 0.5%). We thus hypothesize the adsorbate evolution process at Rh/Ni sites can be listed as follows: Briefly, O-H activation occurs at Rh and Ni sites at ~177 K, ethoxy C-H activation occurs at ~255 K followed by C-C bond cleavage at ~280 K for Rh sites while for Ni sites, the ethoxy C-H activation occurs at ~290 K. Thus, we hypothesize that the observed activity enhancement is attributed to facile C-H activation at Rh adjacent/non-adjacent sites and the newly formed acetaldehyde subsequently diffuses to Ni sites and desorbs. Ongoing DFT calculations from Professor Philippe Sautet and Michael Ngan will provide a complete reaction pathway for

Rh single atoms, Ni single atoms, Rh pairs sites, Ni pair sites and RhNi pair sites, which will provide more insight about this observed activity enhancement on RhNiCu(111) TD-SAA.

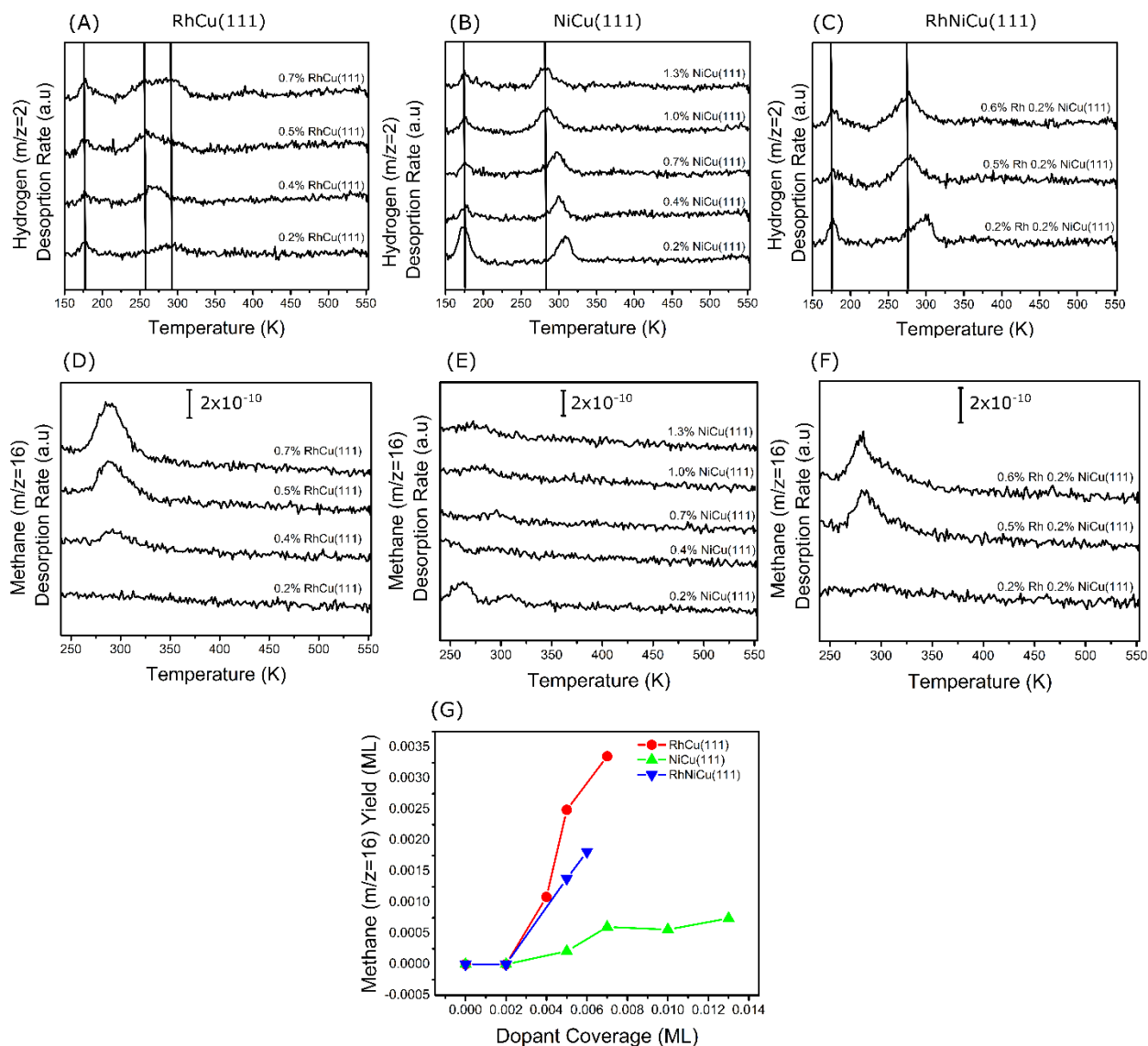


Fig 8. 3 TPD spectra of CH₄ (m/z=16) and H₂ (m/z=2) produced during the ethanol reaction on RhCu (111), NiCu (111) and RhNiCu (111) surfaces. Panels A-C show H₂ evolution as a function of dopant coverages while Panels D-F show CH₄ evolution as a function of dopant coverages. G) Quantifying methane formation as a function of dopant coverages. Methane starts forming when Rh coverage reaches 0.4% while only trace amount of methane formation is observed on NiCu(111). H) Schematic illustration of ethanol decomposition process at Ni and Rh sites.

8.4 Conclusion

This work aims to investigate the synergistic effects between Rh and Ni sites using ethanol as a probe molecule. STM and CO TPD results confirm the coexistence of Rh and Ni sites in the RhNiCu(111) TD-SAA surface. Ethanol TPD results show that 0.5% Rh 0.2% NiCu(111) exhibits higher activity for ethanol dehydrogenation to acetaldehyde than 0.7% NiCu(111) and 0.7% RhCu(111). Furthermore, we investigated the individual role of Rh and Ni sites in the ethanol reaction process as a function of dopant coverage. H₂ and CH₄ TPD traces tell us the active site evolution and Rh non-adjacent/adjacent pair sites start to form when Rh coverage reaches 0.4% and these pair sites are capable of breaking the C-C bond in ethanol to produce CH₄, while Ni sites need to surpass a higher activation barrier to activate the C-C bond. Our hypotheses for the better activity observed in 0.5% Rh 0.2% NiCu(111) were made based on the careful investigation of the RhCu(111) and NiCu(111): Rh pair sites enable low temperature C-H activation and newly formed acetaldehyde molecules subsequently diffuse to Ni sites and desorb. While surface science results provide evidence for the synergy between Rh and Ni sites, ongoing theoretical modeling will calculate the activation barriers for the formation of different intermediates and provide a complete reaction pathway to further demonstrate the observed synergistic effect.

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Chapter 9: Conclusions and Future Directions

9.1 Conclusions

As mentioned in Chapter 1, heterogeneous catalysts play an important role in modern society. However, the complexity of active sites and their surface dynamics under reaction conditions make precise structure-activity relationship assignments challenging. Confining active sites at the single-atom limit provides a reductionist approach to understand the fundamental chemistry for a given catalytic process and thus enables us to rationally design novel materials with improved catalytic performance.¹ Single atom alloys (SAAs), a subclass of single atom catalysts (SACs), have attracted widespread interest owing to their unique properties that enable them to circumvent the conventional linear scaling relationships imposed by Sabatier principle.² One example from our group is the design of a RhCu SAA, an unconventional combination, for highly efficient and selective propane dehydrogenation to produce propylene.³ However, industrially relevant reactions are comprised of multiple elementary steps and it is unlikely for a single site to perform all steps with high efficiency. This necessitates the design of catalysts with multiple sites to reach the activity beyond the top of the volcano plot.^{4,5} In this thesis, I made use of a model surface science approach (Chapter 2) to understand the behavior of different dopants (X=Pd, Pt, Ni and Rh) in a Cu(100) host and apply this knowledge to construct two-dopant single-atom alloys (TD-SAAs) to investigate the synergy between different dopants towards industrially relevant reactions.

In Chapter 3, I investigated the Rh alloying mechanism in Cu(111), Cu(100) and Cu(110) in the single-atom regime. These results show a strikingly different dopant dispersion for Rh in Cu(111) versus the more open Cu(100) and Cu(110) facets. Rh atoms tend to form dense brims above the step edges in Cu(111) while Rh atoms are finely dispersed in the terrace of Cu(100) and

Cu(110) surfaces. This observed dopant dispersion difference was then further investigated by quantifying the energy barrier of different events such as atomic hopping, place exchange, swapping and vacancy filling. DFT results from Profess Stamatakis and Dr. Papanikolaou indicate that the observed difference in alloying mechanism can be attributed to faster hopping rate, relatively higher atomic exchange barriers and stronger Rh binding in the vicinity of the step edges on Cu(111) compared to Cu(100) and Cu(110). The properties of atomically dispersed Rh sites in Cu(100) were further investigated in Chapter 4 using CO TPD and CO RAIRS. I discovered a new peak via TPD, which is assigned to dicarbonyl desorption at 260 K from RhCu(100) which has not yet been observed in RhCu(111). Furthermore, I utilized $^{12}\text{C}^{16}\text{O}$ RAIRS and isotopically labeled $^{13}\text{C}^{16}\text{O}$ to confirm the presence of dicarbonyl species at Rh sites. I assigned three peaks (1926 cm^{-1} , 1917 cm^{-1} and 1884 cm^{-1}), which correspond to $(^{13}\text{CO})\text{-Rh-}(^{13}\text{CO})$, $(^{13}\text{CO})\text{-Rh-}(^{12}\text{CO})$, and $(^{12}\text{CO})\text{-Rh-}(^{12}\text{CO})$ dicarbonyls, after exposing $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}$ mixtures to the 0.7% RhCu(100) surface. Using STM, I visualized the dicarbonyls and conducted localized voltage pulses on these features to reveal CO-free Rh sites. These results provide a general approach for Cu-based SAA characterization and inspired us to investigate two different dopants in Cu(100).

In Chapter 5, I examined the activity of Cu-based SAAs ($\text{X}=\text{Pd}$, Pt , Ni and Rh) towards formic acid decomposition. I found the reactivity trend of these SAAs is: $\text{RhCu}(100) > \text{NiCu}(100) > \text{PtCu}(100) > \text{PdCu}(100)$, which is distinctly different from the monometallic single crystal trend: $\text{Pt}(111) > \text{Pd}(111) > \text{Rh}(111) > \text{Ni}(111)$. DCOOH experiments show that formic acid decomposes via the formate reaction pathway on Cu(100) (O-H activation occurs first followed by C-H activation) and that adding trace amounts of reactive metals ($\text{X}=\text{Pd}$, Pt , Ni and Rh) does not change the reaction pathway. Furthermore, relative CO binding strength acquired by CO TPD can be used as a descriptor to predict the C-H activation capability of dopants. More generally, monometallic

Rh and Ni are not considered as ideal candidates towards selective formic acid decomposition as they bind carboxyl and formate intermediates too strongly which hinders further activation. Overall, this study demonstrates that candidates which are not considered to be optimal catalysts in their bulk phase may show promising catalytic behavior in the single-atom regime.

