

**Atomic-Scale Microscopic and Spectroscopic Insights into the  
Behavior and Interactions of Oxygen, OH and Ethylene on Bare and  
Ni-Promoted Ag(100) Surfaces**

A dissertation submitted by

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## Abstract

The interaction of oxygen with silver surfaces is fundamental to understanding catalytic reactivity in large-scale partial oxidation reactions, particularly as ethylene epoxidation. While Ag(111) and Ag(110) surfaces have been extensively studied, the Ag(100) facet remains comparatively underexplored despite several favorable properties. Using scanning tunneling microscopy (STM), synchrotron X-ray photoelectron spectroscopy (XPS), and density functional theory (DFT), this dissertation investigates formation and behavior of atomic oxygen (O), hydroxyl (OH), ethylene ( $C_2H_4$ ), and related intermediates on Ag(100) and Ni-doped Ag(100) single-atom alloys. On Ag(100), we reveal that, in addition to O adatoms, OH species form readily even under ultra-high vacuum, suggesting their role should be acknowledged in potential oxidation reaction mechanisms on Ag.

To advance chlorine-free ethylene oxide (EO) production, we examine NiAg(100) SAAs, which were previously shown to achieve ~80% EO selectivity without conventional Cl promoters. STM and DFT demonstrate that isolated Ni atoms facilitate  $O_2$  dissociation at cryogenic temperatures, forming  $NiO_2$  species, at a temperature at which  $O_2$  remains intact on Ag(100). This lowered oxygen activation barrier is critical for enhanced catalytic performance of the NiAg SAA. High-pressure XPS performed under simulated epoxidation conditions showed that Ni incorporation suppresses carbon buildup and stabilizes higher oxygen coverage than bare Ag(100).

Together, these findings provide a comprehensive understanding of oxygen species formation, evolution, and behavior on Ag(100) and NiAg(100) surfaces under conditions relevant to oxidation reactions. The demonstrated ability of Ni to promote  $O_2$  activation and

stabilize desired oxygen intermediates without Cl highlights the promise of SAAs for the next generation selective oxidation catalysts. This fundamental insight lays the groundwork for designing more efficient, environmentally sustainable catalysis.

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# Chapter 1:

## Introduction

### 1.1 Overview of Ethylene Epoxidation

#### 1.1.1 Brief History of Ethylene Oxide Production

Ethylene Oxide, EO, was first discovered in 1859 from the synthesis of chloroethanol and potassium hydroxide.<sup>1</sup> However, it was not until the early twentieth century, when French chemist Theodore Lefort managed the successful direct oxidation of ethylene to ethylene oxide due to his use of Ag catalysts.<sup>2</sup> The discovery of Ag as a catalyst occurred in 1931 and quickly led to the industrialization of EO production, particularly during World War II.<sup>2,3</sup> Over the next 80 years ethylene epoxidation, grew to be a landmark industrial reaction and household name in catalysis communities.<sup>2,4,5</sup> However, alumina-supported Ag catalysts have an inherent selectivity toward EO of only ~55%, with the other reacted ethylene combusting to form CO<sub>2</sub> and water.<sup>6,7</sup> Thus, continued improvements to this low selectivity were made through improving reaction conditions, and the use of promoters.

A decade after the first Ag-based catalyst was patented, Cl was found to dramatically enhance the selectivity of the reaction using alkyl chlorides designed to deposit Cl on the catalytic surface.<sup>8,9</sup> The use of Cl as a promoter became common practice for EO production (leading to a 25% increase in selectivity on its own with current technology),<sup>8,9</sup> but its role in the selective mechanism was not understood for many years.<sup>8,10,11</sup> The presence of Cl in both the original synthesis of ethylene oxide, as well as the chlorohydrin process that preceded direct

oxidation on Ag, also emphasize the importance of Cl in selective EO production. In the latter half of the century, Cs and Rh, among other metal-based promoters were discovered and their addition as well as improvements in processing conditions, helped to achieve selectivities ~90%; similar to what we see today.<sup>8,11,12</sup>

### **1.1.2 Ethylene Epoxidation Today and the use of Promoters**

Since its first commercial production of EO in the early 1900s, the total EO production capacity has grown to ~35 million tonnes per year, as of 2023.<sup>2,4</sup> Today, EO is used for a variety of applications from production of consumer goods such as antifreeze and fabrics,<sup>1</sup> to its ubiquitous use in medical device sterilization,<sup>3,13</sup> and for the production of pharmaceuticals.<sup>2,4,14</sup> Due to the unique oxygen adsorption properties of silver,<sup>15</sup> Ag-based catalysts have also been adopted for other partial oxidation reactions such as methanol to formaldehyde,<sup>16,17</sup> and propylene to propylene oxide (PO).<sup>18,19</sup>

Promoters, specifically Cl have been shown to affect EO selectivity by both changing the number of active sites on the surface, as well as changing the chemical nature of different sites.<sup>10,20</sup> Cl tunes the distribution of oxygen species on the Ag surface.<sup>20</sup> Metallic promoters such as Cs and Re, are important for achieving the highest selectivity toward EO with the current Ag-based catalysts.<sup>12,21</sup> Despite their promotional properties, these metal dopants only exhibit their desired effects when used as a co-promoter with Cl.<sup>12,21</sup> This co-dependence of the various promoters makes study of this system and the roles of promoters complex and challenging.<sup>8,22</sup>

### **1.1.3 Current Issues and Future Directions**

Despite the success of the current ethylene epoxidation industry, there are significant issues still plaguing the efficiency and environmental impact of this reaction. The EO production

process has one of the lowest per-pass conversions of industrial reactions run at a similar scale as well as requiring low reactant partial pressures (>50% of the feed is inert).<sup>23</sup> CO<sub>2</sub> is the main byproduct of ethylene epoxidation (10%), which adds to the CO<sub>2</sub> produced from large-volume recycle streams that require energy intensive separation processes.<sup>24,25</sup> These factors all contribute to EO production emitting the most CO<sub>2</sub> of high-volume chemicals on a per volume basis (~1.4 kg CO<sub>2</sub> per 1 kg EO)<sup>24-26</sup> Improvements to EO selectivity and reaction conditions could have a significant impact on the CO<sub>2</sub> emission and energy footprint of ethylene epoxidation.<sup>24,27</sup>

The extensive use of Cl in selective ethylene epoxidation has increasingly raised environmental and safety alarms due to Cl's well documented toxicity especially with regard to its propensity to form ethylene chlorohydrin in this reaction system.<sup>28,29</sup> Additionally, the standard use of Cl as a promoter for industrial EO production has limited study on alternative promoters that can act independently of Cl.<sup>4</sup> However, the compounding of these issues that has occurred as EO demand grows, has sparked a recent shift toward finding new promoters to replace the current Cl-promoted Ag catalyst system.<sup>22,30</sup>

The prolonged research on this reaction has produced a remarkable collection of academic reports that have shed insight on a variety of areas of ethylene epoxidation, from oxygen adsorption properties,<sup>31</sup> to kinetics and reaction dynamics,<sup>25,32</sup> to the use of promoters and their effects,<sup>10,21,30</sup> and the optimized synthesis and surface structure of nanoparticle Ag/Al<sub>2</sub>O<sub>3</sub> catalysts.<sup>23,33-35</sup> The goal of this research has been to understand the interactions between Ag, O<sub>2</sub> and ethylene, and to improve selectivity for this reaction.<sup>4,31</sup> Yet, fundamental questions, such as the nature of the selective active oxygen intermediate, and exact mechanism of selective epoxidation remain unsolved into the twenty-first century.<sup>4,21,31,36</sup>

## **1.2 Debate Over the Active Oxygen Species in Selective Ethylene Epoxidation**

### **1.2.1 Overview**

The reactive nature of oxygen leads to the formation of a diverse array of different O-based species on catalytic surfaces. Oxygen can exist in metal oxides, as O adatoms, in OH and H<sub>2</sub>O, in surface reconstructions, as peroxo and superoxo species, and in carbonaceous species such as CO, CO<sub>2</sub>, carbonate, and alcohols. The range of these types of oxygen and their properties, makes characterization of their presence, role and behavior a complex area of study. Due to this challenge, the exact role of each oxygen species under epoxidation conditions and the identity of the selective species amongst them are still widely debated.<sup>31,36–38</sup> This section will briefly review several proposed identities of selective oxygen as well as other relevant oxygen-based species.

### **1.2.2 Oxygen Adatoms**

The most widely accepted identity for the selective oxygen species in ethylene epoxidation is that O atoms (sometimes referred to as “electrophilic oxygen”) are responsible for reacting with ethylene to form EO. Under reaction conditions, oxygen exists as two broad types, most commonly distinguished with XPS.<sup>36,39,40</sup> The lower binding energy species (528-528.5 eV) consists of O in Ag reconstructions, referred to “nucleophilic oxygen,” and is thought to lead to the complete oxidation of ethylene and formation of combustion products.<sup>39,41</sup> The higher binding energy peak (530-531 eV), consists of electrophilic oxygen, most frequently assigned as atomic oxygen.<sup>32,40–42</sup> It is this higher binding energy species that is thought to be the selective O

species for EO formation. The electrophilic-nucleophilic studies were predominantly led by XPS and DFT, but debate remains over whether or not electrophilic oxygen is O adatoms or a different species.<sup>32,36,43</sup> The crowded 530-531 eV area of O 1s XPS spectra also makes conclusive analysis of these peaks challenging.<sup>42,44</sup>

### 1.2.3 Dioxygen Species

Recently, the singular nature of O itself has been questioned in the selective mechanism of EO formation. Rather, these studies suggest that oxygen is most selective as a peroxo species,<sup>45</sup> or as a dioxygen atomic species.<sup>38,43</sup> O<sub>2</sub> has shown to be selective for directly oxidizing larger olefins,<sup>18</sup> but it is not believed to be the active species for ethylene oxidation.<sup>25</sup> DFT and XPS found a dioxygen species formed on Ag(111) that was active toward both EO and CO<sub>2</sub>.<sup>43</sup> A study performed on Ag nanoparticles also found that an Ag<sub>4</sub>-O<sub>2</sub> species was active toward both reaction pathways.<sup>38</sup> Using Raman and DFT, another group found that diatomic oxygen in the forms of peroxide (O<sub>2</sub><sup>-</sup>), or superoxide (O<sub>2</sub><sup>2-</sup>) forms at high O<sub>2</sub> pressures and play an important role in ethylene epoxidation.<sup>45</sup> The peroxo species demonstrated more favorable EO formation than the superoxo species.

### 1.2.4 Subsurface Oxygen

Subsurface oxygen species have also been reported to play a role in ethylene epoxidation, oxygen activation and the selectivity of EO formation.<sup>46,47</sup> Subsurface oxygen was shown to enhance ethylene adsorption on Ag(100) via DFT calculations,<sup>48</sup> and it was reported that subsurface oxygen can enhance the adsorption of oxygen on Ag(111).<sup>49</sup> Another study supports the claim subsurface oxygen increases the reactivity of the Ag(111) surface, however, they admit their subsurface oxygen coverages of 0.5 and 1 monolayer may be unrealistically high for any

real catalytic system.<sup>50</sup> A recent joint-theoretical and catalytic study proposed that square-pyramidal subsurface oxygen in an O<sub>5</sub> phase on the Ag(100) surface in the form of Ag<sub>4</sub>OAg selectively converts ethylene to EO.<sup>37</sup> They also claim (100) is the only facet and oxygen species combination that can achieve this selective conversion.<sup>37</sup> This phase has a high barrier toward O<sub>2</sub> dissociation, so it must be supplied by O atoms from elsewhere.<sup>37</sup>

There is considerable debate as to the favorability of subsurface oxygen formation and its experimental characterization.<sup>41,46,51–53</sup> EO has been observed on other facets than Ag(100), which suggests that the unique O<sub>5</sub> subsurface species identified is not solely responsible for EO production.<sup>54,55</sup> Several studies performed on Ag surfaces under simulated epoxidation conditions<sup>56,57</sup> or CO oxidation conditions,<sup>58</sup> found that an XPS binding energy peak near 531 eV, previously reported as a subsurface O species,<sup>59</sup> was more consistent with carbonate formation than subsurface oxygen.<sup>56,57</sup> DFT calculations also found that subsurface oxygen is not stable in either the tetrahedral nor the octahedral subsurface sites in Ag(100).<sup>51,52,60</sup>

### 1.2.5 Other O-Containing Species

Sulfur (S), a common impurity found in Ag samples, has also been suggested to play a role in selective oxidation catalysis.<sup>61</sup> It was reported that SO<sub>4</sub><sup>−</sup> might be the true identity of “electrophilic oxygen.” Temperature programmed reaction (TPR), DFT, and XPS showed that SO<sub>4</sub> formed from S impurities on Ag samples.<sup>61</sup> This surface SO<sub>4</sub> species remains unreactive while not in the presence of coadsorbed oxygen. Once coadsorbed oxygen is present, the SO<sub>4</sub> is freed from Ag reconstructions and the resulting species on the unreconstructed surface shares spectroscopic properties associated with electrophilic oxygen,<sup>36</sup> and produces EO during TPR.<sup>61</sup> Despite this result, there are very few other studies that propose sulfur playing a role in selective

epoxidation, and other papers that report electrophilic oxygen also report no presence of trace S impurities.<sup>62</sup>

Carbonate has been commonly observed on Ag surfaces under epoxidation conditions.<sup>11,56,57</sup> There are conflicting fields of thought as to whether the presence of carbonate is indicative of selective<sup>63</sup> or unselective<sup>56</sup> ethylene epoxidation.<sup>64</sup> Carbonate is thought to block Ag surface sites, making less area available for reaction,<sup>57</sup> and it is a precursor to CO<sub>2</sub> formation,<sup>20,65</sup> but it also has been shown to increase the rate of the reaction to EO by stabilizing subsurface oxygen.<sup>58,63</sup>

A surface oxametallacycle, defined as a hydrocarbon backbone including oxygen, bound at both ends to the metal surface, has been often proposed as an intermediate for ethylene epoxidation.<sup>21,7,66–68,55,69</sup> Oxametallacycles of ethylene and oxygen have been demonstrated and proposed in several different ethylene oxidation reaction pathways leading to different products, ranging from ethylene oxide, to combustion products and  $\gamma$ -butyrolactone.<sup>69</sup> Oxametallacycles can form in a variety of arrangements potentially incorporating multiple ethylene molecules or oxygen atoms, but the biggest determinant of selectivity is thought to be whether or not the oxametallacycle binds to one or two Ag surface atoms.<sup>69,70</sup> The ability of a single form of oxametallacycle to proceed through either selective or unselective oxidation pathways through alternate transition states also highlights their potential importance for EO formation.<sup>71</sup> Multiple forms of a surface oxametallacycle have been identified,<sup>70</sup> but experimental evidence of their formation, especially through forward reaction using ethylene, remain limited, likely due to their unstable and ephemeral nature.<sup>21,69,71,72</sup>

### 1.2.6 Water and OH on Ag Surfaces

The interaction of water with oxygen on silver surfaces is relevant to epoxidation studies due to the promotional and deleterious effects water can have on oxidation reactions.<sup>73</sup> Forming exothermically from the reaction of water with surface oxygen, OH specifically plays a role for oxidations on silver as well.<sup>74–76,33,77</sup> Experimental studies of the water and OH interactions with the O-Ag surface have focused on the Ag(110) facet.<sup>76,78–84</sup> On Ag(100), theoretical studies found that the most stable adsorption site for OH is the four-fold hollow site, and that OH formation from the interaction of water and pre-adsorbed oxygen is exothermic.<sup>85,86</sup>

The formation of OH consumes atomic oxygen on the surface,<sup>81</sup> which affects the reaction of ethylene and oxygen by changing the surface makeup of oxygen species and reducing the availability of a potentially selective oxygen species.<sup>73,87</sup> OH has also been shown to hydrogen bond with physisorbed water on the Ag surface, further highlighting its potential role in oxidation reactions.<sup>81</sup> The challenge of clearly distinguishing and identifying surface OH while in the presence of other adsorbates on O-Ag surfaces has limited quantitative experimental work in this area.<sup>73,80,85</sup> This difficulty in characterizing OH on Ag surfaces has also led to it being under looked in potential reaction pathways for oxidation reactions.<sup>4,5</sup>

## 1.3 NiAg Single Atom Alloys for Selective Oxidation Reactions

### 1.3.1 Single-Atom Alloys (SAAs)

Discovered in 2012 and pioneered over the last decade, Single-Atom Alloys (SAAs), consisting of isolated reactive dopant metals alloyed into inter host metals, have shown great

promise as an important area in the next generation of heterogeneous catalysts.<sup>88</sup> The unique properties exhibited by these catalysts largely derive from their unique geometry, which enables facile dissociation of a reactant gas-phase molecule on the isolated dopant atom, followed by weak binding of the reactive intermediate on the host metal surface. This combination of the optimal properties from two classes of metals resulted in catalysts that can break traditional linear scaling relationships via decoupling the transition and final state energies.<sup>89,90</sup> The SAA approach has been successful across a variety of (de)hydrogenation reactions,<sup>88,91–93</sup> but its design makes it ideal for other areas of reactions such as oxidations,<sup>11</sup> which are typically limited by the high O<sub>2</sub> dissociation barrier of Ag.<sup>31</sup>

### 1.3.2 NiAg SAA Catalysts

It was recently discovered that isolated Ni atoms in Ag, in the form of a Single-Atom Alloy, increased ethylene epoxidation selectivity by ~25%.<sup>30</sup> A singular boost in selectivity has only been achieved to this magnitude previously by Cl (also ~25%).<sup>8</sup> This study was a theory-led collaboration that included surface science and nanoparticle catalysis, which highlights the synergy enabled by the SAA approach.<sup>94</sup> The Ni-doped Ag/Al<sub>2</sub>O<sub>3</sub> nanoparticle catalysts demonstrated 85% selectivity toward EO without Cl, and 90% with the addition of Cl.<sup>30</sup>

Ni has been largely unexplored as a selective oxidation promoter, prior to the NiAg SAA report, which may be due to the very small alloying concentration at which it was effective (0.5 atom %).<sup>30,95</sup> However, DFT calculations, using the same SAA framework as for (de)hydrogenation catalysts, searched for dopants in Ag surfaces that exhibited a combination of a low O<sub>2</sub> activation barrier and weak atomic binding energy of atomic oxygen. These calculations found that Ni met both requirements and indicated that it could break the scaling relationships

between oxygen activation and binding that has historically limited Ag-based oxidation catalysts.<sup>31</sup>

Surface studies performed on an NiAg(111) SAA provided further insight into the effects of the Ni sites on O<sub>2</sub> behavior. They found that the presence of Ni leads to the formation of a “Ni-philic” oxygen species with an intermediate binding energy between electrophilic and nucleophilic oxygen in STM.<sup>30</sup> Additionally, Ni was found to reverse segregate from the bulk to the Ag surface upon O<sub>2</sub> exposure at 300 K. From this initial report, the authors hypothesize that Ni’s promotional effect toward EO production on an Ag catalyst is due to its presence increasing the thermal stability of non-selective nucleophilic oxygen allowing the selective electrophilic oxygen species to react more readily with ethylene.<sup>30</sup> This study motivates further investigations on NiAg SAAs for selective oxidation reactions.

## **1.4 Ag(100)**

### **1.4.1 Sticking Probability of O<sub>2</sub>**

The low sticking probability of oxygen on Ag has hindered the consistency of surface science studies of selective oxidation reactions on this system.<sup>96,97</sup> The O<sub>2</sub> sticking coefficient on Ag(100) is  $\sim 10^{-4}$ ,<sup>96</sup> while the most commonly studied facet Ag(111) has an O<sub>2</sub> sticking coefficient of  $\sim 10^{-8}$ .<sup>97</sup> Therefore, it is quite difficult to form oxygen surface species on Ag(111) directly from O<sub>2</sub> exposure in UHV. As a result these studies must turn to O<sub>2</sub> alternatives like NO<sub>2</sub> or O<sub>3</sub> or use high-pressure setups that are subject to contamination.<sup>96,98</sup> Ag(100) is an excellent alternative for clean UHV study of the interaction between O<sub>2</sub> and the Ag surface as O<sub>2</sub> and its

variety of products can be studied directly under a variety of conditions. Ag(110) shares a similar sticking coefficient with Ag(100) making it a good alternative as well.<sup>99</sup>

### **1.4.2 Intrinsic Selectivity Toward Ethylene Oxide**

Ag(100) has also received attention due to its inherent selectivity towards ethylene oxide potentially exceeding other facets.<sup>7,37,66,100</sup> Selectivity studies on the distribution of surface facets in Ag nanowire catalysts reported that higher selectivity toward EO occurred on nanowires with higher concentrations of (100) surface facets.<sup>7</sup> They also found that EO is more selectively formed on Ag(100) than Ag(111), which is supported by DFT calculations as well.<sup>66</sup> This enhanced selectivity on Ag(100) is attributed to different oxygen activation barriers between the facets.<sup>7,66</sup> The subsurface O<sub>5</sub> phase found to be linked with selective EO formation can only form on the Ag(100) facet.<sup>37</sup> Ag(110) has been suggested as equally if not more selective than Ag(100),<sup>9,101</sup> but it also has been cited as less selective than the Ag(111) facet,<sup>102</sup> highlighting the complexity and contradictions of oxygen studies on Ag model catalysts.

### **1.4.3 SAAs on Open Facets and NiAg(100)**

The study of single-atom alloys on single-crystal surfaces has led to the discovery of the facet dependence on the formation of these alloys.<sup>103</sup> SAAs have been extensively studied using surface science in UHV during their short history thus far, and these surface science studies have provided fundamental insight into their structure and reactivity.<sup>88</sup> It was shown on RhCu SAAs formed across (110), (111), and (100) surface facets that there was a stark difference in Rh alloying in Cu(111) than the more open Cu(100) and Cu(110) facets. This difference is due to the existence of two potential alloying mechanisms on SAAs. The first mechanism is place exchange of the dopant atoms directly into terraces on the single crystal host (leading to single atoms

alloyed in the terraces). The other mechanism is the diffusion of the dopant atoms to step edges followed by place exchange at the step edge into the upper terrace (resulting in isolated atoms present in brims above the step edges). Rh alloying into Cu(111) resulted in Rh atoms found in dense brims of the isolated sites above the step edges, whereas on Cu(100) and Cu(110), Rh formed dispersed terrace sites.<sup>103</sup>

As a result of the more dispersed dopant sites in more open facets, these surfaces are more amenable to study with scanning tunneling microscopy (STM), and can potentially achieve a higher dopant surface coverage while still remaining as isolated sites.<sup>104</sup> The combination of isolation of dopant sites, as well as the increased sticking coefficient of O<sub>2</sub> on the (100) facet make the NiAg(100) SAA as well as the bare Ag(100) surface excellent candidates for further study on oxygen speciation and ethylene epoxidation on Ag-based systems.

In this work, the instruments and techniques used in each individual study will be detailed and explained in Chapter 2. Chapter 3 discusses the formation and identification of OH groups on Ag(100) using STM, XPS, and DFT. Chapter 4 presents the demonstration of low temperature oxygen activation on a NiAg(100) SAA using STM and DFT. Chapter 5 shows the comprehensive classification of various oxygen species formed on Ag(100) and NiAg(100) using the combination of STM and XPS. Chapter 6 depicts the direct atom-scale visualization of an oxygen-ethylene oxametallacycle using STM. Chapter 7 looks at high pressure experiments where the effects of simulated reaction conditions on NiAg(100) and Ag(100) were explored with XPS. Chapter 7 will summarize the body of research presented in this dissertation and discuss future directions. Lastly, Appendix 1 features a textbook chapter written on SAAs, their preparation, properties, and applications.

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## Chapter 2.

### Experimental Methods

#### 2.1 Ultra-High Vacuum Chambers

Ultra-high vacuum, defined as pressures  $< 1 \times 10^{-9}$  mbar, is necessary to study surfaces that would no longer remain clean under high-pressure conditions due to quickly adsorbing impinging molecules.<sup>1</sup> The work in this thesis utilized two UHV chambers, one of which is shown in Figure 1. First, a low-temperature scanning tunneling microscope (LT-STM) was used for structural investigations of Ag and NiAg(100). Next, an ambient pressure X-Ray photoelectron spectroscopy (AP-XPS) chamber was used for high pressure reactivity and structural investigations as well as UHV characterization of Ag and NiAg(100).

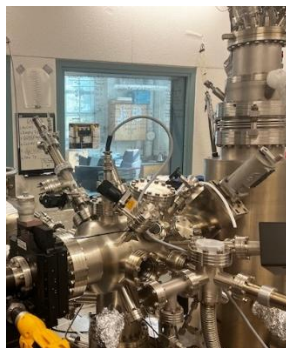


**Figure 2.1.** Low-Temperature STM used in this thesis.

The LT-STM is a commercial chamber (Scienta Omicron) consisting of an STM chamber and a preparation chamber separated by a gate valve. The preparation chamber is equipped with a cold cathode sputter gun (Scienta Omicron, ISE 5) and a hot filament sputter gun (RBD, model 32-165) for sample cleaning. Three electron bombardment evaporators (EFM 3, Scienta Omicron) are used for controlled high-purity metal deposition. A linear manipulator equipped with a pyrolytic boron nitride (PBN) style heater capable of heating to over 1000 K is used to

heat and move the sample. Sample temperatures are calculated based on the applied power using a previous calibration. The STM has a dual-stage cryostat that can be cooled to 78 K with liquid nitrogen or to 5 K with liquid helium. The STM stage is equipped with a PBN heater which can heat the sample to 60 K from liquid helium temperatures or 300 K from liquid nitrogen temperatures. Anneals can also be performed by removing the crystal from the stage and letting it warm naturally in the carousel, manipulator head or wobblestick. Electrochemically etched tungsten tips were used for scanning. The preparation chamber and STM chamber both have collimated and non-collimated high precision leak valves (MDC and Lesker) to expose the samples to gas adsorbates in a controlled manner. The base pressure of the preparation chamber is  $3 \times 10^{-10}$  mbar and the base pressure of the STM chamber is  $<1 \times 10^{-11}$  mbar as monitored by Bayard Alpert style ion gauges (Scienta Omicron). Turbo, ion and titanium sublimation pumps were used to maintain these pressures. All samples were mounted on tantalum sample plates via spot welded tantalum strips or wires.

The Synchrotron XPS chamber is a AP-XPS endstation located at the IOS beamline off of the NSLS-II storage ring at Brookhaven National Lab.<sup>2</sup> It is served by an elliptically polarized undulator source (EPU49). The beamline offers a photon energy range of 250 to 2000 eV with a flux of up to  $10^{13}$  photons/sec and resolving power ( $E/\Delta E$ ) of up to  $10^4$ . The main optical components of the beamline are a horizontally deflecting and focusing mirror (M1B), an adjustable vertical exit slit, a variable line spacing plane grating monochromator (VLS-PGM) with three gratings (150 1/mm, 400 1/mm and 1200 1/nm), and a elliptically cylindrical mirror (M3B) to vertically focus the beam onto the sample over a spot size of 80  $\mu\text{m}$  (horizontal) by 20  $\mu\text{m}$  (vertical). The Ambient Pressure Photoelectron Endstation (APPES) is equipped with a

SPECS Phoibos NAP 150 electron analyzer with a 1-D delay line detector (1D-DLD, Surface Concept).

The main experimental chamber has a base pressure of  $2 \times 10^{-9}$  torr and is designed for a backfilling setup to perform AP-XPS experiments up to 10 Torr. The entrance cone to the first differential pumping stage of the analyzer has a diameter of 300  $\mu\text{m}$ , which is big enough to sample the entire x-ray illuminated spot on the sample, and a 100-nm thick  $\text{Si}_3\text{N}_4$  window separates the beamline vacuum from the APPES main chamber. The analyzer is offset by 70 degrees from the vector of the incident beam. And the sample is aligned such that the incident beam angle and photoelectron emission angle are 50 and 20 degrees from the surface normal. A HAL-100 residual gas analyzer (RGA) is mounted on the second differential pumping stage of the analyzer to monitor gas composition near the sample surface. The chamber is equipped with a SPECS IQE 11/35 ion source for sample cleaning. A four-pocket SPECS EBE-4 electron beam evaporator calibrated with a quartz crystal microbalance is used for controlled high-purity metal deposition. High precision leak valves expose the sample to gas reactants. The chamber pressure is monitored by a combination of a hot cathode ion gauge and Pirani gauge as well as a capacitance manometer for pressures above 50 mTorr. Pfeiffer Turbomolecular pumps maintain the chambers' pressures along the beamline and endstation. The sample is mounted using a STLC sample plate and dock system mounted to a motorized 4-axis manipulator. The manipulator is equipped with a PBN heater (Momentum) which can heat the sample to 1100 K in UHV. The temperature is monitored by a K-type thermocouple placed between the sample and heater.

## 2.2 Model Surface Preparation

Single crystal samples are an excellent tool to achieve highly reproducible results on model systems at the atomic scale. The work presented in this thesis was collected on two Ag(100) single crystals (Princeton-Scientific, 99.999% purity <1 degree polish). Sputtering cycles via argon ion bombardment and thermal annealing were used to clean the samples to less than 1 defect/impurity per 10,000 atoms.<sup>3</sup> Either an RBD hot filament sputter gun or a cold cathode sputter gun were used for cleaning and achieved drain currents of 1 to 20  $\mu$ A. For the STM chamber, annealing was conducted with a PBN heater and temperature calculated via external calibration. For the XPS chamber, annealing was conducted with a PBN heater and temperature measured via a K-type thermocouple attached to the back of the sample. In the TPD chamber, annealing was achieved via resistive heating of tantalum wires, with the temperature measured by a K-type thermocouple laser welded to the back of the crystal.

For STM and NiAg SAA surfaces were prepared via Ni deposition from electron-bombardment evaporation of a high purity Ni rod (Goodfellow, 99.9% purity) using an EFM 3 evaporator. For XPS, Ni deposition was achieved using a four-pocket SPECS EBE-4 electron-beam evaporator. Ni depositions were all done at  $\sim$ 300 K across all three chambers. Manual counting was used to calibrate Ni deposition in the STM, and the Ni 2p peak was measured and corrected to calculate Ni coverage in the XPS chamber.

## 2.3 Scanning Tunneling Microscopy (STM)

STM was invented in the early 1980s by physicists Gerd Binnig and Heinrich Rohrer as a technique to achieve atomic-scale images of conductive surfaces by utilizing the phenomenon of quantum tunneling. They received the Nobel Prize for their invention in 1986.<sup>4</sup> In STM, a sharp conductive tip is brought within  $\sim$ 1 nm of a conductive surface and is rastered across the

surface using piezoelectronic motors.<sup>5,6</sup> At this distance, electrons can tunnel from the tip to the sample (or the sample to the tip depending on the direction of the current). The current's direction is controlled by applying a voltage bias between the sample and the tip. By measuring the intensity of tunneling electrons as a function of position or monitoring the change in the tip-to-sample distance required to maintain a constant tunneling current, high-resolution images of the sample surface can be generated. The intensity of the tunneling current is determined by equation 2.1 shown below, where  $I$  is the tunneling current,  $d$  is the distance between the sample and the tip,  $m_e$  is the mass of an electron,  $\hbar$  is Planck's constant divided by  $2\pi$ ,  $V$  is the potential energy barrier, and  $E$  is the tunneling electron's energy.<sup>4</sup>

Equation 2.1 
$$I \propto e^{-2kd} = e^{[-(8\pi m_e)/\hbar] * d(V-E)}$$

The tunneling current is highly dependent on the distance between the tip and sample which allows highly detailed maps of the surface structure. STM provides topographic information indirectly by measuring the electronic structure (density of states) of the materials. As a result, spectroscopic techniques have been developed to measure the electronic and vibrational properties of the surface and the atoms and molecules adsorbed to it.<sup>5,7</sup>

STMs are mostly used in UHV to keep the sample surface clean and experiments reproducible. STMs can be run in either constant current mode or constant height mode. In constant height mode, the STM tip maintains the same height while it rasters across the surface, and the change in tunneling current is measured. In constant current mode, the more common setup, the STM tip moves up and down as it rasters to maintain a constant set tunneling current. The change in tip-sample distance as a function of position is measured and displayed as an image. This technique can achieve atomic resolution and resolve differences between individual surface atoms.

## 2.4 X-Ray Photoelectron Spectroscopy (XPS)

Modern XPS was pioneered by a group of physicists, including Kai Siegbahn, in the 1960s-80s,<sup>8</sup> and grew in popularity throughout the 1990s as a surface analysis technique.<sup>9,10</sup> XPS can be performed with either monochromatic laboratory x-ray sources or high-flux high-resolution synchrotron radiation sources at beamlines (non-monochromated lab sources can also be used). XPS is possible due to the photoelectric effect that arises when high energy photons (keV range) hit a material and emit electrons (photoelectrons) from the material. If the incident photon has enough energy, many different energy levels of atoms in the sample can be ionized. This process produces a spectrum displaying all accessible energy levels as a distribution of photoelectrons with kinetic energies ( $E_k$ ) dictated by Einstein's law  $E_k = h\nu - E_b - \phi_{\text{spec}}$ , where  $h\nu$  is the energy of the radiation,  $E_b$  is the binding energy of the electron in a particular orbital/level, and  $\phi_{\text{spec}}$  is the work function of the spectrometer/detector.<sup>10</sup> This spectrum, usually portrayed as a function of electron binding energy (BE), contains information on orbitals/energy states where  $BE < h\nu$  for the sample being analyzed. The specific peaks to be analyzed and binding energies to be scanned depend on the sample and experiment. Because XPS spectra are graphed as a function of binding energy, the different chemical binding energies of different electronic states provide insight into the identities and concentration of elements present and their charge/oxidation states among other features. The ability to use XPS to obtain information of the surface and near subsurface of a catalyst by adjusting the photon energy to be surface sensitive is another highly valuable aspect to this technique. It is also important to note that XPS is another technique that can be performed across different pressure regimes. It is usually performed under UHV conditions, but it can be used at ambient, or near-ambient pressures (AP-XPS or NAP-XPS, ~10 torr). This pressure range is highly valuable for model studies as it allows for cross

comparison of reaction environments in UHV or at ambient pressures and bridge the pressure gap.<sup>2</sup>

Reference Ag 3d spectra were taken after acquiring each oxygen or carbon spectrum. Oxygen species coverages were calculated by dividing the corrected O 1s peak areas by the corresponding corrected Ag 3d peak areas. Peaks areas were corrected by dividing the raw areas by their Relative Sensitivity (RSF) value<sup>11</sup> multiplied by the IMFP of the ejected electron found from a universal curve<sup>12</sup> (Equation S1). Carbon C 1s species were only corrected for IMFP. Ag 3d peak areas were also corrected by a first layer correction based on the IMFP to account for the signal only generated for the top level of atoms (Equation S2).

$$\frac{\text{Corrected O1s Peak Area}}{\text{Peak Area}} = \frac{\text{Raw Peak Area}}{\text{R.S.F.} \times \text{I.M.F.P.}}$$

**Equation S1.** Oxygen XPS Correction.

$$\frac{\text{Corrected Ag3d Peak Area}}{\text{Peak Area}} = \frac{\text{Raw Ag3d}_{5/2} \text{ Peak Area} \times \text{First Layer Correction} \times \text{Intensity Factor}}{\text{R.S.F.} \times \text{I.M.F.P.} \times 5/2 \text{ Correction}}$$

**Equation S2.** Silver XPS Correction.

$$\frac{\text{Corrected Ni2p Peak Area}}{\text{Peak Area}} = \frac{\text{Raw Ni2p}_{3/2} \text{ Peak Area}}{\text{R.S.F.} \times \text{I.M.F.P.} \times 3/2 \text{ Correction}}$$

**Equation S3.** Ni XPS Correction.

To investigate different elements, different photon energies were used. Predominantly, 760, 1090 and 500 eV were used to generate photoelectrons with kinetic energies of ~200-300 eV for the O 1s (at 760 eV), Ni 2p (at 1090 eV), and S 2p and C 1s (at 500 eV) core levels, respectively, to maintain similar probing depths. Binding energy calibration was performed on all

spectra with respect to the Fermi edge and metallic Ag 3d<sub>5/2</sub> binding energy measured at each photon energy.<sup>13</sup> XPS data was analyzed with CasaXPS. Each species was assigned and fit according to experimental results and literature values (Table S1). O 1s, C 1s and Ni 2p were fit with a linear background due to their small size, while Ag spectra were fit with a Shirley background.<sup>14</sup>

| Element                       | Component                                                                              | Binding Energy (eV)      | Full Width at Half Maximum (FWHM) | Line Shape (Gaussian: Lorentzian) |
|-------------------------------|----------------------------------------------------------------------------------------|--------------------------|-----------------------------------|-----------------------------------|
| Oxygen (O1s)                  | O in Ag Reconstructions <sup>15-17</sup>                                               | 527.9 – 528.2            | 0.7 – 0.8                         | 30:70                             |
|                               | Ag Oxide Patches (Ag <sub>2</sub> O) <sup>18,19</sup>                                  | 528.5 – 528.7            | 0.8 – 1.0                         | 30:70                             |
|                               | Ag Oxide <sup>25</sup>                                                                 | 529.2 – 529.5            | 1.0 – 1.1                         | 30:70                             |
|                               | NiO <sup>20-23</sup>                                                                   | 529.0 – 529.2            | 0.8 – 0.9                         | 30:70                             |
|                               | NiO <sub>2</sub> <sup>24</sup>                                                         | 531.8*                   | n/a                               | n/a                               |
|                               | Atomic O <sup>11,14,25,26</sup>                                                        | 530.0 – 530.2            | 0.8 – 1.0                         | 30:70                             |
|                               | Carbonate <sup>27,28</sup>                                                             | 530.5 – 530.7            | 0.9 – 1.0                         | 30:70                             |
|                               | OH <sup>20,29,30</sup>                                                                 | 530.9 – 531.1            | 0.8 – 0.9                         | 30:70                             |
|                               | Water <sup>23,31-33</sup>                                                              | 531.5-532.5              | 1.0 – 1.1                         | 30:70                             |
| Silver (Ag3d <sub>5/2</sub> ) | Ag <sup>0</sup> (Metallic Ag) <sup>13,34</sup>                                         | 368.2                    | 0.4                               | 99:1                              |
|                               | Ag Oxide (Ag <sub>2</sub> O) <sup>19,34</sup>                                          | 367.8                    | 0.8                               | 30:70                             |
| Nickel (Ni2p <sub>3/2</sub> ) | Ni <sup>0</sup> (Metallic Ni) <sup>23,35</sup>                                         | 852.6                    | 1.0 – 1.2                         | 30:70                             |
|                               | Ni <sup>2+</sup> (NiO) <sup>23,35</sup>                                                | 853.9                    | 1.0 – 1.2                         | 30:70                             |
|                               | Ni <sup>4+</sup> (NiO <sub>2</sub> ) <sup>36</sup>                                     | 856.1*                   | n/a                               | n/a                               |
| Carbon (C1s)                  | Carbonaceous C <sup>28</sup>                                                           | 284.0 – 284.6            | 1.0 – 1.2                         | 30:70                             |
|                               | Intact C <sub>2</sub> H <sub>4</sub> ( $\pi$ -bound C) <sup>37</sup>                   | 283.2 – 283.4            | 0.8 – 1.0                         | 30:70                             |
|                               | Gas-Phase C <sub>2</sub> H <sub>4</sub> (two peaks) <sup>27</sup> (need one more cite) | 285.5-285.6, 285.8-285.9 | 0.3, 0.8                          | 30:70                             |
|                               | Carbonate/Product <sup>27,28</sup>                                                     | 287.5 – 287.8            | 1.0                               | 30:70                             |

**Table S1.** Summary of fitting parameters for XPS spectra.

\*Not detected within our XPS experiments.

**Note on differing O:OH Ratios:** We found that OH formation from the background is highly dependent on oxygen coverage, temperature, chamber background, and chamber base pressure. As a result, it varies highly between UHV chambers and even varies between experiments on the same UHV chamber.

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## Chapter 3:

### Formation and Dissociation of O and OH on Ag(100)

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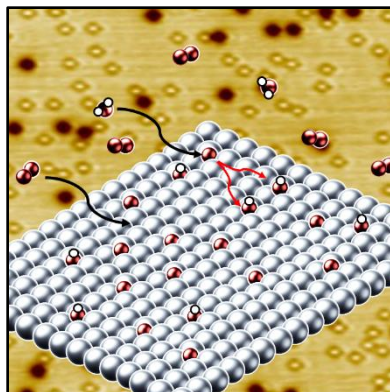
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### 3.1 Abstract

The interaction of oxygen with silver is a key descriptor of catalytic reactivity as silver nanoparticles are ubiquitous in large scale partial oxidation reactions like ethylene epoxidation. Despite Ag(100) being proposed as a selective facet, it is less studied than (111) and (110) surfaces. Using scanning tunneling microscopy and synchrotron X-ray photoelectron spectroscopy, we report that, in addition to the well-known O adatoms formed from O<sub>2</sub> dissociation on Ag(100), hydroxyl groups (OH), at a binding energy of ~531 eV, are also present. The O:OH ratio depends on environmental conditions such as exposure to water and heating. These assignments are consistent with our density functional theory (DFT) calculations, which indicate that the formation of two OH groups from an O atom and H<sub>2</sub>O molecule is exothermic. These results indicate that in addition to O, OH is present even under ultra-high vacuum conditions and therefore should be considered in proposed catalytic pathways.



### 3.2 Introduction

Oxygen on silver is an important catalytic system due to its use in large-scale industrial processes, particularly the partial oxidation of methanol to formaldehyde<sup>1,2</sup> and the epoxidation of ethylene to ethylene oxide.<sup>3,4</sup> As a result, extensive research on this system has been performed in order to understand and improve these reactions, especially ethylene epoxidation.<sup>5,6</sup> Despite decades of investigation into this area, key questions remain, namely the state of the surface, the nature of the selective active oxygen species, and the exact mechanism of selective epoxidation.<sup>6-9</sup> The interaction of water with oxygen on silver surfaces is relevant in this area due to both the promotional and deleterious effects water can have on heterogeneously catalyzed reactions such as oxidations.<sup>10</sup> Forming from the reaction of water with surface oxygen, OH specifically is relevant to oxidations on silver as well.<sup>11-15</sup> Experimentally, studies of water and the interaction of OH with the O-Ag surface have focused on Ag(110).<sup>13,16-22</sup> On Ag(100), theoretical studies found that the most stable adsorption site for OH is the four-fold hollow site, and that OH formation from the interaction of water and pre-adsorbed oxygen is exothermic.<sup>23,24</sup> The challenge of clearly distinguishing and identifying surface OH in the presence of other

adsorbates on O-Ag surfaces has potentially limited the quantitative experimental work in this area.<sup>10,18,23</sup>

Recently, more attention has been called to O-Ag(100)<sup>25-34</sup> due to its inherent selectivity towards ethylene oxide potentially exceeding that of other facets.<sup>35-38</sup> Additionally, the higher sticking probability of oxygen on Ag(100) enables more opportunities to study this system cleanly in UHV without the need for high-pressure cells.<sup>39,40</sup> Using X-ray photoelectron spectroscopy (XPS), previous work demonstrated that the introduction of oxygen at room temperature forms two distinct species on Ag(100) at 530 and 531 eV.<sup>25</sup> In studies on other facets, the 530 eV peak in O 1s spectra on O-Ag surfaces at low coverages is generally assigned as atomic oxygen,<sup>41-43</sup> while there is considerable debate over the nature of the 531 eV species. Various O 1s peaks at ~531 eV have been attributed to several forms of oxygen such as carbonate,<sup>44</sup> molecular oxygen,<sup>45</sup> hydroxyls/hydroxides,<sup>46,47</sup> and subsurface/bulk oxygen.<sup>25,48-50</sup> In order to evaluate and determine the identity of the higher binding energy peak, we turned to scanning tunneling microscopy (STM) experiments and density functional theory (DFT) calculations.