In Chapter 6, I proposed a general characterization approach for two-dopant single atom alloys (TD-SAAs). Using STM, I visualized isolated Rh and Pd sites with atomic resolution. CO RAIRS results show that C-O stretch peaks at Rh and Pd sites in 0.2% RhPdCu(100) match with peaks assigned to CO in Rh sites in 0.4% RhCu(100) and Pd sites in 0.4% PdCu(100), respectively. Also, no bridge bond peak is observed in RhPdCu(100) and C-O stretch peaks of Rh and Pd sites show minimal shifts compared to their SAA counterparts (meaning dipole-dipole interactions are minimized), indicating these sites are separate from each other. Subsequently, I demonstrated the synergy between Rh and Pd sites with iodomethane, toluene and iodobenzene. From the iodomethane experiments, I observed the formation of 1,3-butadiene, a product that involves C-H activation in the methyl group and C-C coupling of the methylene group, occurs ~70 K lower than PdCu(100) while no 1,3-butadiene evolution was observed for RhCu(100). By analyzing methane (an indicator of C-H activation capability) and ethane (C-C coupling capability) TPD traces from iodomethane experiments, we can conclude that the lower temperature 1,3-butadiene formation on RhPdCu(100) originates from the synergistic effect wherein Rh sites facilitate C-H activation and Pd sites enable C-C coupling. To translate this model catalyst knowledge to high surface area nanoparticle studies I studied toluene the decomposition reaction on the aforementioned surfaces. I found that only Rh sites are capable of C-C bond cleavage, but no biphenyl was observed since there are not enough phenyl groups produced. I further investigated biphenyl yield from iodobenzene experiments on Cu(100), PdCu(100) and RhCu(100) to compare the phenyl-phenyl

coupling on different surfaces. The initial results show that Pd sites are better at this type of coupling compared to Rh sites and Cu sites. Ongoing flow reactor studies led by Professor Nathaniel Eagan and Ho-Yi (Kenny) Lam will further test this hypothesis for the toluene reaction on RhPdCu TD-SAA.

In Chapter 7, I utilized formic acid as a probe molecule to understand the synergy between non-adjacent Rh and Ni sites in RhNiCu(100) TD-SAAs. I found that formic acid dehydrogenation is sensitive to dopant coverage and C-H activation (the RLS step) is more facile on higher coverage SAAs. The results show that a 0.3% RhNiCu(100) TD-SAA exhibits similar formic acid dehydrogenation activity as 0.7% RhCu(100) and is better than both 0.3% RhCu(100) and 0.3% NiCu(100). Further investigations show that the low temperature peak (~ 280 K), which corresponds to C-H activation at Rh sites, grows with increasing Ni coverage while Rh coverage (0.07%) and formic acid dosage (0.1 L) were kept constant. It is worth noting that no low temperature peak was observed on a 0.07% RhCu(100) SAA. Furthermore, the low temperature peak appears for 0.07% Rh 0.5% NiCu(100) and 0.07% Rh 0.5% PtCu(100) TD-SAAs while no low temperature peak was observed for 0.07% Rh 0.5% PdCu(100). Based on the fact that Pd sites bind CO less strongly than Pt and Ni, we hypothesized that there is transient CO movement between Rh and Ni/Pt sites that periodically free up Rh sites for increased C-H activation. Ongoing KMC simulations from Professor Michail Stamatakis, Weitian Li and Romain Réocreux will further elaborate upon this observed effect.

In Chapter 8, I studied ethanol dehydrogenation, another important process for acetaldehyde production, on the RhNiCu(111) TD-SAA system. STM confirms that Rh and Ni sites coexist in Cu(111) and CO TPD profiles show that the CO evolution from Rh and Ni sites in the RhNiCu(111) TD-SAA is a linear combination of Rh sites in RhCu(111) and Ni sites in

NiCu(111) SAAs. Furthermore, acetaldehyde from the ethanol reaction evolves at 274 K on 0.5% Rh 0.2% NiCu(111), which is ~ 20 K lower than 0.7% RhCu(111) and 0.7% NiCu(111) SAAs. Acetaldehyde evolution, an indicator of C-H activation capability, is sensitive to dopant coverage, and I found that C-H activation is generally more facile on high coverage SAAs. Specific to Rh sites, ethanol decomposition can either form acetaldehyde which desorbs or reacts further to produce methane and CO, meaning ethanol is a more precise probe for isolated Rh sites/ Rh non-adjacent sites/ Rh adjacent sites (the latter can be abbreviated as pairs). Methane from the ethanol reaction appears when Rh coverage reaches 0.4%, the coverage wherein Rh pairs start to form. Moreover, H₂ peak broadening occurs when Rh coverage reaches 0.5%, indicating C-H activation is more facile on Rh pairs but the newly formed acetaldehyde undergoes C-C bond cleavage to form methane. We therefore hypothesized that Rh pairs facilitate C-H activation, and the produced acetaldehyde can either move to Ni sites to desorb or stay at Rh sites for further C-C bond cleavage. Ongoing DFT calculations from Professor Philippe Sautet and Michael Ngan will investigate the reaction pathway of ethanol decomposition on these sites (Rh single atom sites, Ni single atom sites, Rh-Ni adjacent sites, Rh-Rh adjacent/non-adjacent sites, etc.) and provide a complete mechanistic picture.

9.2 Future Directions

According to Nørskov, the ultimate goal for catalyst design is to tailor catalysts atom-by-atom to precisely modify the catalytic activity.⁶ Single atom alloys, with their atomically resolved active sites, have the potential to achieve this goal.¹ The work in this thesis has demonstrated a catalyst screening approach by first investigating Cu-based SAAs (X=Pd, Pt, Ni and Rh) towards formic acid decomposition and correlating the discovered activity trend with relative CO binding strength. Based on this knowledge, we moved forward to develop TD-SAAs to understand the

synergy between two different dopant sites. Based on the above findings, there are several directions worth to explore:

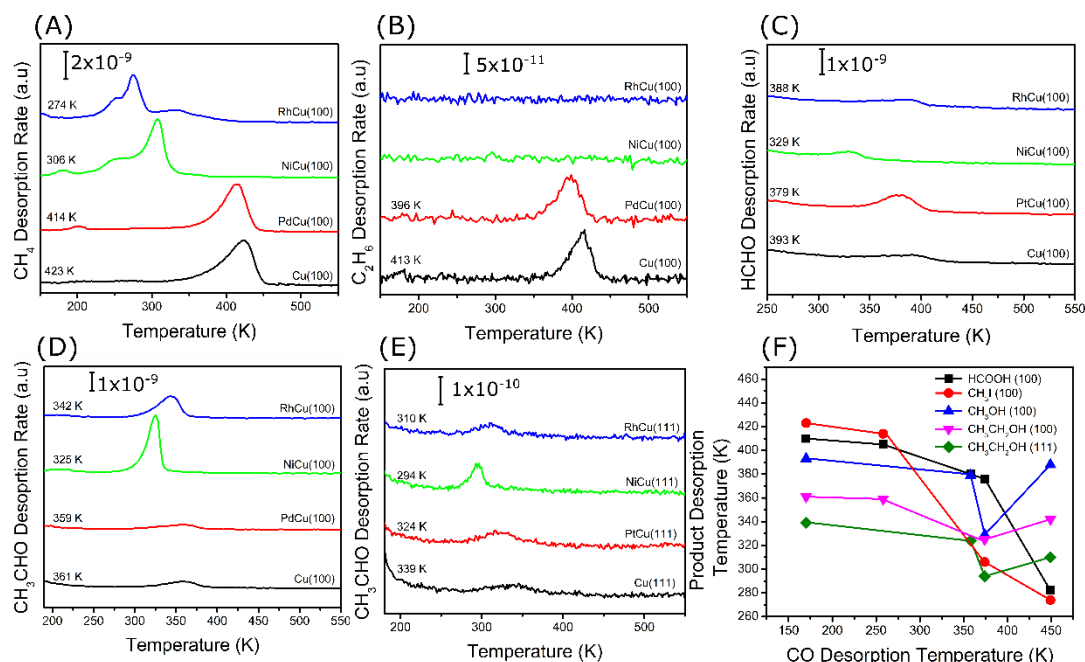


Fig 9. 1 TPD profiles of products from different reactions on Cu-based SAAs (X=Pd, Pt, Ni and Rh). A) Tracking methane from the CH_3I reaction (an indicator of methyl group C-H activation capability); B) ethane from the CH_3I reaction (an indicator of methyl-methyl coupling capability); C) formaldehyde from methanol dehydrogenation; acetaldehyde from ethanol dehydrogenation on D) (100) surfaces and E) (111) surfaces. F) product evolution temperature as a function of CO desorption temperature from dopant sites.

Thorough understanding of the factor/descriptor determining catalytic activity is crucial for future catalyst design.⁶⁻⁸ The results in Chapter 5 show a strong correlation between CO binding strength at the dopant sites in Cu-based SAAs and formic acid decomposition where C-H activation is the RLS on these surfaces. This approach can be expanded to other industrially relevant reactions such as ethanol and methanol dehydrogenation, methyl group C-H activation and C-C coupling. An example is shown in Fig. 9.1. The results show that the trend of HCOOH and methyl group C-H activation capability is: Rh sites > Ni sites > Pt sites > Pd Sites. For methanol and ethanol reactions, in which the C-H activation is the RLS, Ni sites show better activity to produce formaldehyde/acetaldehyde. Further investigations show Rh sites may be too

reactive that lead to deep dehydrogenation to form CO (methanol reaction)/ C-C bond cleavage to form methane and CO (ethanol reaction) and thus the NiCu SAA is a better candidate for ethanol and methanol dehydrogenation reactions.^{9–12} Fig. 9.1 F shows a summary of key product evolution from iodomethane/methanol/ethanol reactions as a function of CO desorption temperature from dopant sites (X=Pd, Pt, Ni and Rh). Moreover, we can expand to other transition metal candidates to achieve fundamental understanding of these elements in the single atom regime.

Moreover, this database can act as a steppingstone to enable us to rationally design novel TD-SAAs (non-adjacent sites) and DAAs (dual-atom alloys with heterodimer sites) to go beyond the top of these volcano plots. For instance, by understanding factors controlling the oxophilicity and carbophilicity of transition metals has led to the successful design of a PtCrAg(111) DAA for ethanol dehydrogenation where O-H activation is achieved by PtCr-adjacent sites.^{13,14} Specifically, DFT results show that Pt binds the dissociated H while Cr stabilizes the ethoxy intermediate. The ultimate goal for TD-SAAs is to find two different dopants that have drastically different properties to activate two different bonds with high efficiency.

9.3 References

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Appendix for Chapter 3

This appendix was modified from the Supplementary Information of following original publication: Wang, Y.; Papanikolaou, K. G.; Hannagan, R. T.; Patel, D. A.; Balema, T. A.; Cramer, L. A.; Kress, P. L.; Stamatakis, M.; Sykes, E. C. H. Surface Facet Dependence of Competing Alloying Mechanisms. *J. Chem. Phys.* **2020**, *153* (24).

A3.1 Cu slabs employed for the DFT calculations

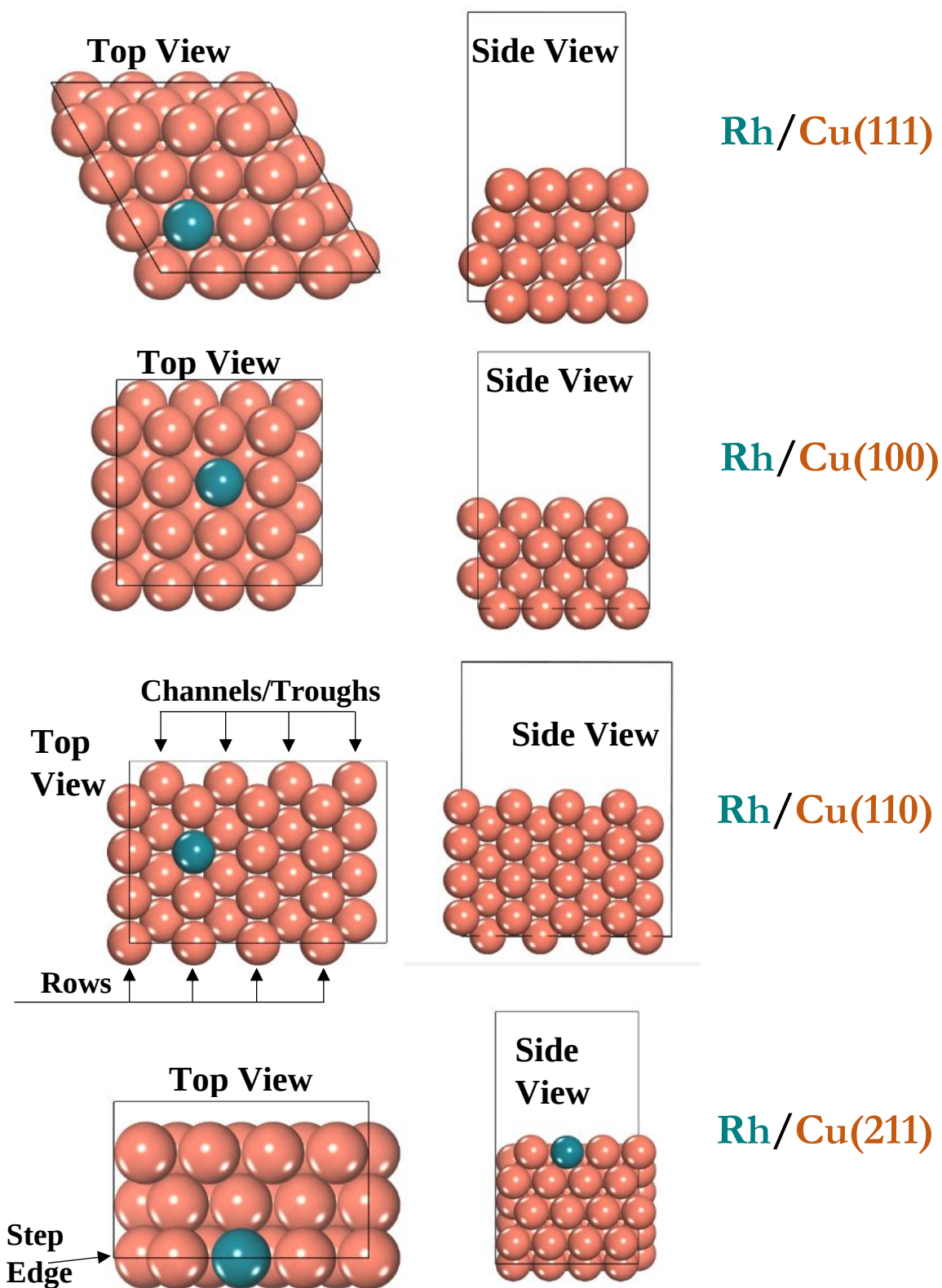


Fig A.3. 1 Top and side views of the DFT slab which was used to model the different Rh/Cu low-index surfaces. The slabs are shown with an embedded Rh atom (shown in teal) in the Cu (shown in orange) matrix.

A.3.2 Rh adatom diffusion over Cu(110)

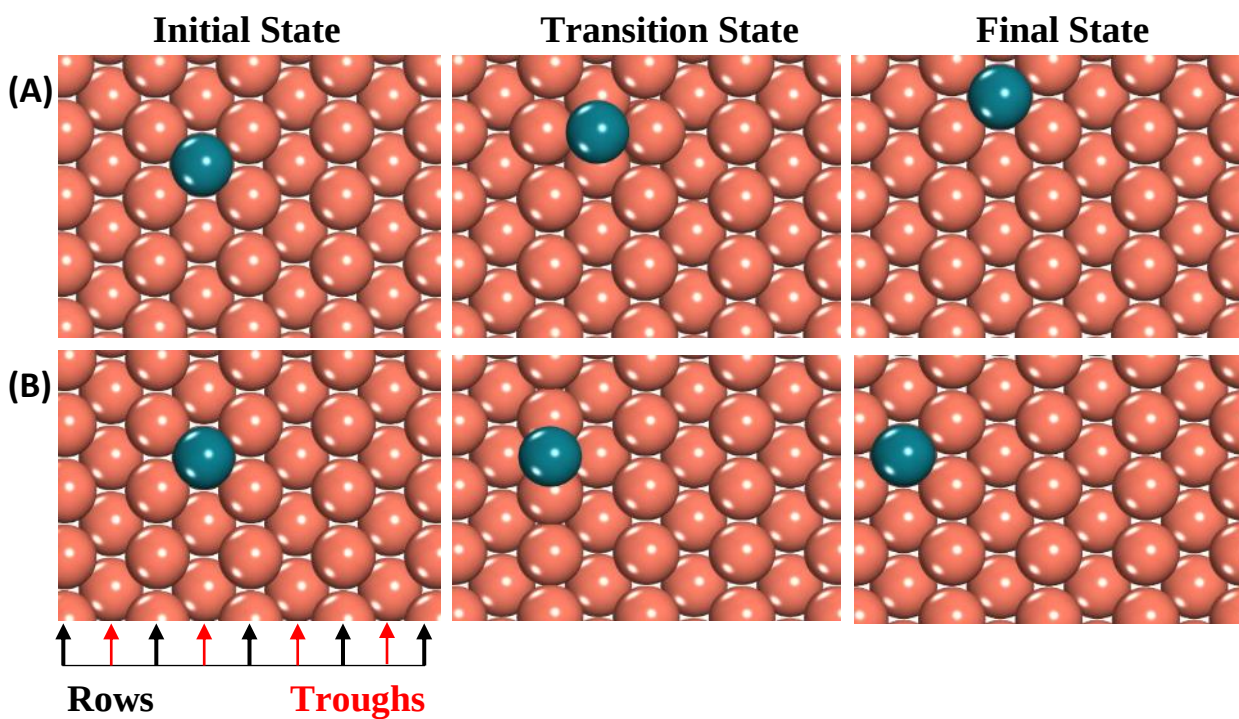


Fig A.3. 2 Top view of Rh adatom diffusion over Cu(110) (A) along a trough and (B) over a row. Cu and Rh atoms are shown in orange and teal, respectively

Appendix to Chapter 4

This appendix was modified from the Supplementary Information of following original publication: Wang, Y.; Schumann, J.; Happel, E. E.; Volkan, C.; Sykes, E. C. H.; Stamatakis, M.; Michaelides, A.; Hannagan, R. T. Observation and Characterization of Dicarbonyls on a RhCu Single- Atom Alloy. *J. Phys. Chem. Lett.* **2022**, *13*, 6316–6322.

A4.1 Experimental and Computational Methods

Low-Temperature Scanning Tunnelling Microscopy (LT-STM). LT-STM experiments were conducted in an (ultra-high vacuum) UHV chamber with a base pressure of $\sim 1 \times 10^{-11}$ mbar using an Omicron LT-STM. Sample cleaning was performed in a connected preparation chamber with a base pressure less than 2×10^{-10} mbar. Repeated cycles of Argon (Airgas 99.99%) ion bombardment (1 keV, 10 μ A) and thermal annealing to 750 K were used for cleaning the Cu(100) single crystal. Rh deposition was performed from a Rh rod (Goodfellow 99.9%) using a flux monitored EFM 3 electron beam evaporator (Scienta Omicron) while the Cu(100) sample temperature was held at ~ 380 K during deposition of a constant Rh flux of ~ 0.01 ML $\cdot$ min $^{-1}$. The STM images were acquired after cryogenically cooling the STM stage to 5 K and exposing the surface to 0.05 L (1 L = 1×10^{-6} Torr $\cdot$ s) of CO (99.99% Airgas) through a collimated leak valve followed by a ~ 220 K anneal.

Temperature-programmed Desorption (TPD). TPD experiments were performed in a separate UHV chamber with a base pressure of $< 1 \times 10^{-10}$ mbar equipped with a quadrupole mass spectrometer (Hidden HAL/3F 301) capable of being advanced to less than 1 mm from the front of the crystal. The Cu(100) crystal was cleaned by repeated cycles of Ar ion sputtering (1 keV, 1.5 μ A) and annealing to 750 K. The RhCu(100) SAA was prepared by a flux monitored EFM 3 (Scienta Omicron) electron beam evaporator at a surface temperature of 300 K. The RhCu(100) surfaces were cooled to 90 K via the liquid nitrogen cryostat and exposed to CO (99.99% Airgas)

or a ^{12}CO and ^{13}CO mixture ($^{12}\text{CO}:^{13}\text{CO} = 3:2$) through a high-precision leak valve. Annealing was done by resistively heating tungsten wires that supported the Cu(100) crystal, and temperatures were measured via a thermocouple spot welded to the back of the crystal. All TPD measurements were run with a heating rate of 2 K/s. The desorption energy (E_{des}) was calculated by the Redhead Equation:¹

$$E_{\text{des}} = RT_p \left(\ln \left(\frac{AT_p}{\beta} \right) - 3.46 \right)$$

where R is the ideal gas constant, T_p the peak temperature, A the pre-exponential factor and β is the heating rate.

Reflection Absorption Infrared Spectroscopy (RAIRS). RAIRS experiments were performed in the same chamber as the TPD experiments using a Bruker Tensor II spectrometer. The grazing-incidence IR beam was directed from the spectrometer onto the crystal and out of the chamber to a mercury-cadmium-telluride (MCT) detector using a series of gold-coated mirrors. The external part of the IR spectrometer was encased with a dry air purge box and the UHV chamber was equipped with ZnSe windows to prevent IR radiation loss. RAIRS spectra were taken at the indicated temperatures and referenced to a background collected at 180 K. Spectra were averaged over 2000 scans with 4 cm^{-1} resolution. Manual background subtraction to account for slight background drift over time was applied to all the IR spectra. Multi-peak fitting with a mixed Gaussian/Lorentzian (25%/75%) line shape was performed with the isotope experiments using CasaXPS. The full width at half maximum for each peak was fixed to 15 cm^{-1} to match experimental conditions.