### 3.3 Results and Discussion

In order to study the species present after Ag(100) is exposed to molecular oxygen, we first performed STM experiments at 78 K. Specifically, we exposed a clean Ag(100) surface to 1,000 Langmuir (L) (1 L =  $1 \times 10^{-6}$  Torr·s) O<sub>2</sub>, which resulted in the formation of two species observed with STM (Figure 1A). These species appear as isolated depressions (18-20 pm depth, red arrow) and isolated protrusions (3-5 pm height, blue arrow). The depressions are consistent

with previous reports of O adatoms formed by the dissociative adsorption of O<sub>2</sub> on Ag(100),<sup>27,28,51</sup> but the identity of the other species appearing as a protrusion was initially unclear. Subsequent XPS measurements (Figure 1B, C) confirmed the presence of two species, one at a binding energy of 530 eV which has previously been assigned to O atoms (red XPS peak)<sup>41–43</sup> and second peak at 531 eV (blue peak) which has been assigned in the literature as subsurface oxygen, hydroxy species, molecular oxygen and carbonate.<sup>25,44–50</sup> As seen in the XPS spectra in Figure 1B, annealing the surface to 400 K reduced the size of the 530 eV peak, but almost completely removed the signal at 531 eV as shown quantitatively in Figure 1C. The appearance of the oxygen feature as a depression in STM, as well as the behavior of the lower binding energy O 1s peak at 530 eV, are consistent with each component representing the same atomic O atoms identified across two different techniques.

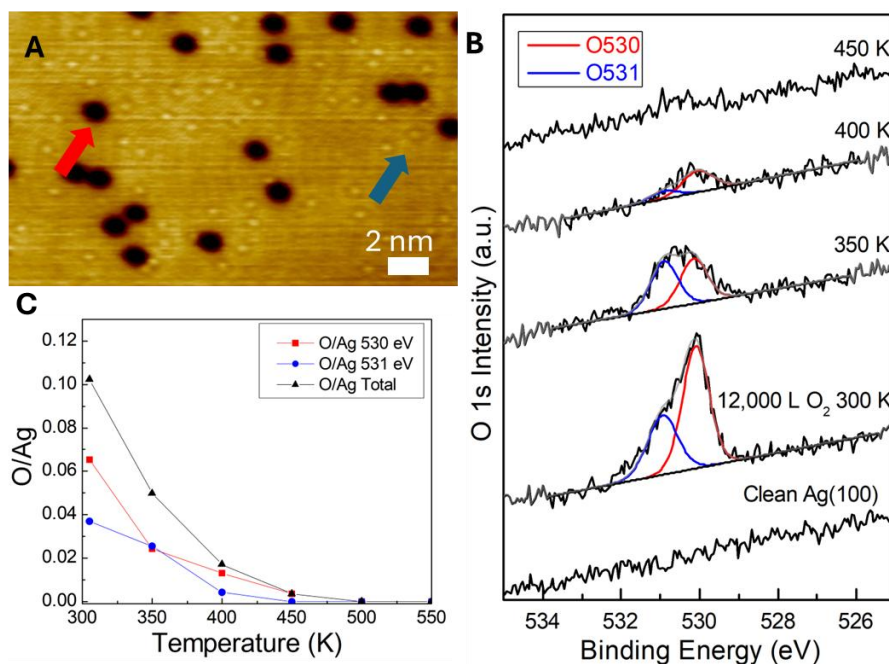


**Figure 3.1.** Products resulting from O<sub>2</sub> dissociation on Ag(100). (A) 78 K STM image of ~1% ML depressions (red arrow) and ~1.5% ML protrusions (blue arrow) resulting from a 1000 L dose of O<sub>2</sub> on Ag(100) at room temperature. Imaging conditions: 10 mV, 1 nA. (B) O 1s spectra of clean Ag(100), 12,000 L O<sub>2</sub> 300 K (7% O530 and 4% O531) on Ag(100), and subsequent anneal. (C) Plot of the coverage of each O 1s component from the fits in A. The difference in O:OH ratio between experiments is due to fluctuation because of environmental differences between chambers.

To determine the identity of the 531 eV (protrusion) species, STM, XPS and DFT were first used to narrow down the number of potential candidates. DFT calculations in which O atoms were placed in octahedral and tetrahedral sites under the Ag surface revealed that any form of subsurface oxygen would be ~2 eV less stable than on the surface (Figure S1), which agrees with other DFT studies on Ag(100).<sup>52–54</sup> Additionally, several attempts were made to stabilize O in the subsurface below the four-fold hollow site, but all resulted in the O spontaneously relaxing

to the surface. In further support of the absence of subsurface oxygen, XPS depth profiling with different photon energies indicates that the attenuation of the two observed species (530 and 531 eV) is consistent with both species being adsorbed on the surface (Figure S2).

Molecular O<sub>2</sub> was ruled out using control experiments in which O<sub>2</sub> was deposited on the sample at 78 K in the STM stage. These experiments indicated that molecular oxygen is not visible in STM images because of its high mobility and weak binding.<sup>55</sup> Adsorbed oxygen molecules are likely present, but diffuse too fast to be imaged.<sup>29</sup> Sulfur, a common impurity in silver samples, was also ruled out by using XPS to check the sample for sulfur, and by using STM to demonstrate that the protrusions do not have the same known bias dependence as sulfur atoms (Figure S3).<sup>56</sup> Similarly, carbonate was ruled out using C 1s clean checks that showed no carbon signal present (Figure S3).

The XPS binding energy of OH on Ag has been reported in the range of 530 to 533 eV.<sup>17,18,46,47,57–59</sup> Our DFT calculations predict a low barrier (0.17 eV) for an oxygen adatom reacting with water to form adsorbed OH groups ( $2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{OH}$ ), as well as a favorable reaction energy (0.56 eV) (Figure 2A). Combined, these data suggest that OH may be the identity of the species observed as isolated protrusions in the STM images and the 531 eV peak in XPS. In this scenario, after O<sub>2</sub> is dosed at 300 K, background water reacts with surface oxygen, leading to the formation of OH groups and a reduction of the number of O adatoms.

STM experiments also demonstrated that the appearance of the two species is highly dependent on the imaging conditions, and under some conditions only one of the species is visible. Specifically, scanning at a bias of 3.00 V leads to only visible protrusions (Figure 2C), while scanning between 300 mV and 1.00 V leads to only visible depressions (Figure 2D). The

depressions appear in different locations than the protrusions, which rules out an inversion effect. The tunneling current did not significantly affect the appearance of either species. However, imaging of both species concurrently and discretely is only possible at conditions of  $\sim 10$  mV and  $\geq 1$  nA (Figure 1A). This selective imaging at the specified conditions allows for easier surface coverage quantification of the two species. Negative sample biases do not exhibit the same effects (Figure S4).

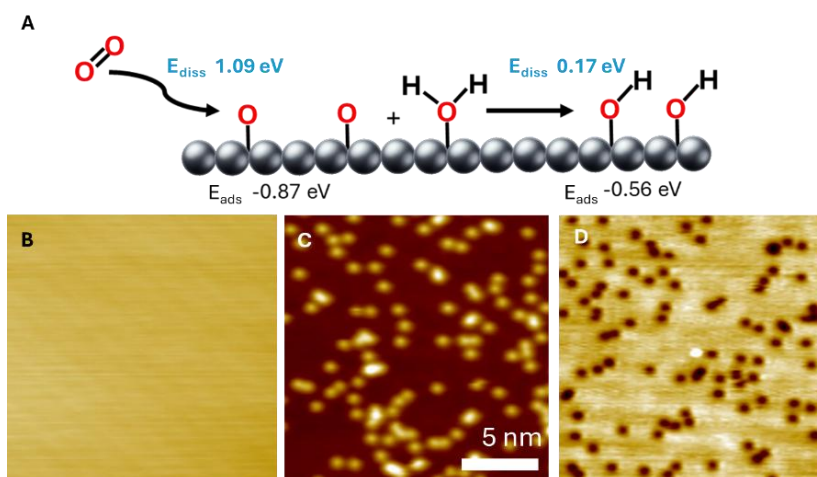


**Figure 3.2.** 78 K STM images of the Ag(100) surface after exposure to  $O_2$  under different imaging conditions. (A) Depiction of oxygen dissociation and reaction with water on the Ag(100) surface and associated reaction energies and activation barriers. Dissociation barriers are shown in blue ( $E_{diss}$ ) and adsorption energies are shown beneath in black ( $E_{ads}$ ). All energy values are relative to gas phase  $O_2$ . (B) 78 K STM image of the bare Ag(100) surface before exposure to  $O_2$ . Imaging conditions: 300 mV, 300 pA. (C)-(D) Images of O adatoms (depressions) and OH groups (protrusions) on Ag(100) imaged at (C) 3.00 V, 300 pA, (D) 300 mV, 300 pA. (C) and (D) are of the same area. At 3.00 V, only protrusions are visible, and at 300 mV only depressions are visible. Surface coverages were 1.0 % O and 1.5 % OH in (C) and (D). All images are 50 by 50 nm, scale bar shown in C.

The bias-dependent appearance of these individual species coupled with DFT-based STM image simulation also supports their identities. Both STM (Figure S4) and simulated STM (Figure S5) images show that OH will always image as a protrusion, but an O adatom will switch from a depression appearance to a protrusion appearance at higher voltage biases ( $>4$  V). These bias-dependent properties further support the assignment of the protrusion (531 eV) species as OH.

In order to examine the adsorption site of the O and proposed OH species we performed high-resolution STM imaging (Figure 3). Images of the O adatom show it binding in the four-fold hollow site of Ag(100) (Figure 3A, B). This adsorption site has been widely shown to be the preferred site for O adatoms on Ag(100),<sup>5,52,53</sup> but has not been imaged with atomic resolution before.<sup>27,28,51</sup> This assignment is consistent with our DFT calculations which indicate that oxygen atoms bind in four-fold hollow sites on Ag(100) (Figure 3E). Figure 3C shows protrusions and depressions imaged in the same frame, and the insets show simulated STM for the appearance of OH (top right) and O (lower), which agrees with our assignments.

With the knowledge that the O adatom depressions are all in four-fold hollow sites, we can overlay a grid of the underlying (100) lattice on a representative STM image and subsequently determine the binding site of the species imaged as protrusions (Figure 3F). As shown in Figure 3F, the protrusions also occupy four-fold hollow sites, which agrees with the DFT-predicted binding site for OH (Figure 3D).

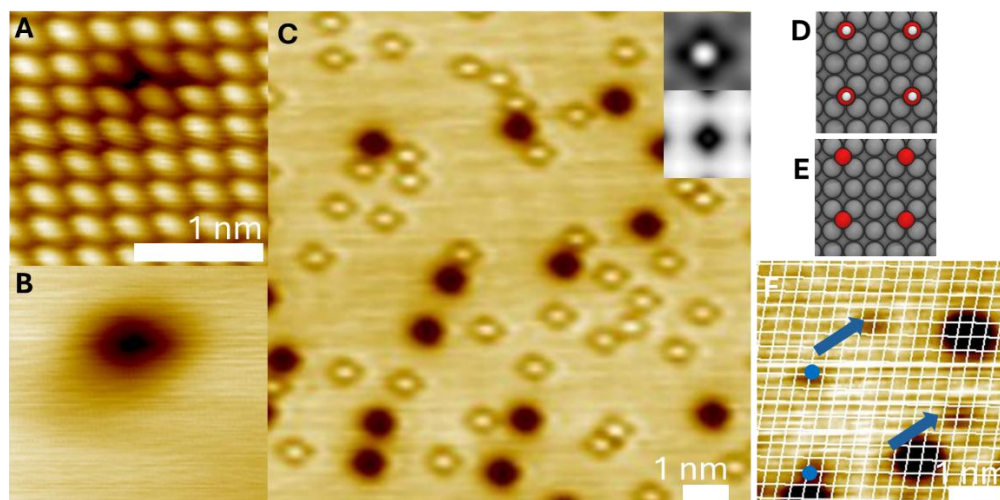


**Figure 3.3.** Binding site characterization of O adatoms and OH groups on O-Ag(100). (A) Atomic resolution 78 K STM image of an oxygen adatom on Ag(100) imaged at 10 mV 1 nA. (B) The same area under typical resolution imaged at 100 mV, 1 nA. Both STM images are the same size and a scale bar is shown in (A). (C) STM image of O and OH on Ag(100) imaged at 100 mV, 1 nA, and a scale bar is shown. Insets are: (top) Simulated STM image of an OH group on Ag(100), (bottom) simulated STM of an O adatom on Ag(100). (D) and (E) are the calculated preferred binding sites for (D) OH and (E) O atoms. (F) STM image of O and OH with the Ag(100) four-fold hollow lattice overlaid. The centers of several OH groups are marked with blue circles or arrows. Imaging conditions: 10 mV, 1 nA, and a scale bar is shown. Images were acquired at 78 K.

Localized STM voltage pulsing further supported the identification of the protrusions as surface hydroxyls. This experiment was performed by moving the tip over the target species and then applying a higher voltage bias.<sup>60</sup> Figure 4 shows representative results of the voltage pulse experiments for protrusions (OH) as well as molecularly adsorbed O<sub>2</sub> for comparison. Figure 4B and C show STM images before and after a pulse was performed. All protrusions (OH) from 4B

were converted to depressions (O). Figure 4A depicts this process in which a 4 V pulse acts to abstract the H atom from the OH group, forming an O adatom. This experiment was attempted using negative sample biases as well, but no dissociation was observed. Additionally, performing pulses on O adatoms produces no reaction. This result added further evidence for the assignment of the protrusions (and the 531 eV feature in XPS by association) as adsorbed surface hydroxyls.

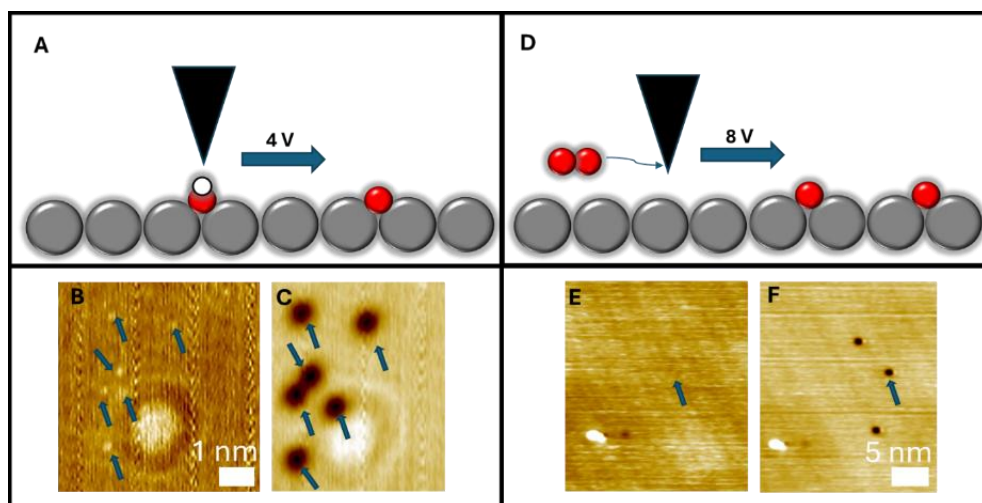


**Figure 3.4.** STM Voltage Pulse Experiments. (A) Depiction of STM tip dissociating OH into O and H using a localized voltage pulse. (B) 78 K STM image of the Ag(100) surface before voltage pulses. OH groups appear as faint protrusions and are marked by blue arrows. (C) 78 K STM image of the same area after 4 V pulses. Each OH is now a depression. Oxygen was dosed at 300 K and the pulse locations are indicated by the blue arrows. (D) Depiction of the STM tip dissociating O<sub>2</sub> into two O adatoms via a voltage pulse. (E) LT-STM image of the Ag(100) surface with oxygen dosed at 78 K. Oxygen is present as molecular oxygen and diffuses too fast at 78 K to be imaged. The pulse location is indicated by the blue arrow. (F) LT-STM image of the same area following one 8 V pulse. Oxygen adatoms have formed as a result of the pulse. No reaction occurred from pulsing on the O adatoms. Imaging conditions: 1.0 nA, 100 mV.

Conversely, figure 4E and F show the effects of tip pulsing on an O<sub>2</sub> covered surface and formation of O adatoms. Dosed at 78 K, molecular oxygen adsorbs intact on Ag(100).<sup>28,61</sup> As noted earlier, when scanning at 78 K, oxygen molecules diffuse too fast to be imaged.<sup>29</sup> However, the oxygen adatoms formed from voltage pulses have a higher diffusion barrier and can be imaged at this temperature (Figure 4F).<sup>62</sup> Negative pulses were performed up to 8 V, but no dissociation of O<sub>2</sub> molecules was induced. This comparison further supports our assignment of the OH species and rules out molecular oxygen as the identity of the protrusions.

In order to understand the formation of the OH species, we performed STM experiments on O-Ag(100) before and after the addition of water (Figure 5). Specifically, 1000 L O<sub>2</sub> was dosed onto a clean Ag(100) crystal at room temperature, and the sample was cooled to 78 K for imaging. The coverage of both O and OH were determined using our species-specific imaging conditions (Figure 5A and B). Using our XPS data for guidance, in which the 531 eV peak assigned to OH disappears almost entirely upon annealing to 400 K, the crystal was annealed to ~400 K (5C and D). After annealing, the surface was occupied solely by O adatoms. Then, 3 L H<sub>2</sub>O was dosed at 78 K. Upon the introduction of water, we observed the formation of more protrusions (OH) and a decrease in depressions (O adatoms) (5E and F). The surface coverages for each step of the experiment are summarized in Figure 5G. As a control, water was dosed onto a bare Ag(100) surface at 78 K and no features (protrusions nor depressions) were observed (Figure S9). The formation of protrusions from the introduction of water and subsequent decrease in O adatoms indicates that when water is introduced, O adatoms react with a water molecule to produce two OH groups. Together these data provide strong evidence that, in addition to the well-known oxygen adatoms on Ag(100) that result from room temperature dissociative adsorption of O<sub>2</sub>, OH species are present and appear in XPS with a binding energy

of 531 eV. These OH groups form from the reaction of water with surface oxygen atoms and can be removed from the surface by annealing to 400 K.

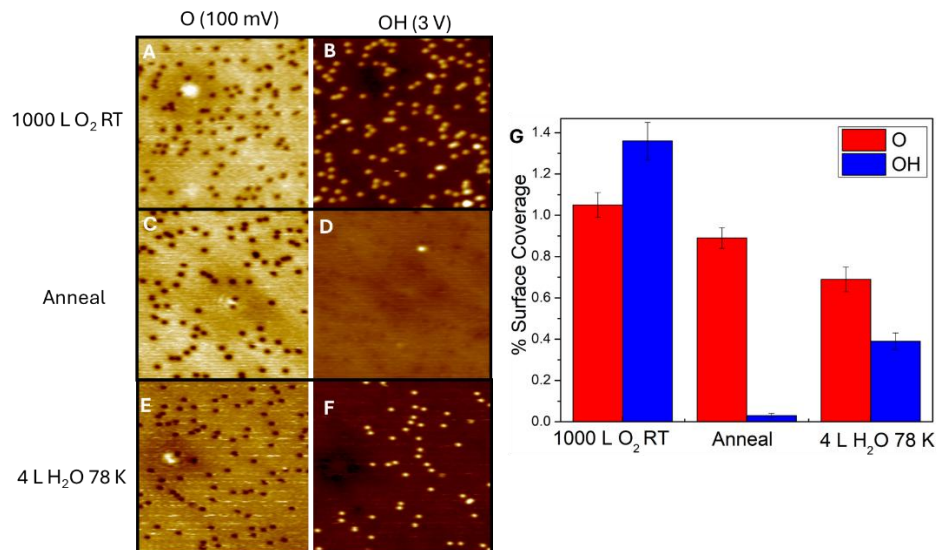


**Figure 3.5.** Reaction of O atoms with H<sub>2</sub>O. (A) 78 K STM image of 1000 L O<sub>2</sub> dosed at RT on Ag(100) imaged at 100 mV. O adatoms are visible as depressions. (B) Same area imaged at 3.0 V where OH groups are visible as protrusions. (C) STM image of O-Ag(100) surface after a 400 K anneal scanned at 100 mV. (D) Same area scanned at 3.0 V showing a significant reduction in the number of OH species. (E) STM image of the post-anneal surface after 3 L H<sub>2</sub>O was dosed at 78 K imaged at 100 mV. (F) Same area imaged at 3.0 V showing an increase in the number of OH species. (G) Quantification of the surface coverages of O and OH for each stage of the experiment. Tunneling current remained constant for all STM images at 300 pA. All images are 50 by 50 nm.

### 3.4 Conclusions

By utilizing a combination of STM, DFT and XPS, we have identified adsorbed OH on the O-Ag(100) surface, which to the best of our knowledge has not been directly imaged. We

showed that these surface hydroxyl species are present alongside the well-characterized O adatoms formed after O<sub>2</sub> exposure on Ag(100), and they can be distinguished via STM and XPS. Atomic-scale STM imaging confirmed that four-fold hollow sites are the preferred adsorption sites of both O adatoms and OH groups. The OH groups, which appear as protrusions in STM across all conditions and produce a 531 eV peak in XPS, are produced from the reaction of preadsorbed oxygen adatoms and water from either the chamber background or a deliberate dose. Voltage pulse experiments helped to confirm the identity of OH by demonstrating their one-way conversion into oxygen adatoms. Importantly, DFT calculations showed that subsurface oxygen is energetically unfavorable under our experimental conditions, and its absence in both STM and XPS further supports this conclusion.

When identifying 531 eV peaks of O 1s XPS spectra on O-Ag, OH should be considered under similar conditions to this study. Additionally, exploration of higher voltages might be important for oxygen studies using STM as OH can only be imaged consistently and discretely at voltages >2.5 V. These findings not only provide the first atomic-scale characterization of OH on Ag(100) but also establish the conditions necessary for studying the interplay between O, OH, and H<sub>2</sub>O on silver surfaces. Given the prominent role of silver in industrial oxidation catalysis, and the importance of water in ethylene epoxidation,<sup>14,15</sup> the reactivity and ubiquitous presence of surface OH on Ag should be considered in proposed reaction pathways and models of catalytic selectivity on O-Ag systems.

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## Chapter 3.6

### Supporting Information

#### 3.6.1 Experimental Methods

##### Scanning Tunneling Microscopy (STM)

78 K STM experiments were conducted in an ultra-high vacuum (UHV) chamber with a base pressure of  $1 \times 10^{-11}$  mbar using a low temperature (LT)-STM (Omicron Nanotechnology). Two Ag(100) single crystals (Princeton Scientific 99.999% purity <1 degree polish) were used for experiments. Sample cleaning was performed in a connected preparation chamber with a base pressure of  $< 5 \times 10^{-10}$  mbar. Repeated cycles of Ar<sup>+</sup> (Airgas 99.99%) ion sputtering (1 keV 10-20  $\mu$ A) and annealing to 825 K were used to clean the Ag(100) crystals. STM images were obtained at 78 K after cryogenically cooling the STM stage. Oxygen (99.9% Middlesex gases) and water (Fisher Scientific HPLC Grade 99%) were dosed through high precision leak valves. Coverages were calculated as an average from ~20 images for each coverage through manual counting of features using an STM image processor (SPIP). Coverages are based on the number of specific features per image divided by the total number of Ag surface atoms in each image. Error bars on coverage were one standard deviation.

##### X-Ray Photoelectron Spectroscopy (XPS)

XPS experiments were performed at beamline 23-ID-2 (IOS) of the National Synchrotron Light Source II (NSLS- II) at Brookhaven National Laboratory.<sup>1</sup> The base pressure for the experimental chamber was  $< 4^{-9}$  torr. All experiments were performed on a Ag(100) crystal

cleaned with Ar<sup>+</sup> ion sputtering and annealing to 825 K until XPS spectra showed no impurities. The heating rate for cleaning and annealing was 40 K/min. High purity O<sub>2</sub> (Matheson, 99.994%) was exposed to the sample via precision leak valve while the sample was heated with a pyrolytic boron nitride heater. Temperature was measured with a K-type thermocouple between the Ag(100) crystal and the heater/sample mount. Reference Ag 3d spectra were taken after acquiring each oxygen spectrum. Oxygen species coverages were calculated by dividing the corrected O 1s peak areas by the corresponding corrected Ag 3d peak areas. Peaks areas were corrected by dividing the raw areas by their Relative Sensitivity (RSF) value<sup>2</sup> multiplied by the IMFP of the ejected electron found from a universal curve<sup>3</sup> (Equation S1). Ag 3d peak areas were also corrected by a first layer correction based on the IMFP to account for the signal only generated for the top level of atoms (Equation S2).

$$\frac{\text{Corrected O 1s Peak Area}}{\text{Peak Area}} = \frac{\text{Raw Peak Area}}{\text{R.S.F.} \times \text{I.M.F.P.}}$$

**Equation S1.** O 1s XPS Correction.

$$\frac{\text{Corrected Ag 3d Peak Area}}{\text{Peak Area}} = \frac{\text{Raw Ag3d}_{5/2} \text{ Peak Area} \times \text{First Layer Correction}}{\text{R.S.F.} \times \text{I.M.F.P.} \times 5/2 \text{ Correction}}$$

**Equation S2.** Ag 3d XPS Correction.

To investigate different elements, different photon energies were used. Predominantly, 760 and 500 eV were used to generate photoelectrons with kinetic energies of ~200-300 eV for the O 1s (at 760 eV) and S 2p and C 1s (at 500 eV) core levels, respectively, to maintain similar probing depths. The latter two elements were only monitored for impurities. Photon energies of 910 and 1090 eV were used for Ag depth profiling. Binding energy calibration was performed on

all spectra with respect to the Fermi edge and metallic Ag 3d<sub>5/2</sub> binding energy measured at each photon energy.<sup>4</sup> XPS data was analyzed with CasaXPS. Each species was assigned and fit according to experimental results and literature values (Table S1). O 1s spectra were fit with a linear background due to their small size, while Ag spectra were fit with a Shirley background.<sup>5</sup>

| Component                   | Binding Energy (eV) | Full Width at Half Maximum (FWHM) | Line Shape (Gaussian/Lorentzian) |
|-----------------------------|---------------------|-----------------------------------|----------------------------------|
| Atomic O <sup>2,5-7</sup>   | 530.0 - 530.1       | 0.8 – 1.0                         | 30:70                            |
| OH <sup>8-10</sup>          | 530.9 - 531         | 0.8 – 0.9                         | 30:70                            |
| Metallic Ag <sup>4,11</sup> | 368.2               | 0.4                               | 99:1                             |

**Table 3.S1.** Summary of fitting parameters for XPS spectra. Symmetric peak shapes were used for all fit peaks.

DFT calculations were performed with the VASP code<sup>12,13</sup> and the PBE exchange-correlation functional. A 400 eV energy cutoff was used for the plane-wave basis set. The projector-augmented wave method<sup>14</sup> was used for core electrons, and the Tkatchenko-Scheffler method was used for dispersion corrections.<sup>15</sup> A  $7 \times 7 \times 1$  k-point grid was used for the  $3 \times 3 \times 1$  supercell. Four layers were used, with the bottom two fixed at their bulk positions. A geometric convergence criterion of 0.03 eV/Å was used, along with an electronic convergence criterion of  $10^{-5}$  eV. Transition state calculations were performed using the dimer method,<sup>16,17</sup> and vibrational calculations confirmed that the final structure contained one significant imaginary frequency corresponding to the reaction coordinate.

**Note on differing O:OH Ratios:** We found that OH formation from the background is highly dependent on oxygen coverage, temperature, chamber background, and chamber base pressure. As a result, it varies highly between UHV chambers and even varies between experiments on the same UHV chamber.

### 3.6.2 Supplementary Figures

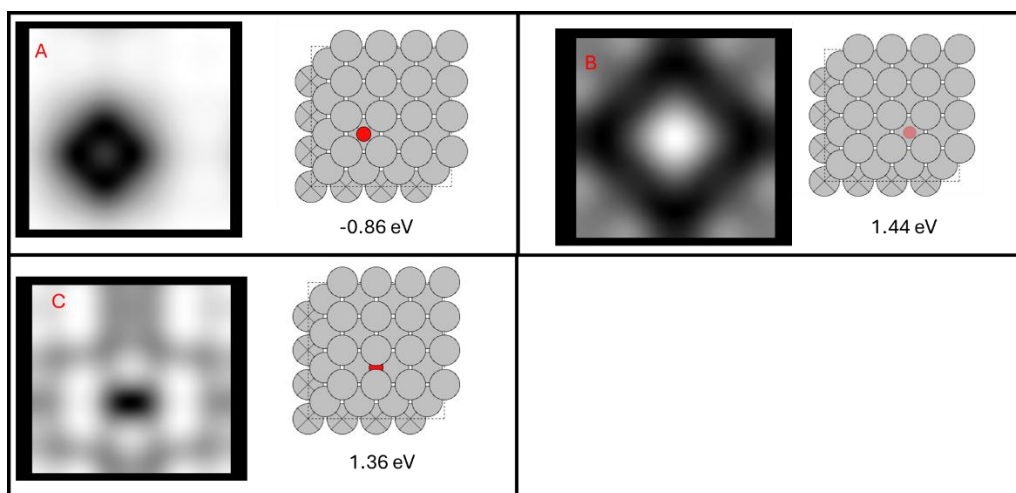


**Figure 3.S1.** Simulated STM images of surface and subsurface atomic oxygen species on Ag(100), along with DFT-calculated adsorption energies relative to gas-phase O<sub>2</sub>. A) Simulated STM image of an oxygen adatom sitting in a 4-fold hollow site and associated depiction of said site. B) Simulated STM image of an oxygen atom in a subsurface octahedral site and associated depiction of said binding site. C) Simulated STM image of an oxygen atom in a subsurface tetrahedral site and associated depiction of said site.

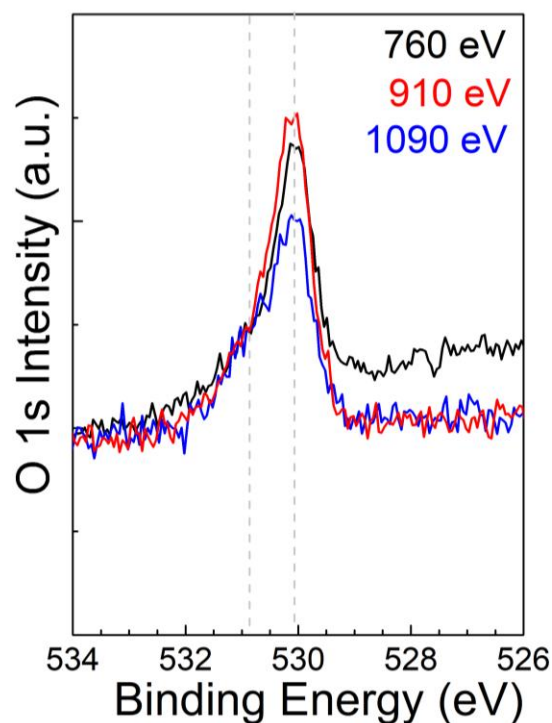


**Figure 3.S2.** XPS depth profiling of O-Ag(100) showing O 1s spectra of Ag(100) after exposure to 12,000 L O<sub>2</sub> at 300 K. Spectra were taken at 3 different photon energies: 760 eV (most surface sensitive, IMFP of ejected electron 0.7 nm, black trace), 910 eV (IMFP of 0.8 nm, red trace) and 1090 eV (most penetrative, IMFP of 0.9, blue trace). The 530 eV peak remains prominent at all energies, and the shoulder at 531 eV is present at each energy. It is observed that the 530 eV peak for atomic oxygen remains unchanged across the three photon energies, which suggests there is no subsurface component to that peak. For the 531 eV peak, there is a higher signal in the 1090 eV and 910 eV traces. This trend suggests that there may be a small amount of subsurface oxygen present in near surface layer of Ag(100) exposed to O<sub>2</sub>, but not an appreciable amount. We therefore treat the 531 eV component as solely an OH peak.

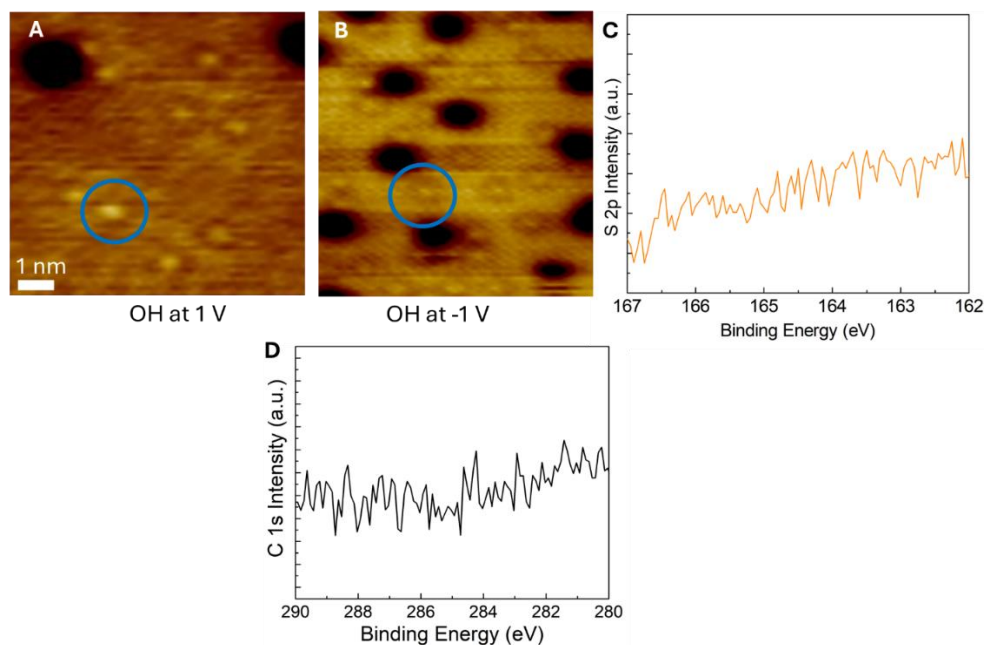


**Figure 3.S3.** XPS and STM evidence against the presence of sulfur (A-C) and carbonate (D). A) 78 K STM image of OH groups imaged with a positive voltage bias. They are present as donut-shaped protrusions. Imaging conditions are 10 mV and 3 nA. B) STM image of OH groups imaged with a negative voltage bias. The OH groups are present as donut shaped protrusions. Imaging conditions are -25 mV and 5 nA. The OH groups do not exhibit a bias-dependence typically seen for adsorbed S atoms.<sup>18</sup> C) XPS scan of the S 2p region taken at 500 eV before experiments on Ag(100) to ensure there were no S impurities present in the sample. D) XPS scan of the C 1s region taken during the O<sub>2</sub> uptake. The lack of C 1s signal suggests there are no C impurities relevant to these experiments, and thus carbonate's presence can be ruled out.

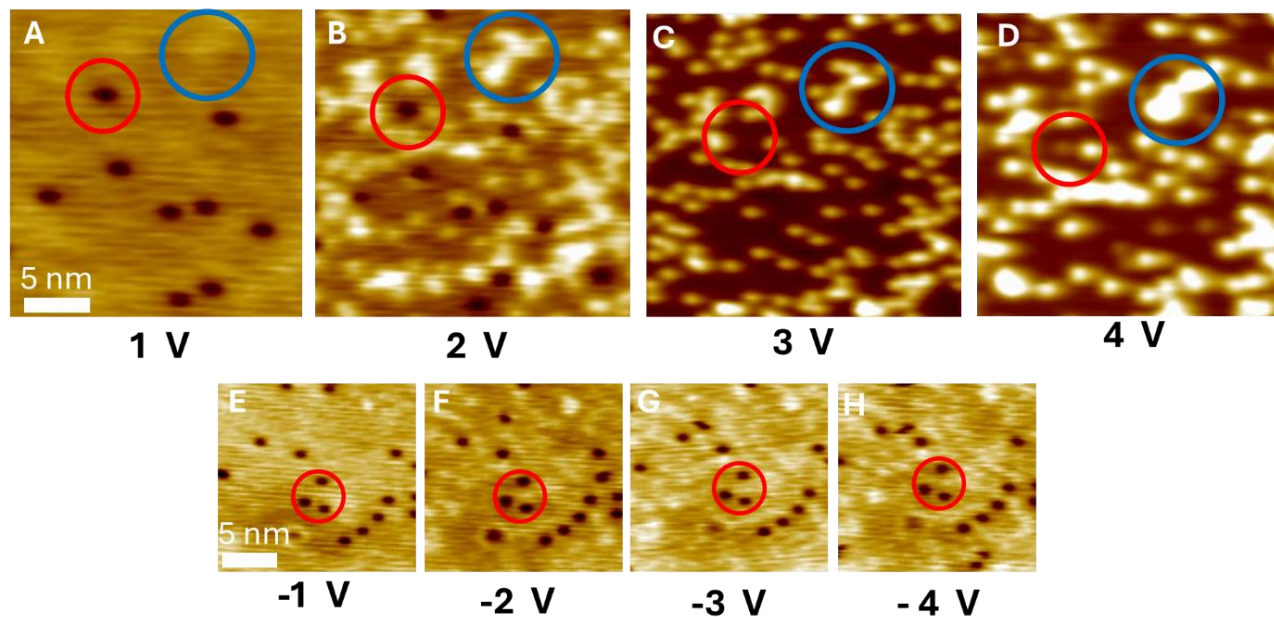


**Figure 3.S4.** Bias-dependent STM appearance of O-Species. A) 78 K STM image of the O-Ag(100) surface taken at 1.00 V. Only O adatom depressions are visible (red circle). B) The same area was imaged at 2.00 V. O adatoms are still visible (red circle) as well as faint OH protrusions (blue circle). C) The same area was imaged at 3.00 V. O adatoms are no longer visible and OH groups are clearer and more discrete. D) The same area was imaged under 4.00 V. O adatoms are visible as dim protrusions and OH groups are visible as bright protrusions (blue circle). All images were taken at 300 pA and a scale bar shown in A. E-H) Equivalent of A-D at negative voltage biases. There is not much voltage dependent change in appearance as with the positive bias regime. OH groups are not visible, and O atoms retain their appearance as depressions. All images were taken at 300 pA and are a scale bar is shown in E.

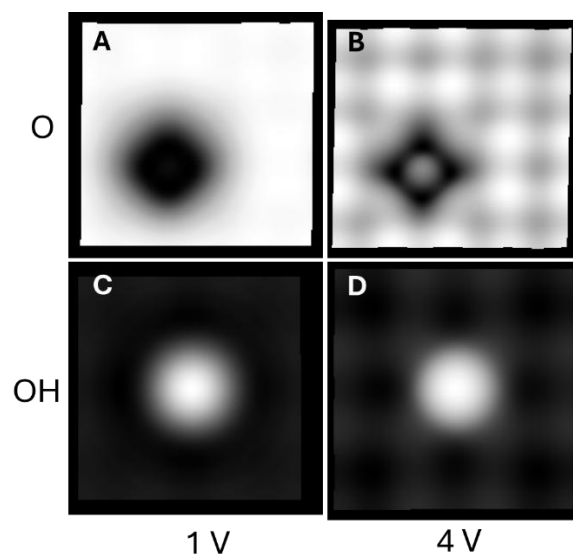


**Figure 3.S5.** Simulated STM image of an O adatom visible as both a protrusion and a depression. A) Simulated STM image under simulated 1 V conditions of an O adatom on Ag(100) showing O as a protrusion. B) Simulated STM image of an O adatom on Ag(100) under simulated 4 V conditions showing O as a depression. C-D) Simulated STM images of OH under the same conditions. OH remains a bright protrusion.

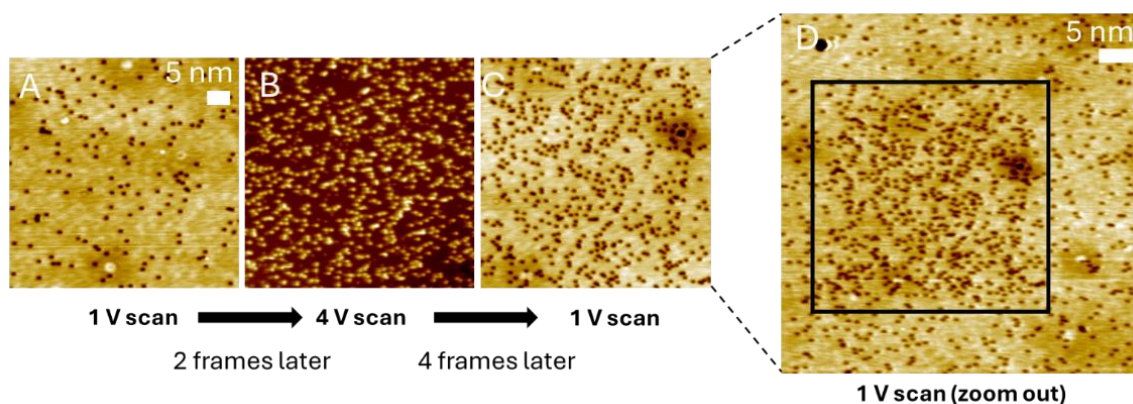


**Figure 3.S6.** Formation of O Adatoms by Scanning at 4 V. A) STM image of 1000 L O<sub>2</sub> dosed at 300 K on Ag(100). Scan was taken at 1.00 V. Oxygen adatom depressions are visible. B) The same area was scanned at 4.00 V. OH groups are visible as bright protrusions and oxygen adatoms are visible as darker protrusions. OH groups were converted to O adatoms by the STM tip while it is held at a 4.00 V bias. C) The same area was scanned at 1.00 V again after 4 frames at 4.00 V. Only oxygen adatom depressions are visible but they have increased in amount/coverage. D) Zoom out of the area shown in A-C. The part of the surface scanned at 4.00 V has a higher oxygen surface coverage (black square) than the surrounding areas due to the voltage-induced conversion of the OH species to O. All images were taken at 300 pA at a temperature of 78 K. Scale bars are shown in A and D.