Density Functional Theory (DFT). The atomistic calculations were performed using periodic DFT as implemented in the Vienna Ab initio Simulation Package (VASP) 5.4.4.²⁻⁴ The

exchange- correlation potential was approximated with the RPBE functional.⁵ The core electrons were modelled using the Projected Augmented Wave (PAW) approach,^{6,7} and the valence density was expanded using a plane wave basis set truncated at 400 eV. We used the lattice constant for Cu of 3.64 Å as determined in our previous work.⁸ A 5-layer p(3x3) slab model and 13x13x1 Monkhorst-Pack k- point meshes was applied. All structures were optimized until forces were less than 0.02 eV/Å, only keeping the two bottom layers of the slab frozen. Frequency calculations were performed for all species on the RhCu surface, freezing the coordinates of the metal atoms at their optimized values. Calculations on the (111) surface termination were performed on a 5-layer p(4x4) slab model using a 7x7x1 Monkhorst-Pack k- point mesh.

Determination of the spillover energy ΔE for a series of 5 different dopants (Rh, Ir, Ni, Pd, Pt) on both (100) and (111) terminated Cu-based SAA was done by calculating the difference of the DFT energies of the dicarbonyl configuration and the separated configuration with both CO molecules in the unit cell as shown in Fig 4.5 c).

$$\Delta E = E_{\text{dicarb}} - E_{\text{separated}}$$

A4.2 Additional Experimental and Computational Results

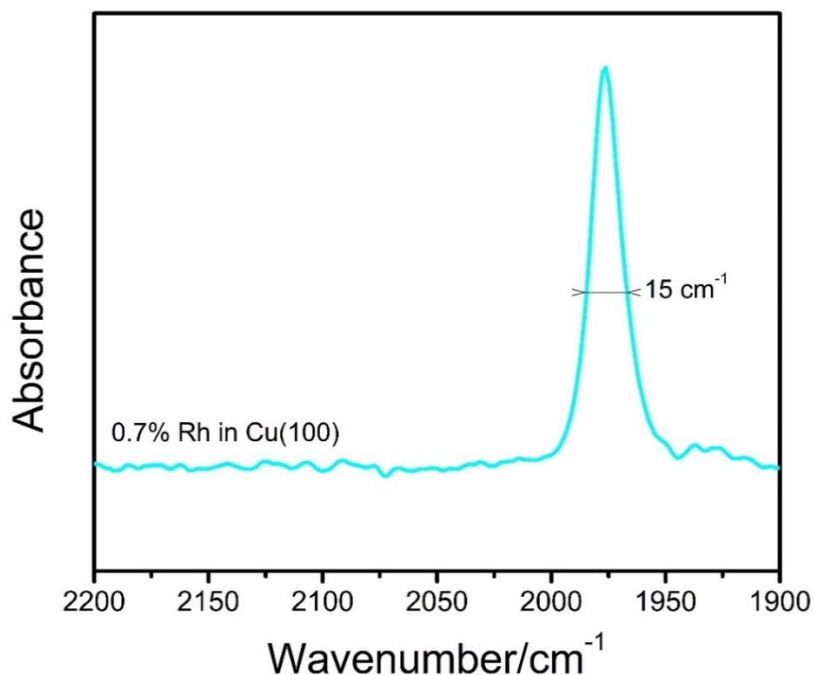


Fig A.4. 1 RAIRS spectra of saturation CO on RhCu (100) SAA with the surface temperature held at 300 K. At this surface temperature only the Rh sites were populated by monocarbonyls while Cu sites are free of CO. The full width at half maximum (FWHM) was measured to be 15 cm^{-1} which demonstrates uniform isolated Rh sites are present at a 0.7% Rh coverage in Cu (100). The FWHM for the previous RAIRS study on a 0.2% RhCu (111) SAA is between 13 cm^{-1} to 24 cm^{-1} (depending on the step density of the Cu (111) surfaces which dictates dispersion of the Rh atoms in the (111) surface).⁹

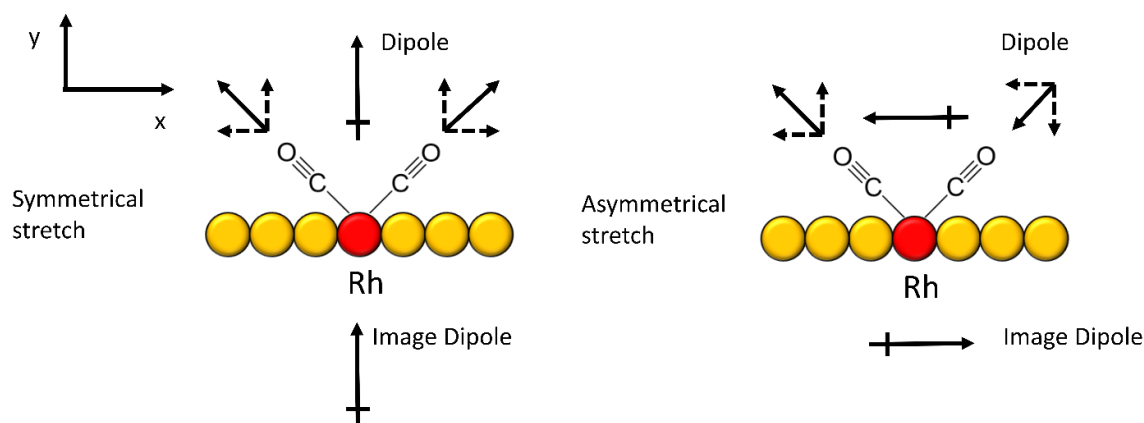


Fig A.4. 2 Schematic illustration of symmetric and asymmetric stretches of a dicarbonyl on Rh single atom sites. For the symmetric stretch, the net dipole component is aligned with the surface-normal (y axis) which is amplified by the Cu (100) metal surface image dipole. For the antisymmetric stretch, the net dipole is aligned with the surface-parallel (x axis) and is screened by the metal surface image dipole.

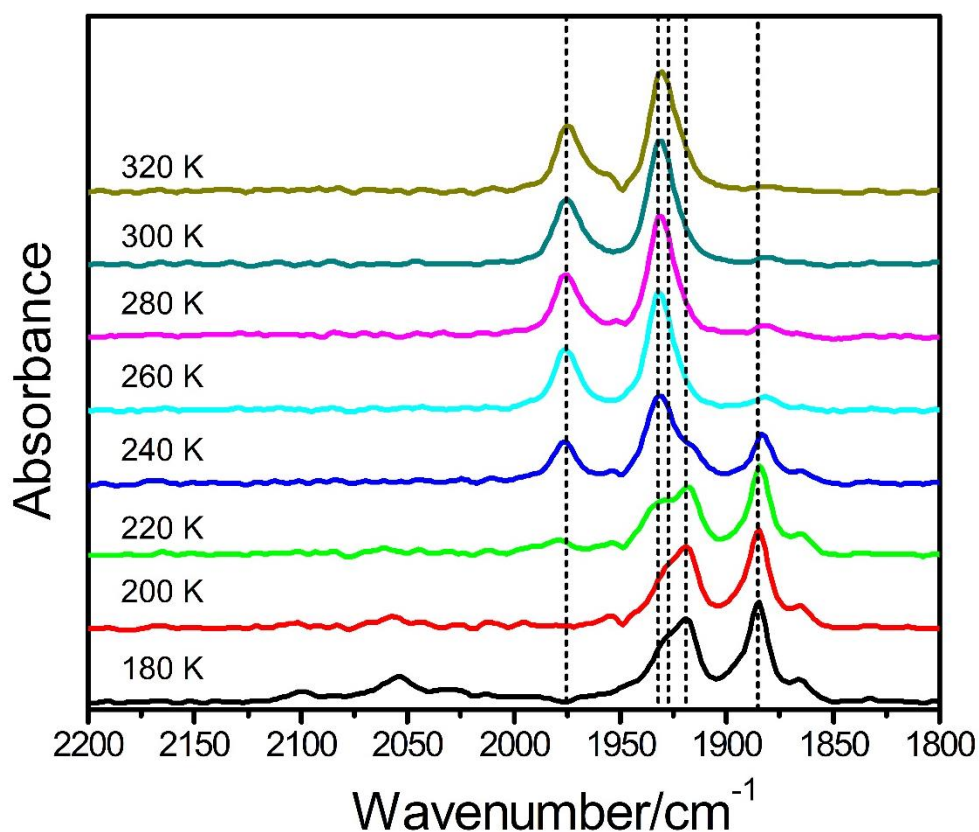


Fig A.4. 3 RAIRS spectra of exposing saturation coverage of a 2:3 ratio $^{13}\text{C}^{16}\text{O}:^{12}\text{C}^{16}\text{O}$ mixture to RhCu (100) and taking the IR spectra over the temperature range 180 K to 320 K without peak fitting.

Table A.4. 1 CO adsorption energies E_{ads} as calculated by DFT, including comparison with RhCu (111) SAA. $E_{\text{ads}} = E_{\text{DFT}} - E_{\text{surf}} - n \cdot E_{\text{COgas}}$, with E_{DFT} being the total energy of the system, E_{surf} the clean slab energy, E_{COgas} the energy of a single CO gas molecule in vacuum and n the number of CO molecules in the system.

	E_{ads} (eV) @ (100) facet	E_{ads} (eV) @ (111) facet
CO @ Cu host	-0.59	-0.48
CO @ RhCu SAA	-1.81	-1.83
2 CO @ RhCu SAA ("dicarbonyl")	-2.90	-2.57
CO @ Rh + CO @ Cu	-2.40	-2.26

Table A.4. 2 CO vibrational frequencies as calculated by DFT and comparison to experiment, as well as wavenumber shifts $\Delta \tilde{\nu}$, relative to respective CO gas phase values of DFT and experiment.

	C-O vibrational freq., DFT (cm ⁻¹)	C-O vibr. freq., experiment (cm ⁻¹)	$\Delta \tilde{\nu}_{\text{DFT}}$	$\Delta \tilde{\nu}_{\text{exp}}$
CO _{gas}	2103	2143	0	0
CO @ Cu(100)	1984	2099	119	44
CO @ RhCu(100) SAA	1934	1978	169	165
¹³ CO @ RhCu(100) SAA	1889	1934	214	209
2 CO @ RhCu(100) SAA (dicarbonyl)	1891	1926	212	217
¹³ CO + ¹² CO @ RhCu(100) SAA	1878	1917	225	226
2 ¹³ CO @ RhCu(100) SAA	1847	1884	256	259

Table A.4. 3 Bader charge analysis for dicarbonyl Rh site, monocarbonyl Rh site and clean Rh site.