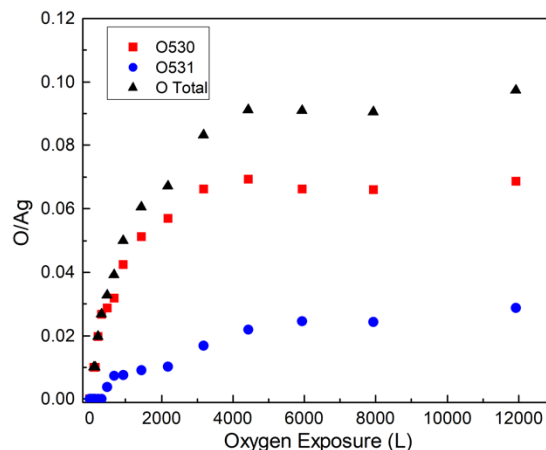


**Figure 3.S7.** XPS-derived 300 K oxygen uptake on Ag(100). Oxygen coverages for the uptake of 12,000 L O<sub>2</sub> dosed at room temperature. Two species are present at 530 eV (red) and 531 eV (blue). The 530 eV peak grows in first, appearing after 70 L O<sub>2</sub> exposure, and the 531 eV peak appears after ~450 L. O 1s spectra were measured at a photon energy of 760 eV.

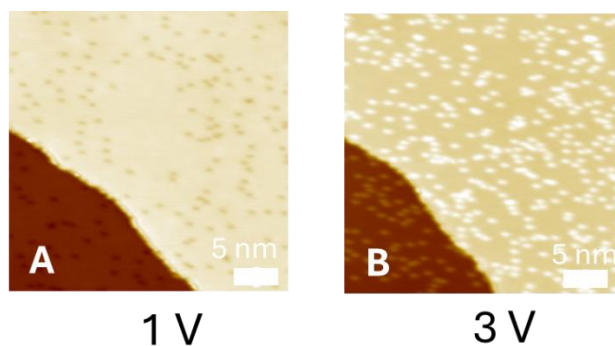


**Figure 3.S8.** STM Images of O and OH at step edges. A) 1 V image of an Ag(100) step edge after being exposed to 1000 L O<sub>2</sub> dosed at room temperature. Oxygen adatoms are visible as depressions on the upper and lower terraces and there is no formation of any brims of oxygen either directly above or below the step edge. B) 3 V image of an Ag(100) step edge on the same area as A. Only OH protrusions are visible. There is no evidence of the formation of brims of OH at the step edge. Both images are 50 x 50 nm (scale bars are shown in both images) and tunneling current was 300 pA. STM performed at 78 K.

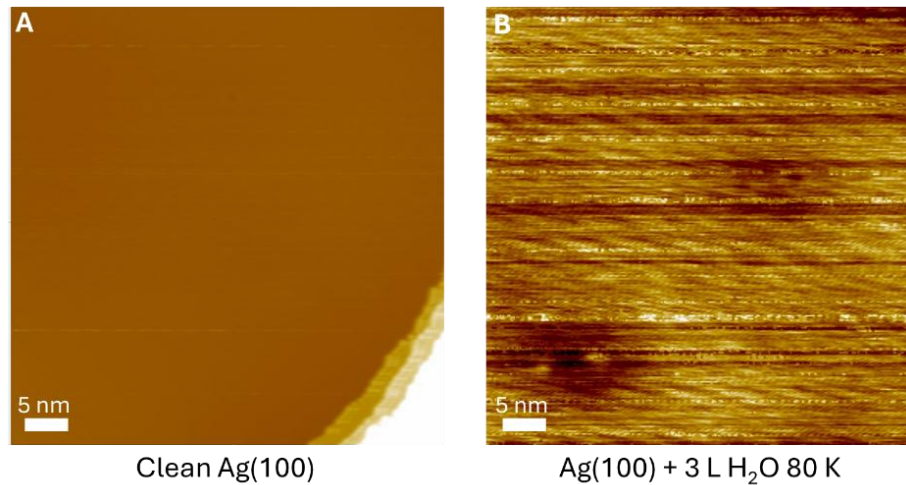


**Figure 3.S9.** STM of H<sub>2</sub>O exposure to clean Ag(100) as a control experiment. A) STM image of a clean Ag(100) surface. B) STM image of the same surface after exposure to 3 L H<sub>2</sub>O at 78 K. The enhanced level of noise in this STM image is due to physisorbed water molecules interfering with the STM tip while scanning. No new features are present. Images were taken at 78 K. Imaging conditions were 300 mV and 300 pA. A scale bar is shown in both images.

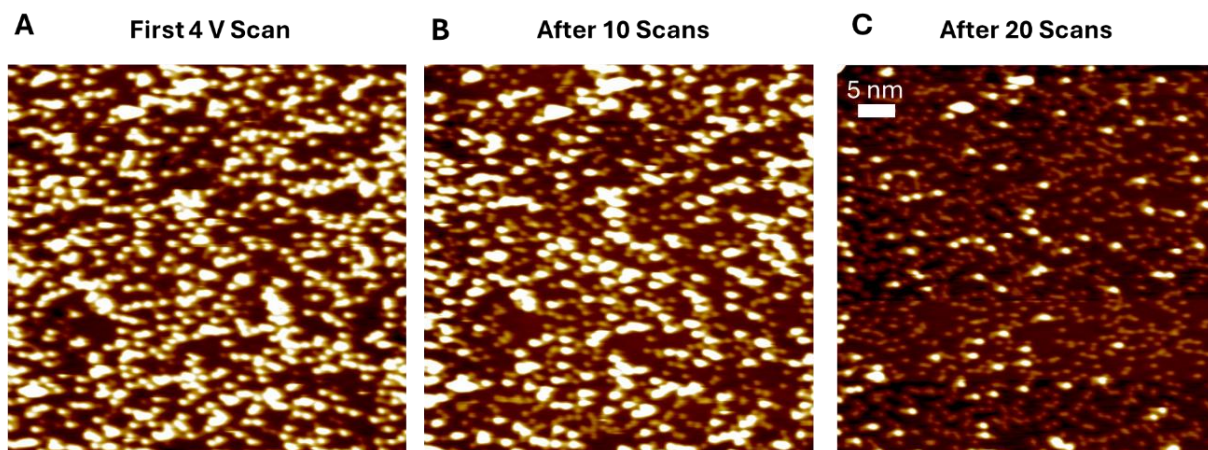


**Figure 3.S10.** STM of conversion of OH to O over time at high voltage bias. A) Initial 4 V scan of Ag(100) after exposure to 1000 L of oxygen at room temperature. OH groups are visible as bright protrusions and oxygen adatoms are visible as darker protrusions. B) The same area after 10 scans at 4.00 V. Many of the OH groups have been converted into O adatoms. C) The same area after 10 additional scans, for a total of 20 scans. The majority of OH groups have now been converted into O adatoms. Tunneling current for all images is 300 pA, the sample temperature was kept at 78 K, and all images are 50 x 50 nm (scale bar is shown in C).

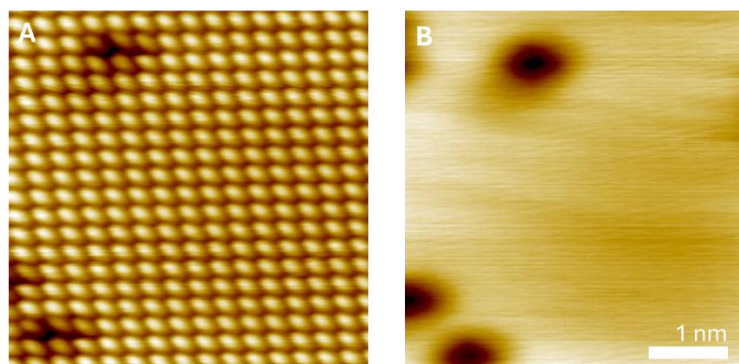


**Figure 3.S11.** Larger scale atomic resolution STM imaging of O adatoms. A) 78 K STM image of oxygen adatoms on Ag(100) under atomic resolution imaged at 10 mV and 1 nA. B) The same area under typical resolution imaged at 100 mV and 1 nA. A scale bar is shown in B.

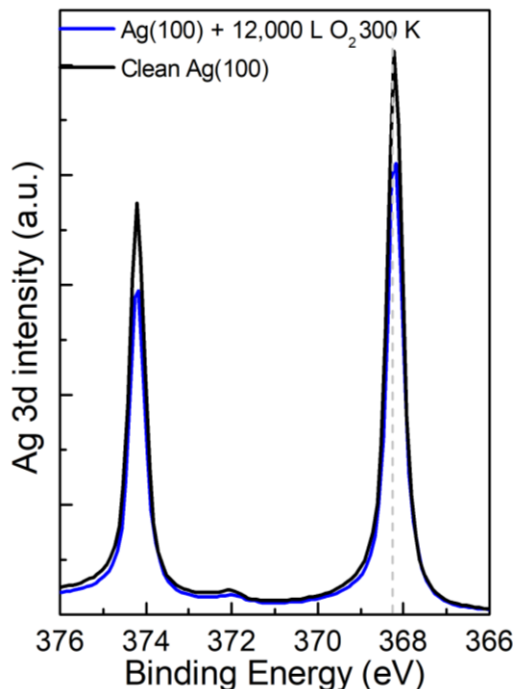


**Figure 3.S12.** Silver XPS. Ag 3d core level spectrum on clean Ag(100) (black trace) overlaid with the Ag 3d core level spectrum after 12,000 L O<sub>2</sub> exposure on Ag(100) (blue trace). The Ag(100) sample and surface remain metallic (Ag 3d<sub>5/2</sub> peak at 368.2 eV) despite the high exposure of oxygen. The overall signal decreases due to higher chamber pressure as a result of repeated oxygen exposures. The spectra were measured at 760 eV photon energy.

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# Chapter 4.

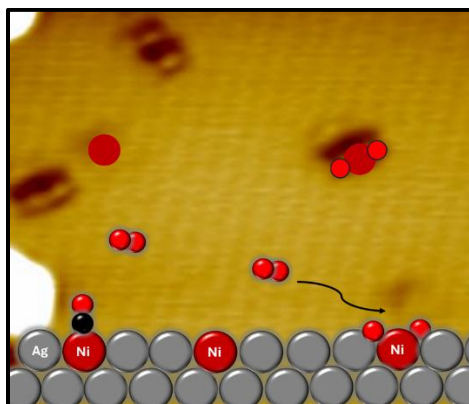
## Low Temperature Oxygen Activation on the NiAg(100) Single-Atom Alloy

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### 4.1 Abstract



Silver-catalyzed ethylene epoxidation remains the only industrially viable route for ethylene oxide (EO) production. However, this process requires chlorine and other promoters to achieve high EO selectivity and generates substantial CO<sub>2</sub> emissions, prompting continued efforts to develop improved catalytic systems. A recent theory-guided approach identified Single-Atom Alloys (SAAs), specifically isolated Ni atoms in a silver matrix, as a promising chlorine-free alternative. NiAg/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalysts achieved ~80% EO selectivity without the need for chlorine or other promoters. To better understand the enhanced reactivity of this NiAg system, particularly the reported reduction in the oxygen activation barrier, we investigated the

interaction of O<sub>2</sub> with a NiAg(100) SAA surface using scanning tunneling microscopy (STM) and density functional theory (DFT). While only molecular O<sub>2</sub> was present on pure Ag(100) at 78 K, a distinct NiO<sub>2</sub> species indicative of O<sub>2</sub> dissociation at Ni atom sites, was identified on NiAg(100) under the same conditions. High-resolution STM imaging and DFT simulations corroborate the formation of this O–Ni–O structure and differentiate it from other possible adsorbates. These findings provide direct experimental evidence for the lowered oxygen activation barrier in the NiAg system and the formation of reactive atomic oxygen at cryogenic temperatures.

## 4.2 Introduction

Ethylene epoxidation is an important industrial reaction (global market size of ~40 billion USD annually), due to the high demand of its product, ethylene oxide (EO), important for a wide range of applications from consumer goods to healthcare sterilization.<sup>1–4</sup> Ag-based catalysts on alumina supports are the sole means of industrial EO production.<sup>5–7</sup> However, Ag/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalysts have an inherent selectivity of only ~50% toward EO with the remaining reacted ethylene producing CO<sub>2</sub> and water.<sup>8–10</sup> Therefore, these catalysts rely on a series of promoters, primarily chlorine, to increase selectivity up to ~90% toward EO.<sup>3,10–14</sup> The use of chlorine can lead to corrosion, safety and environmental concerns, which has motivated research into alternative promoters.<sup>15–18</sup> Given that CO<sub>2</sub> is a byproduct of EO production, and the enormous scale at which this reaction is run, even minor improvements in selectivity could lead to significant reduction in CO<sub>2</sub> emissions and energy costs.<sup>5,15,19</sup> Both of these issues motivate

continued study on understanding and improving ethylene epoxidation on Ag catalysts.<sup>1,2,8,201,8,21–25</sup>

Recently, a joint theoretical, surface science, and catalytic study revealed that the addition of trace amounts of Ni enhance the EO selectivity of Ag/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalysts by 25%, the same increase as Cl provides but without the need for constant co-flow as is the case for Cl.<sup>18</sup> Specifically, DFT calculations were used to screen a range of single-atom dopants in Ag in search of a metal that breaks scaling relationships by achieving a low barrier to oxygen activation while maintaining moderate atomic oxygen binding energy,<sup>18</sup> similar to single-atom approaches to (de)hydrogenation performed previously.<sup>26–30</sup> Ni was found to meet these criteria, and the effect was experimentally demonstrated using surface science that informed the design of Al<sub>2</sub>O<sub>3</sub>-supported NiAg nanoparticles that exhibited ~80% selectivity toward EO under industrially relevant conditions without the presence of Cl.<sup>18</sup>

Due to the low sticking probability of oxygen on Ag(111) ( $10^{-6}$ ),<sup>11,31</sup> surface science studies in ultra-high vacuum (UHV) conditions using molecular oxygen are challenging.<sup>32,33</sup> Consequently, the decreased O<sub>2</sub> activation barrier induced by the presence of isolated Ni atoms has not been directly demonstrated on NiAg(111), and active nickel-oxygen sites have not been characterized. The more open (100) facet has a higher sticking probability of O<sub>2</sub> ( $\sim 10^{-4}$ ), which provides more opportunity to study O-NiAg and O-Ag without the need for high pressure cells or toxic oxygen substitutes.<sup>34,35</sup> Ag(100) has also been suggested to potentially have inherent selectivity toward EO greater than other facets, which makes it a good surface for further study of NiAg as a selective oxidation catalyst.<sup>36–39</sup> Lastly, the study of SAA active sites with Scanning Tunneling Microscopy (STM) is generally easier on more open facets as the dopant atoms tend to alloy as diffuse sites across terraces rather than as dense brims at step-edges.<sup>40</sup>

To experimentally demonstrate how Ni lowers the O<sub>2</sub> activation barrier on Ag in an NiAg SAA, we used a combination of STM and Density Functional Theory (DFT) to study the effects of oxygen on NiAg(100) and Ag(100) at low temperature. In this work, we form and characterize an atomically-resolved O-Ni-O species formed at 78 K on NiAg(100), a temperature at which oxygen only binds molecularly on bare Ag(100).<sup>41,42</sup> This O-Ni-O species provides direct evidence of the decreased oxygen activation barrier on NiAg(100) as well as potentially providing insights into the higher EO selectivity observed on NiAg catalysts. Through these experiments, we further the understanding of NiAg as a selective oxidation catalyst and display its exciting oxygen-related properties.

### 4.3 Results and Discussion

In order to investigate the oxygen activation barrier on the NiAg(100) SAA surface we used 78 K STM and imaged the surface before and after the introduction of O<sub>2</sub>. First, a NiAg(100) single-atom alloy was synthesized by doping ~1% Ni at 300 K onto a clean Ag(100) surface and then characterized by cooling the sample to 78 K for STM imaging (Figure 1 A-C). On the as deposited NiAg (100) surface, three features are observable in STM: CO-covered Ni atoms (orange arrows), ejected silver islands (green arrows), and bare Ni atoms (red arrows). Ni atoms place exchange with surface Ag atoms and small Ag islands are formed from silver atoms ejected from the surface during the alloying of Ni at room temperature.<sup>40</sup> The Ni atoms all occupy surface sites, directly replacing surface Ag atoms. The CO-bound Ni atoms were identified by using voltage pulses experiments that desorb the CO molecules from atop the Ni sites as after the pulses the appearance changes to that of bare Ni atoms in Ag(100) (Figure S1).<sup>43</sup>

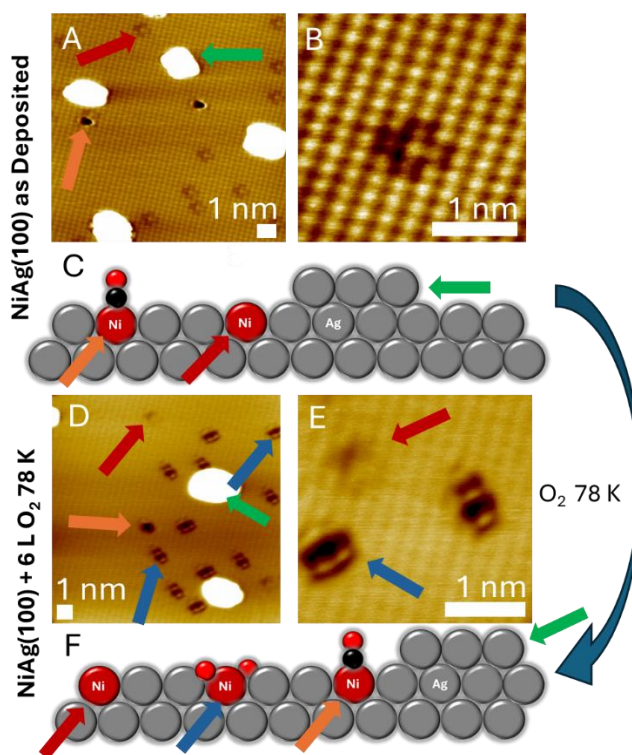


**Figure 4.1.** Overview of low temperature oxygen activation on 1% NiAg(100). A) Atomically resolved STM image of the as prepared NiAg(100). Bare Ni single-atom sites are visible as “cross” features (red arrow), CO-capped Ni sites (orange arrow) appear as depressions and ejected Ag islands are visible as white protrusions (green arrow). B) High resolution STM image of a bare Ni single-atom site in Ag(100). The Ni atom occupies a site in the Ag lattice, replacing an Ag atom. C) Schematic of the NiAg(100) surface features with arrows that correspond to the STM images. D) STM image of NiAg(100) after exposure to 6 Langmuir (L) ( $1 \text{ L} = 1 \times 10^{-6} \text{ Torr}\cdot\text{s}$ )  $\text{O}_2$  at 78 K. Bare Ni sites, CO-capped Ni sites and Ag islands are still visible. O-Ni-O sites are present as well (blue arrow) as rectangular depressions. E) STM image of Bare Ni and O-Ni-O sites under atomic resolution on NiAg(100). Imaging conditions were 10 mV 1 nA, for each image and scale bars are shown. All images were acquired at 78 K. F) Corresponding schematic of STM data in panels D and E.

To study the effects of oxygen dissociation, the sample was exposed to O<sub>2</sub>. While holding the NiAg(100) at 78 K 6 L (1 L = 1 x 10<sup>-6</sup> Torr/s) of O<sub>2</sub> were dosed. After the dose, in addition to the features found on the as-deposited surface, we observed a new species. This species appears as rectangular depressions and is only formed after exposure to O<sub>2</sub>. This nickel-oxygen species has two-fold symmetry, and as would be expected on a square packed (100) surface, two equivalent orientations are observed (Figure 1E). We therefore hypothesize that these species are composed of two O atoms bound to one Ni atom. Importantly, we note that the surface remained at 78 K during O<sub>2</sub> exposure and imaging, meaning that Ni atoms can dissociate O<sub>2</sub> at this low temperature.

To evaluate the STM results, DFT was used to calculate energy barriers and compare O<sub>2</sub> activation on NiAg(100) to Ag(100) (Figure 2). On bare Ag(100), the O<sub>2</sub> activation barrier is 1.09 eV and the binding energy is -0.87 eV. For NiAg(100), the barrier is only 0.26 eV with respect to gas phase O<sub>2</sub> and the binding energy for two O atoms bound to an Ni atom increases to -1.48 eV. Isolated Ni atoms were found to prefer to bind two O atoms, whereas Ag prefers to bind only a single O atom per Ag atom (Figure S2).<sup>41,44</sup> The barrier height is much higher on the bare surface, which explains why oxygen only adsorbs molecularly at 78 K on Ag(100).<sup>45,46</sup> On NiAg(100), the lower barrier allows the oxygen-oxygen bond to be broken at cryogenic temperatures. This comparison represents a significant result, as O<sub>2</sub> dissociation is the rate limiting step in many selective oxidation reactions on Ag-based heterogeneous catalysts.<sup>5,9,18,47</sup> Ni also binds oxygen 0.6 eV stronger than Ag, which explains the lack of O atom spillover to Ag sites at this temperature. DFT calculations and the atomically resolved STM images demonstrate

that O atoms bind in four-fold hollows on both Ag(100) and the NiAg(100) SAA, in agreement with the literature for Ag(100).<sup>41,44,47</sup>

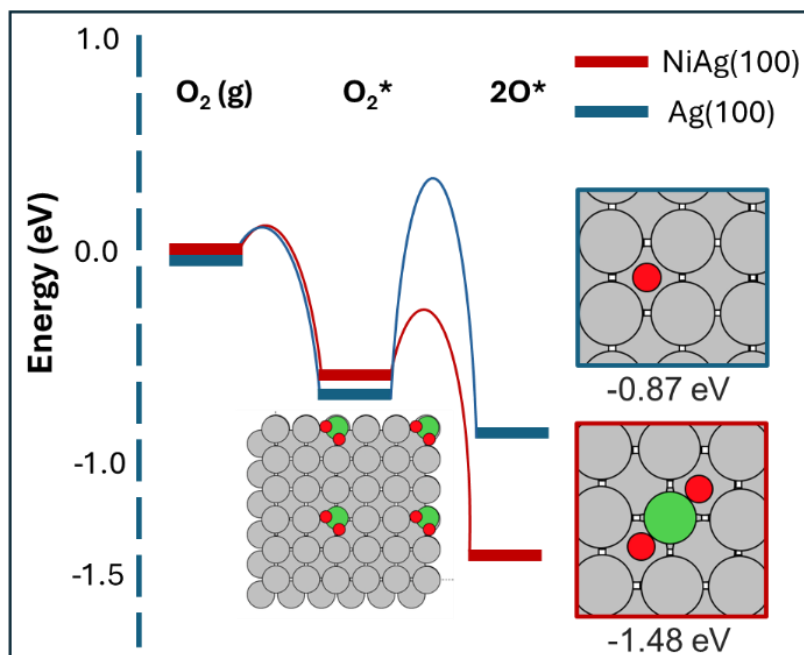


**Figure 4.2.** Oxygen activation energetics calculated by DFT. The activation barriers, transition states, and stabilities/reaction energies are shown for both NiAg(100) (red, defined as isolated dopant Ni sites in the Ag surface) and Ag(100) (blue). The activation barrier for oxygen on bare Ag(100) is much higher than on NiAg(100). Additionally, Ni prefers to bind two oxygen atoms rather than a single oxygen atom as is the case for bare Ag. The  $O_2^*$  transition state is similar on both systems, but lower in energy for NiAg(100).

To both demonstrate these DFT results experimentally and to further understand the effects of the 78 K oxygen dose on NiAg(100), further STM experiments were performed on Ag(100) and NiAg(100). These results are depicted in Figure 3. First, a control experiment in which 6 L of oxygen was dosed onto a clean Ag(100) surface while holding it at 78 K was

performed (Figure 3 A-B). STM did not detect any features as expected, due to the high barrier for oxygen dissociation and the fast diffusion of physisorbed O<sub>2</sub> at this temperature (3B).<sup>42,45,46</sup> By contrast, NiO<sub>2</sub> features appeared in STM images after the same oxygen exposure on NiAg(100), confirming the much lower O<sub>2</sub> dissociation barrier on the SAA (Figure 3 C-D).

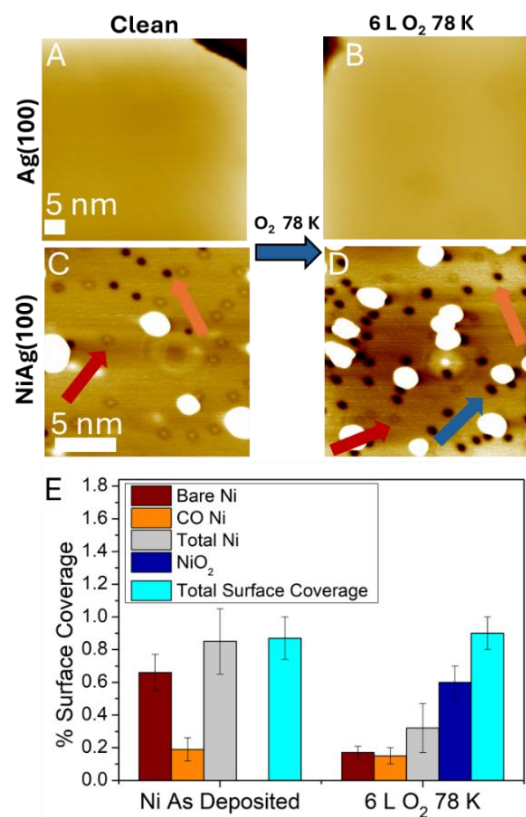


**Figure 4.3.** STM Comparison of oxygen doses on Ag(100) held at 78 K (A-B) and NiAg(100) (C-D). SSTM image of the clean Ag(100) surface. No features are observable on the surface. A) STM image of the Ag(100) surface after exposure to 6 L O<sub>2</sub> at 78 K. O<sub>2</sub> is present on the surface, but at this temperature it cannot be imaged.<sup>42,45,46</sup> C) STM image of the NiAg(100) surface as deposited. Three features are present: Bare Ni atoms (donuts), CO-capped Ni atoms (depressions), and islands of ejected Ag formed during the alloying of Ni (bright white features). D) STM image of NiAg(100) after exposure to 6 L O<sub>2</sub> at 78 K. Typical scanning conditions were 100 mV and 300 pA, and a scale bar is shown in each image. All STM performed at 78 K. E) Surface coverage of different features observed in STM on NiAg(100) before and after 78 K oxygen exposure. Error bars are a single standard deviation. The NiO<sub>2</sub> species were distinguished from the CO depressions using high bias voltage scanning conditions to desorb the CO molecules but not the NiO<sub>2</sub> (Figure S3).

The distribution of species present on the NiAg(100) surface before and after O<sub>2</sub> exposure was quantified with STM (Figure 3E). On the as-deposited surface, 0.8% Ni was present as either bare Ni atoms (0.6 %) or CO-bound Ni atoms (0.2%). Upon introduction of oxygen, the amount of CO-bound Ni atoms remained the same, the number of bare Ni sites decreased by ~0.4%, and the new NiO<sub>2</sub> species increased by ~0.5%. These results further support that these features arise due to dissociative adsorption of oxygen at the Ni atom sites and that O<sub>2</sub> cannot displace the CO bound to Ni atoms at this temperature.

To further support the identity of proposed structures, DFT-simulated STM was combined with atomic resolution experimental STM images (Figure 4). Figure 4 A-B shows the O-NiAg(100) system under atomic resolution (A) and typical (B) STM imaging conditions. With typical resolution the bare Ni sites are less defined (red arrows), but still observable and the NiO<sub>2</sub> sites appear somewhat rectangular in shape with two orientations (blue arrows). Figure 4 C shows a simulated STM image of the NiO<sub>2</sub> species. Oxygen-nickel species with different stoichiometries and structures are shown in Figure S4. This simulated NiO<sub>2</sub> (where the bright areas are oxygen atoms, and the Ni atom is gray in the center) is similar to the oxygen feature observed with STM. In particular, the orientation of the species and the location of its bright and dark areas are in good agreement and support our assignment as NiO<sub>2</sub>.

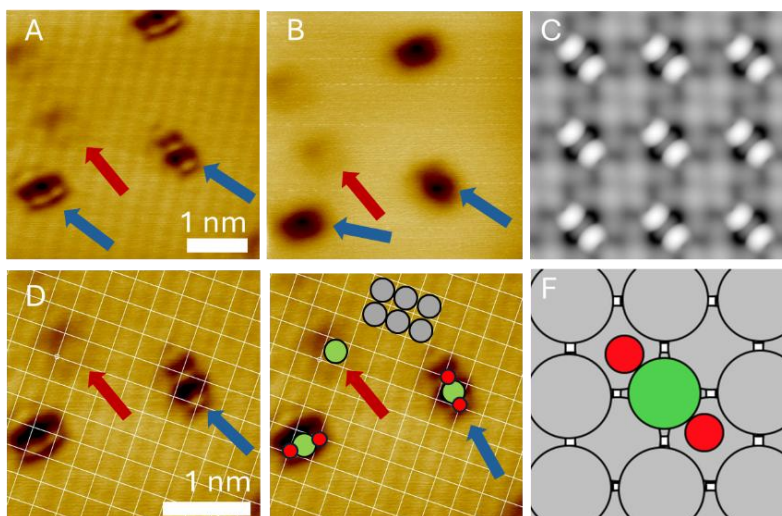


**Figure 4.4.** DFT-simulated STM and experimental atomic-resolution images. A) 78 K STM image of the NiAg(100) surface after exposure to O<sub>2</sub>. Bare Ni sites appear as cross-shaped features (red arrow) and NiO<sub>2</sub> is present as rectangular features that run diagonally to the (100) lattice (blue arrows). Imaging conditions were 10 mV 1.0 nA. B) The same area imaged under typical resolution (300 mV, 1 nA). Bare Ni sites appear fainter than in A but retain the same shape. NiO<sub>2</sub> sites appear as depressions under these conditions but retain their rectangular shape. A scale bar is shown in A. C) Simulated STM image of O-Ni-O features on Ag(100). The bright areas are oxygen atoms while the central gray area is an Ni atom. D, E) Atomic resolution 78 K STM image of the system with a grid showing the 4-fold hollows sites of the Ag(100) lattice. E shows the surface with Ni and O atoms overlaid at their preferred sites as calculated with DFT. The location of Ni (green), oxygen (red) and silver (gray, only some Ag atoms are highlighted) sites are shown. Imaging conditions were 10 mV 1 nA, and a scale bar is shown in D. F) DFT-calculated preferred binding site of dissociated O<sub>2</sub> on Ag(100). The oxygen atoms sit in four-fold hollow sites each side of the Ni dopant atom.

To test if the O-Ni-O assignment is consistent with the size and orientation of our observed species, the Ag(100) lattice was overlaid on an atomic resolution STM image (Figure 4 D-E). The DFT-calculated preferred adsorption site for oxygen on NiAg (Figure 4F) was used as a reference. Figure 4E shows that for both orientations of the NiO<sub>2</sub> species. The brighter areas of the feature align with four-fold hollow sites on opposite sides of a surface Ni atom. This structure agrees with our DFT predictions and provides further evidence for the formation of an NiO<sub>2</sub> species with an O-Ni-O structure at 78 K on NiAg(100).

#### 4.4 Conclusions

This study provides direct, atomically resolved evidence that isolated Ni atoms embedded in an Ag(100) surface dramatically lower the activation barrier for molecular oxygen dissociation. Using low-temperature scanning tunneling microscopy (STM) and corroborative density functional theory (DFT) calculations, we observed the formation of a distinct NiO<sub>2</sub> species on the NiAg(100) SAA following O<sub>2</sub> exposure at 78 K, a condition under which only molecular oxygen adsorbs on pure Ag(100). The rectangular STM features, their orientation on the Ag(100) lattice, and their structural alignment with DFT-predicted NiO<sub>2</sub> configurations support this assignment. The combination of STM imaging and DFT energetics revealed that isolated Ni atoms not only facilitate O–O bond scission at cryogenic temperatures but also preferentially stabilize the resulting atomic oxygen in four-fold hollow sites, in contrast to the weaker binding of molecular O<sub>2</sub> on Ag at 78 K. Our findings confirm that single-atom Ni dopants break conventional scaling relations in oxidation catalysis by simultaneously enabling facile O<sub>2</sub> activation and maintaining moderate oxygen binding strength. Beyond providing the

first direct imaging of dissociated oxygen on a SAA surface, this work illustrates the power of combining surface science techniques with theoretical modeling to elucidate the behavior of catalytic sites at the atomic scale. The ability of NiAg SAAs to activate oxygen under mild conditions offers exciting opportunities for broader application of these SAAs for selective oxidation reactions.

## Acknowledgements

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## 4.5 References

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## Chapter 4.6

### Supporting Information

#### 4.6.1 Experimental Methods

##### Scanning Tunneling Microscopy

78 K STM experiments were conducted in an ultra-high vacuum (UHV) chamber with a base pressure of  $1 \times 10^{-11}$  mbar using a low temperature (LT)-STM (Omicron Nanotechnology). An Ag(100) single crystal (Princeton Scientific 99.999% purity <1 degree polish) was used for experiments. Sample cleaning was performed in a connected preparation chamber with a base pressure of  $< 5 \times 10^{-10}$  mbar. Repeated cycles of  $\text{Ar}^+$  (Airgas 99.99%) ion sputtering (1 keV 10-20  $\mu\text{A}$ ) and annealing to 825 K were used to clean the Ag(100) crystals. STM images were obtained at 78 K after cryogenically cooling the STM stage. Oxygen (99.9% Middlesex gases) was dosed through high precision leak valves. Ni was deposited via hot filament evaporation from a high-purity Ni rod. Coverages were calculated as an average from  $\sim 20$  images for each coverage through manual counting of features using an STM image processor (SPIP). Coverages are based on the number of specific features per image divided by the total number of Ag surface atoms in each image. Error bars on coverage were one standard deviation.

## 4.6.2 Supplementary Figures

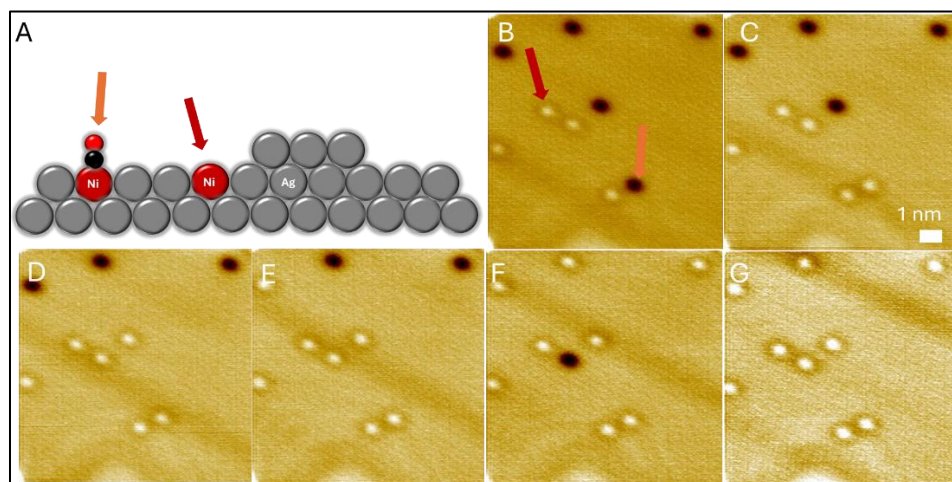


**Figure 4.S1.** STM Pulse Sequence of CO molecules on NiAg(100). A) Depiction of NiAg(100) surface after Ni deposition. CO-Bound Ni (orange arrows) and bare Ni atoms (red arrows) are present). B-G) 78 K STM of a 5.0 V pulse sequence where CO molecules are desorbed one-by-one from Ni atoms in NiAg(100). CO-bound atoms appear as depressions and bare Ni atoms appear as donut-shaped protrusions. In F, a CO molecule readsorbed to a previously bare Ni atom. Scanning conditions were -100 mV and 800 pA, and a scale bar is shown in C.

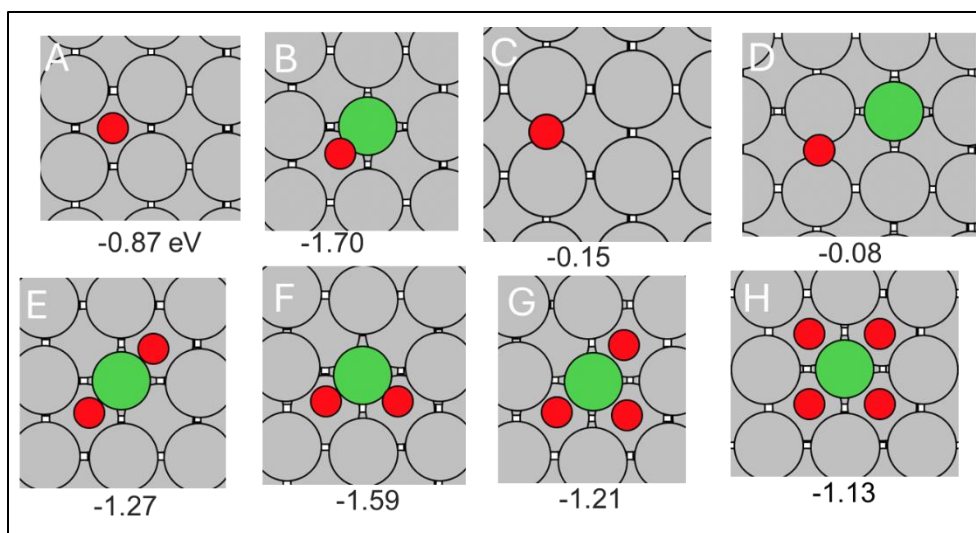


**Figure 4.S2.** DFT-calculated binding sites and associated adsorption energies for oxygen atoms in various configurations on Ag(100) and NiAg(100). F is calculated to be more stable than E, but this discrepancy is likely due to a DFT-based error due to DFT's poor performance with respect to transition metal oxides.

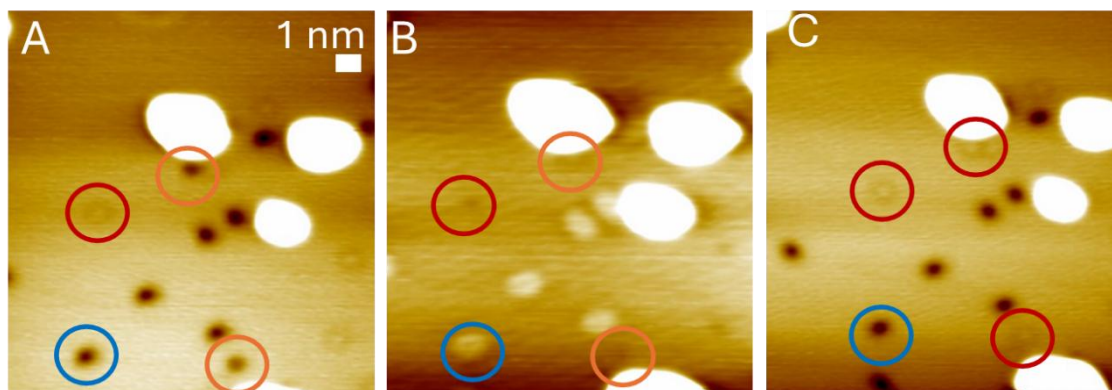


**Figure 4.S3.** Higher bias voltage scanning on O-NiAg(100). A) STM of NiAg(100) after O<sub>2</sub> exposure at 80 K. Bare Ni atoms (red circle donut protrusion), O-Ni-O sites (blue circle, rectangular depressions) and CO-bound Ni atoms (orange circles, light depressions) are all present. Scanning conditions were 100 mV 300 pA. B) 3.0 V (300 pA) scan of the same surface and same area. Ni atoms now appear as faint depressions. O-Ni-O appears as rectangular shallow depressions. The CO bound to Ni atoms have been desorbed due to the high voltage. C) 100 mV scan (300 pA) after two 3 V scans. The appearances of the various species is the same as in A. However, now there are no CO-bound Ni atoms. As the only depressions present are O-Ni-O sites, and the Ni atoms previously under CO are visible, we can distinguish between the two species and count the STM features to determine surface coverage. Images are 14.2 nm<sup>2</sup> with a scale bar shown in C.

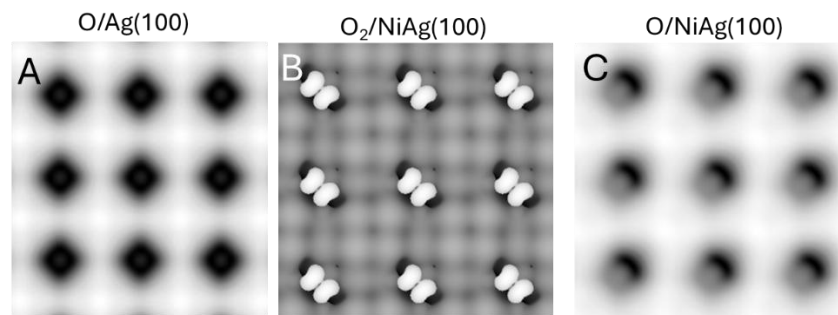


**Figure 4.S4.** Simulated STM of other species. A) Simulated STM of O-Ag(100). O adatoms appear as square depressions in a four-fold hollows. B) Simulated STM image of O<sub>2</sub> molecules on NiAg(100). The oxygen molecules appear as protrusions with slight depressions on their edges. C) Simulated STM image of O adatoms on Ni atoms in NiAg(100). Ni appears gray and the oxygen adatom is bound in the four-fold hollow and appear as a small depression. Each of these species has a different appearance than the O-Ni-O species observed in this work. The Ag-bound oxygen atoms appear as square depressions rather than the rectangular depressions observed on O-Ni-O. The oxygen molecules appear as predominantly protrusions rather than the mix of protrusion and depression seen with O-Ni-O experimentally and seen with simulated STM (Figure 4). The single oxygen atoms bound to Ni appear as single depressions, whereas with O-Ni-O the depression area extends to multiple atoms on either side of Ni (Figure 4).

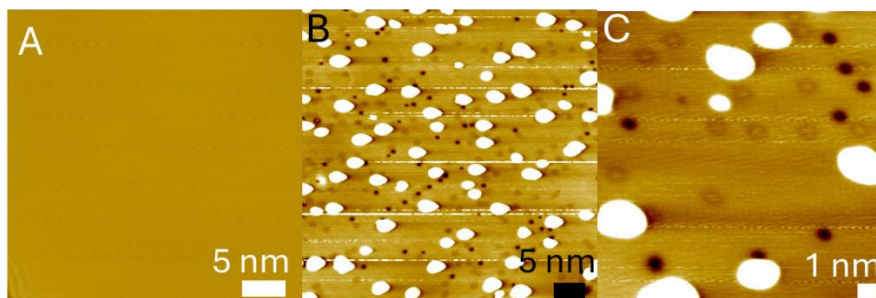


**Figure 4.S5.** STM of the Ag(100) surface before and after Ni deposition. A) Bare Ag(100) surface after cleaning. No impurities or other species are present. B) Ag(100) after deposition of ~1% Ni on Ag(100). Ejected Ag islands, CO-bound Ni and bare Ni atoms are present. C) Zoom of the NiAg(100) surface. A scale bar is included with each image, and typical imaging conditions were 300 mV and 300 pA. Imaging performed at 78 K.