	Rh charge
Clean Rh site	-0.38
CO @ Rh site	-0.14
2 CO @ Rh sites (dicarbonyl)	+0.02

A4.3 References

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Appendix for Chapter 5

A 5.1 Additional experimental data

Table A.5. 1 Imaging conditions for Cu-based SAAs

	Zoom out view	Zoom in view
PdCu(100) SAA	100 mV 0.5 nA	-3 mV 9 nA
PtCu(100) SAA	-50 mV 0.5 nA	-3 mV 15 nA
NiCu(100) SAA	300 mV 0,3 nA	20 mV 30 nA
RhCu(100) SAA	300 mv 0.3 nA	-12 mV 0.5 nA

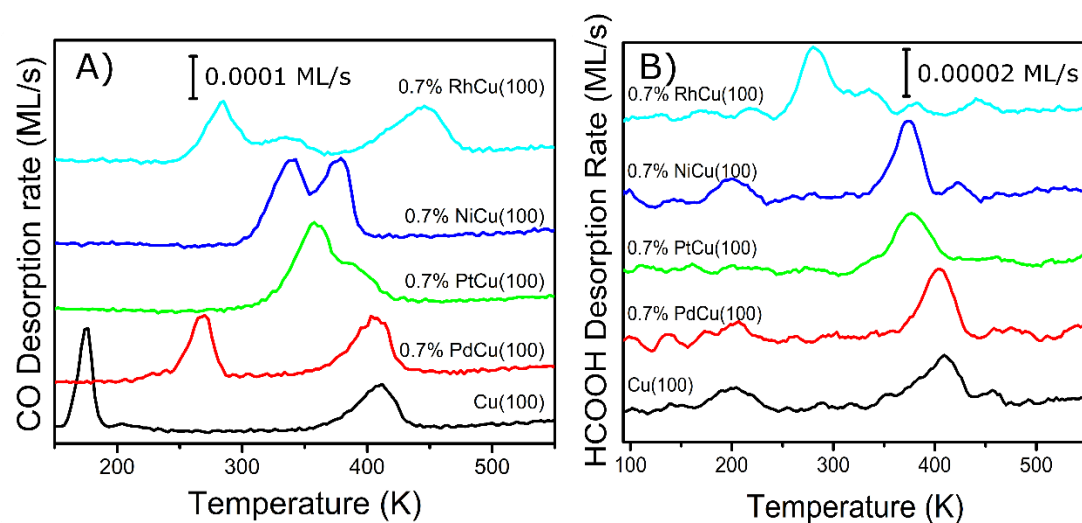


Fig. A.5. 1 Tracking other products formed after exposing 0.1 Langmuir [1 Langmuir (L) = 10^{-6} torr·s] of HCOOH to the as-prepared SAAs. A) TPD spectra of CO ($m/z = 28$) evolution from the formic acid reaction on different surfaces. B) TPD spectra of HCOOH ($m/z = 46$) evolution from the formic acid reaction on different surfaces.

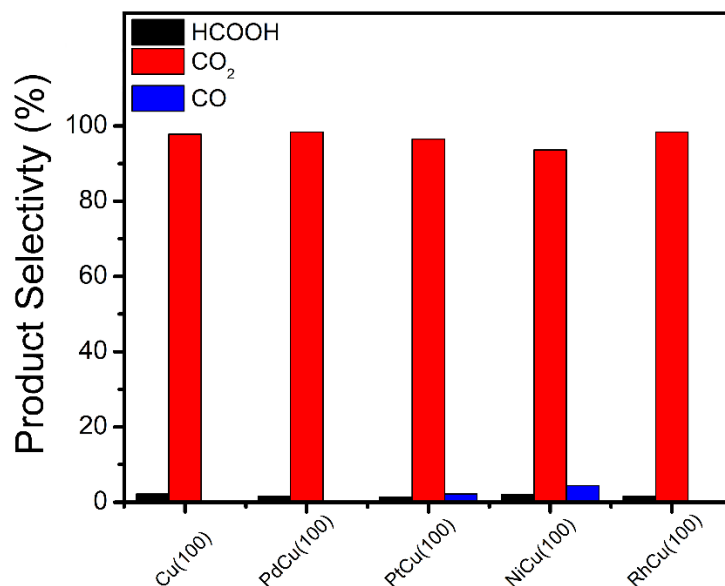


Fig. A.5. 2 Products selectivity of the investigated surfaces after exposing them to 0.1 Langmuir of HCOOH and tracking the desorption of HCOOH ($m/z = 46$), CO₂ ($m/z = 44$), and CO ($m/z = 28$). All of the investigated surfaces exhibited a selectivity of over 94% in producing CO₂

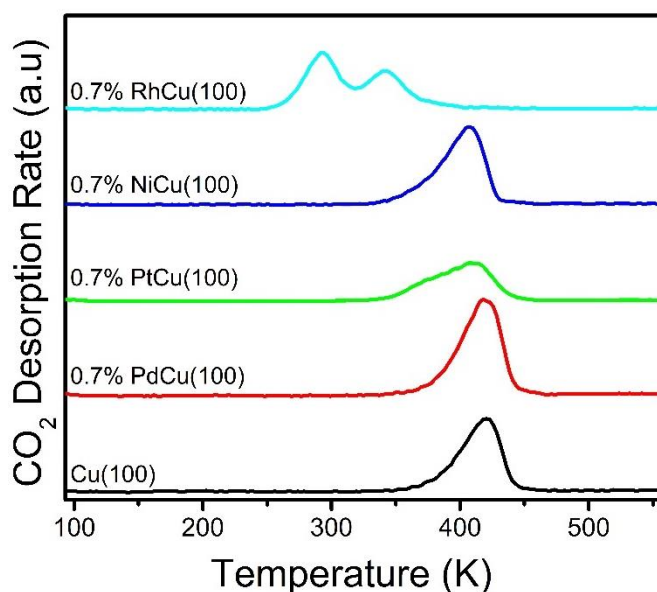


Fig. A.5. 3 TPD spectra of CO₂ desorption after exposing 0.1 Langmuir DCOOH exposed to different surfaces. CO₂ desorption from Cu (100), PdCu (100), PtCu (100), NiCu (100) and RhCu (100) are 420 K, 420 K, 410 K, 407 K and 291 K, respectively. The CO₂ desorption temperature of different surfaces are the same as D₂ desorption temperature from those surfaces as shown in Figure 5.2B, illustrating that C-H activation is the rate limiting step on all investigated surfaces.

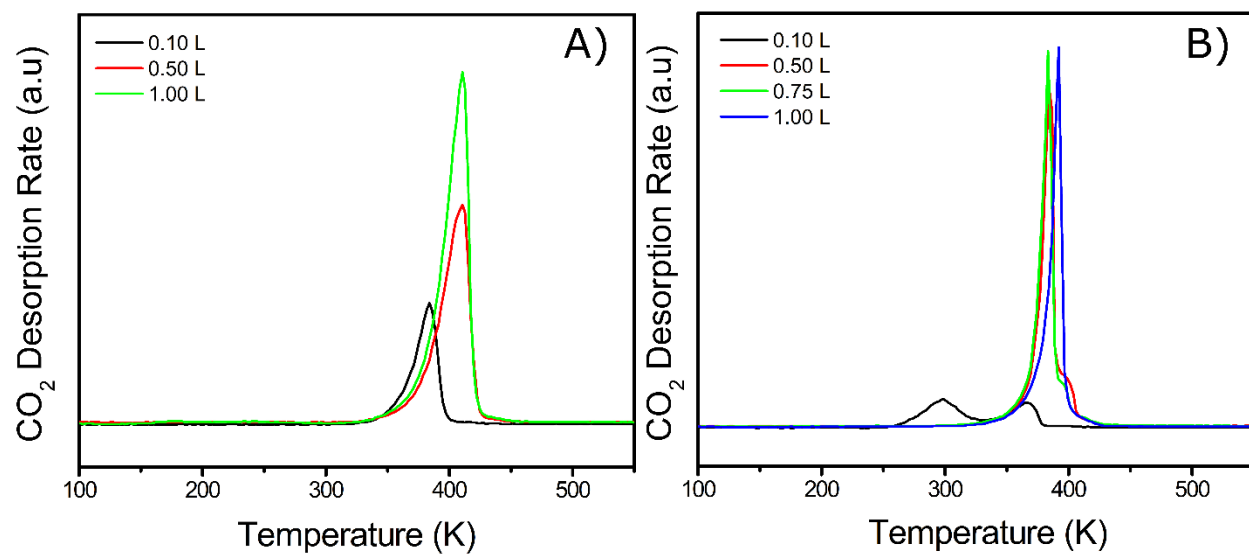


Fig. A.5. 4 TPD Spectra of CO₂ desorption after exposing to HCOOH as a function of HCOOH coverage A) NiCu and B) RhCu.

Appendix for Chapter 6

A6.1 Experimental methods

Low-Temperature Scanning Tunnelling Microscopy (LT-STM). LT-STM experiments were conducted in an UHV chamber with a base pressure of $\sim 1 \times 10^{-11}$ mbar using an Omicron LT-STM. Sample cleaning was performed in an adjacent preparation chamber with a base pressure less than 2×10^{-10} mbar. Repeated cycles of Ar (Airgas 99.99%) ion bombardment (1 keV, 10-20 μA) and thermal annealing to 750 K were used for cleaning the Cu(100) single crystal. Rh/Pd deposition was performed from Rh/Pd rods (Goodfellow 99.9%) using a flux monitored EFM 3 electron beam evaporators (Scienta Omicron), while the Cu(100) sample temperature was held at 380 K during deposition of a constant Rh /Pd flux of $\sim 0.01 \text{ ML} \cdot \text{min}^{-1}$. For RhPdCu DAA, Pd was deposited first followed by Rh deposition. The STM images were acquired after cryogenically cooling the STM stage to 80 K.

Temperature-programmed Desorption (TPD). TPD experiments were performed in a separate UHV chamber with a base pressure of $< 1 \times 10^{-10}$ mbar equipped with a quadrupole mass spectrometer (Hidden HAL/3F 301) capable of being advanced to less than 1 mm in front of the crystal. The Cu(100) crystal was cleaned by repeated cycles of Ar ion sputtering (0.5 keV, 1.5 μA) and annealed to 750 K. The PdCu(100)/ RhCu(100) SAAs were prepared by a flux monitored EFM 3 (Scienta Omicron) electron beam evaporators at a surface temperature of 380 K. For dopant metals coverage quantification, the as-prepared surfaces were cooled to 90 K via a liquid nitrogen cryostat and exposed to CO (99.99% Airgas) through a high-precision leak valve. For C-H activation and C-C coupling capability studies, the as-prepared surfaces were cooled to 90 K via the liquid nitrogen cryostat and exposed to CH₃I (99.0% Sigma Aldrich) through a high-precision leak valve. Annealing was done by resistively heating Ta wires that support the Cu(100) crystal,

and temperatures were measured via a thermocouple spot welded to the back of the crystal. All TPD measurements were run with a heating rate of 2 K/s. Reactivity of the SAA surfaces was examined by dosing 4 Langmuir [1 Langmuir (L) = 10^{-6} torr·s] CH_3I (0.03 equivalent monolayers). CH_4 , C_2H_6 , C_4H_6 were tracked using $m/z = 16, 30$ and 54 , respectively.

Reflection Absorption Infrared Spectroscopy (RAIRS). RAIRS experiments were performed in the same chamber as the TPD experiments using a Bruker Tensor II spectrometer. The grazing-incidence IR beam was directed from the spectrometer onto the crystal and out of the chamber to a mercury-cadmium-tellurium (MCT) detector using a series of gold-coated mirrors. The external part of the IR spectrometer was encased with a dry air purge box and the UHV chamber was equipped with ZnSe windows to prevent IR radiation loss. RAIRS spectra were taken at the indicated temperatures and referenced to a background collected at 90 K. Spectra were averaged over 2000 scans with 4 cm^{-1} resolution. Manual background subtractions that accounted for slight background drift over time were applied to all the IR spectra.

A6.2 Additional Experimental results

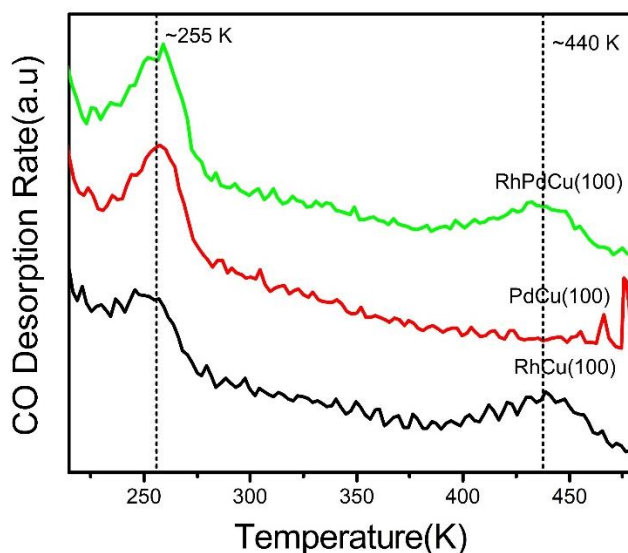


Fig A.6. 1 TPD spectra were obtained for the saturation CO exposure on PdCu (100) SAA, RhCu (100) SAA, and RhPdCu (100) TD-SAA. In the TPD spectra of RhCu (100) SAA, two distinct CO desorption peaks can be observed. However, in the TPD spectra of PdCu (100) SAA, only one peak is seen. It is challenging to differentiate between the desorption of dicarbonyl from Rh sites and monocarbonyl from Pd sites in the CO TPD trace of RhPdCu (100) TD-SAA.

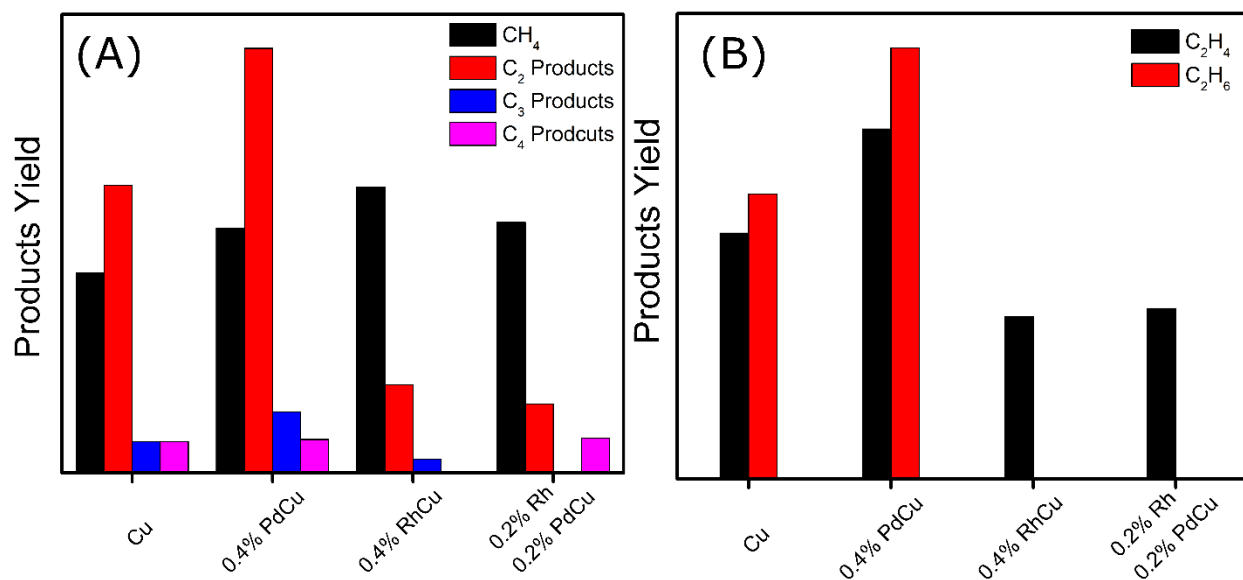


Fig A.6. 2 Products distribution after exposing to 4 Langmuir [1 Langmuir (L)= 10^{-6} torr·s] of CH₃I at 90 K to different surfaces. A) C₁-C₄ Products distribution on different surfaces (1/10 factor was applied for methane yield). B) Acetylene, ethylene and ethane distribution on different surfaces.

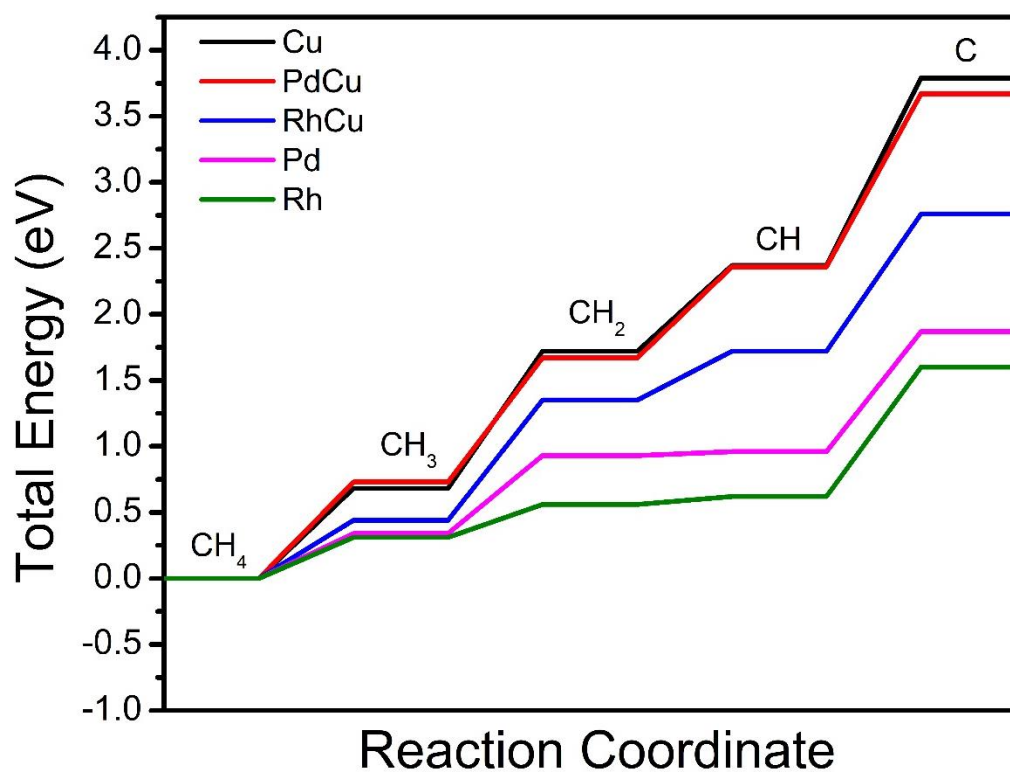


Fig A.6. 3 Thermochemical potential energy surfaces methane activation on different surfaces (Cu, PdCu SAA and RhCu SAA).² The activation barrier for CH_3 dehydrogenation affects products distribution on different surfaces.

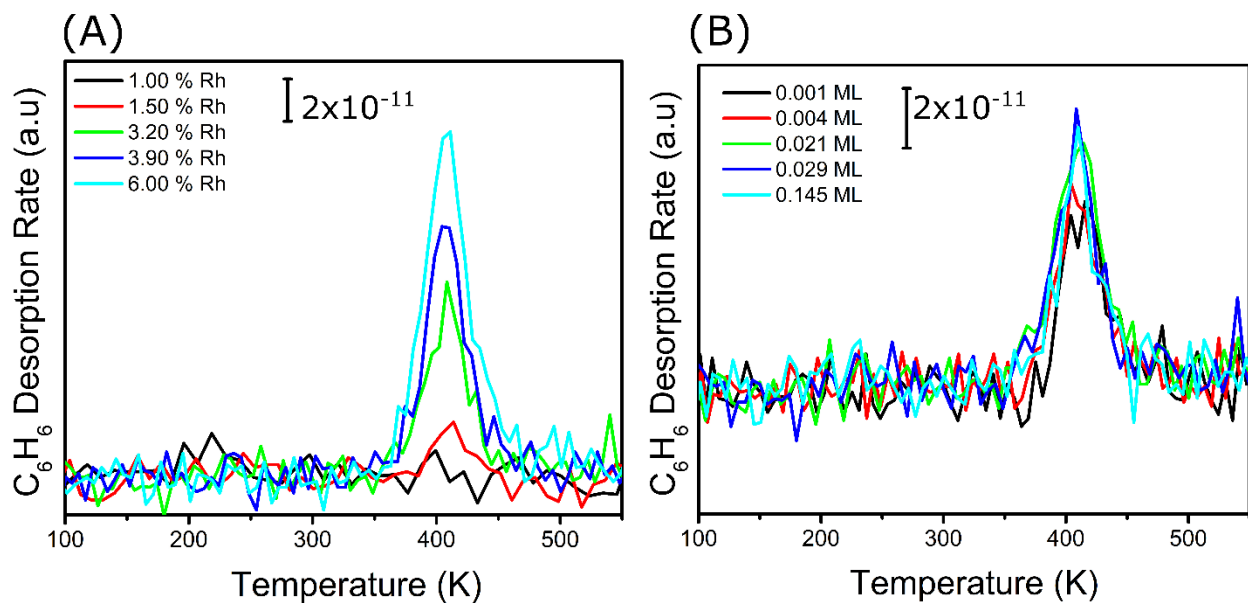


Fig A.6. 4 TPD spectra of exposing A) 0.5 Langmuir [1 Langmuir (L)= 10^{-6} torr·s] of toluene at 90 K Cu (100) surfaces with different Rh coverages (1.00-6.00%). B) different amounts of toluene (0.001-0.145 ML) at 90 K to 3% RhCu (100).

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Appendix for Chapter 7

A7.1 Experimental methods

Low-Temperature Scanning Tunnelling Microscopy (LT-STM). LT-STM experiments were conducted in an UHV chamber with a base pressure of $\sim 1 \times 10^{-11}$ mbar using an Omicron LT-STM. Sample cleaning was performed in an adjacent preparation chamber with a base pressure less than 2×10^{-10} mbar. Repeated cycles of Ar (Airgas 99.99%) ion bombardment (1 keV, 10-20 μ A) and thermal annealing to 750 K were used for cleaning the Cu(100) single crystal. Rh/Pd deposition was performed from Rh/Ni rods (Goodfellow 99.9%) using a flux monitored EFM 3 electron beam evaporators (Scienta Omicron), while the Cu(100) sample temperature was held at 380 K during deposition of a constant Rh /Ni flux of ~ 0.01 ML $\cdot$ min $^{-1}$. For RhPdCu DAA, Pd was deposited first followed by Rh deposition. The STM images were acquired after cryogenically cooling the STM stage to 80 K.