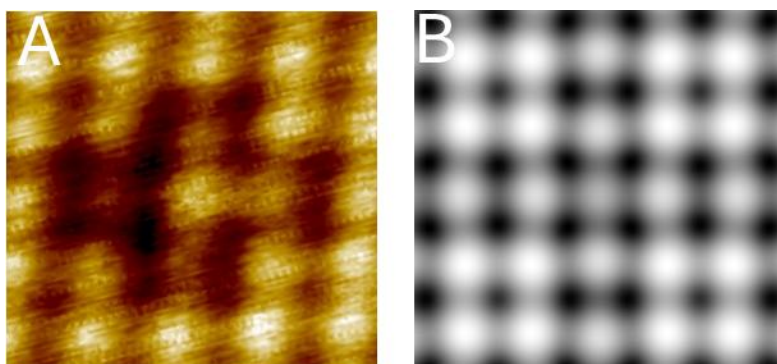


**Figure 4.S6.** Simulated STM of isolated Ni atom in NiAg(100). A) Atomic resolution STM of an isolated Ni atom in NiAg(100). Scanning conditions were 10 mV and 1 nA, and the image is 1.5 by 1.5 nm large. B) DFT-based simulated STM image of an Ni site (gray atom in the center) in NiAg(100). Both images share the same + shape with four adjacent Ag atoms affected by the Ni atom in the center.

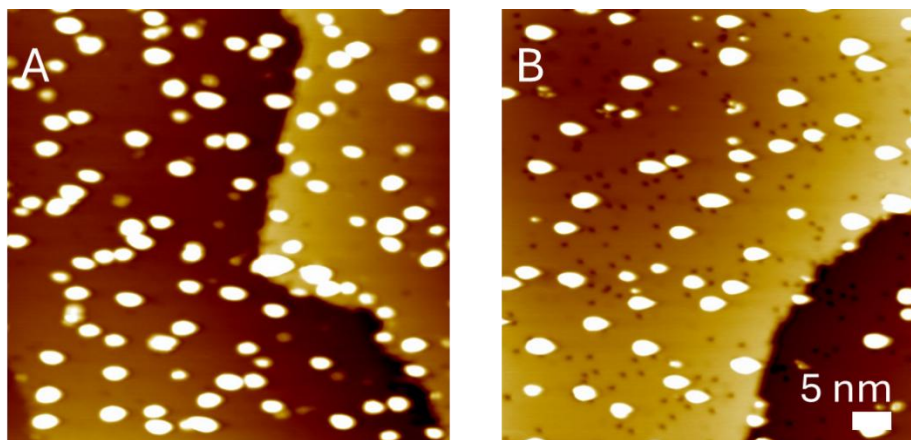


**Figure 4.S7.** STM NiAg(100) and O-NiAg(100) step edge comparison. A) Step edge on NiAg(100) as deposited. Bare Ni sites, Ag islands and CO-bound Ni sites are present. There is no clustering of Ni at the step edge. B) Step edge on NiAg(100) after exposure to 6 L O<sub>2</sub> at 78 K. Bare Ni sites, Ag islands, CO-bound Ni sites and O-Ni-O sites are present. No clustering of Ni or O was observed at the step edges. Scanning conditions were 100 mV and 300 mA for each image. Images are 50 by 50 nm, and a scale bar shown in B.

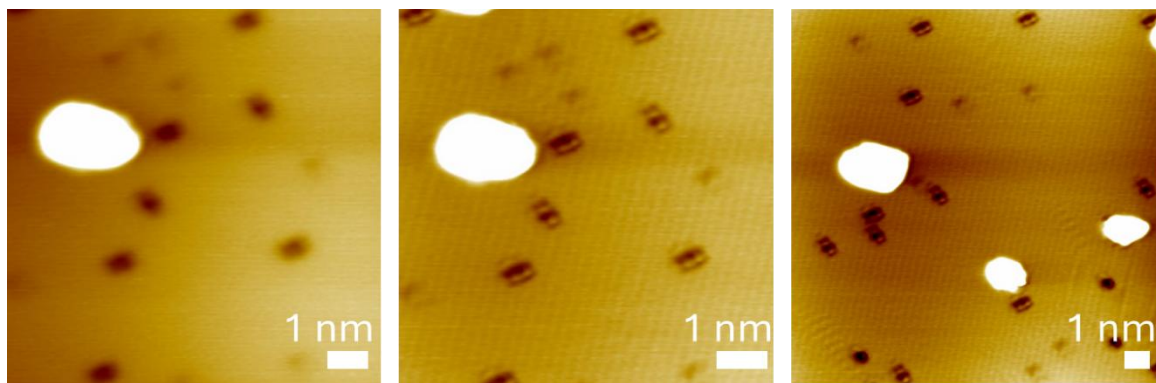


**Figure 4.S8.** Additional 78 K STM Images. A) STM image of NiAg(100) after 6 L O<sub>2</sub> exposure under standard resolution. Scanning conditions were 100 mV and 1 nA. B) Same area under atomic resolution. Scanning conditions were 10 mV and 1 nA. C) Separate area under atomic resolution. Scanning conditions were 10 mV and 1 nA. Scale bars are shown in each image.

## Chapter 5.

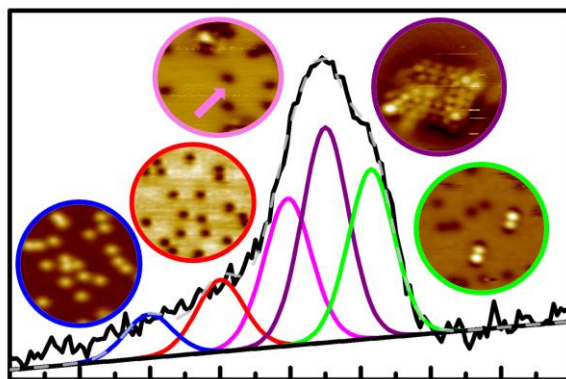
# Characterization of Oxygen Species Formed on the NiAg(100) Single-Atom Alloy

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### 5.1 Abstract

Ethylene epoxidation, a high-value industrial reaction, has long been hindered by its reliance on Ag-based catalysts. These catalysts lack both high inherent selectivity toward ethylene oxide (EO) and viable alternatives to replace them as industry standard. Currently, Ag-based catalysts rely on Cl as a promoter to achieve suitable selectivity, but the safety and environmental concerns raised by Cl and the high volume of CO<sub>2</sub> emitted by this reaction have driven study into alternative promoters. Recently, isolated Ni atoms in an Ag surface were found

to be a promising new oxidation catalyst, with 25% greater selectivity than bare Ag without Cl. However, detailed understanding of oxygen on this system remains limited. To gain further insight into the higher EO selectivity observed on NiAg, we combined high resolution scanning tunneling microscopy (STM), with synchrotron X-ray photoelectron spectroscopy (XPS), to visualize and characterize the oxygen species formed on a NiAg(100) SAA. We observe that the presence of Ni significantly affects the speciation of oxygen on Ag(100). Upon O<sub>2</sub> exposure, isolated Ni atoms are fully oxidized, forming distinct NiO and NiO<sub>2</sub> species, and other forms of oxygen absent on Ag(100). XPS and STM corroborate the assignment of each species by correlating data across two surface-sensitive techniques. Together, these results provide mechanistic insight into oxygen's unique behavior on the NiAg(100) single-atom alloy and support Ni's promise as a promoter for selective oxidation reactions.

## 5.2 Introduction

Ethylene epoxidation is a large scale industrial reaction of great economic importance.<sup>1-4</sup> Currently, alumina-supported Ag nanoparticles are the industrial standard but Ag itself has a low intrinsic selectivity of ~55% toward ethylene oxide (EO), with CO<sub>2</sub> as the main byproduct.<sup>5-10</sup> To reach ~90% selectivity these Ag-based industrial catalysts rely on a series of promoters, primarily Cl, co-fed as alkyl chlorides, along with other promoters like Cs and Re.<sup>3,10-14</sup> The complex synergistic effects among these multiple additives makes understanding the reaction mechanism very challenging, motivating many academic studies and the search for alternative, less toxic and corrosive promoters instead of Cl that can achieve comparable or better performance.<sup>1,8,15-23</sup>

While single-atom alloys (SAAs) were initially explored for hydrogenation and dehydrogenation reactions,<sup>24–27</sup> their potential in oxidation catalysis has barely been explored.<sup>28,29</sup> However, it was very recently discovered that isolated Ni in Ag, in the form of a NiAg SAA, increased ethylene epoxidation selectivity by 25%, the same as ubiquitously used Cl.<sup>23</sup> Despite years of industrial R&D, Ni went undiscovered as a promotor, probably due to the very small concentrations it is effective at (0.5 atom %).<sup>23</sup> This result motivates fundamental studies of the types of oxygen and the effect of Ni in these very dilute alloys. The relatively high O<sub>2</sub> sticking coefficient ( $\sim 10^{-4}$ ),<sup>30</sup> and favorable EO selectivity<sup>31–34</sup> of the Ag(100) facet make it ideal for studying these effects on model single crystals without the need for O<sub>2</sub> alternatives like NO<sub>2</sub> or O<sub>3</sub> or the use of high-pressure setups which can be subject to contamination.<sup>30,35</sup>

In this work, we used high-resolution X-Ray photoelectron spectroscopy (XPS) and 78 K scanning tunneling microscopy (STM) to characterize the species formed on Ag(100) and NiAg(100) SAAs after O<sub>2</sub> exposure. We identified multiple species including O adatoms, OH groups, NiO and NiO<sub>2</sub> complexes and semi-ordered Ag oxide patches. Density functional theory (DFT) calculations supported the assignment of the newly observed nickel-oxygen species present and their surface binding geometries. By correlating data from XPS and STM, we provide atomic-scale characterization of the types of oxygen not found on bare Ag(100), offering new insight into the role of Ni in selective oxidation catalysis.

### 5.3 Results and Discussion

To examine oxygen species on NiAg(100), we began with STM imaging at 78 K after depositing  $\sim 1\%$  Ni onto an Ag(100) surface held at 300 K (Figure 1). The resulting surface exhibited three distinct features: bare Ni atoms (highlighted by red arrows), CO-bound Ni atoms

(gold arrows), and Ag islands (purple arrows) formed during alloying (Figure 1D and F).<sup>36</sup> As Ni alloys into the Ag(100) surface, it undergoes direct place exchange with Ag atoms, and ejects them from the surface. These Ag atoms diffuse and cluster to form the ejected Ag islands we observe in STM.<sup>37,38</sup> These islands are 260 pm high in STM, the same as the expected step edge height for Ag(100).<sup>39,40</sup> This observed height is consistent with a 1-layer high formation where the ejected Ag atoms sit in four-fold surface hollows.<sup>39</sup> Due to the bulky presence of ejected Ag islands, STM imaging is difficult after Ni-deposition, so the coverage was kept low to optimize scanning.

CO is observed in STM at 78 K, where CO, always present in the chamber background adsorbs onto some Ni atoms.<sup>41,42</sup> CO typically images as a depression in STM, which is consistent with our observations of Ni atoms appearing as a protrusion and CO-bound Ni appearing as a depression.<sup>43,44</sup> These observations confirmed successful Ni incorporation and SAA formation. Upon exposure to 1000 Langmuir (L) ( $1 \text{ L} = 1 \times 10^{-6} \text{ Torr}\cdot\text{s}$ )  $\text{O}_2$ , the surface changes significantly, and all the Ni atoms become oxidized as we will discuss in detail (Figure 1E).

To better interpret our STM results, we used synchrotron XPS to monitor the oxidation of Ni on NiAg(100) under increasing  $\text{O}_2$  exposures (Figure 1B). We used higher Ni concentrations for synchrotron experiments to achieve resolvable XPS signal. This higher coverage is still representative of the NiAg nanoparticle catalysts which could have up to 10% Ni at the surface due to Ni's oxophilicity.<sup>23</sup> As-deposited Ni (8%) remained metallic with a binding energy of 852.6 eV.<sup>45</sup> However, after a 3000 L  $\text{O}_2$  dose at 300 K, all the Ni was oxidized to  $\text{Ni}^{2+}$  with a binding energy of 853.9 eV.<sup>45</sup> The charge of the Ni atoms under these conditions suggests that they are all bound to O atom(s). The absence of C1s peaks confirmed that no CO-bound Ni was

present because unlike the 78 K STM experiments, CO does not bind to NiAg(100) at 300 K.<sup>42,46</sup> No C1s peaks were detected on the clean surface either (Figure S1.).

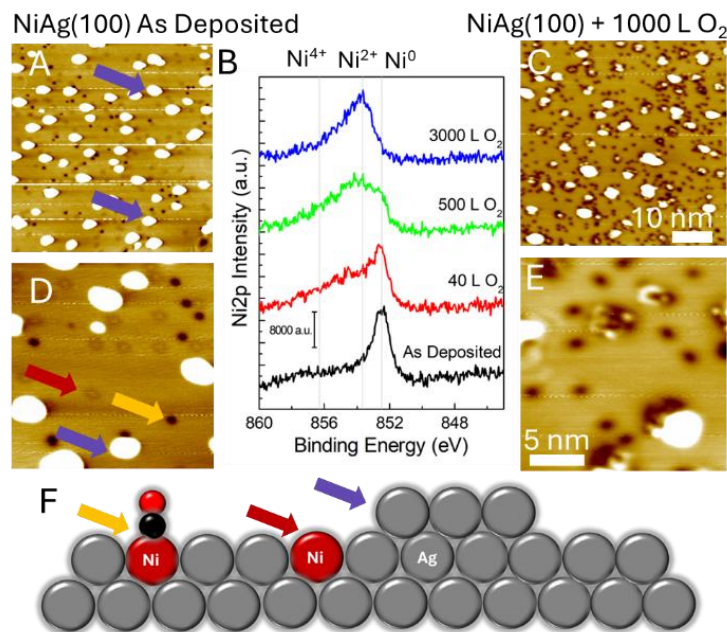


**Figure 5.1.** Overview of NiAg(100) before and after oxidation. A) STM image after depositing 1% Ni onto Ag(100) at 300 K. The white protrusions are Ag islands formed during alloying of Ni (purple arrows). Imaging condition: 100 mV, 1 nA. B) XPS spectra showing Ni 2p<sub>3/2</sub> peak shifts from metallic Ni<sup>0</sup> (852.6 eV) to oxidized Ni<sup>2+</sup> (853.9 eV) after 3000 L O<sub>2</sub> exposure. Ni<sup>4+</sup> (856.1 eV) was not observed. C) STM image after 1000 L O<sub>2</sub> exposure. D) High-resolution STM image of the NiAg(100) surface showing bare Ni atoms (red arrow), CO-bound Ni (gold arrow), and Ag islands (purple arrow). E) High-resolution STM image of the oxidized surface. F) Schematic of the as-deposited NiAg(100) surface. STM images A and E are 50 by 50 nm, and B and F are 14.5 by 14.5 nm. Scale bars and imaging conditions are specified for each panel. STM performed at 78 K, and typical imaging conditions were 100 mV and 1 nA.

We further explored the oxidative behavior of NiAg(100) using STM and XPS as a function of O<sub>2</sub> exposure (Figure 2). By cross-referencing XPS O1s peaks and with STM images on

NiAg(100) after exposure to O<sub>2</sub>, we identified O adatoms (530 eV, red),<sup>47–50</sup> NiO (529 eV, pink),<sup>23,51,52</sup> NiO<sub>2</sub>, semi-ordered Ag oxide patches (528.6 eV, purple),<sup>53,54</sup> OH groups (531 eV, Blue),<sup>51,55,56</sup> oxygen in Ag reconstructions (528 eV, green),<sup>57–59</sup> and water (532 eV, cyan).<sup>60–62</sup> The determination of their assignments will now be discussed in detail.

The first peak we identified was that at 530 eV in the O 1s spectra. When O<sub>2</sub> reacts with Ag(100) at room temperature it forms O adatoms on the Ag surface. These O adatoms have been well documented as depressions in STM,<sup>48,63,64</sup> and have been linked to O 1s peaks around 530 eV (“electrophilic oxygen”).<sup>49,58,65,66</sup> Our own results are consistent with the formation of O atoms on our surfaces and their link to the 530 eV peak (red trace) observed in XPS. On Ag(100) O adatoms and OH are known to be present at both 78 K and room temperature.<sup>23,57,67</sup> OH formation on Ag(100) through the reaction of O adatoms and water from the chamber background is favorable.<sup>2–74,31,75</sup> OH binding energy is also cited in the range of 531–532 eV most commonly.<sup>51,55,56</sup> Together these details led us to assign the 531 eV peak to OH. Due to its temperature dependent nature, O in Ag reconstructions is difficult to characterize in STM (Figures S2, S3).<sup>68</sup> However, we were able to identify the peak at 528 eV due to its properties being consistent with other studies on O in Ag reconstructions (nucleophilic oxygen, binding energy 528–528.5).<sup>49,57</sup> To determine the identity of the peak at 532 eV, we considered water due to its ability to be stabilized by OH groups, which we identified, and by its presence only at 300 K, as well as the cited binding energy for water on Ag is between 531 and 533 eV.<sup>60–62</sup> Water was not observed in STM due to its fast diffusion at 78 K.<sup>69</sup> Notably, the 529 eV and 528.6 eV peaks were absent from the Ag(100) surface, so we turned to additional STM and XPS experiments to verify their identities.

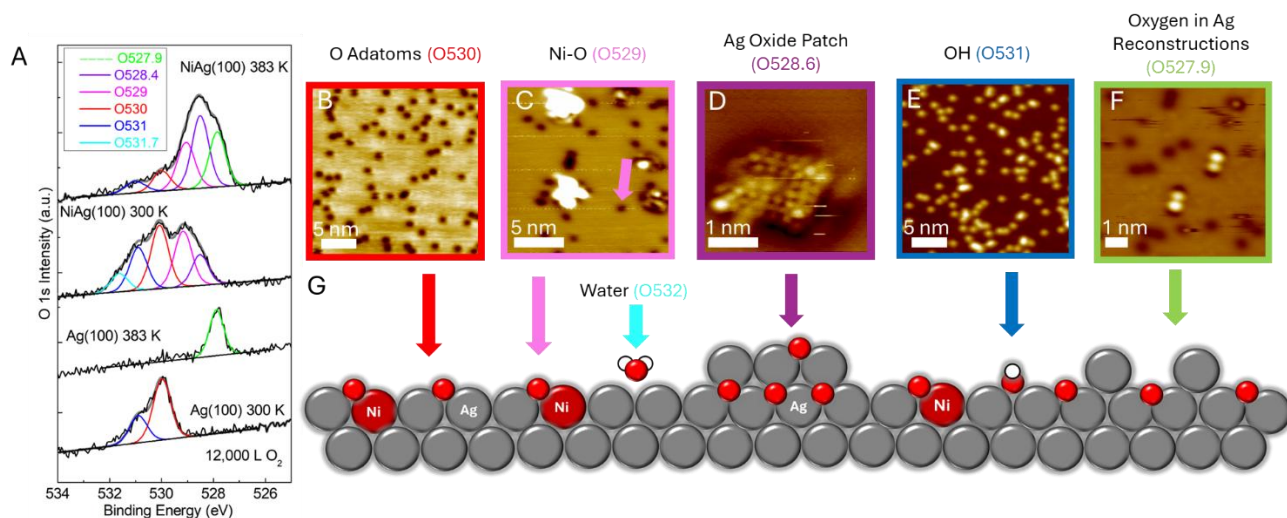


**Figure 5.2.** Overview of the different oxygen species present on NiAg(100). A) O1s XPS after 12,000 L O<sub>2</sub> exposure on Ag(100) and NiAg(100) at 300 and 383 K, and 8% NiAg(100) at 300 K and 383 K. 6 XPS peaks were identified: 528 eV (green), 528.6 eV, 529 eV (pink), 530 eV, (red) 531 eV, and 532 eV (cyan). B-F) STM images of these individual species. B) STM of the 530 eV species assigned to O adatoms on Ag(100). C) STM image of NiO (pink arrow). STM of an Ag oxide patch NiAg(100). E) STM image of OH groups formed on Ag(100). F) STM of reconstructed oxygen formed on Ag(100). G) Schematic of identified oxygen species. Scale bars and imaging conditions are provided for each panel. STM performed at 78 K, and typical imaging conditions were 100 mV 300 pA. For the OH image, a 3 V bias voltage was used.

To better understand the NiO<sub>x</sub> species, we carried out DFT calculations of O adsorption on NiAg(100) (Figure 3). O prefers to bind in the four-fold hollow near Ni atoms in NiAg(100), which is similar to how O atoms bind to Ag(100) (Figure 3B),<sup>70</sup> but with significantly stronger binding energy (-0.87 eV vs -1.47 eV). DFT calculated that Ni prefers to bind two O atoms in a linear O-Ni-O structure (Figure 3E), which is consistent with what we observe in STM also demonstrated confirmed with STM. At room temperature, after O<sub>2</sub> exposure, all Ni remains as

$\text{Ni}^{2+}$ , and the size of the O 1s 529 eV peak observed in XPS is consistent with the size of the  $\text{Ni}^{2+}$  peak, which suggests a 1:1 Ni:O ratio at Ni sites.

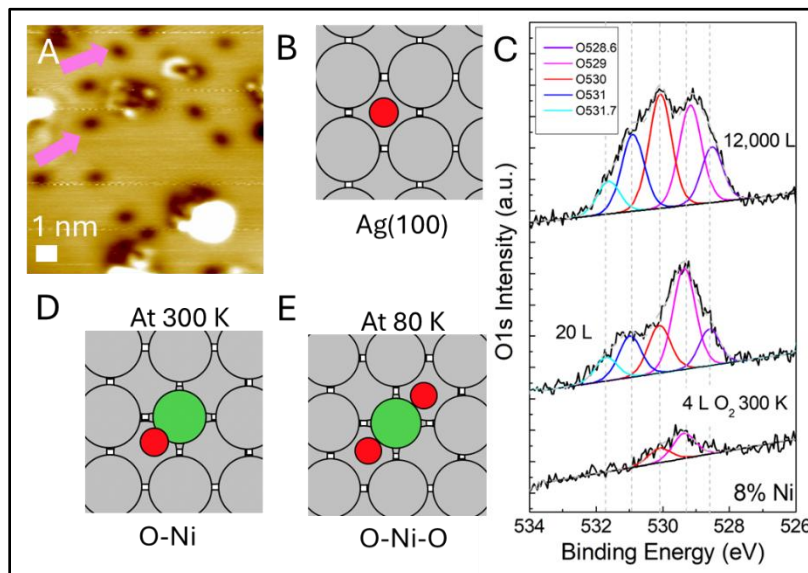


**Figure 5.3.** Characterization of  $\text{NiO}_x$  species. A) 78 K STM image of  $\text{NiAg}(100)$  exposed to 1000 L  $\text{O}_2$  at 300 K. Ni-O species are marked (pink arrows). Imaging conditions were 100 mV, 500 pA, and a scale bar is shown. B) DFT model of O binding site on  $\text{Ag}(100)$ . C) XPS spectra of O1s peaks during increasing  $\text{O}_2$  exposure at 300 K. D)-E) DFT models of one O atom and two O atoms bound to Ni, showing preferred hollow-site binding and O-Ni-O formation at 78 K.

Next, we used high-resolution 78 K STM to characterize the semi-ordered Ag oxide patches that we observed after  $\text{O}_2$  was introduced (Figure 4). On the as-deposited  $\text{NiAg}(100)$  surface, one-atom-high Ag islands appeared as 260 pm protrusions (4A, orange arrow).<sup>39,40</sup> Upon exposure to 1000 L  $\text{O}_2$  at 300 K, these islands were transformed into semi-ordered Ag oxide patches (4B-F, purple arrows). The XPS spectra of a similarly oxidized surface exhibited peaks at 528.6 eV, consistent with the Ag oxide patches observed in STM (Figure 3D).<sup>53,54</sup> This oxide feature forms when O adatoms oxidize ejected Ag islands during  $\text{O}_2$  exposure. The resulting oxide patches exhibited a much lower apparent height ( $\sim 110$  pm), and under high resolution,

their semi-ordered structure was discernable (Figure 4C-F). In these STM images, brighter areas are hypothesized to be ejected Ag, and the darker areas correspond to oxygen atoms.<sup>35,48,71</sup> The observed decrease in apparent STM height supports the identification of these islands as oxide patches because oxides are less conductive than metallic Ag, and this reduced conductivity results in lower apparent STM height.<sup>72</sup> To further support this assignment, we performed voltage pulse experiments to break apart the Ag islands, after which O atoms appeared on Ag in the surrounding area (Figure S4). We hypothesize that the structure of these islands is predominantly Ag<sub>2</sub>O, with defect sites composed of metallic Ag based on the binding energy of the O 1s feature,<sup>54</sup> and the appearance of the oxide patches under high resolution STM.<sup>71</sup>

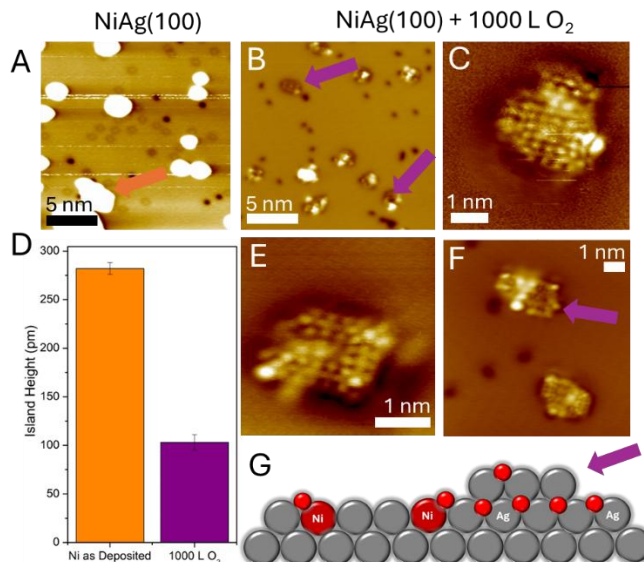


**Figure 5.4.** STM of Ag-oxide patches (528.6 eV). A) STM of as-deposited NiAg(100) with 260 pm high Ag islands (orange). B) STM after 1000 L O<sub>2</sub> exposure at 300 K; islands are ~110 pm high (purple), indicating oxide formation. Imaging conditions were 100 mV 300 pA for A and B, and the z-scale is the same. C) High resolution STM of an oxide patch with bright (Ag) and dark (O) regions. D) Height comparison pre- and post- oxidation. E)-F) Additional oxide patch STM images. Imaging conditions were 100 mV 100 pA for the high-resolution oxide patch images, and 100 mV 1 nA for typical imaging conditions G) Proposed surface structure of the oxidized Ag island patches based on STM and XPS data All STM images done at 78 K, and scale bars are shown.

Lastly, we used high-voltage STM to investigate OH formation on Ag(100) and NiAg(100) (Figure 5). The highest binding energy peaks observed on Ag(100) and NiAg(100) after O<sub>2</sub> exposure were at 531 and 532 eV and were assigned to OH groups and water molecules respectively, in agreement with previous literature.<sup>51,55,56,60</sup> As noted earlier, water cannot be imaged with STM at 78 K, so it was only observed using XPS. In contrast, OH can be imaged on these surfaces at 78 K, but only effectively under high-voltage scanning conditions (>2.5 V). On

Ag(100), when O<sub>2</sub> is dosed at room temperature or below, water physisorbed from the chamber background can react with adsorbed O atoms to form two OH groups.<sup>73–78</sup> On NiAg(100) the presence of Ni leads to the formation of strongly bound NiO<sub>2</sub> sites as the surface cools to 78 K (Figure 3). NiO<sub>2</sub> limits the availability of O for OH formation due to sequestering O atoms. To further explore the effect of Ni on OH formation, we studied a “corked” NiAg(100) surface, where CO at 78 K was dosed onto the as-deposited NiAg(100) surface to block Ni sites.<sup>79</sup> Upon O<sub>2</sub> exposure, the CO-corked NiAg(100) surface showed an increase in surface OH in STM, compared to the non-corked sample (Figure S5).

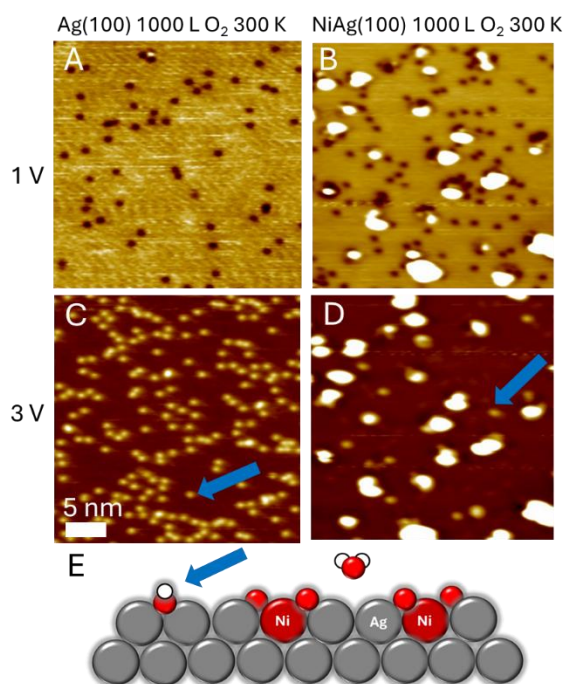


**Figure 5.5.** STM of OH groups (531 eV) on Ag(100) and NiAg(100). A-B) Ag(100) after 1000 L O<sub>2</sub> exposure showing, O adatoms, NiO<sub>2</sub> and Ag features at. 1 V. C-D) High-voltage (3 V) STM of the same surfaces in A and B reveals symmetric OH protrusions (blue arrows). E) Schematic of OH (blue arrow) adsorption and nearby oxygen species on NiAg(100). Imaging was performed at 78 K, tunneling current was 1 nA, and a scale bar is shown in C.

## 5.4 Conclusions

In this study we join synchrotron X-ray photoelectron spectroscopy with high-resolution scanning tunneling microscopy to systematically characterize and visualize the diverse oxygen species formed on NiAg(100) SAAs after O<sub>2</sub> exposure under UHV conditions. These species included O adatoms, OH groups, semi-ordered Ag oxide patches, NiO and NiO<sub>2</sub>; the latter three of which were absent from Ag(100) after identical O<sub>2</sub> exposures. Upon O<sub>2</sub> exposure, we also observed the complete oxidation of isolated Ni, as evidenced by both Ni 2p XPS and monitoring distinct features in STM. By correlating O1s peak binding energies from XPS with atomic-scale STM features, we confidently assign these species and establish a detailed classification of oxygen states not found on Ag(100). DFT calculations support the formation of O–Ni–O species at low temperatures and confirm that oxygen atoms bind preferentially to four-fold hollow sites adjacent to Ni atoms over equivalent sites in the Ag(100) matrix. Additionally, the transformation of ejected Ag islands into semi-ordered oxide patches emphasizes the dynamic nature of the Ag surface in oxidative conditions. The comprehensive identification of oxygen species observed on the NiAg(100) SAA advances the understanding of oxygen activation and reactivity on Single-Atom Alloy catalysts. The distinct reactivity of Ni sites and their impact on oxygen adsorption and speciation on Ag provide insight relevant to understanding selective oxidation reactions as well as a strong foundation for future studies of NiAg(100) under epoxidation conditions.

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## Chapter 5.6

### Supporting Information

#### 5.6.1 Experimental Methods

##### Scanning Tunneling Microscopy (STM)

78 K STM experiments were conducted in an ultra-high vacuum (UHV) chamber with a base pressure of  $1 \times 10^{-11}$  mbar using a low temperature (LT)-STM (Omicron Nanotechnology). An Ag(100) single crystal (Princeton Scientific 99.999% purity <1 degree polish) was used for experiments. Sample cleaning was performed in a connected preparation chamber with a base pressure of  $< 5 \times 10^{-10}$  mbar. Repeated cycles of Ar<sup>+</sup> (Airgas 99.99%) ion sputtering (1 keV 10-20  $\mu$ A) and annealing to 825 K were used to clean the Ag(100) crystals. STM images were obtained at 78 K after cryogenically cooling the STM stage. Oxygen (99.9% Middlesex gases) was dosed through high precision leak valves. Ni was deposited via hot filament evaporation from a high-purity Ni rod. Coverages were calculated as an average from ~20 images for each coverage through manual counting of features using an STM image processor (SPIP). Coverages are based on the number of specific features per image divided by the total number of Ag surface atoms in each image. Error bars on coverage were one standard deviation.

##### X-Ray Photoelectron Spectroscopy (XPS)

XPS experiments were performed at Beamline 23-ID-2 (IOS) of the National Synchrotron Light Source II (NSLS- II) at Brookhaven National Laboratory.<sup>1</sup> All experiments were performed on a Ag(100) single crystal ) (Princeton Scientific 99.999% purity <1 degree polish) cleaned with Ar<sup>+</sup> ion sputtering and annealing to 825 K until XPS spectra showed no

impurities. The heating rate for cleaning and annealing was 40 K/min. High purity O<sub>2</sub> (Matheson, 99.994%) was exposed to the sample via precision leak valve while the sample was heated with a pyrolytic boron nitride heater. Temperature was measured with a K-type thermocouple between the Ag(100) crystal and the heater/sample mount. Reference Ag 3d spectra were taken after each oxygen spectrum. Ni was deposited via hot filament evaporation from a high-purity Ni rod calibrated by a quartz mass balance. Oxygen and Ni species coverages were calculated by dividing the corrected O 1s peak areas by the corresponding corrected Ag 3d peak areas. Peaks areas were corrected by dividing the raw areas by their Relative Sensitivity Factor (RSF),<sup>2</sup> multiplied by the IMFP of the ejected electron found from a universal curve<sup>3</sup> (Equation S1, S2). In addition, Ag 3d peaks were taken at reduced intensity and then corrected to full intensity area using reference spectra taken at the beginning of each experiment. Ag 3d peak areas were also corrected by a first layer correction based on the IMFP to account for the signal only generated by the top level of atoms (Equation S3).

$$\frac{\text{Corrected O 1s Peak Area}}{\text{Peak Area}} = \frac{\text{Raw Peak Area}}{\text{R.S.F.} \times \text{I.M.F.P.}}$$

**Equation 5.S1.** O 1s XPS Correction.

$$\frac{\text{Corrected Ag 3d Peak Area}}{\text{Peak Area}} = \frac{\text{Raw Ag 3d}_{5/2} \text{ Peak Area} \times \text{First Layer Correction}}{\text{R.S.F.} \times \text{I.M.F.P.} \times 5/2 \text{ Correction}}$$

**Equation 5.S2.** Ag 3d XPS Correction.

$$\frac{\text{Corrected Ni 2p Peak Area}}{\text{Peak Area}} = \frac{\text{Raw Ni 2p}_{3/2} \text{ Peak Area}}{\text{R.S.F.} \times \text{I.M.F.P.} \times 3/2 \text{ Correction}}$$

**Equation 5.S3.** Ni 2p XPS Correction.

To investigate different elements, different photon energies were used. Predominantly, 760, 1090 and 500 eV were used to generate photoelectrons with kinetic energies of ~200-300 eV for the O 1s (at 760 eV), Ni 2p (at 1090 eV), and S 2p and C 1s (at 500 eV) core levels, respectively, to maintain similar probing depths. The latter two elements were only monitored for impurities. Binding energy calibration was performed on all spectra with respect to the Fermi edge and metallic Ag 3d<sub>5/2</sub> binding energy measured at each photon energy.<sup>4</sup> XPS data was analyzed with CasaXPS. Each species was assigned and fit according to experimental results and literature values (Table S1). O 1s spectra and Ni 2p were fit with a linear background due to their small size, while Ag spectra were fit with a Shirley background.<sup>5</sup>

| Element                        | Component                                            | Binding Energy (eV) | Full Width at Half Maximum (FWHM) | Line Shape (Gaussian: Lorentzian) |
|--------------------------------|------------------------------------------------------|---------------------|-----------------------------------|-----------------------------------|
| Oxygen (O 1s)                  | O in Ag Reconstructions <sup>6-8</sup>               | 527.9 – 528.0       | 0.7 – 0.8                         | 30:70                             |
|                                | Ag Oxide Patches (Ag <sub>2</sub> O) <sup>9,10</sup> | 528.5 – 528.7       | 0.8 – 1.0                         | 30:70                             |
|                                | NiO <sup>11-14</sup>                                 | 529.0 – 529.2       | 0.8 – 0.9                         | 30:70                             |
|                                | NiO <sub>2</sub> <sup>15</sup>                       | 531.8*              | n/a                               | n/a                               |
|                                | Atomic O <sup>2,5,16,17</sup>                        | 530.0 – 530.1       | 0.8 – 1.0                         | 30:70                             |
|                                | OH <sup>11,18,19</sup>                               | 530.9 – 531         | 0.8 – 0.9                         | 30:70                             |
|                                | Water <sup>14,20-22</sup>                            | 531.7 – 532.1       | 1                                 | 30:70                             |
| Silver (Ag 3d <sub>5/2</sub> ) | Ag <sup>0</sup> (Metallic Ag) <sup>4,23</sup>        | 368.2               | 0.4                               | 99:1                              |
|                                | Ag Oxide (Ag <sub>2</sub> O) <sup>10,23</sup>        | 367.8*              | n/a                               | n/a                               |
| Nickel (Ni 2p <sub>3/2</sub> ) | Ni <sup>0</sup> (Metallic Ni) <sup>14,24</sup>       | 852.6               | 0.8                               | 30:70                             |
|                                | Ni <sup>2+</sup> (NiO) <sup>14,24</sup>              | 853.9               | 1.0                               | 30:70                             |
|                                | Ni <sup>4+</sup> (NiO <sub>2</sub> ) <sup>25</sup>   | 856.1*              | n/a                               | n/a                               |
| Carbon (C 1s)                  | CO-Ni <sup>26</sup>                                  | 285.9 *             | n/a                               | n/a                               |

**Table 5.S1.** Summary of fitting parameters for XPS spectra.

\*Not detected within our XPS experiments.

**Note on differing O:OH Ratios:** We found that OH formation from the background is highly dependent on oxygen coverage, temperature, chamber background, and chamber base pressure. As a result, it varies highly between UHV chambers and even varies between experiments on the same UHV chamber.

## 5.6.2 Supplementary Figures

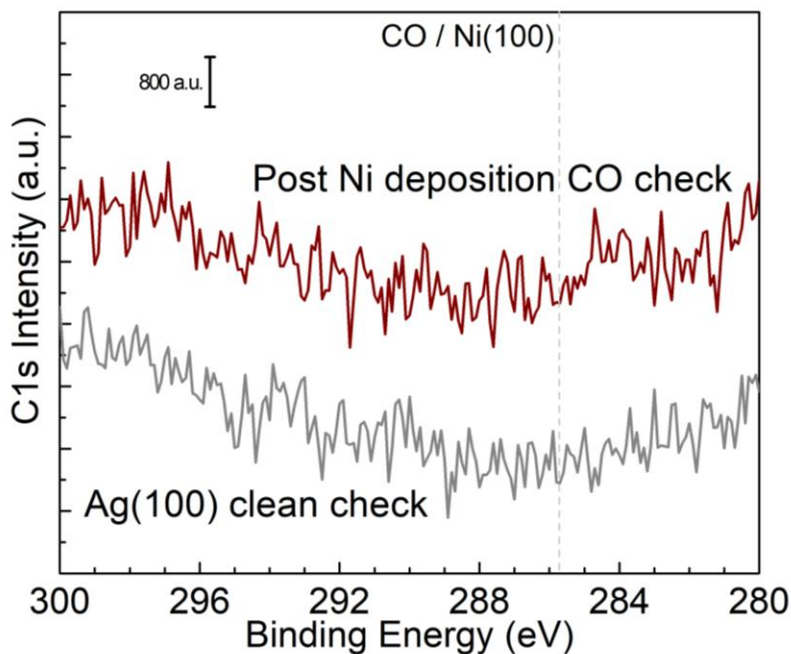


**Figure 5.S1.** C 1s XPS spectra for as-deposited NiAg(100) taken at 300 K. C 1s spectra were taken at 500 eV beam energy to check for the presence of CO-bound Ni after Ni deposition, as well as to check for C impurities. The lower trace (gray) is a C 1s spectrum after cleaning, and the top was taken post Ni deposition. No C features were observed in either case, consistent with O 1s and Ni 2p results. There is a small peak around 284 eV after Ni deposition due to carbon contamination from the Ni source. The binding energy of CO to atop Ni(100) sites is shown for reference.<sup>26</sup>

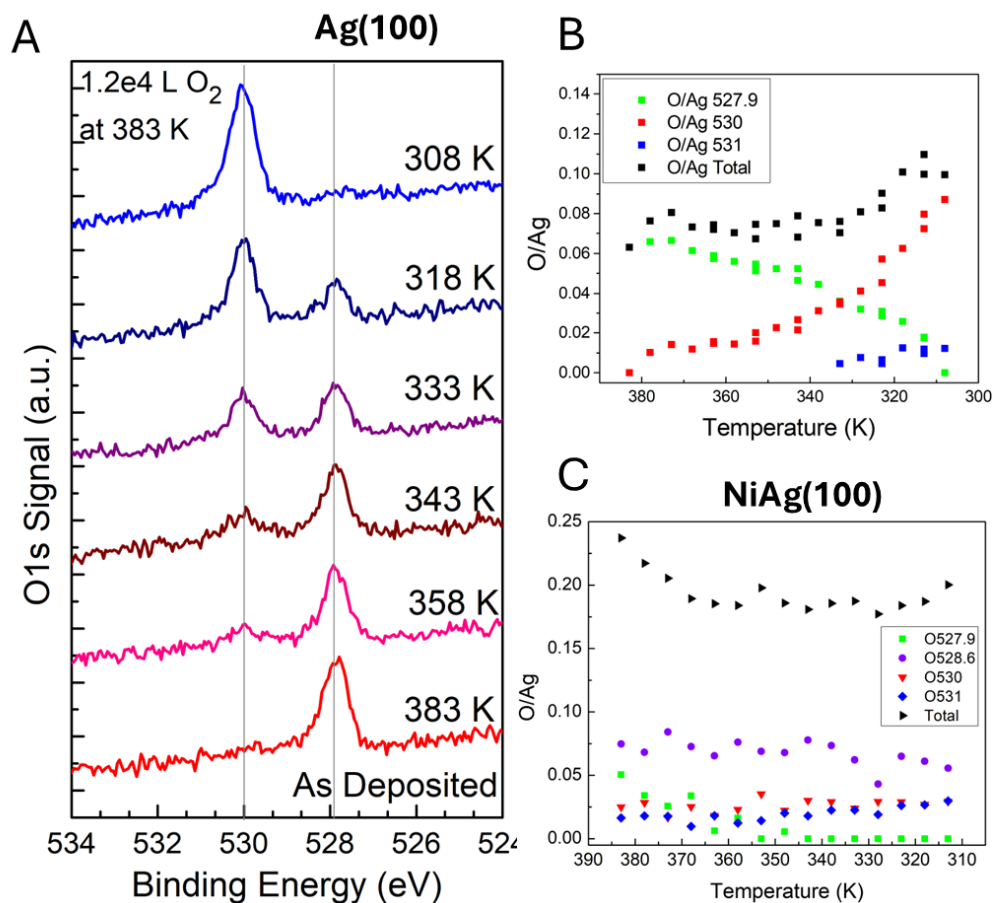


**Figure 5.S2.** Temperature dependence of the 528 eV peak in O 1s spectra. A) O 1s spectra of 12,000 L O<sub>2</sub> dosed at 383 K (red trace, bottom) on Ag(100), and subsequent incremental cooling to 308 K (blue trace, top). The 528 eV peak, representing reconstructed oxygen, disappears as the sample cools down. Conversely, the 530 eV peak, representing atomic O adatoms, grows in during cooling as the reconstructed oxygen converts into adatoms due to no longer being stable at lower temperatures. Spectra taken at 760 eV beam energy. This phase transition on Ag(100) has been observed previously in literature.<sup>27</sup> B) Plot of surface coverage of various oxygen species present during the experiment shown in A. Once the sample cools below 340 K, a shoulder peak at 531 eV grows in. This peak represents OH, which can readily form from adsorbed O adatoms reacting with water in the chamber background. This OH formation leads to an increase in overall oxygen coverage as the sample cools. C) Plot of equivalent experiment

shown in A, B but for NiAg(100) (12,000 L O<sub>2</sub> dosed at 383 K and cooled incrementally to room temperature). The behavior of the various O species is similar on NiAg(100). The reconstructed oxygen peak (528 eV) disappears during cooling, and the 530 and 531 eV peaks grow in, consistent with observations on Ag(100). The other peaks present did not change significantly during cooling.