Temperature-programmed Desorption (TPD). TPD experiments were performed in a separate UHV chamber with a base pressure of $< 1 \times 10^{-10}$ mbar equipped with a quadrupole mass spectrometer (Hidden HAL/3F 301) capable of being advanced to less than 1 mm in front of the crystal. The Cu(100) crystal was cleaned by repeated cycles of Ar ion sputtering (0.5 keV, 1.5 μ A) and annealed to 750 K. The NiCu(100)/ RhCu(100) SAAs were prepared by a flux monitored EFM 3 (Scienta Omicron) electron beam evaporators at a surface temperature of 300 K. For RhNiCu(100)/RhPtCu(100)/RhPtCu(100) DAAs, the second dopants (X=Ni, Pt and Pd) were deposited first followed by Rh deposition. For dopant metals coverage quantification, the as-prepared surfaces were cooled to 90 K via a liquid nitrogen cryostat and exposed to CO (99.99% Airgas) through a high-precision leak valve. For formic acid decomposition activity study, the as-

prepared surfaces were cooled to 90 K via the liquid nitrogen cryostat and exposed to HCOOH (99.0% Fisher Scientific) through a high-precision leak valve. Annealing was done by resistively heating Ta wires that support the Cu(100) crystal, and temperatures were measured via a thermocouple spot welded to the back of the crystal. All TPD measurements were run with a heating rate of 2 K/s. Reactivity of the SAA surfaces was examined by dosing 0.1 Langmuir [1 Langmuir (L) = 10^{-6} torr·s] HCOOH (0.06 equivalent monolayers). HCOOH was tracked using $m/z = 46$. Products, CO₂ and H₂ were tracked using $m/z = 44$ and 2, respectively, and CO and H₂O were tracked using $m/z = 28$ and 18 respectively.

Reflection Absorption Infrared Spectroscopy (RAIRS). RAIRS experiments were performed in the same chamber as the TPD experiments using a Bruker Tensor II spectrometer. The grazing-incidence IR beam was directed from the spectrometer onto the crystal and out of the chamber to a mercury-cadmium-tellurium (MCT) detector using a series of gold-coated mirrors. The external part of the IR spectrometer was encased with a dry air purge box and the UHV chamber was equipped with ZnSe windows to prevent IR radiation loss. RAIRS spectra were taken at the indicated temperatures and referenced to a background collected at 90 K. Spectra were averaged over 2000 scans with 4 cm⁻¹ resolution. Manual background subtractions that accounted for slight background drift over time were applied to all the IR spectra.

A7.2 Additional Experimental results

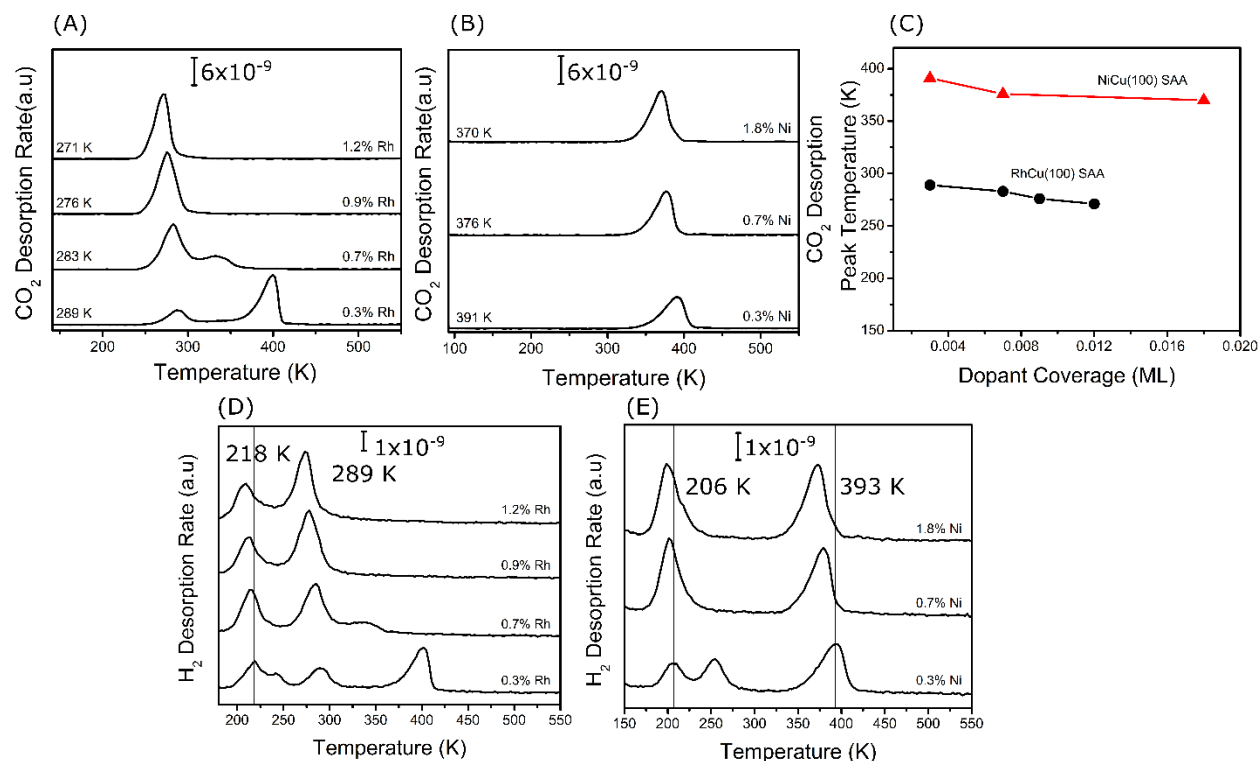


Fig A.7. 1 Formic acid dehydrogenation is sensitive to dopant coverage. TPD spectra showing CO₂ evolution from formic acid reaction on A) RhCu (100) surface as a function of Rh coverage and B) NiCu (100) surface as a function of Ni coverage. Each surface was exposed to 0.1 Langmuir [$1 \text{ Langmuir (L)} = 10^{-6} \text{ torr}\cdot\text{s}$] of HCOOH at 90 K. C) CO₂ desorption temperature peak against dopant coverage; TPD spectra showing H₂ desorption from formic acid reaction on D) RhCu (100) surface as a function of Rh coverage and B) NiCu (100) surface as function of Ni coverage. H₂ trace are good indicators to probe the presence of ensemble sites as Rh/Ni ensemble binds H₂ more strongly.¹

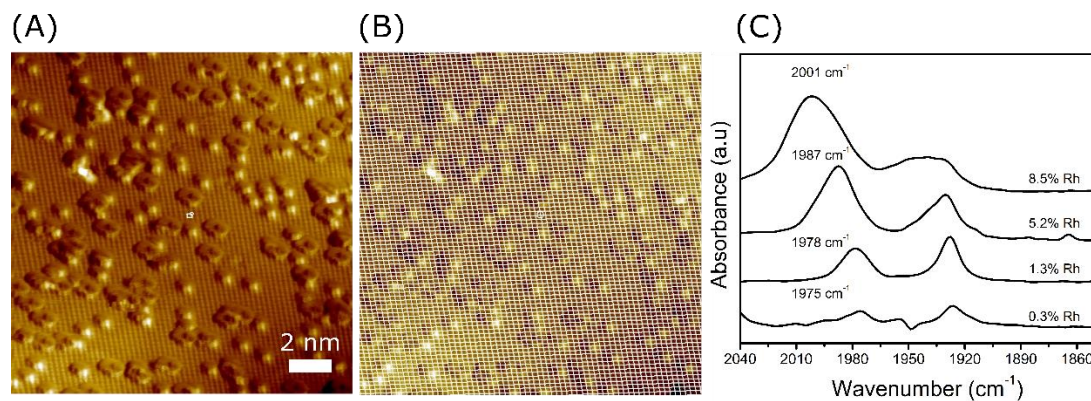


Fig A.7. 2 Further illustration of single atom regime for Rh in Cu(100) host. A) STM image of 5% Rh in Cu (100) where Rh sites with CO/without CO appear as sombrero shapes and protrusions, respectively. B) same STM image after imposing Cu (100) grid. It can be seen that Rh sites are

separate from each other. C) CO RAIRS of as-prepared RhCu(100) surfaces(Rh coverage ranging from 0.3% to 8.5%) exposed to saturation amount of CO at 90 K. IR spectra acquired at 240 K. CO atop peak ranging from 1975 cm^{-1} to 2001 cm^{-1} . It can be seen that CO atop peak shows little shift for Rh coverage ranging from 0.3% to 5.2%, indicating that Rh sites are separate from each other thereby dipole-dipole interactions are minimized (similar case was observed for Pd sites in Cu (111) host).² Furthermore, the FWHM reflects the uniformity of active sites and can be used to determine the homogeneity of the active sites.³ The FWHM of 0.3% RhCu(100), 1.3% RhCu(100), 5.2% RhCu(100) and 8.5% RhCu(100) are 12.2 cm^{-1} , 16.1 cm^{-1} , 21.2 cm^{-1} and 31.0 cm^{-1} , respectively. Noted that previous studies show that the FWHM of monocarbonyl on Rh sites in 0.2% RhCu (111) is 24.0 cm^{-1} . This tells us that Rh atoms are better dispersed in Cu(100) host which is consistent with the alloying mechanism study reported in our group (Rh atoms exhibit better dispersion on the terraces of Cu(100) and Cu(110) surfaces, while they tend to form dense clusters along the upper step edges in Cu (111))^{4,5} Also, it is more likely that the single atom regime for RhCu(100) is below $\sim 5.2\%$ Rh coverage.

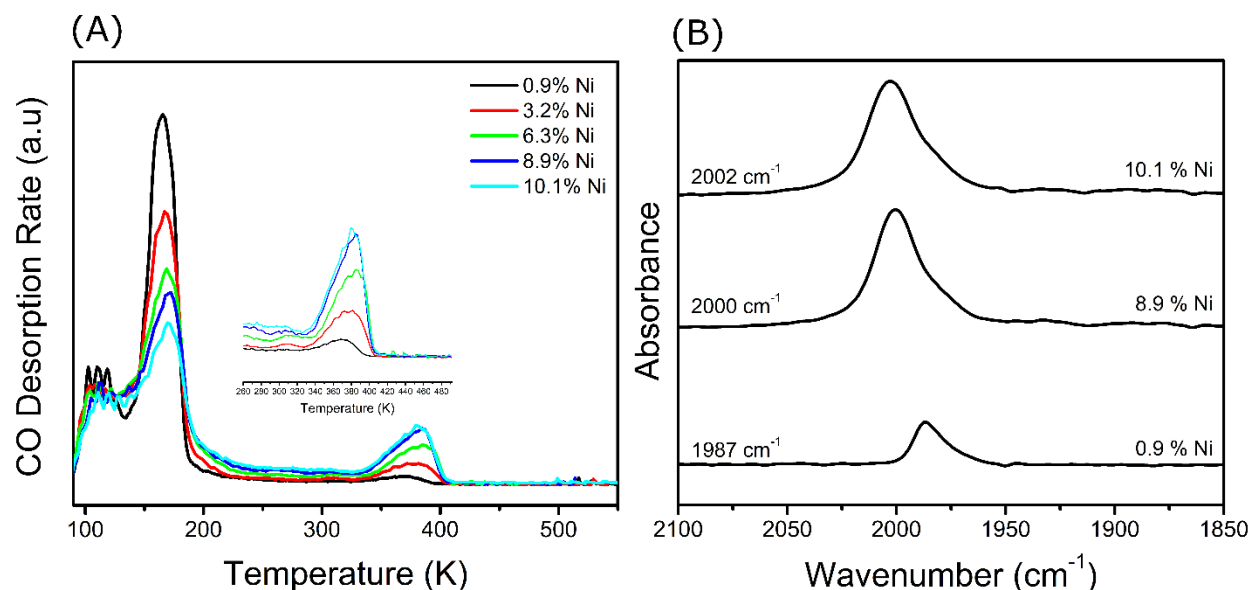


Fig A.7. 3 Further illustration of single atom regime for NiCu (100) system. A) TPD spectra of exposing saturated amounts of CO to as-prepared NiCu (100) surface by varying Ni coverage. B) RAIRS spectra of saturation CO on NiCu (100) as a function of Ni coverage. The FWHM of 0.9% NiCu (100), 8.9% NiCu (100) and 10.1% NiCu (100) are 16.5 cm^{-1} , 23.0 cm^{-1} and 25.7 cm^{-1} , respectively. According to Gates and coworkers' study, the FWHM reflects the uniformity of the dopant sites.³ Previous studies in our group show that the FWHM of atomically dispersed Ni in Cu (111) (Ni coverage $< 3\%$) is 24.3 cm^{-1} .⁶ This result tells us that Ni are better dispersed in Cu (100) and more likely to form atomically dispersed sites at higher coverage in Cu (100) host.

A7.3 References

1. Patel, D. A. *et al.* Mechanistic Insights into Nonoxidative Ethanol Dehydrogenation on NiCu Single-Atom Alloys. *ACS Catal.* 4290–4303 (2023) doi:10.1021/acscatal.3c00275.
2. Kruppe, C. M., Krooswyk, J. D. & Trenary, M. Polarization-Dependent Infrared Spectroscopy of Adsorbed Carbon Monoxide to Probe the Surface of a Pd/Cu(111) Single-Atom Alloy. *J. Phys.*

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3. Hoffman, A. S., Fang, C. Y. & Gates, B. C. Homogeneity of Surface Sites in Supported Single-Site Metal Catalysts: Assessment with Band Widths of Metal Carbonyl Infrared Spectra. *J. Phys. Chem. Lett.* **7**, 3854–3860 (2016).
 4. Hannagan, R. T. *et al.* Combining STM, RAIRS and TPD to Decipher the Dispersion and Interactions Between Active Sites in RhCu Single-Atom Alloys. *ChemCatChem* **12**, 488–493 (2020).
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 6. Patel, D. A. *et al.* Atomic-Scale Surface Structure and CO Tolerance of NiCu Single-Atom Alloys. *J. Phys. Chem. C* **123**, 28142–28147 (2019).

Appendix for Chapter 8

A8.1 Additional Experiments results

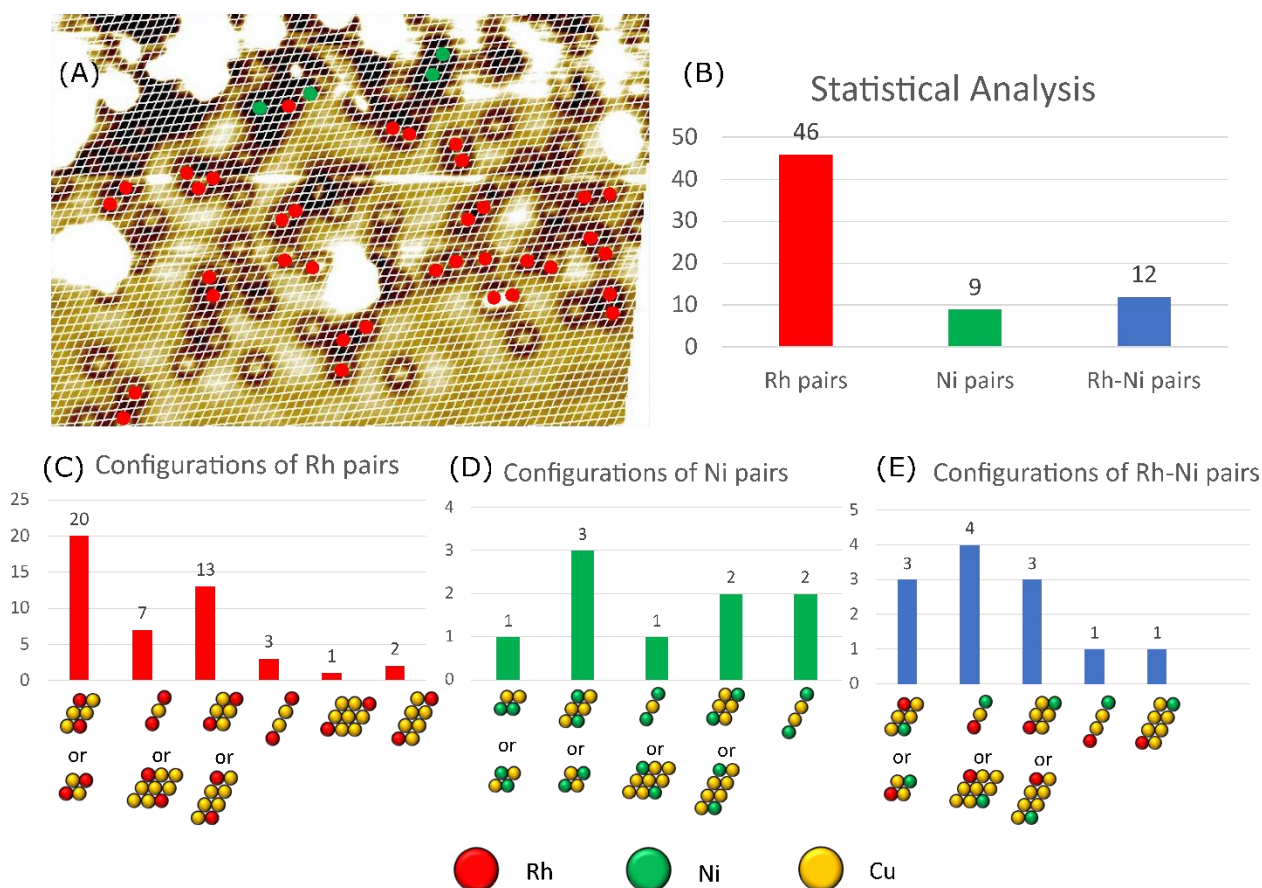


Fig A.8. 1 Statistical analysis of 0.5% Rh 0.2% NiCu (111) TD-SAA. A) The representative STM image shows a 0.5% Rh and 0.2% NiCu (111) TD-SAA, where the unit cell of Cu (111) is imposed, and the dopant metals are assumed to replace Cu atoms in Cu (111). In this image, non-touching dimers, referred to as pairs, can be observed. B) The summary of 300 dopant atoms reveals that Rh pairs are predominant compared to Ni pairs and Rh-Ni hetero-pairs. Configurations of C) Rh pairs D) Ni pairs E) Rh-Ni hetero-pairs.

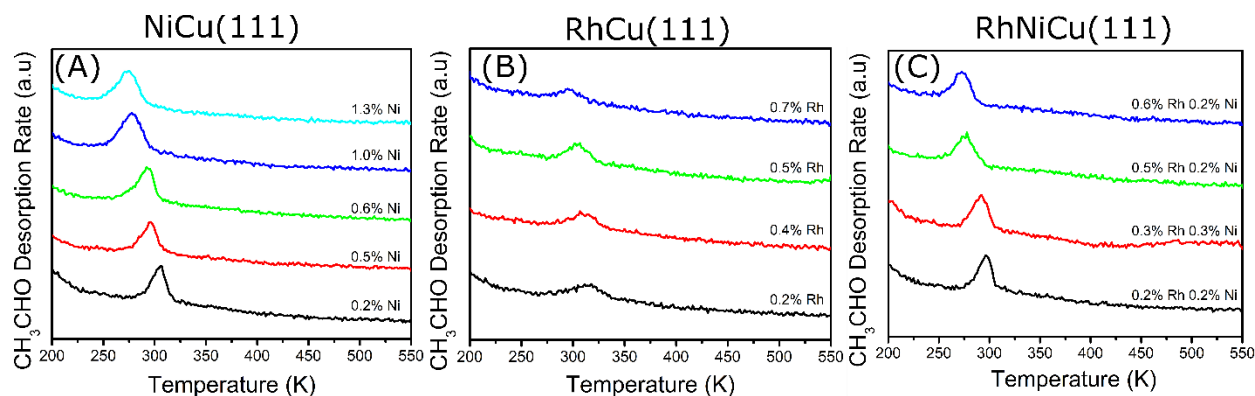


Fig A.8. 2 Acetaldehyde yield after exposing 20 Langmuir [1 Langmuir (L)= 10^{-6} torr·s] of ethanol to different surfaces at 160 K. Acetaldehyde desorption peak temperature shifts to lower temperature as dopant coverage increases. A) NiCu (111) SAA B) RhCu (111) SAA C) RhNiCu (111) TD-SAA

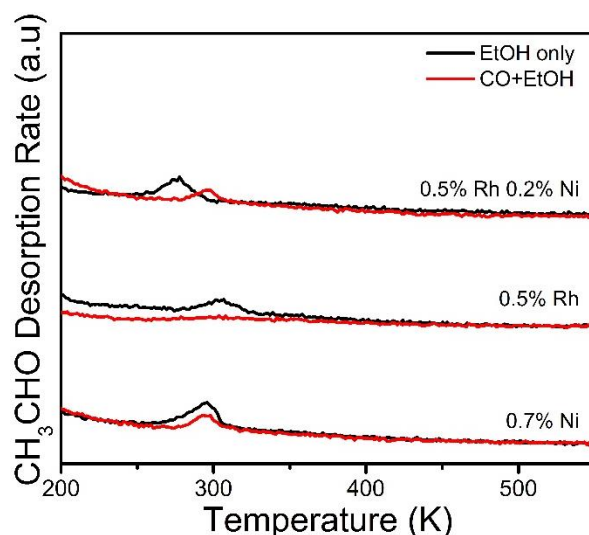


Fig A.8. 3 Comparing acetaldehyde yield from ethanol reactions with (red trace)/without (black trace) CO coking on different surfaces (NiCu (111), RhCu (111) and RhNiCu (111)). The observation that the desorption of acetaldehyde shifts to a higher temperature on RhNiCu (111) TD-SAA after CO coking indicates that the observed activity enhancement on RhNiCu (111) TD-SAA is not a result of Rh sites binding to background CO and freeing up the Ni sites.