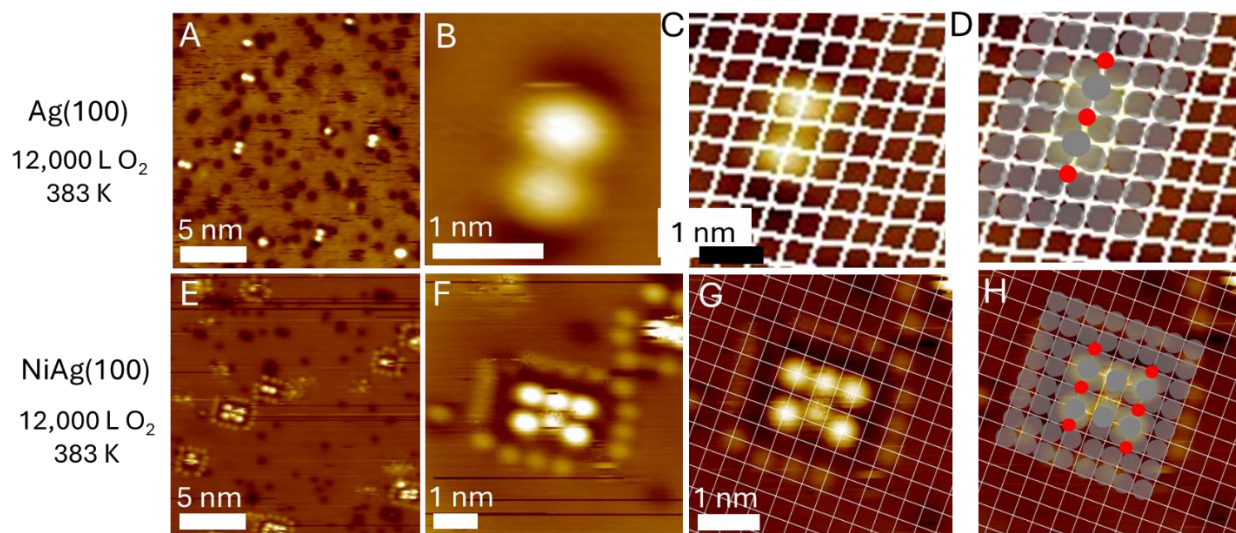


**Figure 5.S3.** STM of O in Ag reconstructions species. A-D) small patches of p(2x2) formed on Ag(100) exposed to 12,000 L O<sub>2</sub> at 383 K and cooled to 78 K. E-H) STM small patches of p(2x2) formed on 1% NiAg(100) exposed to 12,000 L O<sub>2</sub> at 383 K and cooled to 78 K. A) Ag(100) after a large O<sub>2</sub> dose. O adatoms, and reconstructed O present as p(2x2) monomers and dimers are visible. B) Zoomed image of p(2x2) dimer. C) p(2x2) dimer with atomic Ag(100) grid overlaid. D) Dimer with atoms overlaid. The Ag(100) surface matrix is shown transparently. Ejected Ag atoms are shown above as well as O atoms. This structure is consistent with the p(2x2) reconstruction observed in literature.<sup>28,29</sup> The ejected Ag atoms are in four-fold hollow sites in line with the oxygen atoms. E) Representative image of NiAg(100) after a large O<sub>2</sub> dose. Atomic O adatoms, NiO<sub>2</sub> sites and reconstructed O, in the form of p(2x2) patches, are present. F)

Zoomed image of p(2x2) patch. The smaller protrusion features surrounding the reconstruction are hypothesized to be Ag<sub>2</sub>O.<sup>30</sup> G) p(2x2) patch with atomic Ag(100) grid overlaid. H) p(2x2) reconstruction overlaid. The Ag(100) surface matrix is shown transparently. Ejected Ag atoms are depicted and the location of oxygen atoms in the reconstruction is overlaid. This structure is consistent with the p(2x2) reconstruction observed in literature with some defects present.<sup>28,29</sup> The middle Ag atoms appear to be bound in four-fold hollow sites. These ejected Ag atoms were originally part of the Ag islands formed during alloying. All images were taken at 78 K and scale bars are included. Typical imaging conditions were 100 mV 1 nA.

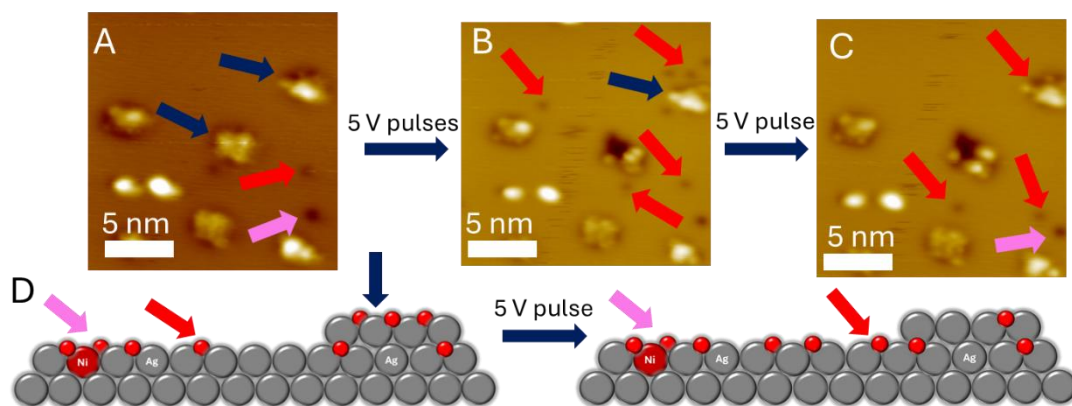


**Figure 5.S4.** Voltage pulse experiments on oxide patches. Voltage pulse experiments were used to gain insight into the makeup of the semi-ordered Ag oxide patches. A) STM image of NiAg(100) surface after exposure to 1000 L O<sub>2</sub> at 300 K. Semi order Ag oxide patches are present as well as atomic O (red arrow) and NiO<sub>2</sub> (pink arrow). The location of two 5 V pulses performed on semi-ordered Ag oxide patches are shown with blue arrows. B) The same area as A imaged after the voltage pulses. More O atoms are present because they have been ejected from the Ag islands, and the Ag islands appearance has changed. The location of an additional 5 V pulse is also shown. C) Same area imaged after the additional voltage pulse. The O adatoms have

moved around and the Ag oxide island has altered further. All images were taken at 78 K and scale bars are included. The imaging conditions were 100 mV 300 pA for the entire sequence. D) Scheme of voltage sequence on NiAg(100) with species and pulses labeled.

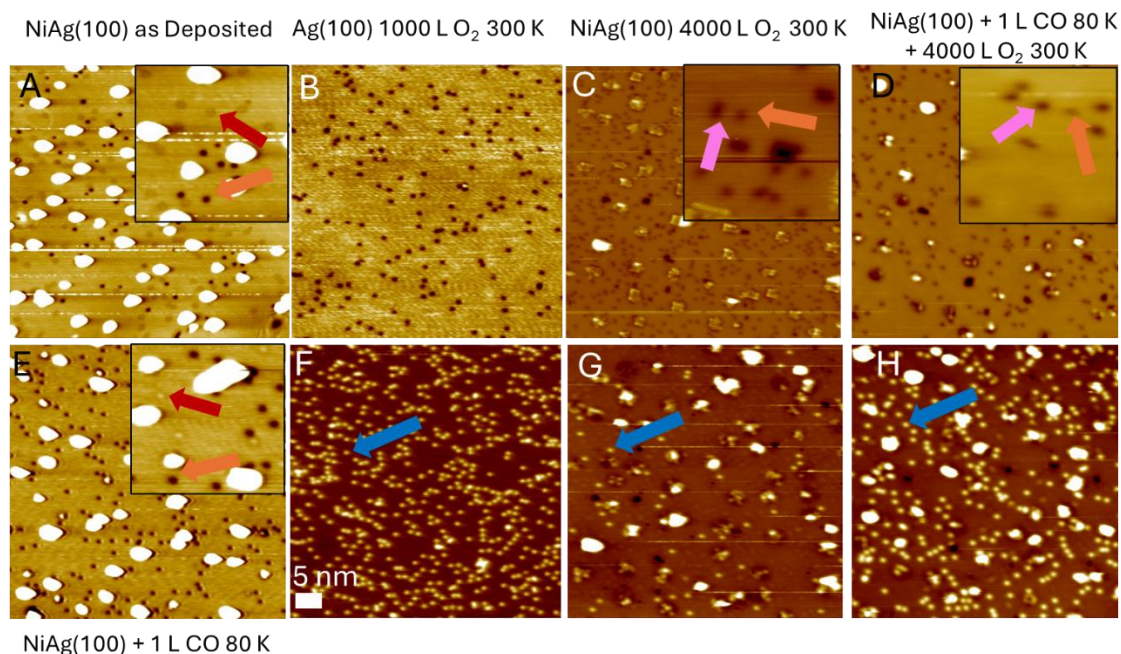


**Figure 5.S5.** Effect of CO-Corking on OH formation. A) STM image of NiAg(100) as deposited. Ag islands, Bare Ni atoms (red arrow, inset), and CO-bound Ni atoms (orange arrow, inset) are present. Imaging conditions were 100 mV 1 nA. B) STM image of Ag(100) after exposure to 1000 L O<sub>2</sub> at 300 K. O Adatoms are present. C) STM image of NiAg(100) after exposure to 4000 L O<sub>2</sub> at 300 K. O adatoms, NiO<sub>2</sub> (pink arrow, inset), CO-bound Ni (Orange arrow, inset) and semi-oxidized Ag islands are present. D) STM image of NiAg(100) + 1 L CO 80 K + 4000 L O<sub>2</sub> 300 K. The same features are present under these conditions as D, but there are fewer O adatoms present (see inset). E) STM image of NiAg(100) + 1 L CO dosed at 80 K. Ag islands, Bare Ni atoms (red arrow, inset), and CO-bound Ni atoms (orange arrow, inset) are present. The number of bare Ni atoms is decreased significantly. F) Same area as B at 3 V scanning conditions. OH groups (blue arrows) are present. G) Same area as C at 3 V conditions.

OH groups and Ag islands are visible. H) Same area as B at 3 V under imaging conditions. OH groups and Ag islands are visible. The coverage of OH groups is visibly higher than NiAg without pre-dosed CO. Thus, we hypothesize that CO prevents Ni atoms from binding O<sub>2</sub>, which causes O<sub>2</sub> to react with the Ag(100) surface; populating the surface with O adatoms. O adatoms are more reactive toward OH than strongly bound NiO<sub>2</sub>; leading to higher OH production. All images were taken at 78 K, and all images are 50 nm<sup>2</sup> excluding insets. A scale bar is included in F. Imaging conditions were 3 V 500 pA for OH images and 100 mV 1 nA for O images.

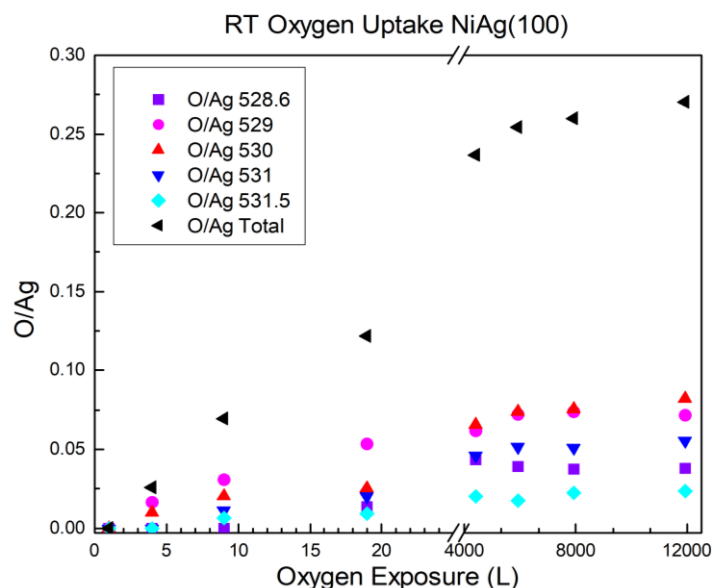


**Figure 5.S6.** XPS-Derived 300 K O<sub>2</sub> uptake on NiAg(100). Surface coverage of O species during 300 K O<sub>2</sub> uptake on 8% NiAg(100) as shown in Figure 3. After the NiO peak at 529 eV saturates (pink), the predominant species formed are more atomic oxygen adatoms (red) and OH groups (blue) as well as oxidized Ag islands (purple). O coverages were determined as described in the XPS Experimental Methods.

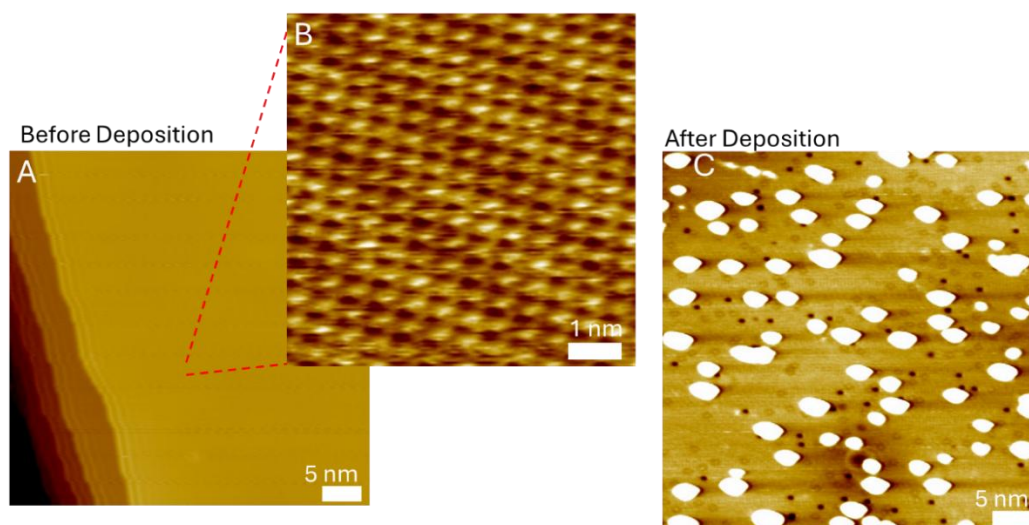


**Figure 5.S7.** The Ag(100) surface before and after Ni deposition. A) Bare Ag(100) after cleaning. B) Atomic resolution image of the Ag(100) lattice. Imaging conditions 10 mV 1 nA. C) Ag(100) after deposition of ~1% Ni at 300 K. All images were taken at 78 K and scale bars are included. For typical imaging conditions, 300 pA and 300 mV were used.

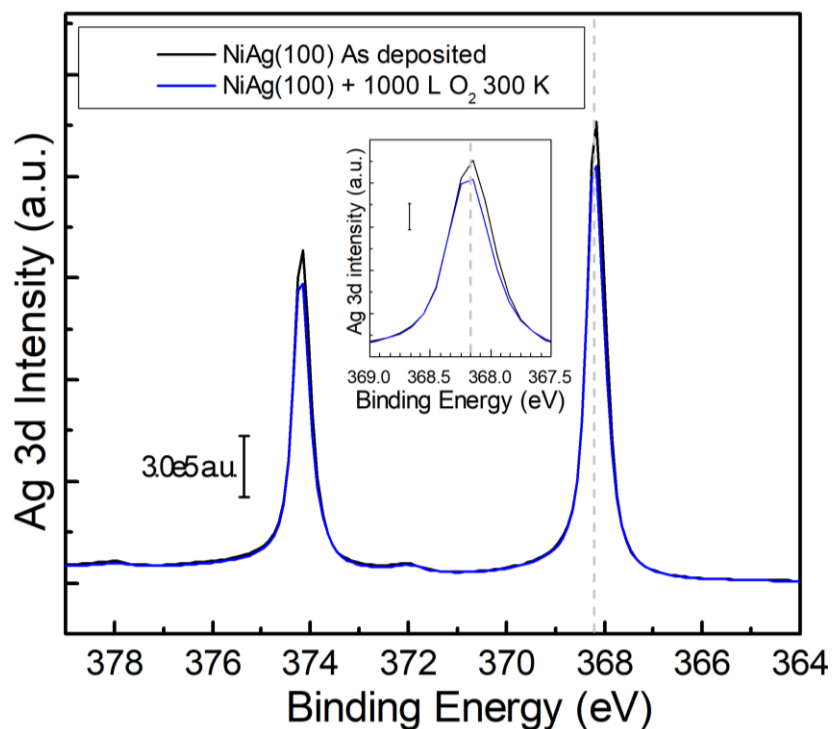


**Figure 5.S8.** Ag 3d XPS taken at 760 eV before (black trace) and after (blue trace) 12,000 L O<sub>2</sub> exposure on NiAg(100). The Ag 3d 5/2 peak starts as metallic at 368.2 eV.<sup>4,23</sup> Upon high O<sub>2</sub> exposure in UHV, the Ag 3d 5/2 peak remains at 368.2 eV, and the shape of the spectrum remains the same as well. The slight decrease in signal is due to an increase in chamber pressure caused by consecutive large O<sub>2</sub> doses. The formation of oxide patches observed in O1s XPS is not detectable in the Ag 3d spectra due to the large Ag signal.

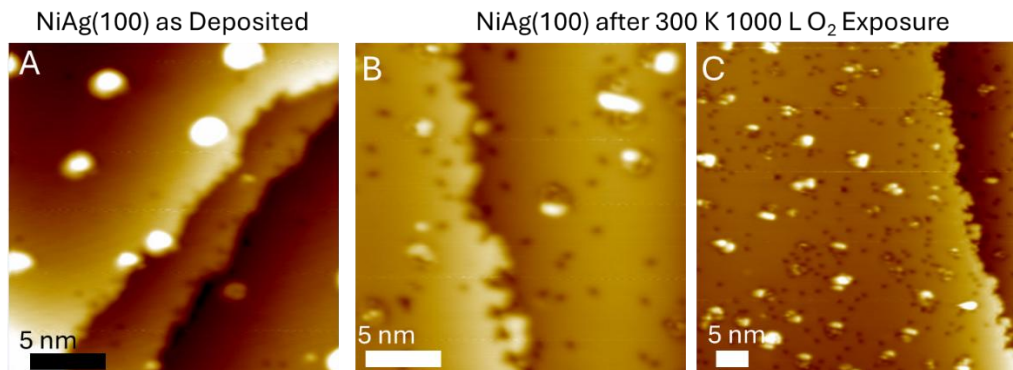


**Figure 5.S9.** STM Comparison of step edges on NiAg(100) before and after O<sub>2</sub> exposure. A) Step edge of Ag(100) after 1% Ni deposition at 300 K. Ejected Ag islands only form above the step edges, and Ni is present as dispersed bare and CO-bound sites. No brims or step reconstructions are present. B) Step edge of NiAg(100) after exposure to 1000 L O<sub>2</sub> at 300 K. The step edge appears more corrugated after O<sub>2</sub> exposure, likely due to the beginning of step oxidation. No brims are observed on the step edge. C) Zoomed out image of the area in B. Imaging conditions All images were taken at 78 K and scale bars are included. Typical imaging conditions were 300 mV and 300 pA.

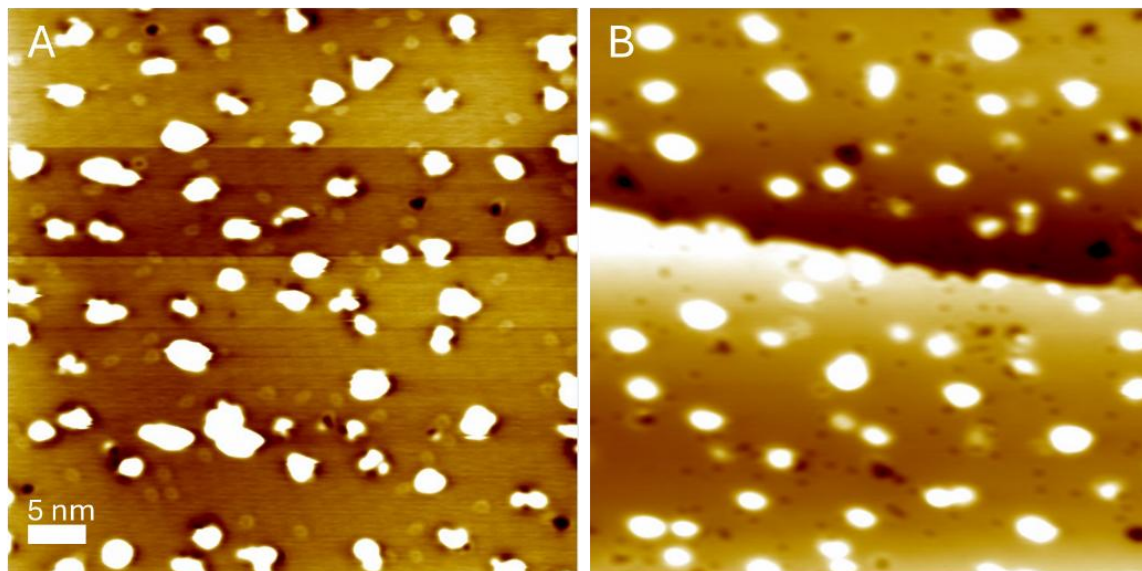


**Figure 5.S10.** Further evidence of O-Ni-O site formation with high-voltage STM. A) 2 V STM Image of 1000 L O<sub>2</sub> on NiAg(100). Imaging conditions were 3 V 300 pA. The two opposite orientations of the NiO<sub>2</sub> sites are more clear at this voltage. Oxygen adatoms are not visible at this voltage. B) 5 V STM Image of a step edge on NiAg(100) after O<sub>2</sub> exposure. Imaging conditions were 5 V, 300 pA. At 5 V, the Ni sites appear symmetric at this voltage, as the oxygen atoms bound to Ni cannot be imaged effectively. At higher voltage, oxidized islands appear as depressions, while metallic Ag islands remain protrusions. Both images were taken at 78 K, and a scale bar is included in A.

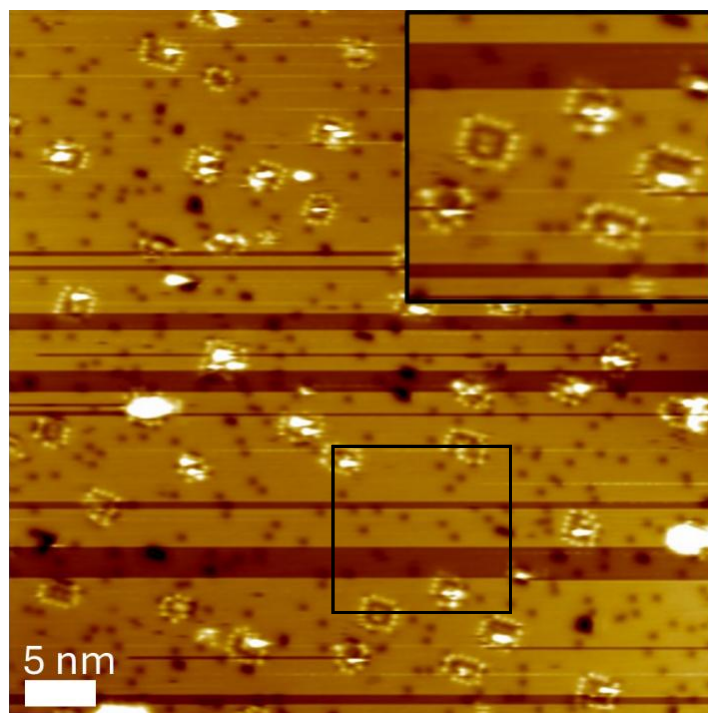


**Figure 5.S11.** Additional STM of O in reconstructions. 4000 L O<sub>2</sub> 383 K dosed on NiAg(100). Under these tip and imaging conditions, the borders of Ag oxide are more clearly visible while the reconstructed oxygen is less distinct. Imaging conditions 500 mV 500 pA. Oxygen adatoms, NiO<sub>2</sub> and unreacted Ag islands are also present. Some Ag islands appear to be semi-metallic and semi-oxidized Taken at 78 K. A scale bar is included in the bottom left. Inset is 10 nm by 10 nm and shows a zoomed in version (black boxes) of this surface.

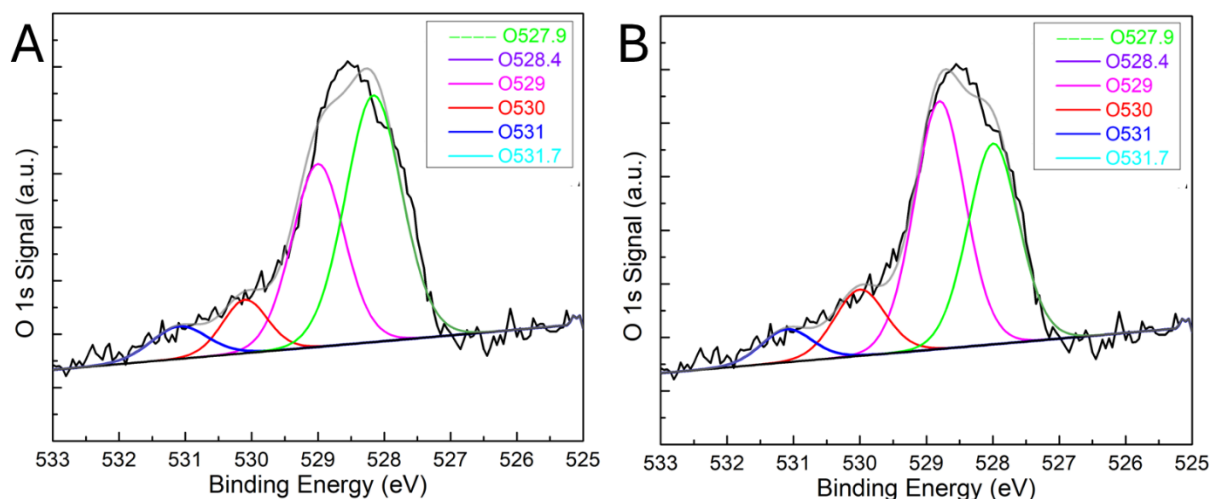


**Figure 5.S12.** Alternative O 1s peak fitting schemes for 12,000 L O<sub>2</sub> exposure on NiAg(100) at 383 K. A Shows the removal of the 528.4 peak and subsequent widening of the FWHM (to 1.0) of the other 4 peaks. The envelope no longer correctly represents the experimental peak shape. B shows four peaks as well with wider FWHMs, but the 529 eV peak was fit at a lower binding energy. The envelope no longer correctly represents the experimental peak shape in this case too.

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## Chapter 6.

# Structure and Behavior of Oxametallacycle Ethylene Intermediates on Ag(100)

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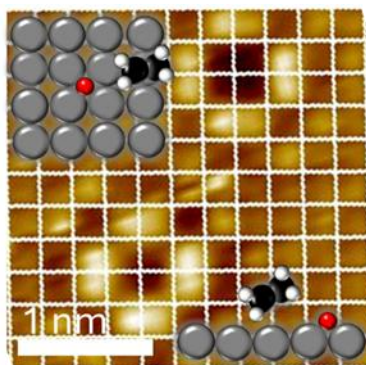
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### 6.1 Abstract

The study of the interactions between oxygen and Ag is key to understanding the catalytic reactivity of large scale partial oxidation reactions, particularly ethylene epoxidation. Decades of research have greatly enhanced our knowledge of ethylene epoxidation, but fundamental questions such as the selective active intermediate and oxygen species remain unanswered. Many potential ethylene epoxidation intermediates have been proposed, including various iterations of an oxametallacycle, described as a cyclic structure incorporating oxygen and ethylene bound to the Ag surface. Experimental evidence of oxametallacycles and their role in ethylene epoxidation is limited due to their unstable nature and the low sticking probability of oxygen on Ag. In this work, we used atomic-resolution scanning tunneling microscopy (STM) to form and characterize both O- and OH-based oxametallacycles at 78 K on an Ag(100) surface exposed to O<sub>2</sub> and ethylene. Using Density Functional Theory (DFT) calculations in combination with STM movies, we were able to elucidate the diffusion properties of the observed species and found that ethylene decreases the diffusion barrier of OH groups on Ag(100), while not affecting the O

diffusion barrier. These results provide valuable insight into the roles oxametallacycles and OH groups may play in selective epoxidation by clearly capturing their behavior at the atomic scale.



## 6.2 Introduction

Partial oxidation reactions on Ag are an important area of catalytic study due to the exclusive use of Ag-based catalysts in large-scale industrial processes, primarily ethylene epoxidation to form ethylene oxide (EO).<sup>1,2</sup> As the main byproduct of this reaction is CO<sub>2</sub> and selectivity (~90%) has not improved significantly in years, prolonged research on this system has strived to understand the interactions between Ag, O<sub>2</sub> and ethylene to improve selectivity for this reaction.<sup>3,4</sup> However, key questions remain such as the nature of the selective active intermediate and exact mechanism of selective ethylene epoxidation.<sup>4-7</sup>

Recently, it has been proposed that the formation of surface oxametallacycles between an O atom, ethylene molecule and Ag atom, or combination thereof, are key intermediates for selective ethylene epoxidation.<sup>8-14</sup> Oxametallacycles on Ag surfaces have been demonstrated and proposed in several different ethylene oxidation reaction pathways leading to different products, ranging from ethylene oxide, to combustion products to even  $\gamma$ -butyrolactone.<sup>14</sup> Multiple forms of an oxametallacycle have been identified through these studies, but experimental evidence of their formation and properties remain limited, especially without the use of ethylene substitutes.<sup>8,14-16</sup> Readily formed from water reacting with O adatoms on Ag surfaces, OH

groups are also relevant to oxidation reactions on Ag, and their role remains underexplored.<sup>17–21</sup> Ag(100) is a good choice of surface for clean ultra-high vacuum (UHV) study of the interactions of O<sub>2</sub>, water and ethylene on Ag due to its comparatively high sticking coefficient of O<sub>2</sub> and inherent selectivity toward EO than other facets.<sup>9,10,22–25</sup> Scanning tunneling microscopy (STM) is a powerful analytical tool that allows for atomic-scale imaging of complex catalytic systems, however, studies of ethylene and O<sub>2</sub> on Ag(100) are scarce compared to other facets.<sup>26–28</sup>

To better understand the formation and role of oxametallacycle intermediates in selective ethylene epoxidation, we used STM and density functional theory (DFT) calculations. In this work, we form and characterize both O-ethylene and OH-ethylene moieties at 78 K that exhibit behavior different than O adatoms and OH groups. We use 78 K STM movies to observe unique interactions between the different ethylene complexes under atomic-resolution and DFT calculations to determine the structure of the various species. These results provide exciting experimental atomic-scale evidence of multiple types of oxametallacycles and as well as insight into their role in ethylene oxidation. The different behavior of the OH-ethylene species compared to the O-ethylene species, and their interactions with one another suggest OH plays a role in ethylene oxide selectivity.

### 6.3 Results and Discussion

To examine the formation of oxametallacycle species on Ag(100) we used 78 K STM to first characterize the Ag(100) surface after exposure to O<sub>2</sub> (Figure 1). The clean Ag(100) sample was exposed to 1000 L (1 L = 1x10<sup>-6</sup> Torr,s) O<sub>2</sub> at 300 K, which led to O adatoms (red arrow) and OH groups (blue arrow) forming on the surface (1B). Water from the chamber background reacts exothermically with adsorbed O atoms to form OH at 300 K.<sup>29–31</sup> O adatoms are well characterized on Ag(100) in STM,<sup>32–34</sup> and are known to bind in four-fold hollow sites on

Ag(100).<sup>3,35,36</sup> Ethylene (3 L) was dosed onto the oxygen-covered Ag(100) surface while it remained held at 78 K. The only species present after ethylene exposure were O-ethylene (pink arrow) and OH-ethylene (cyan arrow) moieties (Figure 1C). No O or OH features remained following the ethylene dose. The two different complexes in 1C shared the same cross-shape with four distinct lobes surrounding a darker square center, but their apparent heights in STM (depicted as relative brightness) differed.

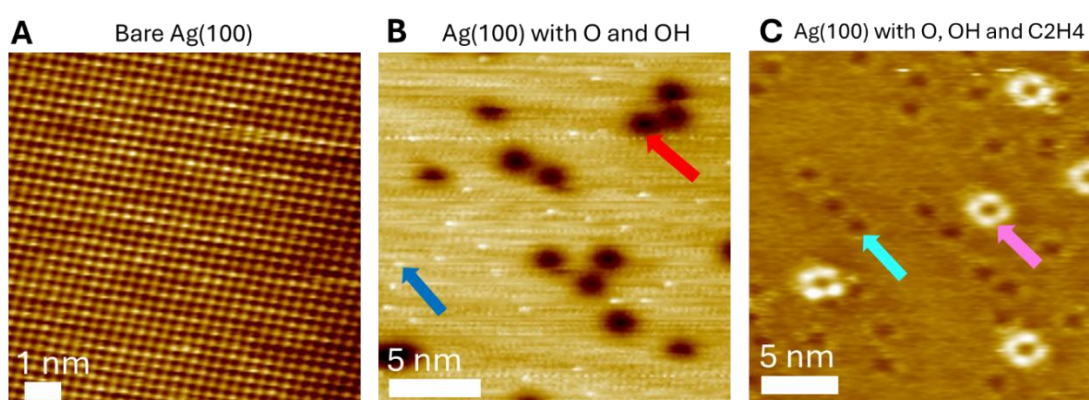


**Figure 6.1.** STM Overview of Ag(100) before and after exposure to O<sub>2</sub> and ethylene (C<sub>2</sub>H<sub>4</sub>). A) Atomic resolution STM of the bare Ag(100) surface. B) STM of Ag(100) after 1000 L O<sub>2</sub> exposure at 300 K. Depressions are O adatoms (red arrow) and small bright protrusions are OH groups (blue arrow). C) STM image of Ag(100) after oxygen exposure + 3 L C<sub>2</sub>H<sub>4</sub> dosed at 78 K. Cross features are O-ethylene (pink arrow) and OH-ethylene (cyan arrow) moieties. The OH-based features appear fainter than their O-based counterparts in STM. Typical Imaging conditions were 10 mV 1 nA for atomic resolution and 100 mV 500 pA for standard resolution. STM performed at 78 K.

To determine the nature of these oxygen-ethylene features, we performed DFT calculations of O and ethylene co-adsorption on Ag(100) (Figure 2). These calculations found that ethylene bound to Ag is stabilized (-0.06 eV) by an O adatom bound to a nearby four-fold

hollow. A second ethylene molecule interacting with an O atom is not stabilized, so each O atom prefers to bind a single ethylene molecule. The Ag(100) lattice was overlaid on STM images to confirm that the structure predicted by DFT, and the spacing between the O atom in the center of the feature and ethylene molecule in STM match and are consistent with an ethylene atom interacting with an O atom in a four-fold hollow. In addition to the O-ethylene spacing, the orientation of ethylene with respect to the O adatom is consistent with DFT as well. The combination of the symmetric four-lobes, the uniform appearance across the surface, and the ethylene binding orientation predicted with DFT calculations, suggest that the cross feature observed in STM appears as such due to a time-resolved effect caused by fast rotation of a single ethylene molecule around an O atom (Figure 2E-G) or OH group.

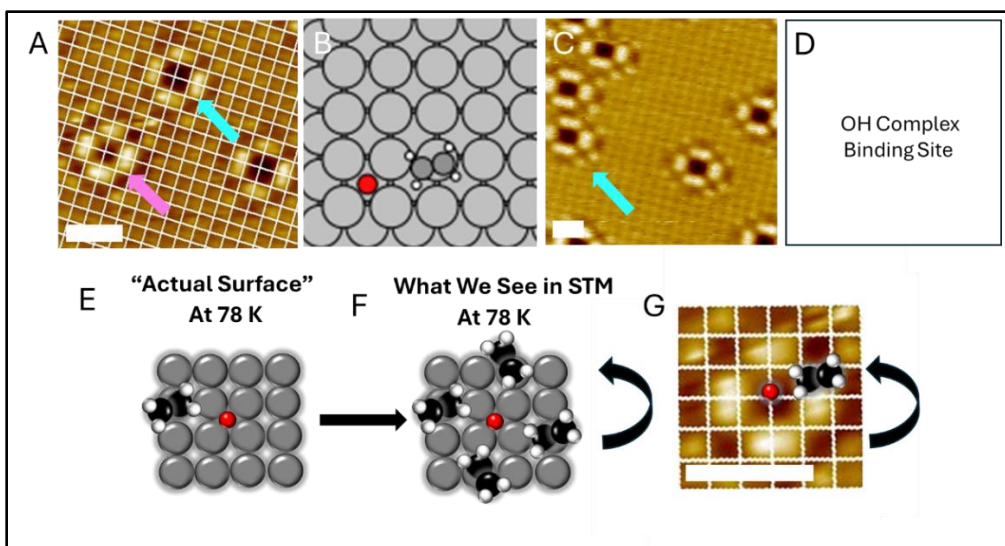


**Figure 6.2.** STM and DFT characterization of O- and OH-ethylene moieties. A) Atomic resolution STM image of O- (bright, pink arrow) and OH-ethylene (dimmer with a darker center, cyan arrow) species with Ag(100) grid showing four-fold hollow sites overlaid. The bright lobes on the O moiety are a single ethylene molecule circling the O adatom (dark depression) in the center of the site. B) DFT-calculated preferred O and ethylene binding orientation. The O adatom binds in a four-fold hollow site and stabilizes the nearby ethylene molecule by 0.06 eV compared to bare Ag. Other binding structures are included in the supporting information (Figure S1). C) Atomic resolution STM of OH-ethylene moieties. The OH groups appear as dark depressions in four-fold hollows in the center of the revolving ethylene molecule. D) \*\*DFT of the preferred binding orientation of OH and ethylene. E-F) Schematic demonstrating the true stoichiometry of the O-ethylene moiety and why we observe it as a cross feature in STM. G) Atomic-resolution STM of a single O-ethylene moiety with an O atom and ethylene molecules. Imaging conditions were 100 mV 1 nA. for each image. All scale bars are 1 nm in length, and all STM was performed at 78 K.

To examine the interactions of these O-ethylene and OH-ethylene moieties we recorded STM movies to track their behavior over time at 78 K (Figure 3). First, we monitored O and OH on Ag(100) after O<sub>2</sub> exposure (A-G). O atoms (A-C) were present as both permanently stationary atoms (red circle) and atoms that undergo tip-induced diffusion during scanning (blue circles). OH groups cannot be imaged consistently below tunneling biases of 2.5 V. Therefore, we used 3 V scanning conditions, however the O adatoms do not appear at 3 V (D-G). OH groups do not undergo tip induced diffusion, unlike O atoms, but they are occasionally buffeted by the tip during scanning (orange circle). Upon the introduction of ethylene, the two types of ethylene moieties, behaved differently than the O species on their own. The O-ethylene species (pink circles) remained stationary, while the OH-ethylene moiety (blue circles) underwent tip induced diffusion. These observations offered an interesting contrast to the diffusion behavior of O and OH where OH remains stationary, while the majority of O atoms present underwent diffusion. Also of note is that the surface coverage of O-ethylene moieties is much lower than the initial coverage of O atoms (Figure S2).

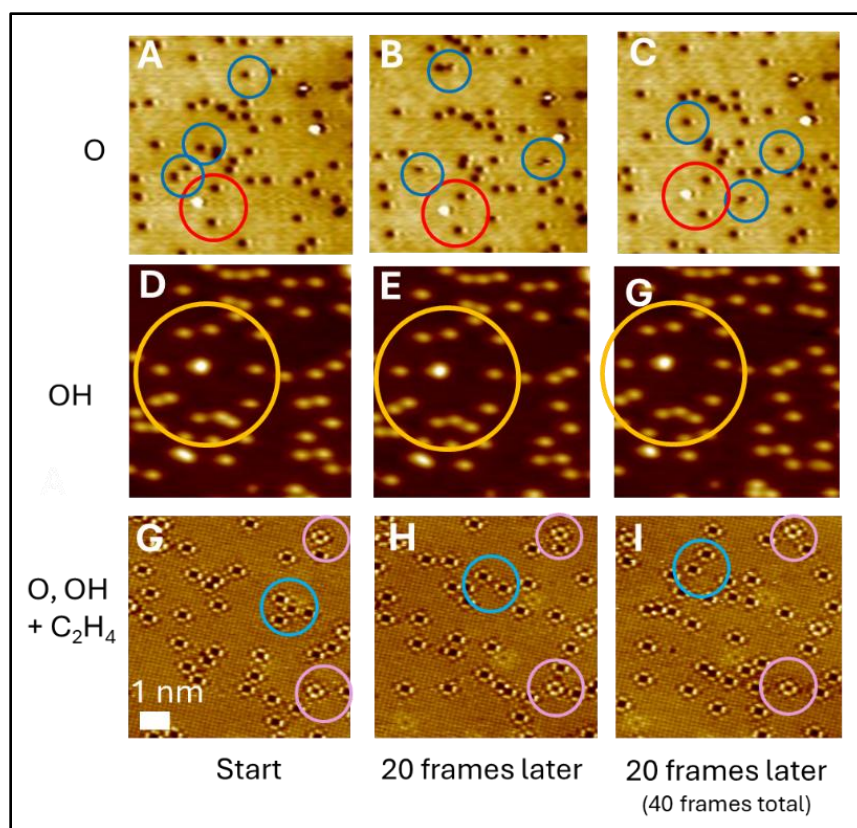


**Figure 6.3.** STM observed movement of O, OH, and their respective ethylene moieties at 78 K. A-C) STM images of 1.1% O on Ag(100). Each image is 20 frames apart (20 minutes of scanning time), stationary O adatoms are circled (red). Most O atoms (blue circles) undergo tip-induced diffusion. All O atoms appear as depressions. Imaging conditions were 1 V, 1 nA. D-F) STM images of 1.9% OH on the same surface. A 3 V tunneling bias was used to image OH exclusively, as O adatoms do not appear under these conditions. The tunneling current was 1 nA. The circle shows several OH groups, which do not diffuse, but some are moved slightly by the tip as seen in the transition from D to E. G-I) STM of 3 L ethylene dosed at 78 K onto the oxidized Ag(100) surface. Bright cross features (red circles) do not move and are made of four lobes and a dark square center. Dark cross features (blue circles) do move under the tip. Imaging conditions were 100 mV, 1 nA, and a scale bar is included in. Full movies of each set of images are included with the supporting information. STM was performed at 78 K.

We used DFT to determine the diffusion barriers of these species and provide more insight into their behavior (Figure 4). The diffusion barrier for O atoms on Ag(100) was found to be 0.72 eV from a four-fold hollow to a bridge site. As this is a relatively high barrier, O atoms would not be expected to diffuse at 78 K, so we believe the diffusion we observe in STM is tip-induced. OH groups have an even higher diffusion barrier on Ag(100), which is consistent with their stationary appearance in STM at 78 K. The effect of ethylene's interaction with O and OH on their respective diffusion barriers is a complex calculation for DFT to perform, so we used our experimentally derived rates from STM to shed insight. The O-ethylene moieties were not observed to move, similar to the minority O atom species (Figure 3, darker feature), so ethylene did not appear to affect the O diffusion barrier. Conversely, the OH-ethylene moiety was observed diffusing around the surface, while the OH groups remained stationary. This change in behavior suggests that ethylene lowered the OH diffusion barrier on Ag(100).

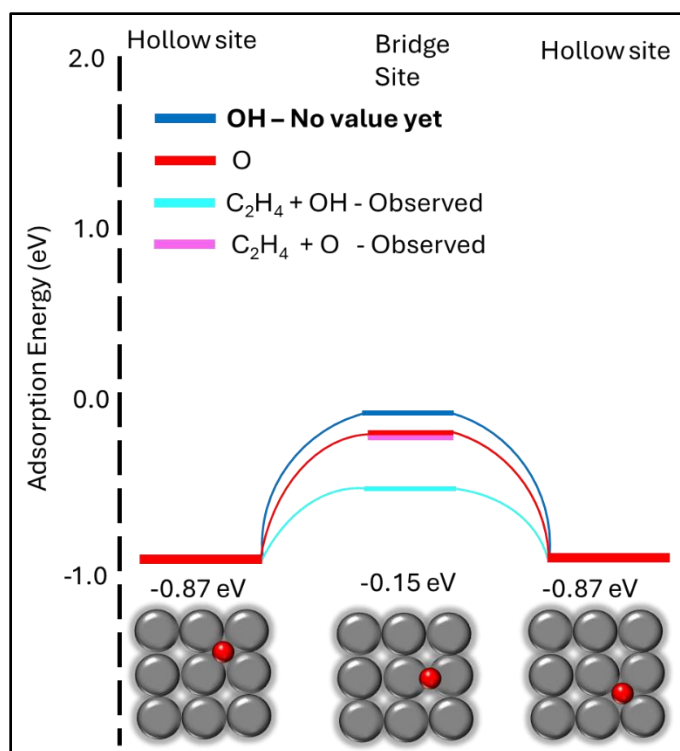


**Figure 6.4.** Diffusion barriers of observed species. \*\*\*Waiting for data.

Ethylene's effect on the diffusion of OH groups led to unique interactions between the different ethylene moieties, which led us to investigate further using atomic-resolution STM at 78 K (Figure 5). Two notable actions were consistently observed: OH-ethylene “dimer” formation and OH-ethylene – O-ethylene “dimer” formation. During the OH “dimer” interaction (A-D), two OH-ethylene moieties (red circles) diffused close to one another (A), formed an intermediate dimer species with two overlapping ethylene lobes (B), underwent a fast diffusion action to another area on the surface (C), and reformed the intermediate species (D). These results were consistent with ethylene lowering the diffusion barrier of OH on Ag(100), as the overlap of two ethylene molecules between two OH-ethylene moieties induced a large diffusion action across the surface. No monomer OH-ethylene moieties underwent similar movements.

Through STM, we also found that the OH-ethylene moieties interact differently with O-ethylene moieties (Figure 5, E-G). When an OH-ethylene moiety diffused close to an O-stabilized ethylene site, one ethylene lobe overlapped between the two species (A). This overlap induced a change in appearance of the O-ethylene moiety, where the lobes now only occupied a single Ag atom site each rather than two (F). The OH-ethylene moiety changed orientation by 90° with regard to the O adatom, and the O-ethylene moiety's appearance returned to its initial state. This interaction is also consistent with ethylene lowering the diffusion barrier of OH, as the OH-ethylene moiety does undergo a fast diffusion movement when it overlaps with another ethylene molecule. However, the ethylene molecule is bound stronger to O than OH (Figure 2), so only the OH-ethylene monomer moves, rather than both species. These actions occur repeatedly during prolonged scanning of the surface under these conditions (see Supporting Information for STM movies). No such interaction between two O-ethylene moieties was observed due to their low surface coverage and stationary nature. The formation of these “dimer” intermediates between O, OH and two ethylene molecules is also notable due to oxametallacycles containing multiple O atoms or ethylene molecules have been proposed.<sup>14,15</sup>

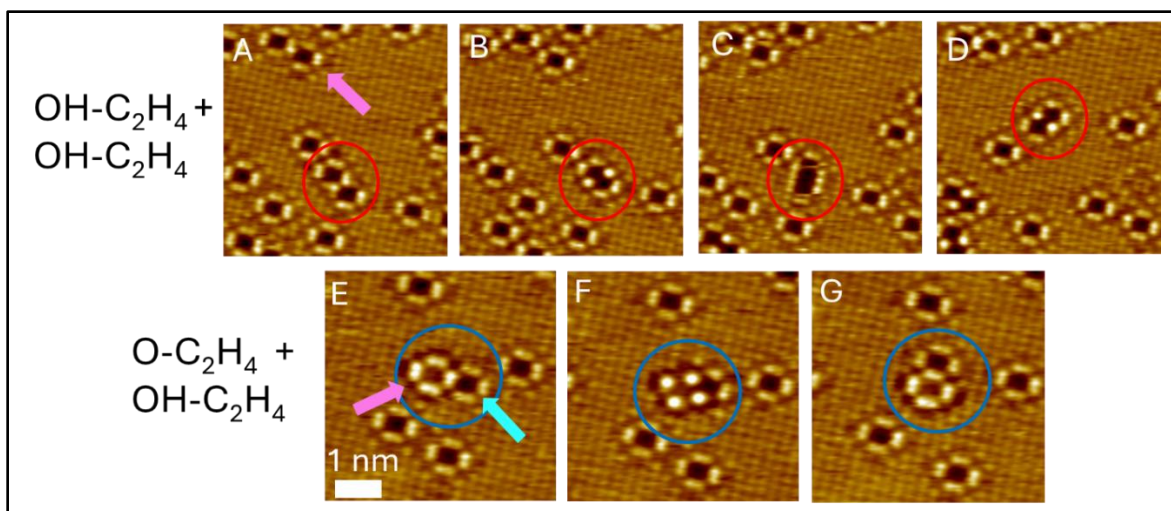


**Figure 6.5.** STM of unique interactions of O- and OH-ethylene moieties. A-D) STM images of movement sequence for OH-ethylene moieties interacting on Ag(100). Each sequential image was taken two frames later. All species shown are OH-ethylene moieties. A and B show two monomer moieties (red circle) diffusing close to one another and forming an intermediate dimer complex (B). Once this dimer formed, it performed a fast jump across the surface (C) and then separated back into monomers (D). E-G) STM images of movement sequence for O-ethylene + OH-ethylene moiety interaction on Ag(100). E) An O-ethylene moiety (brighter feature, pink arrow) begins to interact with an OH-ethylene moiety (darker feature, cyan arrow). There is overlap of one lobe of each feature, and each lobe occupies two Ag atoms. F) The proximity with the OH moiety causes a shift in appearance of the O-ethylene moiety. The lobes of the O complex are now brighter and only occupy one silver atom in the lattice. Two lobes are overlapping between the two complexes, and their centers are now two atoms away. G) The two complexes separate again. The OH complex's position in relation to the O complex is now  $90^\circ$  from its position in E with one lobe still overlapping. There is no interaction between two O-ethylene moieties. Imaging conditions were 100 mV 1 nA for each sequence. All STM performed at 78 K. A scale bar is shown in E, and all images are the same size.

## 6.4 Conclusions

Through atomic-resolution STM and DFT calculations we identified multiple ethylene oxidation intermediates in the form of O- and OH-ethylene oxametallacycles. These are the first direct images of O-ethylene intermediates on Ag(100) to the best of our knowledge. We demonstrated that ethylene is stabilized by both O atoms and OH groups on the Ag(100) surface through both DFT calculations and STM imaging. We also found that ethylene appears to lower the diffusion barrier of OH, leading to increased surface interactions. These interactions include the formation of intermediate “dimer” species, which could be a notable result in the broader discussion on selective ethylene epoxidation. The ubiquity of OH on the Ag(100) surface after O<sub>2</sub> exposure and its unique interactions with ethylene shown in this work, highlight the importance of considering OH in proposed catalytic selectivity models for ethylene epoxidation on O-Ag systems.

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# Chapter 6.1

## Supporting Information

### 6.6.1 Experimental Methods

78 K STM experiments were conducted in an ultra-high vacuum (UHV) chamber with a base pressure of  $1 \times 10^{-11}$  mbar using a low temperature (LT)-STM (Omicron Nanotechnology). A Ag(100) single crystal (Princeton Scientific 99.999% purity <1 degree polish) was used for experiments. Sample cleaning was performed in a connected preparation chamber with a base pressure of  $< 5 \times 10^{-10}$  mbar. Repeated cycles of Ar<sup>+</sup> (Airgas 99.99%) ion sputtering (1 keV 10-20  $\mu$ A) and annealing to 825 K were used to clean the Ag(100) crystals. STM images were obtained at 78 K after cryogenically cooling the STM stage. Oxygen (99.9% Middlesex gases) ethylene (99.9% Sigma) were dosed through high precision leak valves. Coverages were calculated as an average from ~20 images for each coverage through manual counting of features using an STM image processor (SPIP). Coverages are based on the number of specific features per image divided by the total number of Ag surface atoms in each image. Error bars on coverage were one standard deviation.

## 6.6.2 Supplementary Figures

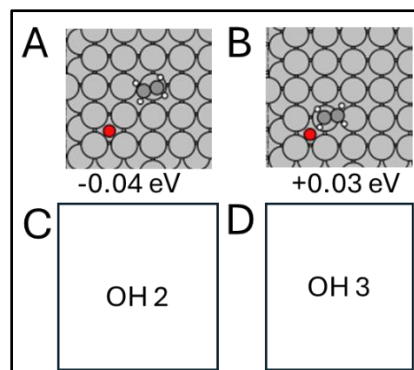


**Figure 6.S1.** DFT-calculated alternate binding orientations for ethylene and O species on Ag(100). A-B) Alternative interactions between an O atom in a four-fold hollow and a nearby ethylene molecule and the associated decrease or increase in stability of the ethylene molecule. C-D) Alternative interactions between an OH group in a four-fold hollow and an ethylene molecule, and the associated decrease or increase in stability of the nearby ethylene molecule.\*\*\* Waiting for some data for this from collaborators.

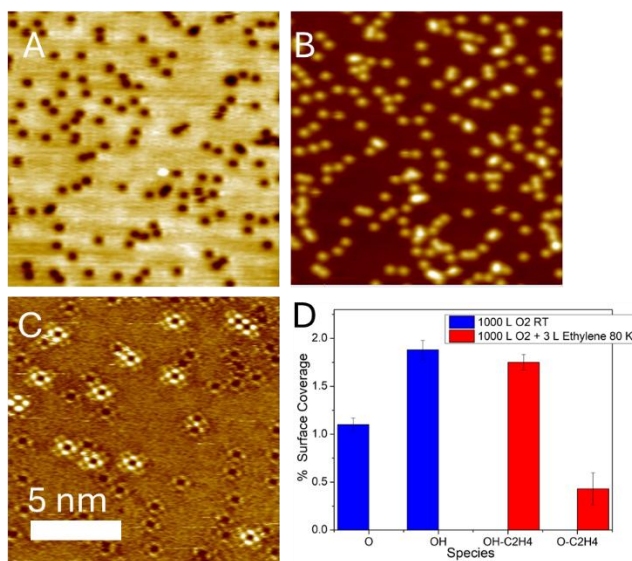


**Figure 6.S2.** Surface coverage evidence for species assignments. A) STM image of Ag(100) after exposure to 1000 L O<sub>2</sub> at 300 K. O adatoms are present. Scanning conditions 1 V 1 nA. B) same area as A scanned at 3 V 1 nA, OH atoms are present. C) STM image of the sample from A and B after a 3 L ethylene dose performed at 78 K. OH- (darker) and O-ethylene moieties (brighter) are present. Scanning conditions 100 mV 1 500 pA. D) Bar graph comparing surface coverages of the four features observed in these experiments. The correlation between the coverage of the O-based features with the ethylene-based features helps us to confidently assign the ethylene moieties to O and OH. All STM performed at 78 K.

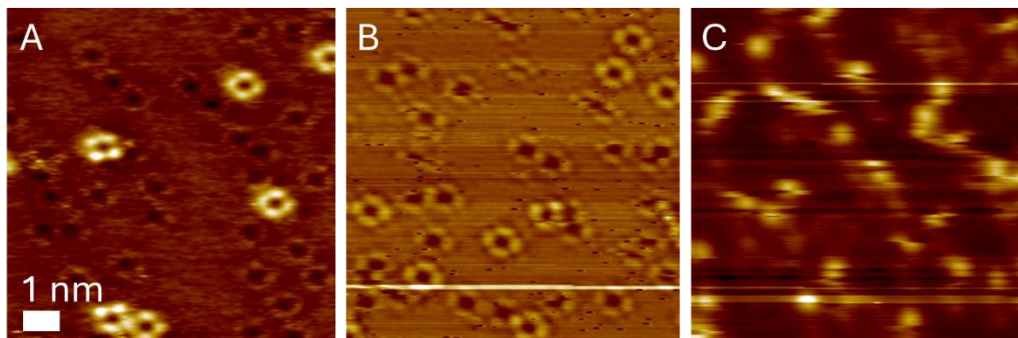


**Figure 6.S3.** High-voltage scanning with ethylene on the surface. A) STM image of the Ag(100) surface after exposure to 1000 L O<sub>2</sub> at 300 K and 3 L ethylene at 78 K. The ethylene-oxygen species were distinct and visible under these scanning conditions (1 nA, 100 mV). B) 1 V 1 nA scan of a different area of the same Ag(100) sample. The two types of cross features were harder to distinguish at this voltage. C) STM image of the same area as B under 3 V 1 nA conditions. At 3 V, it was difficult to resolve any features. Thus, we avoided high voltage scanning for this system. All STM scanning was done at 78 K, and a scale bar is shown in A for all three images.

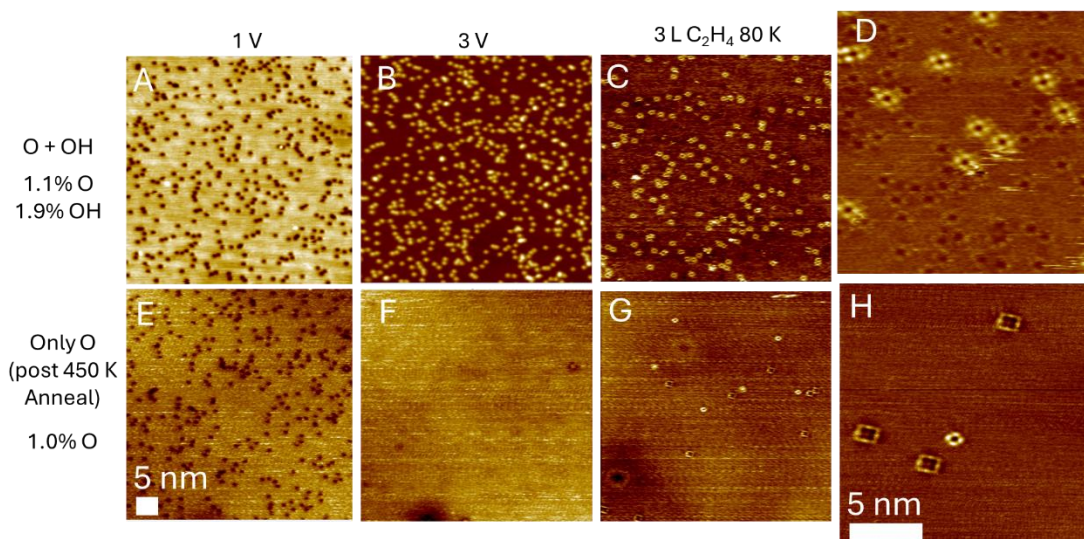


**Figure 6.S4.** STM comparison of ethylene exposure with and without prior anneal. To further support the identity of the dark ethylene moiety, we performed a control experiment where the surface was annealed to 450 K post O<sub>2</sub> exposure (E-H). This anneal caused the OH groups to react, reform water and desorb, leaving only O adatoms on the Ag(100) surface. After ethylene exposure on the O-only surface, only bright cross features were formed (G, H). The lack of OH on the pre-ethylene surface and absence of darker cross features post ethylene exposure is consistent with the darker ethylene moieties being associated with OH and the brighter ones with O. All STM performed at 78 K. Typical imaging conditions were 100 mV 1 nA, a scale bar is shown in E for images A-C and E-G which are all the same size, and in H for D and H.

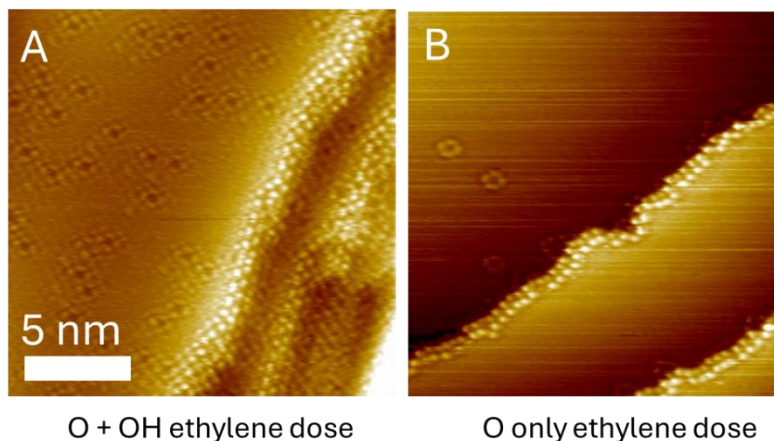


**Figure 6.S5.** STM Step edge comparison after ethylene exposure. A) Step edge on Ag(100) after exposure to 1000 L O<sub>2</sub> at 300 K and 3 L ethylene at 78 K. The ethylene sticks to the top and bottom of the step edge, but no O-features are found on the step edge. OH-ethylene moieties are visible on the terrace. B) Step edge on Ag(100) after 1000 L O<sub>2</sub> exposure at 300 K, anneal to 450 K, and subsequent 3 L ethylene dose at 78 K. The step edge itself looks the same as in A, coated in ethylene, but there are much fewer O-ethylene moieties on the terrace. This difference is due to the anneal removing all OH from the surface. Scanning conditions were 100 mV 500 pA, and a scale bar is shown. All STM performed at 78 K.

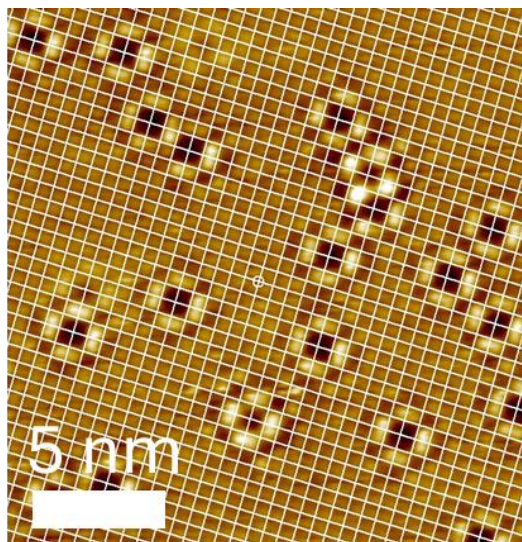


**Figure 6.S6.** Larger image of ethylene-covered O-Ag(100) surface with Ag(100) grid overlaid. Atomic-resolution 78 K STM image of Ag(100) exposed to 1000 L O<sub>2</sub> at 300 K and 3 L ethylene at 78 K. The dark center of each feature is an O atom or OH group in a four-fold hollow site and the four lobes surrounding each center is one ethylene molecule revolving around the O atom or OH group. The STM scan speed is lower than the rate at which the ethylene molecules move.

## Chapter 7.

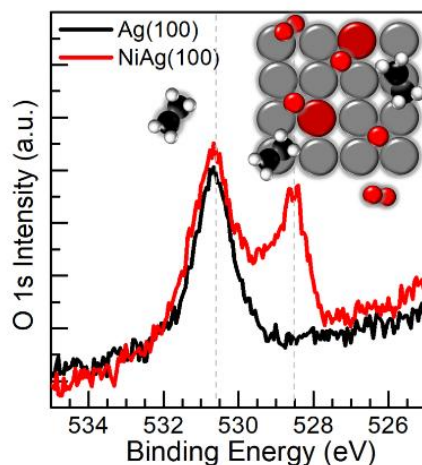
# Behavior of O and C Under Simulated Ethylene Epoxidation Conditions on the NiAg(100) SAA

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### 7.1 Abstract

The dependence of ethylene oxide, a valuable commodity chemical, on Ag-based catalysts, has consistently plagued the improvement of ethylene epoxidation. These catalysts suffer from a low inherent selectivity toward ethylene oxide and currently rely on Cl as a promoter to achieve viable selectivity. However, the toxicity of Cl as well as the large volume of

CO<sub>2</sub> continuously produced by this reaction, have motivated study into alternative promoters. Isolated Ni atoms in an Ag surface were recently reported as a promising new oxidation catalyst, demonstrating 25% higher selectivity than bare Ag without Cl. This result has inspired fundamental studies of NiAg SAAs to better understand the effect of Ni on O<sub>2</sub> speciation and ethylene selectivity on Ag. In this work, we used near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) to simulate epoxidation conditions for a NiAg(100) SAA and characterize the various surface species formed. We found that the Ni-doped surface is more resilient against carbon build up from ethylene and maintains a much higher surface coverage of oxygen than the bare Ag(100) surface. The insight into epoxidation on NiAg(100) provided by this study is crucial for a complete understanding of Ni's unique role in selective oxidation.

## 7.2 Introduction

Ethylene epoxidation is a large-scale industrial reaction essential for the production of a variety of consumer goods and other applications such as the sterilization of medical surfaces.<sup>1-5</sup> Ag-based catalysts are the sole means of production of ethylene oxide (EO) industrially, however they suffer from low intrinsic selectivity (~55%), and must rely on a series of promoters led by Cl, cofed as alkyl chlorides, to achieve sufficient selectivity (~90%).<sup>6-11</sup> The complex synergistic effects of Cl and the additional promoters such as cesium and rhenium makes understanding the selective reaction mechanism difficult, and the use of Cl raises environmental and safety concerns.<sup>10-14</sup> These factors have led to a pivot in research direction and a search for less toxic alternative promoters to achieve comparable or superior performance to Cl for selective ethylene epoxidation.<sup>1,9,12-20</sup>

Single-Atom Alloys (SAAs), consisting of isolated reactive dopant atoms alloyed into a dilute host metal, were initially explored for (de)hydrogenation reactions.<sup>21–24</sup> However, their ability to break traditional linear scaling relationships for fundamental reaction steps is promising for oxidation reactions, typically limited by O<sub>2</sub> activation.<sup>25–27</sup> Recently, it was reported that an NiAg SAA consisting of isolated Ni in Ag increased ethylene epoxidation selectivity by 25% toward ethylene oxide, the same selectivity boost provided by Cl.<sup>20</sup> The exciting discovery of Ni as a selective oxidation promoter in Ag was generally unexpected due to its absence in studies on alternative promoters despite years of industrial and academic research; possibly due to the very small concentrations it was selective at.<sup>20,28</sup> This motivates fundamental studies of the effect of Ni on oxygen speciation and ethylene reactivity on these dilute bimetallic alloys. The comparatively high sticking O<sub>2</sub> sticking coefficient ( $\sim 10^{-4}$ ),<sup>29</sup> and EO selectivity<sup>30–33</sup> of the Ag(100) facet compared to similar surfaces, make it ideal for studying these effects on model single crystals without requiring O<sub>2</sub> alternatives like NO<sub>2</sub> or O<sub>3</sub>, oxygen cracking, or the use of high-pressure setups which are susceptible to contamination.<sup>29,34</sup>

In this work, we use synchrotron near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) to characterize the NiAg(100) surface under simulated reaction conditions and compare it to Ag(100) to elucidate the effects of Ni on oxygen and ethylene and their interactions. The use of XPS allows us to bridge the pressure gap between ultra-high vacuum (UHV) conditions and industrially relevant pressures.<sup>35</sup> Through these experiments, we identify a variety of oxygen and carbon species formed under epoxidation conditions, and through a cross comparison of the bare and Ni-doped Ag(100) surfaces we find that NiAg(100) is a more robust system and resistant to carbon build up. The presence of Ni also increased the coverage and diversity of oxygen on the surface including the formation of an NiO<sub>x</sub> species. We also observed

that carbonate is the dominant O species present under these reaction conditions on both surfaces, and that the majority of the surface remains metallic on both systems as well. Together, these reaction studies provide fundamental understanding into the role of Ni in selective oxidation catalysis.

### 7.3 Results and Discussion

To investigate Ag(100) and NiAg(100) under epoxidation conditions, we first began by characterizing these surfaces under oxidative conditions using XPS (Figure 1). A clean Ag(100) sample held at 383 K was exposed to 12,000 Langmuir (L) ( $1 \text{ L} = 1 \times 10^{-6} \text{ Torr}\cdot\text{s}$ )  $\text{O}_2$ , which led to a small O peak forming at 528 eV (green trace) representing O atoms in an Ag reconstruction.<sup>36–38</sup> This assignment is supported by the lower binding energy peak in O 1s spectra (commonly referred to as nucleophilic oxygen), being well characterized in the literature, and although exact structures differ, most studies agree that the 528 eV peak is produced by O atoms in Ag surface reconstructions.<sup>12,36,37</sup>

Upon increasing the oxygen exposure to the mTorr range, the 528 eV peak increased dramatically, and four additional peaks formed as well. The identity of these peaks was determined by cross referencing previous studies under similar conditions on Ag surface, and through careful analysis of each peak and the environment in which it formed. Beginning from the lowest binding energy peak, the 529.3 eV peak (navy trace) was assigned to Ag oxide based on its correlation with both AgO and Ag<sub>2</sub>O in literature,<sup>39,40</sup> as it is present only at high pressure, and its appearance coincided with an Ag oxide shoulder peak in the Ag 3d spectra. However, we were unable to determine its exact identity, so we will refer to this peak as Ag<sub>x</sub>O. In O 1s spectra,

530 eV peaks are consistently assigned as electrophilic oxygen.<sup>37,41–43</sup> Debate remains over whether or not electrophilic oxygen is made up of O adatoms, or a different species.<sup>12,41,44</sup> However, similarities to previous STM and XPS studies on Ag(100) and our own experiments strongly support the 530 eV peak we observe (red trace) as O adatoms.<sup>42,45–47</sup> Specifically, the a 530.0 eV peak observed on Ag(100) exposed to O<sub>2</sub> in XPS was directly correlated with O adatoms observed in STM under the same conditions.<sup>42,45–47</sup>

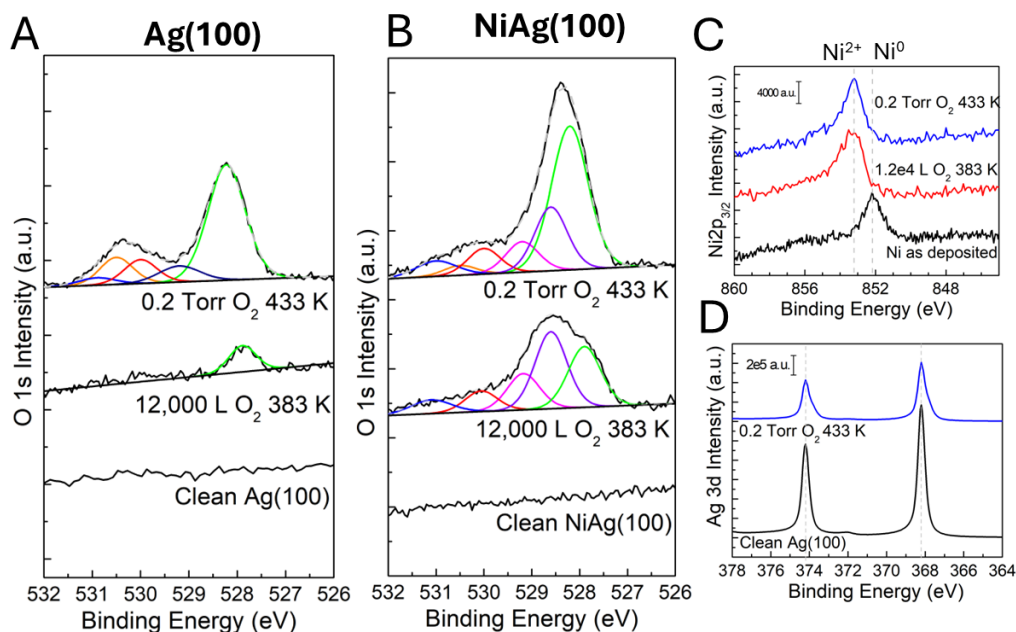


**Figure 7.1.** XPS overview of O<sub>2</sub> exposure on Ag(100) and NiAg(100). A-B) O 1s spectra showing Ag(100) and ~7% NiAg(100) after exposure to O<sub>2</sub> in UHV at 383 K and in sitting in 200 mTorr of O<sub>2</sub> at 433 K. On Ag(100) five distinct peaks were identified under these conditions at: 528 eV (green), 529.3 eV (navy), 530 eV (red), 530.6 eV (orange), and 531 eV (royal blue). In UHV, only the 528 peak was present. On NiAg(100), six distinct peaks were identified as well. Of these peaks, two were unique to NiAg(100): 528.6 eV (purple), and 529 eV (pink). The overall surface coverage of oxygen is higher on NiAg(100) in both UHV and high pressure. The predominant species is O in reconstructed Ag (or nucleophilic O) in both systems as expected on Ag surfaces at higher temperatures. C) Ni 2p<sub>3/2</sub> spectra showing the oxidation of Ni sites during oxygen exposure on NiAg(100). All Ni is oxidized to Ni<sup>2+</sup> (853.9 eV) from Ni<sup>0</sup> (852.6 eV) during oxygen exposure in UHV, and in 200 mTorr O<sub>2</sub> the same oxidation is observed. D) Ag 3d spectra showing the oxidation of Ag in 200 mTorr O<sub>2</sub> at 433 K. A slight shoulder is formed at 367.8 eV consistent with oxidized Ag.

For the higher binding energy peaks, we looked for potential contaminants in order to identify the oxygen species. In high pressure environments, contamination from carbon based species is common.<sup>35,47</sup> Carbon-based oxygen species are reported to have binding energies between 531-533 eV.<sup>48</sup> carbonate is the most common carbon-oxygen species to form under oxidative conditions (binding energy 530.4-530.7), so we assigned the 530.6 eV peak (orange trace) as carbonate.<sup>49-51</sup> Water from the chamber background readily reacts with adsorbed O atoms on Ag(100) to rapidly populate the surface with OH groups.<sup>52,53</sup> The oxygen-exposed Ag surface is covered in a significant amount of O atoms (530 eV), which create an ideal environment for OH formation. Additionally, the binding energy of OH peak in O 1s spectra is commonly reported between 531 and 532 eV.<sup>54-56</sup> Therefore we assigned the 531 eV peak (royal blue trace) to OH.<sup>54-56</sup> The overall distribution of O species observed in our experiments on Ag(100) at high pressure is consistent with literature.<sup>49,50</sup>

Next, ~6% Ni was alloyed into a clean Ag(100) sample held at 300 K. The as deposited Ni remained metallic, but upon exposure to O<sub>2</sub>, all the Ni (852.6 eV) was oxidized to Ni<sup>2+</sup> (853.9 eV (Figure 1C)).<sup>57</sup> The O1s spectra taken during O<sub>2</sub> exposure on NiAg(100) displayed six distinct peaks, and overall the amount of O on the NiAg(100) surface was much higher than on Ag(100). The 528, 530, 530.6 and 531 eV peaks are present on the bare Ag(100) surface as well, but two unique peaks at 528.6 (purple) and 529.1 eV (pink) were observed in addition. The 529 eV peak was assigned to NiO<sub>x</sub> due to its agreement with literature values for NiO<sub>x</sub> species, its presence only on the Ni-doped surface, and correlation with the Ni 2p spectra.<sup>20,56,58</sup> The 528.6 eV species was assigned as semi-ordered Ag oxide patches.<sup>39,40</sup> When Ni alloyed into the Ag(100) surface, it place exchanged with Ag atoms, and these Ag atoms clustered and formed Ag islands after they were ejected.<sup>59</sup> These Ag islands are detectable by Scanning Tunneling Microscopy (STM), but

not with XPS. However, upon oxygen exposure, the formation of the peak at 528.6 eV is consistent with the partial oxidation of these ejected Ag islands based on STM evidence,<sup>60</sup> and binding energy agreement with literature.<sup>40</sup> Lastly, Ag3d spectra revealed the formation of an oxidized shoulder in 0.2 Torr O<sub>2</sub> on NiAg and Ag(100), but not under UHV conditions (Figure 1D, Figure S1).

After establishing the surface makeup under purely oxidative conditions, we introduced ethylene to allow us to study Ag(100) and NiAg(100) under simulated reaction conditions (Figure 2). We increased the overall chamber pressure to from 0.2 Torr of O<sub>2</sub> to 0.7 Torr with a 2.5:1 ratio of ethylene to O<sub>2</sub> which is the industrial standard ratio.<sup>20</sup> The introduction of ethylene led to the increase in the size of the higher binding energy O1s peaks (>530 eV) on both surfaces. On NiAg(100) the lower binding energy peaks (528, 529 eV) remained, whereas the 528 and 529 eV peaks were consumed on Ag(100). This difference in O species distribution under reaction conditions is due to Ni's effect on the interaction of O<sub>2</sub> with the Ag surface. The oxygen distribution on Ag(100) is consistent with similar epoxidation studies on Ag surfaces where the dominant O 1s species have binding energies between 530 and 531 eV.<sup>49,50</sup> The C1s spectra, revealed that three surface C peaks are present under these conditions, and a gas-phase ethylene feature was observed as well.<sup>50</sup> The Ag(100) surface exhibited a higher C coverage than NiAg(100). On Ag(100), ~60% of the surface remained as metallic Ag, and ~50% of the surface remained as metallic Ag on NiAg(100).

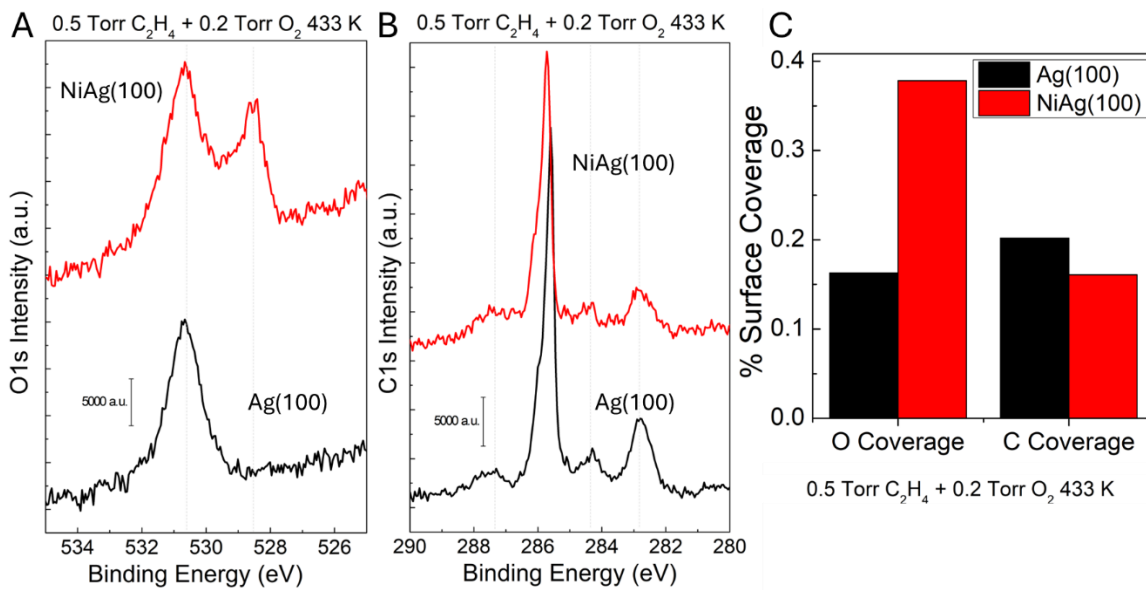


**Figure 7.2.** Overview of Ag(100) and NiAg(100) under epoxidation conditions. A) O 1s spectra comparing Ag(100) (black trace) to NiAg(100) (red trace) under simulated reaction conditions (0.5 Torr C<sub>2</sub>H<sub>4</sub> + 0.2 Torr O<sub>2</sub> at 433 K). On Ag(100) there is one prominent feature near 531 eV, while on NiAg(100) in addition to the 531 eV area, there is a second feature between 528 and 529 eV. B) C 1s spectra comparing Ag(100) (black trace) to NiAg(100) (red trace) under reaction conditions. Both spectra show the same four main peaks, 283 eV, 284 eV, 286 eV (gas phase ethylene) and 287 eV. The peaks appear larger on Ag(100). C) Bar graph comparing surface coverages for each element across each species. The O coverage is higher for NiAg(100), while Ag(100) has a higher C coverage.

With the general trends of C and O coverage under reaction conditions on Ag(100) and NiAg(100) characterized, we turned to a deeper analysis of the XPS spectra to further elucidate the state of the surfaces under reactive conditions (Figure 3). On Ag(100) the primary O 1s species observed under reaction conditions was carbonate (530.6 eV, gold trace), but O adatoms (530 eV, red trace), OH groups (531 eV, blue trace) and a new peak at 532 eV (cyan trace) were present in lesser amounts. To determine the identity of the 532 eV peak, we again considered

potential contaminants as a source. Physisorbed intact water has been reported in a binding range of 532 to 534 eV.<sup>61–63</sup> As we also observe considerable quantities of OH groups on these surfaces, and water can be stabilized on the Ag surface by OH groups.<sup>64</sup> Therefore, we assigned the 532 eV peak as water due to binding energy correlation and the presence of OH. On the Ni-doped surface, the carbonate peak was the largest as well. NiO<sub>x</sub> and semi-ordered Ag oxide patches were observed at lower binding energy, which explains the stark difference in shape between the O1s spectra on Ag(100) vs NiAg(100). Notably, the Ag oxide species formed on Ag(100) in 0.2 Torr O<sub>2</sub> was no longer present under reaction conditions, but the semi-ordered oxide patches on NiAg(100) (purple trace) persisted under epoxidation conditions. The 530, 531 and 532 eV peaks are each larger on NiAg(100).

The dominant coverage of carbonate in the O1s spectra is consistent with the size of the 287 eV peaks in the C1s spectra, and the coverage ratio was ~ 3:1 O to C, consistent with a carbonate species.<sup>49,51</sup> Other work has highlighted the potential importance of carbonate intermediates/species for selective oxidation reactions.<sup>49,50,65</sup> Four other C1s peaks were observed. The two 286 eV peaks (Figure 3B, gray traces) are from gas phase ethylene, so they do not affect the surface chemistry and will not be discussed further in this work.<sup>50</sup> The other two peaks at 283 and 284.5 eV are due to intact ethylene and “carbonaceous C” likely in the form of hydrocarbon fragments, as supported by their binding energy agreement with other epoxidation studies.<sup>49,50,66</sup> The peak at 283 eV can be produced by a carbide species, or SiC, but the survey scan revealed no corresponding peaks elsewhere on the spectrum (Figure S2).<sup>67</sup>

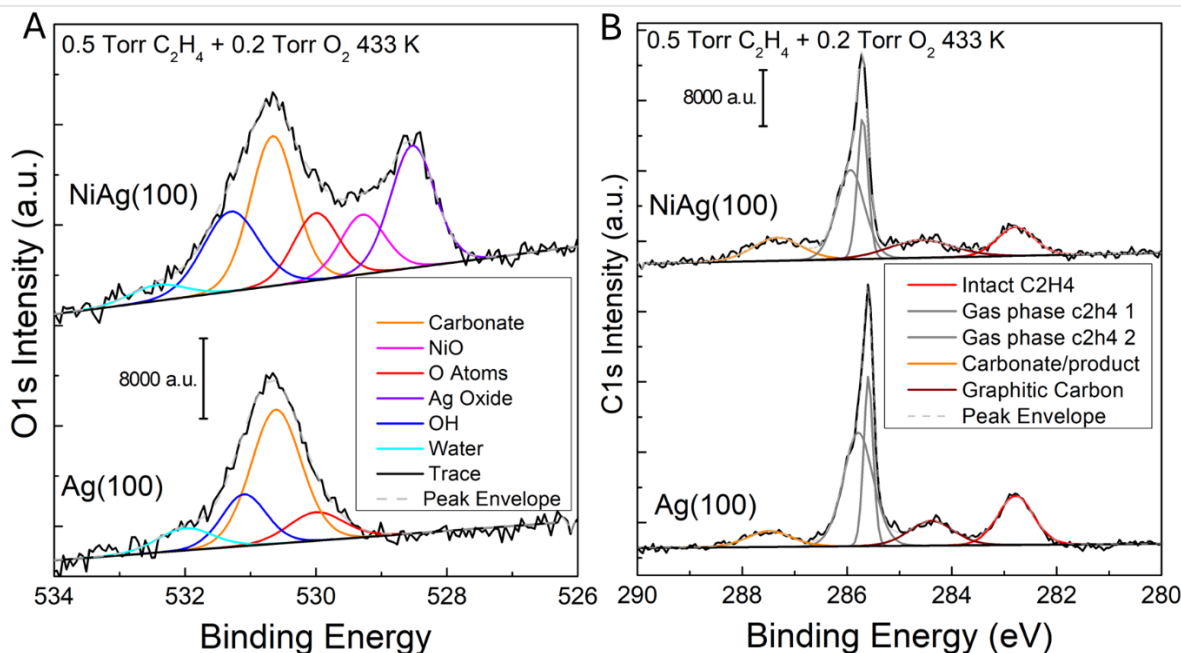


**Figure 7.3.** O 1s and C 1s peak fits for reaction conditions. A) O 1s XPS spectra for Ag(100) (bottom) and NiAg(100) (top). Six distinct peaks were observed: 528.6 eV (purple trace,  $\text{Ag}_x\text{O}_y$ ), 529.2 eV (pink,  $\text{NiO}_x$ ), 530 eV (red, O adatoms), 530.6 eV (orange, carbonate), 531 eV (blue, OH), and 532 eV (cyan, water). The 529 and 528.6 eV peaks were not present on the Ag(100) sample, and the amount of OH and O adatoms is greater on NiAg(100). B) Fit C 1s XPS spectra for Ag(100) (bottom) and NiAg(100) (top). Both Ag(100) and NiAg(100) exhibited the same range of C 1s peaks. Two gas phase peaks at 285.5 and 285.7 eV (gray traces) correspond to gas phase ethylene. The 283 (red) and 284 eV (maroon) peaks are consistent with intact ethylene molecules and carbonaceous C respectively. The 287 eV peak (orange) is consistent with formed products or surface carbonate. The intact ethylene peak is the largest C 1s surface peak observed for each system under these conditions.

To better understand our two surfaces under epoxidation conditions, we studied the effect of returning the sample to UHV after high pressure conditions, and the effect of an anneal on the post-reaction surface (Figure 4). For this process, we closed the chamber off from the gas

sources, pumped down into UHV, annealed to 800 K and cooled back down to 433 K. After each step we took O 1s and C 1s spectra (as well as Ni 2p spectra for NiAg(100), and Ag 3d spectra for reference). For O, closing off both gases led to an increase in oxygen on the surface for Ag(100), particularly as carbonate, while O on NiAg(100) remained unchanged. Pumping down to UHV pressures did not affect Ag(100), and the 528.6 eV peak on NiAg(100) was consumed. Post 800 K anneal; no O signal was observed on either surface.

The amount of C on the surface increased once the gas sources were closed off to Ag(100). The C1s spectra taken in UHV also showed an increase in C coverage, but less dramatically. These results are consistent with ethylene building up on the surface due to a lower availability of oxygen to react with and burn off the excess C species. This effect was not observed on NiAg(100), suggesting that the presence of Ni atoms creates a more reactive surface that is less prone to carbon buildup and more active for ethylene epoxidation. As further evidence for the enhanced reactivity of the Ni-doped surface, after annealing each sample no carbon was observed on NiAg(100), but a significant amount remained on Ag(100) (~30%). The remaining carbon is consolidated in one 284 eV peak, however this peak has shifted in binding energy from 284.5 eV to 284.0 eV. This shift is consistent with the sintered carbon formation following the anneal.<sup>68</sup>

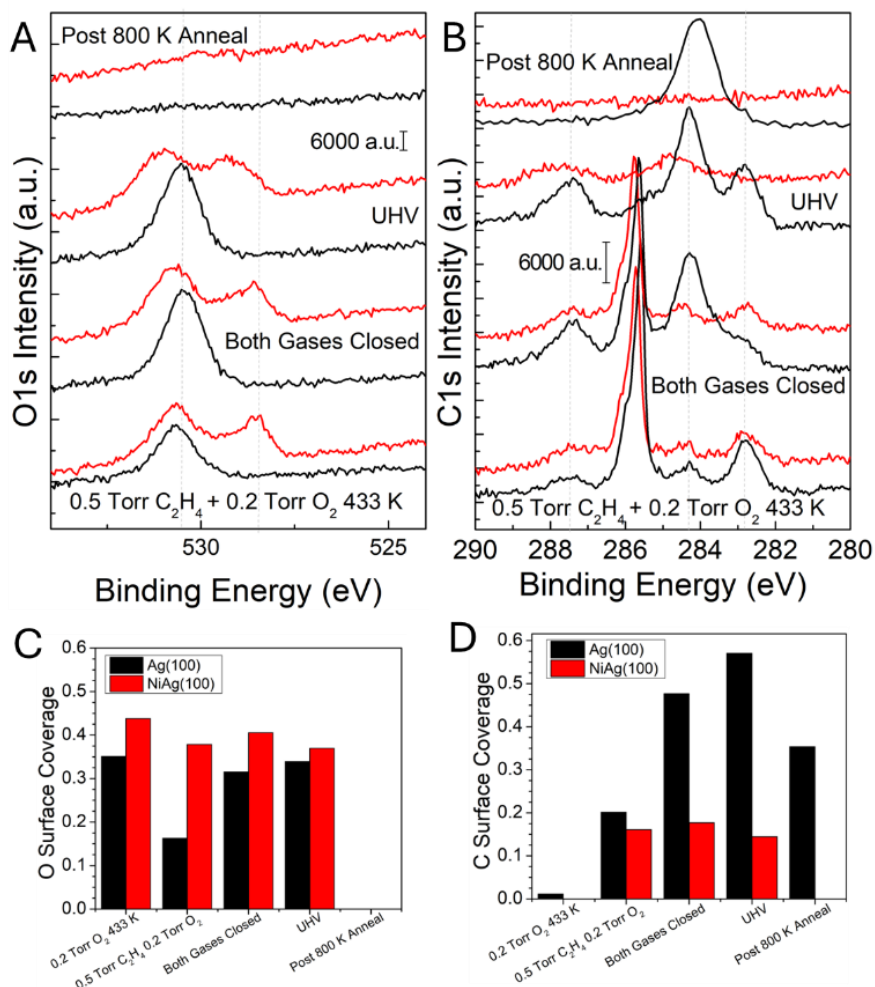


**Figure 7.4.** Effect of pumping down and annealing after reactive condition experiments. A) O 1s spectra depicting the transition from simulated reaction conditions in the mTorr range to UHV ( $<5 \times 10^{-9}$  Torr), and subsequent anneal for Ag(100) (black traces) and NiAg(100) (red traces). The higher binding energy peak grows on each surface when gas pressure is reduced. No O remained after the 800 K anneal. B) C 1s spectra for the same process. On NiAg(100), The amount of C NiAg(100) remained consistent once C<sub>2</sub>H<sub>4</sub> was introduced. No C was present after the 800 K anneal. On Ag(100), the amount of C grew significantly O<sub>2</sub> pressure was reduced and reached a maximum coverage of ~50% in UHV before the anneal. Unlike NiAg(100), after the 800 K anneal, a large C peak at 284 eV is present on Ag(100). C) Bar graph depicting oxygen coverage throughout the experiment. D) Bar graph depicting carbon coverage throughout the experiment.

Lastly, we performed temperature oscillation experiments on Ag(100) and NiAg(100) under near-ambient reaction conditions to test the comparative “robustness” of each surface (Figure 5). For this comparison, we held each sample under reaction conditions (0.5 Torr ethylene, 0.2 Torr O<sub>2</sub>, heated and cooled the sample in a small range around our initial temperature (433 K), and monitored progression of the C and O species on each surface with XPS. The Ag(100) surface quickly accumulates more C once the sample is heated or cooled. Once this C build up began (predominantly in the 283 eV peak, but observed across all three surface peaks), the carbon coverage does not decrease, even upon returning to 433 K. Conversely, on NiAg(100) the surface retained a similar C coverage throughout the oscillations. In general, heating led to an increase in the 283 eV peak, while cooling led to an increase in the 287 and 284 eV peaks in the C 1s spectra.

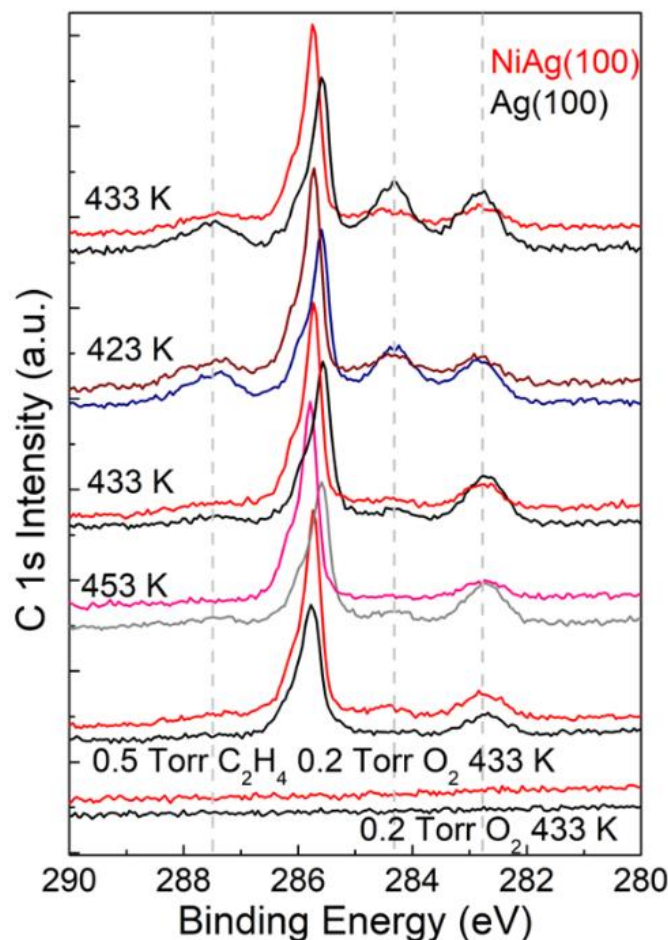


**Figure 7.5.** Effect of temperature oscillations on carbon coverage. C 1s spectra depicting the change in carbon coverage for Ag(100) (black traces) and NiAg(100) (red traces) in simulated reaction conditions (0.5 Torr C<sub>2</sub>H<sub>4</sub> + 0.2 Torr O<sub>2</sub> at 433 K) and over a range of temperatures surrounding 433 K while maintaining the same gas ratio and pressure. The sample was heated up to 453 K, back to 433 K, down to 423 K and back to 433 K, and the carbon coverage was monitored throughout. On Ag(100), both heating and cooling the sample from 433 K lead to an increase in surface coverage, particularly at the 284 and 283 eV peaks. On NiAg(100), a slight increase in carbon coverage was observed during the temperature oscillations, but the surface remained largely the same. Important peaks are marked with dashed gray guiding lines.

## 7.4 Conclusions

We utilized synchrotron X-ray photoelectron spectroscopy to study an NiAg(100) SAA under simulated epoxidation conditions and compare the resulting oxygen and carbon species to those formed Ag(100) in the same environment. We found that carbonate dominates the surface in epoxidation conditions in each system, but a variety of O species are formed. The presence of Ni led to a much higher O coverage under reaction conditions, and all surface oxygen and carbon species were reacted off on NiAg(100), while the Ag(100) surface remained coated in carbon. The increased robustness of the Ni-doped surface was supported by temperature oscillation experiments as well that showed NiAg(100) was resistant to carbon buildup at a range of temperatures, while carbon quickly accumulated on Ag(100). Both the classification of the oxygen and carbon species present under reaction conditions, and the comparative robustness observed on NiAg(100) provide important insight into Ni as a selective epoxidation promoter.

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## **Chapter 7.6.**

### **Supporting Information**

#### **7.6.1 Experimental Methods**

##### **Scanning Tunneling Microscopy (STM)**

78 K STM experiments were conducted in an ultra-high vacuum (UHV) chamber with a base pressure of  $1 \times 10^{-11}$  mbar using a low temperature (LT)-STM (Omicron Nanotechnology). An Ag(100) single crystal (Princeton Scientific 99.999% purity <1 degree polish) was used for experiments. Sample cleaning was performed in a connected preparation chamber with a base pressure of  $< 5 \times 10^{-10}$  mbar. Repeated cycles of Ar<sup>+</sup> (Airgas 99.99%) ion sputtering (1 keV 10-20  $\mu$ A) and annealing to 825 K were used to clean the Ag(100) crystals. STM images were obtained at 78 K after cryogenically cooling the STM stage. Oxygen (99.9% Middlesex gases) was dosed through high precision leak valves. Ni was deposited via hot filament evaporation from a high-purity Ni rod. Coverages were calculated as an average from ~20 images for each coverage through manual counting of features using an STM image processor (SPIP). Coverages are based on the number of specific features per image divided by the total number of Ag surface atoms in each image. Error bars on coverage were one standard deviation.

##### **X-Ray Photoelectron Spectroscopy (XPS)**

XPS experiments were performed at Beamline 23-ID-2 (IOS) of the National Synchrotron Light Source II (NSLS- II) at Brookhaven National Laboratory.<sup>1</sup> All experiments were performed on a Ag(100) crystal cleaned with Ar<sup>+</sup> ion sputtering and annealing to 825 K

until XPS spectra showed no impurities. The heating rate for cleaning and annealing was 40 K/min. High purity O<sub>2</sub> (Matheson, 99.994%) was exposed to the sample via precision leak valve while the sample was heated with a pyrolytic boron nitride heater. Temperature was measured with a K-type thermocouple between the Ag(100) crystal and the heater/sample mount. Reference Ag 3d spectra were taken after each oxygen spectrum. Ni was deposited via hot filament evaporation from a high-purity Ni rod calibrated by a quartz mass balance. Oxygen and Ni species coverages were calculated by dividing the corrected O1s peak areas by the corresponding corrected Ag 3d peak areas. Peaks areas were corrected by dividing the raw areas by their Relative Sensitivity Factor (RSF),<sup>2</sup> multiplied by the IMFP of the ejected electron found from a universal curve<sup>3</sup> (Equation S1, S2). In addition, Ag 3d peaks were taken at reduced intensity and then corrected to full intensity area using reference spectra taken at the beginning of each experiment. Ag 3d peak areas were also corrected by a first layer correction based on the IMFP to account for the signal only generated by the top level of atoms (Equation S3).

$$\frac{\text{Corrected O 1s Peak Area}}{\text{Peak Area}} = \frac{\text{Raw Peak Area}}{\text{R.S.F.} \times \text{I.M.F.P.}}$$

**Equation 7.S1.** O 1s XPS Correction.

$$\frac{\text{Corrected Ag 3d Peak Area}}{\text{Peak Area}} = \frac{\text{Raw Ag 3d}_{5/2} \text{ Peak Area} \times \text{First Layer Correction}}{\text{R.S.F.} \times \text{I.M.F.P.} \times 5/2 \text{ Correction}}$$

**Equation 7.S2.** Ag 3d XPS Correction.

$$\frac{\text{Corrected Ni 2p Peak Area}}{\text{Peak Area}} = \frac{\text{Raw Ni 2p}_{3/2} \text{ Peak Area}}{\text{R.S.F.} \times \text{I.M.F.P.} \times 3/2 \text{ Correction}}$$

**Equation 7.S3.** Ni 2p XPS Correction.

$$\frac{\text{Corrected O 1s Peak Area}}{\text{Peak Area}} = \frac{\text{Raw Peak Area}}{\text{R.S.F.} \times \text{I.M.F.P.}}$$

**Equation 7.S4.** C 1s XPS Correction.

To investigate different elements, different photon energies were used. Predominantly, 760, 1090 and 500 eV were used to generate photoelectrons with kinetic energies of ~200-300 eV for the O 1s (at 760 eV), Ni 2p (at 1090 eV), and S 2p and C 1s (at 500 eV) core levels, respectively, to maintain similar probing depths. The latter two elements were only monitored for impurities. Binding energy calibration was performed on all spectra with respect to the Fermi edge and metallic Ag 3d<sub>5/2</sub> binding energy measured at each photon energy.<sup>4</sup> XPS data was analyzed with CasaXPS. Each species was assigned and fit according to experimental results and literature values (Table S1). O 1s, C 1s and Ni 2p spectra were fit with a linear background due to their small size, while Ag spectra were fit with a Shirley background.<sup>5</sup>

| Element                       | Component                                                                              | Binding Energy (eV)      | Full Width at Half Maximum (FWHM) | Line Shape (Gaussian: Lorentzian) |
|-------------------------------|----------------------------------------------------------------------------------------|--------------------------|-----------------------------------|-----------------------------------|
| Oxygen (O1s)                  | O in Ag Reconstructions <sup>6-8</sup>                                                 | 527.9 – 528.2            | 0.7 – 0.8                         | 30:70                             |
|                               | Ag Oxide Patches (Ag <sub>2</sub> O) <sup>9,10</sup>                                   | 528.5 – 528.7            | 0.8 – 1.0                         | 30:70                             |
|                               | Ag Oxide <sup>25</sup>                                                                 | 529.2 – 529.5            | 1.0 – 1.1                         | 30:70                             |
|                               | NiO <sup>11-14</sup>                                                                   | 529.0 – 529.2            | 0.8 – 0.9                         | 30:70                             |
|                               | NiO <sub>2</sub> <sup>15</sup>                                                         | 531.8*                   | n/a                               | n/a                               |
|                               | Atomic O <sup>2,5,16,17</sup>                                                          | 530.0 – 530.2            | 0.8 – 1.0                         | 30:70                             |
|                               | Carbonate <sup>18,19</sup>                                                             | 530.5 – 530.7            | 0.9 – 1.0                         | 30:70                             |
|                               | OH <sup>11,20,21</sup>                                                                 | 530.9 – 531.1            | 0.8 – 0.9                         | 30:70                             |
|                               | Water <sup>14,22-24</sup>                                                              | 531.5-532.5              | 1.0 – 1.1                         | 30:70                             |
| Silver (Ag3d <sub>5/2</sub> ) | Ag <sup>0</sup> (Metallic Ag) <sup>4,25</sup>                                          | 368.2                    | 0.4                               | 99:1                              |
|                               | Ag Oxide (Ag <sub>2</sub> O) <sup>10,25</sup>                                          | 367.8                    | 0.8                               | 30:70                             |
| Nickel (Ni2p <sub>3/2</sub> ) | Ni <sup>0</sup> (Metallic Ni) <sup>14,26</sup>                                         | 852.6                    | 1.0 – 1.2                         | 30:70                             |
|                               | Ni <sup>2+</sup> (NiO) <sup>14,26</sup>                                                | 853.9                    | 1.0 – 1.2                         | 30:70                             |
|                               | Ni <sup>4+</sup> (NiO <sub>2</sub> ) <sup>27</sup>                                     | 856.1*                   | n/a                               | n/a                               |
| Carbon (C1s)                  | Carbonaceous C <sup>19</sup>                                                           | 284.0 – 284.6            | 1.0-1.2                           | 30:70                             |
|                               | Intact C <sub>2</sub> H <sub>4</sub> ( $\pi$ -bound C) <sup>28</sup>                   | 283.2 – 283.4            | 0.8 – 1.0                         | 30:70                             |
|                               | Gas-Phase C <sub>2</sub> H <sub>4</sub> (two peaks) <sup>18</sup> (need one more cite) | 285.5-285.6, 285.8-285.9 | 0.3, 0.8                          | 30:70                             |
|                               | Carbonate/Product <sup>18,19</sup>                                                     | 287.5 – 287.8            | 1.0                               | 30:70                             |
|                               | CO-Ni <sup>29</sup>                                                                    | 285.9 *                  | n/a                               | n/a                               |

**Table S1.** Summary of fitting parameters for XPS spectra.

\*Not detected within our XPS experiments.

## 7.6.2 Supplementary Figures

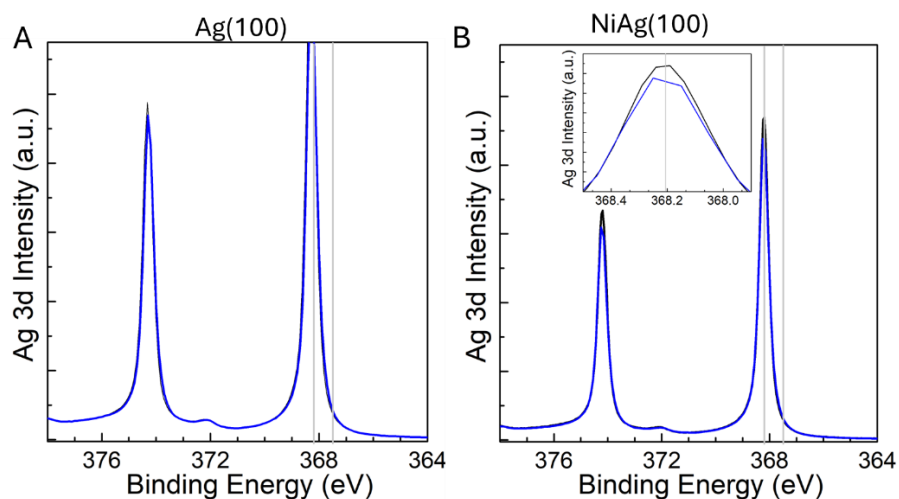


**Figure 7.S1.** Ag 3d spectra of (A) Ag(100) and (B) NiAg(100) before O<sub>2</sub> exposure (black trace) after 12,000 L O<sub>2</sub> exposure at 383 K (blue trace). No oxide peak formation was observed and the Ag 3d<sub>5/2</sub> peak remained metallic at metallic at 368.2 eV.<sup>4,25</sup>. The only difference between the oxidized and non-oxidized spectra was a slight decrease in signal due to poor chamber pressure from large O<sub>2</sub> doses. Inset is a zoom in of the metallic Ag 3d<sub>5/2</sub> peak. Ag 3d spectra taken at 760 eV photon energy.

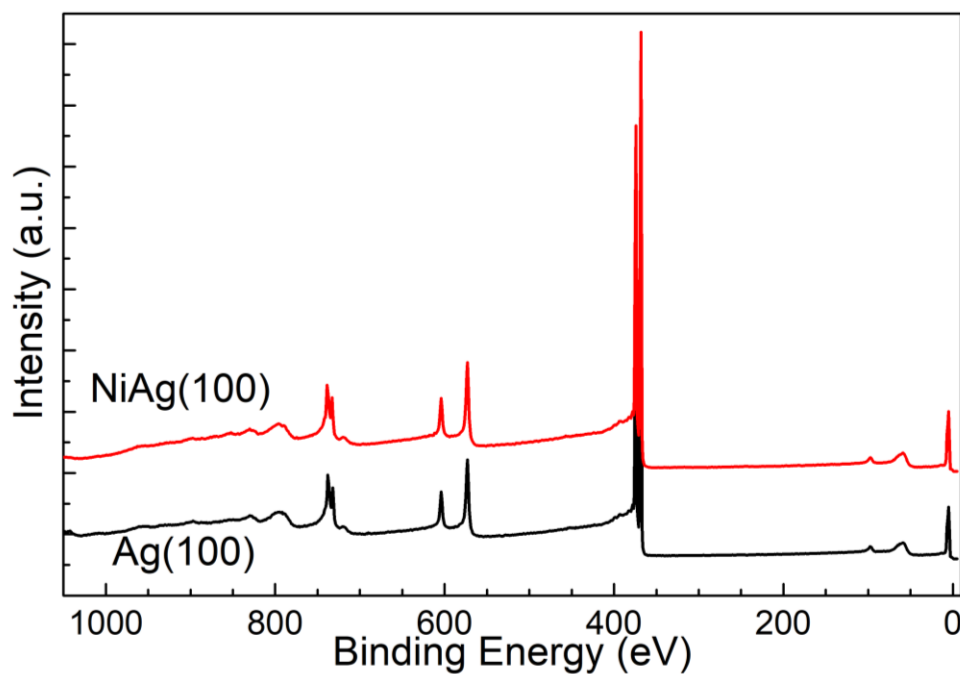


**Figure 7.S2.** Survey scans of Ag(100) and NiAg(100) (post Ni deposition) demonstrating lack of impurities in the sample. The only peaks present are from Ag, and a small Ni peak is present on NiAg(100). Notably there were no C, S or Si impurities. Survey scan taken from 1090 eV photon energy.

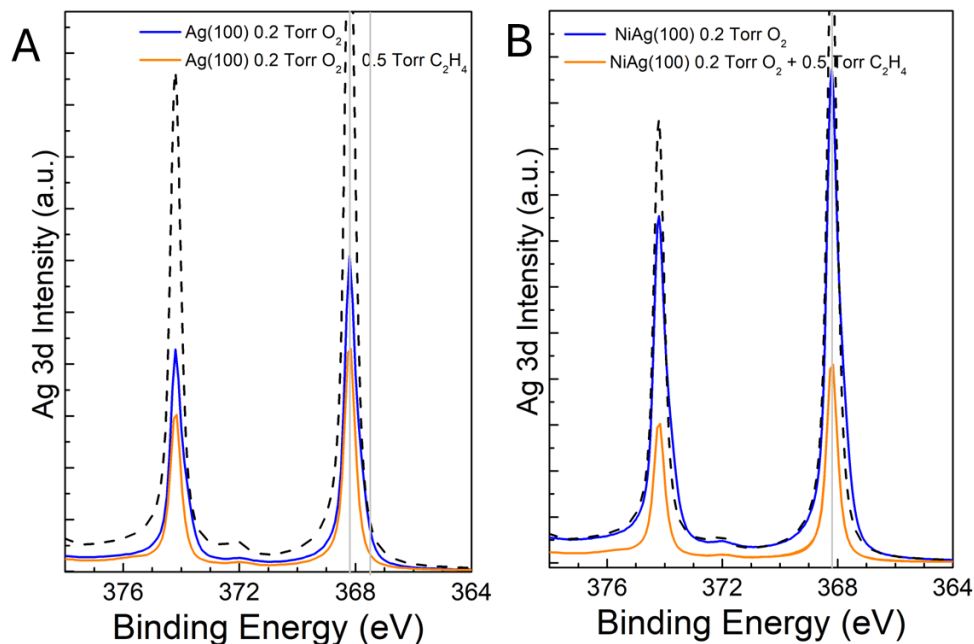


**Figure 7.S3.** Ag 3d spectra of Ag(100) (A) and NiAg(100) (B) under clean conditions (dashed black trace), oxidized conditions (blue trace), and simulated epoxidation conditions (orange trace). The signal decreases significantly as the pressure increases up to 0.7 Torr. The Ag 3d peaks remain metallic throughout, however a slight oxide shoulder forms under epoxidation conditions on each surface at 367.8 eV (rightmost gray guiding line). Spectra taken at 760 eV photon energy.

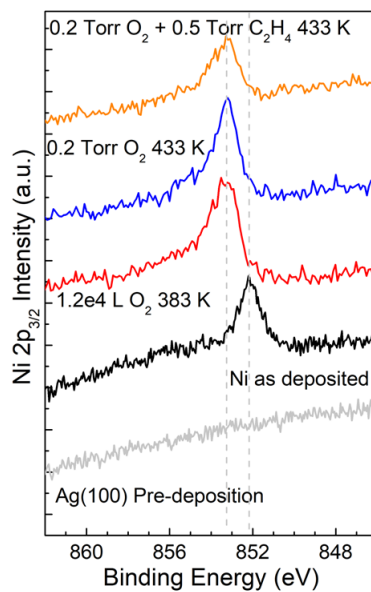


**Figure 7.S4.** Ni  $2p_{3/2}$  spectra showing the oxidation of  $\sim 6\%$  Ni to  $\text{Ni}^{2+}$  during exposure to  $\text{O}_2$ . Ni remains fully oxidized under reaction conditions (orange trace). Spectra taken at 1090 eV photon energy.

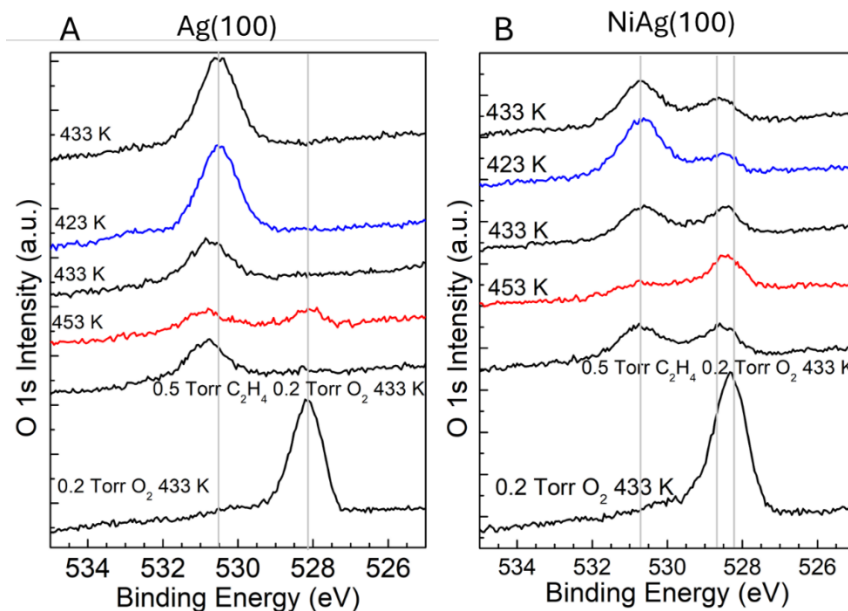


**Figure 7.S5.** O  $1s$  spectra showing the effects of temperature oscillation on the O species on (A) Ag(100) and (B) NiAg(100) under 0.2 Torr  $\text{O}_2$  and 0.5 Torr ethylene. This experiment was performed as described in Figure 5 of the main text. Spectra taken at 760 eV photon energy.

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## **Chapter 8:**

### **Conclusions and Future Directions**

#### **8.1 Conclusions**

The various studies on Ag(100) surfaces exposed to O<sub>2</sub> presented in this dissertation can be grouped under two fundamental research questions: What selective oxygen species form under epoxidation conditions? And how does Ni change the behavior of oxygen and promote selective EO formation? These questions motivated each individual research chapter included in this work. Each chapter works to establish further understanding of the O-Ag system and helps to answer one or both questions. As discussed in Chapter 1, these topics are important to understanding and improving industrial oxidation reactions such as ethylene epoxidation. Debate remains surrounding the nature of the active oxygen species for ethylene epoxidation, and the use of Cl as a promoter for EO production continues to raise alarms. The use of Single-Atom Alloys (SAAs) has introduced an exciting approach for the next generation of heterogeneous catalysts and led to the discovery of isolated Ni atoms in Ag as a selective promoter for ethylene epoxidation. The discovery of these catalysts is theory driven, and the elucidation of their fundamental properties has been led by surface science studies on model catalysts. As shown in Chapter 2, this thesis employed surface science techniques (Namely STM and XPS) to investigate complex catalytic systems on an atomic scale. These studies demonstrated the potential of SAAs, while shedding insight into under looked areas of oxidation reactions on Ag.

Chapter 3 detailed the discovery and behavior of OH groups formed on Ag(100) after exposure to O<sub>2</sub>. Here, I presented the difficulties associated with identifying OH groups on Ag

surfaces. Their relevance to the study of oxidation reactions on Ag catalysts was highlighted using STM, XPS and DFT. Chapter 4 demonstrated the lower O<sub>2</sub> activation barrier induced by Ni atoms on Ag(100). Atomic-resolution STM identified an NiO<sub>2</sub> species at 78 K where two atomic oxygen atoms were bound to opposite four-fold hollow sites around an Ni atom. On bare Ag(100), oxygen remains as molecular O<sub>2</sub> at this temperature. Chapter 5 described the speciation of O on NiAg(100) SAAs and identified a variety of species by correlating O 1s peaks observed in XPS with STM features observed under similar conditions. Chapter 6 portrayed atomic-resolution STM images of the interactions between oxygen and ethylene; resulting in the formation of an oxametallacycle or O-Ethylene moiety. To bridge the pressure gap between UHV model studies and relevant reaction conditions, Chapter 7 depicts the study of Ag(100) and NiAg(100) under high pressures of O<sub>2</sub> and ethylene. Through these experiments, NiAg(100) was shown to be more resistant to carbon build up than Ag(100), which highlights the unique oxygen properties Ni atoms impart onto the Ag surface. Overall, this work uses surface science to make exciting atomic-scale discoveries regarding oxidations on Ag(100) and inform the next generation of catalysts

## 8.2 Future Directions

The main future research direction stemming from this work is to perform Temperature Programmed Desorption (TPD) experiments on Ag(100). Using similar exposures and conditions, these experiments would directly assess the reactivity of Ag(100) and the NiAg(100) SAA toward O<sub>2</sub>, water and ethylene. Cross referenced with the STM and XPS data presented in this dissertation, TPD results could yield generous insight into the effects of OH and Ni on

selective oxidation reactions. Another direction for research on these systems is to study the effects of ethylene exposure on NiAg(100) using STM. This work used STM to explore both ethylene on O-covered Ag(100) and NiAg(100) exposed to O<sub>2</sub>, but ethylene and O<sub>2</sub> were not coadsorbed onto NiAg(100) and studied under STM. Another development could be to expand the scope of oxidation reactions studied on a NiAg SAA. The partial oxidation of methanol to formaldehyde is also performed industrially on Ag-based catalysts, and the exciting oxygen-based effects that isolated Ni atoms have on Ag(100) suggests that Ni could have promotional effects on other oxidation reactions as well.

# **Appendix 1:**

## **Single-Atom Alloy Catalysts:**

### **More Than Just the Sum of Their Parts**

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**Note:** This textbook chapter was submitted in 2022 to be published in a book detailing the chemistry of Single-Atom Catalysts and Single-Atom Alloys. All figures are reproduced herein with permission from the publisher. The chapter manuscript is produced unchanged from final submission barring formatting and figure labeling.

#### **A1.1 Abstract:**

Single-Atom Alloys (SAAs) utilize precious catalytically active metals at the ultimate limit of atom-efficiency by doping them in nanoparticles of a second metal. The negative mixing enthalpy of the two elements provides the driving force for active site isolation. This unique atomic-scale geometry of SAAs allows the transition state and the binding site of the reaction intermediates to be decoupled, enabling both facile dissociation of reactants and weak binding of intermediates, two key factors for efficient and selective catalysis. The spillover of reaction intermediates to the host metal offers opportunities for bifunctionality in the reaction mechanism that allow linear scaling relationships that limit the performance of traditional metal catalysts to be broken. SAAs have been demonstrated to catalyze many reactions including selective

hydrogenation, dehydrogenation, C-C coupling, CO oxidation/NO reduction, water-gas shift, oxygen reduction, CO<sub>2</sub> reduction, hydrodechlorination, and hydrosilylation, and are also of use in both photo- and electro-catalysis.

**Key words:**

Single-atom alloy, catalyst, bimetallic, single-site, metal alloy, spillover, linear scaling, free atom like states, hydrogenation, dehydrogenation

## **A1.2 Introduction**

Historically, paradigm shifting developments in the field of heterogenous catalysis have been few due to the complexity and non-uniformity of their active sites. Unlike homogenous and enzymatic catalysts which have extremely well-defined active sites, heterogenous catalysts expose a variety of active sites which can result in lower selectivity to desired products. This complexity arises from the range of nanoparticle sizes and shapes found in catalysts which contain different metal facets, and their associated defects such as kinks, steps and reconstructions.<sup>1</sup> Considerable research has focused on understanding the relationship between structure and reactivity in these heterogenous catalytic systems in order to improve catalytic performance.<sup>2</sup> However, the immense complexity of heterogeneous catalysts in general presents a major challenge in their rational design.<sup>3</sup> As a result, the vast majority of modern catalysts have been developed through “trial and error” approaches.<sup>4</sup>

Single-atom catalysts (SACs) are a class of heterogenous catalyst comprised of isolated metal atoms on a support (often a metal oxide or a 2D material). SACs have shown great potential in alleviating this active site heterogeneity problem due to their more uniform distribution of single metal atom sites. Single-atom alloys (SAAs), first reported by Sykes and coworkers, comprise isolated catalytic dopant atoms in a more inert metal host.<sup>5</sup> Unlike the majority of heterogeneous

catalysis, SAAs were discovered through fundamental surface science experiments, rather than traditional catalyst development, where multiple catalyst samples are synthesized and tested. Then, these model catalyst surface science results were used to inform nanoparticle catalyst synthesis, characterization and testing under industrially relevant conditions.<sup>6-8</sup> The well-defined nature of the active sites in SAAs, which can be directly visualized in the model catalyst studies and in nanoparticle analogs, has enabled highly accurate theoretical modeling with Density Functional Theory (DFT).<sup>6,7</sup> Thus far, most of the work on these SAA materials has focused on trace amounts of group 8, 9 and 10 transition metals (Pd, Pt, Rh, Ni, Ru) alloyed into group 11 metals (Cu, Ag, Au)<sup>6,7,9,10</sup> although other metal combinations appear to also form catalytically interesting SAAs.<sup>11-</sup>

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SAA catalysts offer several unique properties including improved activity/selectivity over monometallic catalysts, resistance to deactivation via coke formation, the ability to escape linear scaling relationships, unique free-atom like electronic structures, resistance to CO poisoning, and amenability to rational design, all of which will be discussed in depth in this chapter. For the purposes of this chapter, as well as in our review of the literature on SAAs, we used the following definition: *SAAs are bimetallic single-site heterogenous catalysts in which small amounts of one metal are atomically dispersed in the surface of a different metal.*<sup>15</sup> In terms of the naming convention for SAAs in this chapter, we list the dopant element first followed by the host metal. For example, a NiAg SAA denotes single nickel atom sites in a silver metal host.

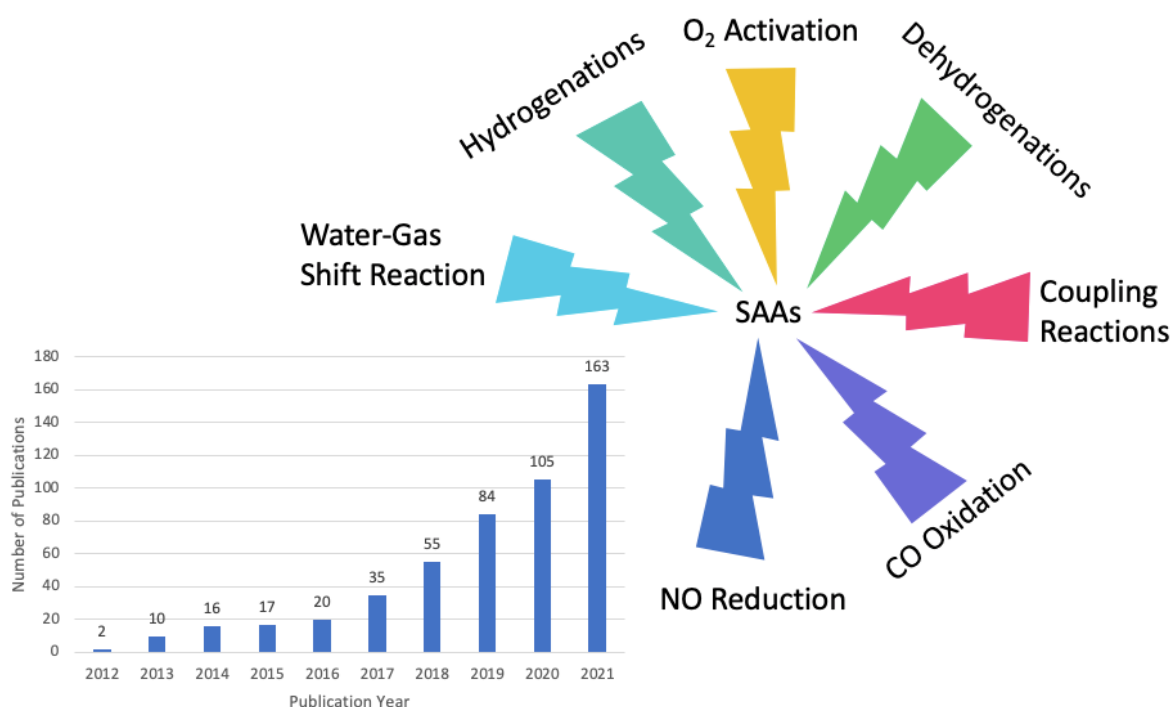


**Figure A1.1.** Visualization of the different classes of reactions catalyzed by SAAs. Inset shows SAA publications per year demonstrating the continued growth of studies in this field.

This chapter will first cover a brief background and history of the field of SAAs followed by a discussion of how to prepare and characterize SAAs in both model single-crystal and nanoparticle forms. Then, we go on to describe the general properties of SAAs. Finally, we comment on the feasibility of industrial scaleup and highlight new directions in future SAA research.

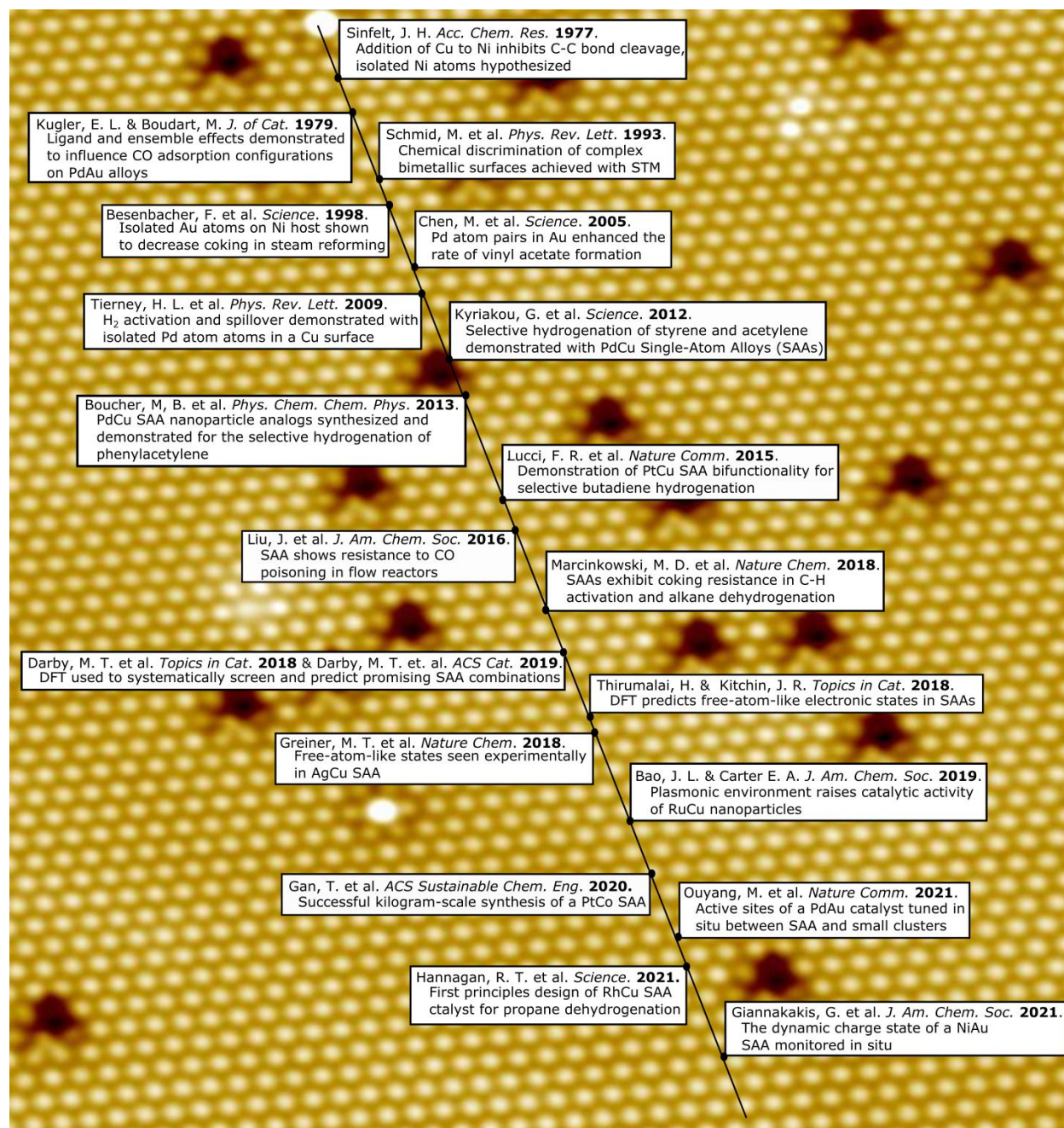


**Figure A1.2** Timeline of significant milestones in the history of SAAs, as well as important discoveries made in the decades prior that helped set the groundwork for SAAs as a new class of heterogenous catalysts.

## A1.1 Timeline

The use of bimetallic alloys to catalyze heterogeneous reactions has a long history that predates the formulation of single-atom alloys as a class of catalyst.<sup>16</sup> For instance, in the late 1970's and early '80's Sinfelt and coworkers showed that diluting an active metal such as Ni in Cu led to a decrease in the active metal ensemble size.<sup>17</sup> They hypothesized this relationship could result in the formation of isolated atoms but lacked direct experimental evidence to support this. Towards the end of the century, advances in Scanning Tunneling Microscopy (STM) enabled the Varga group to map out complex bimetallic surfaces with atomic resolution and elemental contrast.<sup>18</sup> In 1999, Besenbacher et al. used STM to conclusively identify the presence of Au monomers in the surface of Ni and demonstrate how these isolated Au atoms lowered the reactivity of the Ni surface and inhibited coke formation.<sup>19</sup> Then in 2005, Goodman and coworkers examined the PdAu surface alloy and discovered that certain facets of Au had appropriately spaced Pd monomer pairs that were hypothesized to enhance the rate of vinyl acetate formation.<sup>20</sup>

In 2009, Tierney et al. demonstrated that isolated Pd atoms in the surface of Cu(111) were active for hydrogen dissociation and spillover of the dissociated H atom to Cu sites.<sup>21</sup> In 2012, Kyriakou et al. showed, using model systems, that this dissociated hydrogen could be used for selective hydrogenations and coined the term *single-atom alloys* to describe these materials.<sup>5</sup> The first nanoparticle analogs of SAAs were successfully synthesized by Boucher et al. in 2013 and shown to be active for selective hydrogenations in agreement with the UHV model system studies.<sup>8</sup> This was a significant step for SAAs as it demonstrated that information from UHV model systems could be used to inform the design of nanoparticle catalysts, bridging the materials and pressure gaps between model studies and high surface area catalysts.

The last decade has seen a dramatic increase in SAA studies with both fundamental and applied approaches. For example, Lucci et al. were able to establish the bifunctional nature of SAAs by using CO to block the active site and demonstrating that the hydrogenation step occurs on the host surface vs. H<sub>2</sub> dissociation which occurs at the Pt atom.<sup>22</sup> Following up on this study, Liu and coworkers demonstrated that while the Pt sites can be blocked with CO under certain conditions, PtCu SAAs are far more resistant to CO poison than traditional Pt-based materials due to the weakened binding of CO to isolated Pt atoms compared to Pt ensembles.<sup>23</sup> In 2018, Marcinkowski et al. established PtCu SAAs as highly selective and stable C-H activation catalysts that are remarkably coke resistant.<sup>24</sup> These first demonstrations of CO tolerance and coking resistance illustrate the potential for SAAs to overcome these two major issues faced in many important heterogeneously catalyzed reactions. Furthermore, the well-defined active sites in SAAs has made accurate modeling with theory possible, and several theory groups have begun to systematically screen the thermodynamic stability of SAAs, as well as the energetics of key reaction steps in a wide variety of SAAs.<sup>25–27</sup> Furthermore, Thirumalai et al. predicted that the dopant atom in SAAs often hybridizes weakly with the host metal and exhibits unique “free-atom” like d-states.<sup>26</sup> This unique “free-atom” like electronic structure was confirmed experimentally by Greiner et al. the same year.<sup>28</sup> The role of theory has also been instrumental in the more recent developments in the field, and in 2021 Hannagan et al. reported a first-principles-guided design approach in the development of a working RhCu dehydrogenation catalyst.<sup>29</sup>

### A1.1.2 Methods

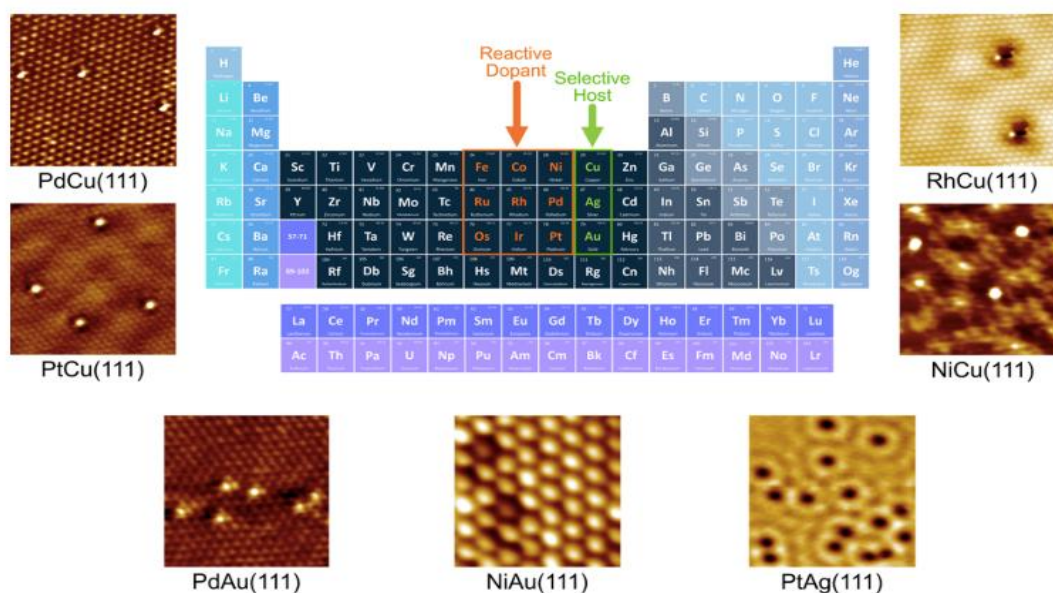


**Figure A1.3.** Periodic table illustrating the SAA approach of adding small amounts of a reactive dopant metal into a less reactive, more selective host metal. Atomically resolved STM images of the SAAs pictured are courtesy of Sykes and coworkers. The isolated dopant atom sites appear in STM images as either protrusions or depressions depending on imaging conditions and the alloy itself. Reproduced with permission from ref 15. Copyright 2020 American Chemical society.

SAAs are a class of single-site catalyst consisting of reactive dopant metal atoms dispersed in a less reactive metal host.<sup>6,7,9</sup> The thermal stability of SAAs that keeps the dopant sites isolated is due to the strong host-dopant interactions that lead to mixing. This thermodynamic driving force for isolated sites is crucial in the prevention of clustering/sintering that afflicts other types of single-atom catalysts at elevated temperatures.<sup>30</sup> As Figure 3 shows, many different SAAs have been reported in the literature including PdCu,<sup>31</sup> PtCu,<sup>32</sup> RhCu,<sup>33</sup> NiCu,<sup>34</sup> PdAu,<sup>35</sup> NiAu<sup>36</sup> and PtAg<sup>37</sup> among others. Many of these SAA systems, such as NiCu, have been prepared both as single crystal model catalysts and as actual nanoparticle or nanoporous catalysts.<sup>34,38</sup> In this section

we will review how SAAs are prepared experimentally as both model catalysts studies in UHV and nanoparticle or nanoporous catalysts. Then we will discuss the instrumental techniques used to characterize the model catalysts and nanoparticle catalysts respectively.

## **A1.3 Preparation**

### **2.1.1 Model catalyst preparation (UHV)**

A joint single-crystal surface science and scanning probe microscopy approach making use of well-defined UHV conditions was used to realize many of the unique properties of SAAs. UHV (ultra-high vacuum), is a pressure regime defined by pressures between  $10^{-9}$  and  $10^{-12}$  mbar which allows for highly reproducible experiments largely free from the effects of impurities or background gases. Working in UHV has given researchers a deeper understanding of the fundamental steps that drive observed catalytic activity on larger more complex nanoparticles.<sup>39–</sup>  
<sup>41</sup> Furthermore, UHV studies also enable many surface sensitive probes (such as low energy electron and ion-based techniques) to be used and obtain conclusive results on the well-defined single crystal model catalysts. For these model system UHV studies, SAAs are prepared by depositing small amounts of one metal onto a single crystal of another, creating a bimetallic alloy in the process. In these vacuum conditions, cleanliness with less than 0.01% impurities can be achieved and maintained, which is essential when studying such dilute systems.<sup>6,7</sup>

For UHV deposition, filament style or electron beam evaporators are used to deposit trace amounts of the reactive dopant onto a clean single crystal of the host metal held at a constant alloying temperature. For an electron beam style evaporator, a metal rod or pellets of the dopant metal, is/are vaporized by an electron beam generated from a filament. For a filament style evaporator, a wire of the dopant metal is wrapped around and heated by a tungsten filament causing some of the dopant atoms to vaporize. With both evaporator styles, small amounts of high purity

dopant can be deposited onto well-defined single crystals held at an elevated temperature to promote alloy formation. The alloying temperature (typically around 400 K) must be high enough to promote mixing of the metals but not too hot such that the dopant segregates entirely into the bulk of the host metal.<sup>31</sup>

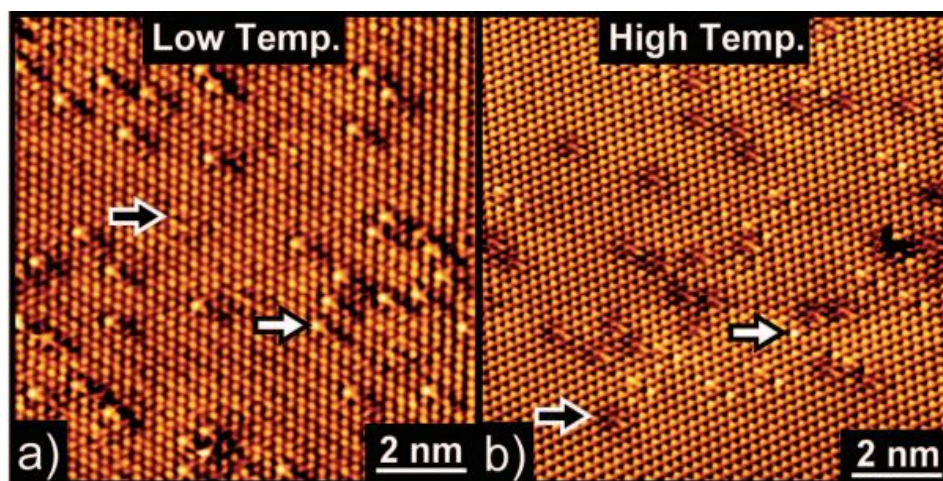


**Figure A1.4.** STM images showing that both surface and subsurface Pd atoms are observed in a Cu(111) surface over a range of deposition temperatures. Subsurface Pd appears as depressions perturbing the appearance of up to 7 surface atoms (black arrows). Surface Pd appears as single atom protrusions (white arrows). Low temperature depositions, such as that shown in (a) at 350 K, yield more surface Pd atoms (90% surface vs 10% subsurface Pd) than higher temperature depositions. Depositions at higher temperatures, such as that shown in (b) at 500 K, have a higher prevalence of subsurface Pd atoms (30% surface vs 70% subsurface Pd). Both images are of a 0.01 ML Pd dose. Reproduced with permission from ref 31. Copyright 2009. American Chemical Society.

In UHV, it is generally not expected that the dopant atoms rearrange or reconstruct under low temperature and pressure conditions, which leads to the metastable nature of model bimetallic species. This enables researchers to prepare different metastable states of the dopant metal to test

specific active site configurations. This control over the ensemble size and structure is a significant advantage over flow reactor conditions/experiments where the initial structure and final structure tested before and after the reaction might be the same, but active sites that are formed dynamically under reaction conditions that drive the reaction would be missed by normal characterization techniques. For example, Zhang and coworkers found that NiAu nanoparticles temporarily lose their core-shell structure during CO<sub>2</sub> hydrogenation.<sup>42</sup> Using environmental transmission electron microscopy (ETEM) they observed the transformation of core-shell NiAu into a NiAu alloy during the reaction and then its return to the core-shell configuration post reaction.<sup>42</sup> This intermediate alloy state is responsible for the reaction, but traditional characterization techniques would only be able to observe the original and final core shell structures rather than the true active site of the catalyst. In UHV, this phenomenon is less of an issue, as at lower temperatures/pressures the restructuring is not likely to occur.

Generally, due to this type of restructuring under ambient conditions, the true nature of the active site cannot be determined without challenging in-situ experiments. However, In UHV experiments, depending on the alloying/deposition conditions, different active sites (including a range of metastable ones) can be formed and tested. Controlling the amount of dopant metal deposited on the surface can dictate whether isolated sites or ensemble sites form on the surface of the host metal.<sup>32,34,43</sup> Controlling the alloying temperature also allows for subsurface or surface alloys to be synthesized.<sup>31,35</sup> For example with PdCu, low alloying temperatures ~ 350 K were shown to promote surface alloying of Pd atoms, while at 500 K, subsurface Pd atoms were more prevalent (Figure 4).<sup>31</sup> Each of these different alloy types represents different potential active sites (subsurface, isolated and ensemble) that can then be tested for reactivity via desorption measurements. In summary, these active sites can be controllably formed in UHV and their

structure directly related to their catalytic activity, allowing for a high level of understanding of structure-function relationships that would not be achievable in flow reactor conditions. On model single crystal catalysts, it is also possible to reliably measure the number of active sites which is much more difficult on NP samples, making the calculation of accurate turnover frequencies (TOFs) on NPs difficult.

STM studies performed to study the alloying mechanism of model SAAs have revealed two primary alloying mechanisms in single crystal hosts. These mechanisms are 1) place exchange of the dopant atoms directly into terraces on the single crystal host (leading to single atoms alloyed in the terraces), and 2) diffusion of the dopant atoms to step edges followed by place exchange at the step edge into the upper terrace (resulting in isolated atoms present in brims above the step edges).<sup>32,44</sup> Additionally, Wang and coworkers found that the alloying behavior of Rh with Cu is dependent on the specific facet of Cu host that it is alloying with.<sup>44</sup> Rh alloying into Cu(111) resulted in Rh atoms found in the dense brims of the isolated sites above the step edges, whereas on Cu(100) and Cu(110), Rh alloyed directly into terrace sites.

An important general takeaway from the preparation of these model single-crystal SAAs is this ability to image them using STM. The STM imaging allows for the characterization of the atomic scale structure of the SAAs, which in turn, is able to provide direct evidence of their isolated active sites and thereby demonstrate the successful preparation of model single-atom alloys. These images of the isolated sites can then be correlated with activity of the SAAs, thus furthering the understanding of their catalytic behavior in producing atomic-scale structure function relationships. Most of this work has been conducted under UHV conditions to date, however, STM is not limited to UHV conditions. For instance, Maroun et al. have prepared a model PdAu SAA via electrochemical reduction of a Pd and Au mixture onto Au(111).<sup>45</sup> Using in-situ STM, they

were able to observe the atomic-scale structure of the catalyst surface under reaction conditions. While STM in liquids or at elevated pressures is challenging, it offers the exciting opportunity to understand any dynamic effects that may occur on these surfaces under realistic conditions.

### **2.1.2 Nanoparticle Preparation and Synthesis**

To test SAA performance under more industrially relevant reaction conditions, the transition from model systems to practical catalysts must be made. A variety of methods have been used to synthesize nanoparticle SAA analogs in either supported or unsupported forms. Generally, techniques used for the synthesis of SAA nanoparticles have been previously used for synthesis of bimetallic alloys and have been optimized for the formation of SAAs. Most reported SAAs have been synthesized via galvanic replacement, sequential reduction, or incipient wetness coimpregnation. These are the main methods for SAA nanoparticle formation we will focus on, but other methods for potential bimetallic nanoparticle synthesis including controlled surface reaction and strong electrostatic adsorption are detailed in reference.<sup>15</sup> Both supported (nanoparticle) and unsupported (nanoporous) forms of SAA catalyst syntheses are possible from many of these methods.

#### **2.1.2.1 Galvanic Replacement**

Guided by UHV experiments, Boucher et al. employed galvanic replacement to synthesize the first PdCu SAA nanoparticle catalysts.<sup>8</sup> Galvanic replacement has been previously employed to synthesize other surface alloys, and is of particular interest due to its simplicity and the fact that it does not require an external source of electricity.<sup>46,47</sup> The technique is a multistep process controlled by the reduction potential. When the overall potential of the reaction is positive, selective deposition of the dopant metal atom in the host metal occurs via atom-by-atom exchange,

resulting in the desired isolated surface sites of the dopant metal. To achieve this positive reaction potential, prereduction of the host metal is required for the formation of a metallic substrate. The host metal atoms become oxidized upon contact with the dopant metal ions. As the dopant metal ions are reduced, the oxidized atoms of the host metal surface dissolve in the solution. A general requirement of this process is that the dopant metal needs to be more noble than the host metal in nature. The high precision of galvanic replacement makes it a valuable tool for the synthesis of SAA catalysts such as PdCu,<sup>48</sup> PtCu,<sup>49</sup> PdCu,<sup>8</sup> PdGa<sup>50</sup> RhCu,<sup>29</sup> NiCu<sup>51</sup> and RhGa.<sup>52</sup> Despite all of its advantages, galvanic replacement does have some drawbacks. Certain limitations arise when the substrate (host metal) is a noble metal such as Au. In this scenario, Au's resistance to oxidation results in a considerably negative semireduction potential ( $\text{Au}^0 \rightarrow \text{Au}^{3+} + 3\text{e}^-$ ,  $E^0 = -1.5 \text{ V}$ ) which leads to a negative overall reduction potential. As such, the galvanic replacement pathway is rendered unfavorable.

#### 2.1.2.2 Sequential Reduction

For metal combinations where the reduction potentials are unfavorable (often Au host systems), sequential reduction is a viable alternative. Sequential reduction is an important two-step technique for bimetallic nanoparticle formation when the substrate is a noble metal. It has been used effectively for the deposition of small amounts of dopant metals such as Ni and Pd onto the already synthesized host metal (usually Au) nanoparticles.<sup>53,54</sup> First, Au nanoparticles are synthesized via the reduction of a gold precursor such as  $\text{HAuCl}_4$ , in an ethylene glycol solution containing  $\text{NaHCO}_3$  at 90 °C. Then appropriate amounts of the dopant metal precursor and reducing agents (e.g. hydrazine for  $\text{NiCl}_2$ , ethylene glycol for  $\text{Pd}(\text{NO}_3)_2$ ) are added via sequential reduction. This process leads to the formation of unsupported nanoparticles in ethylene glycol

which can then be supported on a desired support. The chemical reactions occurring during this process are not well understood, but the atomic dispersion of the dopant is dictated by the thermodynamic preference for site isolation. A positive aggregation energy of the two metals will result in a SAA configuration due to the dopant's thermodynamic preference to be surrounded by host metal atoms. Other precursors and reactants have also been used that have been shown to yield monodisperse host nanoparticles.<sup>55</sup> An advantage of sequential reduction is that the alloy formation is ensured because it occurs in solution prior to deposition of metal particles on the support. This is a significant advantage of this technique because an important aspect of catalysis research is decoupling the effect of metal alloy nanoparticles from that of metal atoms on the support which can act as single-atom catalysts themselves. For dopant host combinations with favorable thermodynamics of site isolation, sequential reduction is a powerful method of preparing SAAs without also directly loading dopant onto the support.

### **2.1.2.3 Incipient Wetness Coimpregnation**

The previous two synthesis methods involve multiple steps, various pretreatments and an array of glassware, which may deter their widespread use for SAA preparation. Incipient wetness coimpregnation is a simple, one-pot technique that has been used to make some SAAs such as PdCu and PdAg.<sup>56,57</sup> The simplicity and efficiency of this technique give it a significant advantage over the other techniques discussed here and make it a leading technique for industrial-scale synthesis of SAAs. In fact, the vast majority of the current SAA literature uses incipient wetness coimpregnation for nanoparticle synthesis. In incipient wetness coimpregnation, metal precursors are mixed in solution and an appropriate amount is added dropwise to fill the pores of the support. The appropriate amount of solution is dictated by the pore volume of the support, and if this volume is exceeded, diffusion limitations result. Similar to simple incipient wetness impregnation, a broad

particle size distribution is expected. When two precursors are mixed (coimpregnation), inhomogeneous alloys can form, however no such case has been reported in the catalyst preparation papers that have used this technique for SAA synthesis.<sup>58,59</sup> Another potential issue of this technique could be the migration of dopant metal atoms from the particles to the support, which would prevent clear study of the alloy, but this issue has not been observed or discussed to date.

#### **2.1.2.4 Other Preparation Techniques**

While many methods exist for SAA nanoparticle synthesis, galvanic replacement, incipient wetness coimpregnation and sequential reduction are the leading techniques in this regard. Some other techniques which show promise, but have more limited reported demonstrations, include strong electrostatic adsorption, controlled surface reaction, electroless deposition and coreduction. For more information on these techniques see reference <sup>15</sup>. SAA nanoparticle synthesis is a quickly developing area, and as more studies and syntheses are performed, further advantages and limitations to each technique will be better understood, particularly with regard to their scalability. For instance, Gan et al. demonstrated that the ball milling method for synthesizing unsupported SAA nanoparticles was successful on a kilogram scale, and PdCo, RuCo, IrCo and RhCo SAAs were prepared in this manner.<sup>11</sup>

#### **A1.2.2 Characterization**

In order to characterize SAA systems, a variety of techniques have been employed. In this section we will discuss the techniques used to characterize both model single-crystal systems and their nanoparticle counterparts. For both types of materials, the characterization techniques fall into three main categories: microscopy, infrared spectroscopy (IR), and X-ray based techniques.

For model systems, Temperature-Programmed Desorption (TPD) is another vitally important technique, and both material regimes also rely on probe molecule experiments to answer further characterization questions. *It is important to note that no one technique is capable of completely verifying atomic dispersion or the local environment in a single-atom catalyst.* Instead, information from two, or ideally many, techniques is needed to form an accurate picture of their working. The individual techniques have their own limitations, as mentioned above, but by combining many of these techniques together, their respective information gaps can be filled. Overall, microscopy is still regarded as the most convincing of all these instrumental tools when it comes to single-atom catalysts as it is able to provide clear visual evidence for the isolation of the active site dopant species, and as many scientists have said, “seeing is believing.”<sup>60</sup>

### **2.1.2 Nanoparticle characterization and testing**

While there are many techniques that yield information about atomic-dispersion in model and nanoparticle catalysts, early microscopy studies which directly visualized site isolation are often credited with sparking dramatic research interest in single-site catalysts.<sup>21,61,62</sup> Unlike UHV studies where STM is used, for imaging of high surface area SAA catalyst samples, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) has been used. TEM techniques rely on beams of electrons to image the materials. The difference between traditional TEM and STEM is that TEM uses transmitted electrons to create an image while STEM uses reflected electrons to create an image.<sup>63</sup> Using a HAADF detector increases the resolution by enhancing the contrast between different elements in the sample.<sup>63</sup> An example HAADF-STEM image is shown in Figure 5.

STEM is an important technique as it is able to provide atomic-scale images of practical SAA catalysts, however a major drawback of this technique is that the two metals may not be able

to be distinguished from one another. Depending on the resolution of the microscope, there must be a large enough difference in atomic number for the two metals to be able to be independently resolved, known as the “z-difference.”<sup>59,64</sup>

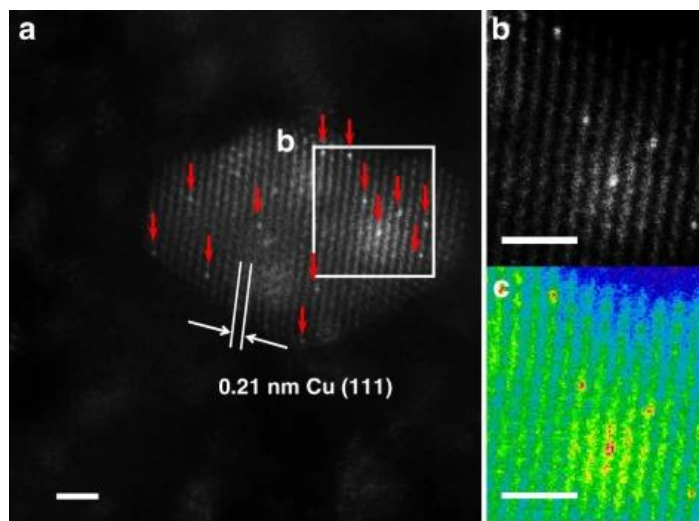


**Figure A1.5.** HAADF-STEM images of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported PtCu SAA. (a) typical region of the reduced 0.1Pt10Cu/Al<sub>2</sub>O<sub>3</sub> catalyst, showing isolated Pt atoms dispersed on Cu(111). Pt atoms are highlighted by red arrows. (b) and (c), the enlarged image and colored intensity map from the selected region in (a). The lattice spacing of Pt/Cu SAA is 0.21 nm which is consistent with that of Cu(111). Scale bars 1 nm. Adapted with permission from ref 59. Copyright 2018 Springer Nature.

Another important tool for characterization of nanoparticle SAA catalysts is infrared (IR) spectroscopy. IR spectroscopy has two major attributes that make it a valuable characterization technique. The first is that it provides a deeper understanding of the coordination environment of dispersed metal atoms by way of characteristic stretching frequencies of probe molecules such as CO. The other significant advantage of IR spectroscopy is that it provides a bridge between surface science studies of model single-crystal catalysts performed with reflection absorption infrared

spectroscopy (RAIRS), and studies performed on their high surface area, nanoparticle catalyst counterparts with diffuse reflectance infrared Fourier transformed spectroscopy (DRIFTS). IR has very high resolution (typically  $2\text{--}4\text{ cm}^{-1}$ ) which allows spectra of bound molecules to provide unique fingerprints of active sites where very similar but non identical samples can be differentiated. Probe molecules such as NO and CO bind in specific conformations that indicate the type of surface site present in the catalyst.<sup>33,53,59,65</sup> These different conformations are distinguishable based on their IR stretching frequencies. For example, characteristic CO stretch frequencies for CO binding atop a dopant atom in a SAA are typically in the  $2000\text{--}2110\text{ cm}^{-1}$  range.<sup>33,34,59</sup> Likewise, bridge bound CO molecules have characteristic stretches around  $1850\text{--}1900\text{ cm}^{-1}$ .<sup>33,34</sup>

By its nature, IR on metal samples is sensitive to molecules on the surface as well as the gas phase, but importantly it can also be performed in a way as to eliminate gas phase effects and thus give surface specific information. It is widely applied as a means of in situ/operando confirmation that the dopant metal in question resides as isolated atoms in the surface of the host material in both single-atom catalysts and SAAs. The dopant metal atom typically binds CO more strongly than the host metal, so the appearance of very narrow IR peaks that are associated with CO binding atop isolated active minority metal surface atoms, confirmation that a SAA has been formed.<sup>25,59,66</sup> One disadvantage of IR characterization for these catalysts is that the probe molecules can cause changes to the surface itself (see Section 3.1 for more detail).<sup>67</sup> In such circumstances, or in cases when the probe molecule only binds weakly to the dopant metal (e.g. CO on Pd atoms in an Au surface),<sup>68</sup> the use of cryogenic conditions is recommended to produce cleaner spectra and deconvolute restructuring effects. Identification of probe molecules that do not

affect the surface structure would extend the capabilities of IR for analyzing the surface structure of SAAs.

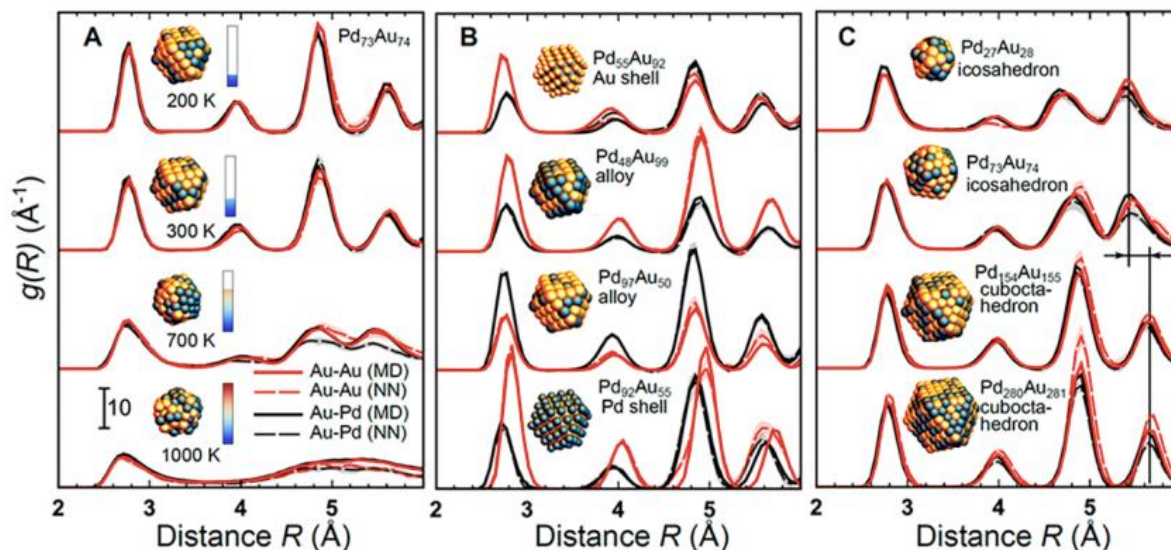


**Figure A1.6.** EXAFS spectra confirming theoretical molecular dynamics (MD) calculations performed with a neural network (NN). Au-Au and Au-Pd partial radial distribution functions (PRDFs) yielded by NN from Au L<sub>3</sub>-edge MD-EXAFS spectra are compared with the true PRDFs calculated directly from MD coordinates for nanoparticles at different temperatures (A), with different compositions (B), and different sizes and crystallographic structures (C). In (A), all results correspond to cuboctahedral Pd<sub>73</sub>Au<sub>74</sub> nanoparticle. For all cases in (B) and (C), the corresponding temperature is 300 K. PRDFs shifted vertically for clarity. Reproduced with permission from ref 69. Copyright 2018 American Chemical Society.

X-ray absorption spectroscopy (XAS) is potentially the most powerful technique for in situ or operando determination of the coordination environment of the dopant metal atom in single-site catalysts.<sup>70</sup> A wide range of reactor cells and beamline setups allow for catalysts to be monitored under gas or liquid phase environments, high temperatures and pressures as well as in vacuo.<sup>71,72</sup>

Extended X-Ray absorption fine structure (EXAFS) offers the ability to identify the presence of bonds between the host atoms themselves as well as dopant-host and dopant-dopant bonds. This bond identification is crucial for understanding the structure of single-atom catalysts.

One limitation of EXAFS for SAAs is that the experiments need to be conducted at synchrotron facilities with high photon flux beamlines and with detectors capable of mapping the metal atoms that are present at very low loadings (a few ppm). Particularly in the case of alloys diluted to the single atom limit, added complexities can arise that make obtaining clear spectra challenging. Due to polydispersity (mixed particle size) and disorder effects at the single atom limit, single atoms may be confused with contributions from small clusters or nanoparticles.<sup>73</sup> Also, similar edge energies between metal pairs such as NiCu and PdAg also present unique challenges as it makes distinguishing individual EXAFS features more difficult.<sup>51,74</sup> In these cases, fitting only the first coordination shell is possible, or occasionally linear fitting combination analysis of the XANES part of the spectrum is chosen to study the atomic dispersion. XANES stands for X-ray absorption near edge structure, and it refers to the analysis part of an XAS spectrum. It is also important to note that XAS is usually a bulk, rather than a surface, technique and therefore cannot give a full picture of the coordination environment of the dopant metal in the surface layer without making careful assumptions about the nanoparticle size and dopant distribution. Some studies on PdAu alloys have used molecular dynamics in combination with X-ray spectroscopy to overcome some of these limitations and understand the variation in local environments of dopant atoms (Figure 6).<sup>69,75</sup> The high-energy-resolution fluorescence detection technique (HERFD) can be used in conjunction with XANES to obtain further information about SAAs. For instance, HERFD was able to successfully determine the charge state of a NiAu SAA.<sup>76</sup>

Additionally, XAS can be turned into a semi-surface sensitive technique via modulation excitation spectroscopy, and this method has been used to successfully identify surface species.<sup>77,78</sup>

Although not an instrumental technique in itself, probe molecule reaction testing is an incredibly valuable analytical tool that has gone largely unused in the field of single-atom catalyst characterization. Probe reaction testing can aid further in determination of the atomic dispersion of the active dopant metal. Probe reactions have been extensively used for surface site characterization in traditional heterogeneous catalysis. Some examples of specific applications are CO temperature-programmed reaction to react with and thus titrate active OH groups on a support,<sup>79</sup> ethylene hydrogenation to estimate the metallic surface area of exposed Pt,<sup>80</sup> and DME carbonylation to probe the local active site structure in zeolites,<sup>81</sup> among others. Another example of these probe studies is from Cao et al. where they used the water-gas shift reaction to report on the atomic dispersion of Au atoms stabilized by oxygen and alkali ions.<sup>82</sup> A linear relationship between the loading of Au atom sites, verified via EXAFS, and the reactivity under water-gas shift conditions was observed.

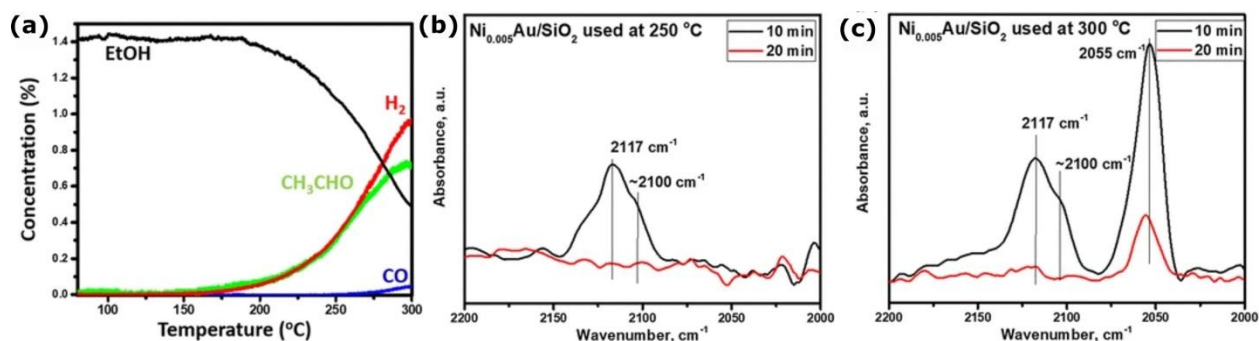


**Figure A1.7.** (a) Temperature-programmed surface reaction profile of ethanol on silica supported  $\text{Ni}_{0.0005}\text{Au}/\text{SiO}_2$ . Reaction conditions 400 mg catalyst, 2% ethanol balanced in He. He flow rate 50 mL/min. (b, c) CO-DRIFTS spectra of used silica supported  $\text{Ni}_{0.0005}\text{Au}$  for ethanol dehydrogenation at (b) 250 °C and (c) 300 °C. CO adsorption took place at room temperature and spectra were recorded after removal of gaseous CO peaks upon He purging. Adapted with permission from ref 53. Copyright 2018 Springer Nature.

Evidence that this probe molecule reaction testing approach works well for characterizing alloy catalysts can be found in the study of NiAu SAAs for the nonoxidative dehydrogenation of ethanol.<sup>53</sup> The loss of selectivity to acetaldehyde above 280 °C, as shown in Figure 7a is correlated with the growth of Ni clusters, which was confirmed via CO-IR of the used catalyst as well as by UHV and DFT studies performed later.<sup>76</sup> The CO-IR, Figure 7b and c, shows a new feature at 2055  $\text{cm}^{-1}$  which corresponds to CO on small Ni ensembles. This example is an important demonstration that probe molecule reactions can be used as another way to characterize SAAs and their structural evolution under different reaction conditions.

Lastly, it is important to note that in addition to characterization before and after reactions, *in situ* studies need to be conducted in order to understand how the surface structure changes under reaction conditions. For instance, environmental TEM and EXAFS can provide

information on the evolution of catalyst structure in response to reaction conditions. Evidence of site isolation under reaction conditions is the ultimate demonstration of an SAA, and is therefore a predominant goal in these experimental studies.

### **2.2.2 Model catalyst characterization and testing**

Working heterogeneous catalysts have a high degree of difficulty associated with understanding their reaction mechanisms due to the complexity of the materials and the associated reaction mechanisms. As a result of this complexity, a significant effort has been made to use surface science techniques on simplified model single-crystal systems in UHV to better understand reaction steps and environments.<sup>83</sup> Using surface science techniques to investigate model single-crystal catalysts gives important information that nanoparticle studies are unable to. They are able to quantify the number of active sites; visualize with molecular-scale resolution the reactants, intermediates and products; as well as gain direct visual evidence of the atomic-scale structure of the alloy surfaces and associated active site. SAAs in particular have benefitted from this approach and were in fact discovered using model single-crystal systems. Together, the fields of surface science, catalysis and theory form a feedback loop that can be effectively used to gain a deeper understanding of the structure and reactivity of SAA materials while informing new catalyst design.<sup>6,7</sup> This approach was recently leveraged to design an RhCu SAA catalyst for C-H activation from first principles.<sup>29</sup>

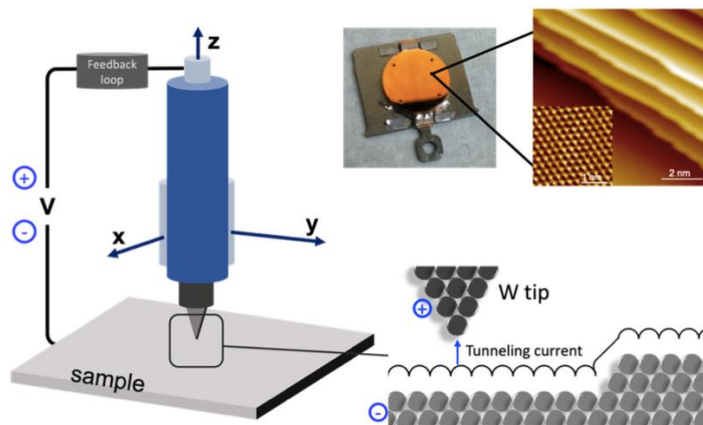


**Figure A1.8.** Schematic diagram of an STM. The image on the left shows the tungsten STM tip and the three piezoelectric positioners that allow precise control over the  $x$ ,  $y$  and  $z$  positions of the STM tip. The STM tip moves across the surface in a rastering motion while measuring the tunneling current which can provide topographic and electronic information about the surface. The upper right image shows a Cu(111) single crystal mounted to a sample plate with a representative STM image of Cu(111) with multiple monoatomic step edges, and the inset shows an atomically resolved terrace where the hexagonal 111 lattice is observable.

Model SAAs are best understood using a combination of STM and temperature-programmed desorption (TPD) techniques. For instance, STM studies are able to visualize the atomic-scale structure of the surface. STM has picometer resolution in the  $z$  direction, so metal atoms of different elements can be clearly seen and differentiated in the images. This ability to identify individual metal atoms in STM images was first demonstrated by Varga and coworkers on a variety of bimetallic surfaces.<sup>18,84</sup> Beyond just imaging the surface of the model alloy to determine its atomic-scale structure, using STM on model single-crystal catalysts provides the ability to image reaction intermediates, including species as small as hydrogen, as well as the ability to manipulate adsorbed reaction intermediates and probe their preferred adsorption sites.

The ability to study and manipulate the position of adsorbates has enabled STM to provide both definitive evidence of the spillover of reaction intermediates (such as hydrogen and alkyl species), and, coupled with TPD, demonstrate bifunctional reaction mechanisms (see Section 3.4).

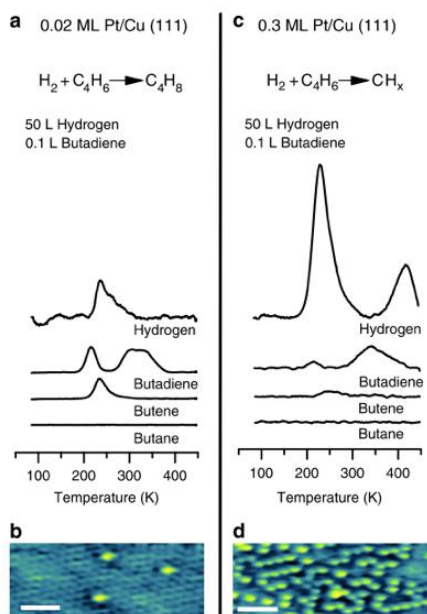


**Figure A1.9.** TPD spectra showing different product selectivity for butadiene hydrogenation as a function of Pt ensemble size. Single Pt atoms are 100% selective to butenes, whereas 1D chains lead to butadiene composition that liberates hydrogen at  $\sim 400$  K. (a) TPD trace from adsorption of  $\text{H}_2$  and butadiene on 0.02 monolayers (ML) of PtCu(111) and on (c) 0.3 ML PtCu(111). (b) STM image of 0.02 ML and (d) 0.3 ML PtCu(111). Reproduced with permission from ref 49. Copyright Springer Nature 2015.

The atomic-scale structure of these model alloys derived using STM can then be related to their catalytic properties using TPD. In a TPD experiment, a model system with a known atomic scale structure is exposed to reactants and heated until those reactants undergo reaction or desorb. Many temperature-programmed surface reactions are reaction rate limited, meaning that the products desorb spontaneously once formed. In this case the desorption temperature of the product

can be related to the activation energy of the reaction step. Alternatively, other reactions are desorption rate limited, meaning the products remain adsorbed after forming and only desorb at higher temperatures when their bond to the surface is broken. In this case, their desorption temperature does not yield the activation energy of the reaction step, rather it yields the product desorption barrier, so it is important to determine whether a given reaction is reaction rate or desorption rate limited prior to further analysis. Furthermore, quantitative comparison of the amounts of different products which desorb provides information about the reaction selectivity.<sup>85</sup> While STM is important to determine the atomic-scale structure of the model SAAs, TPD is complementary in providing the reactivity and selectivity of the model SAAs.

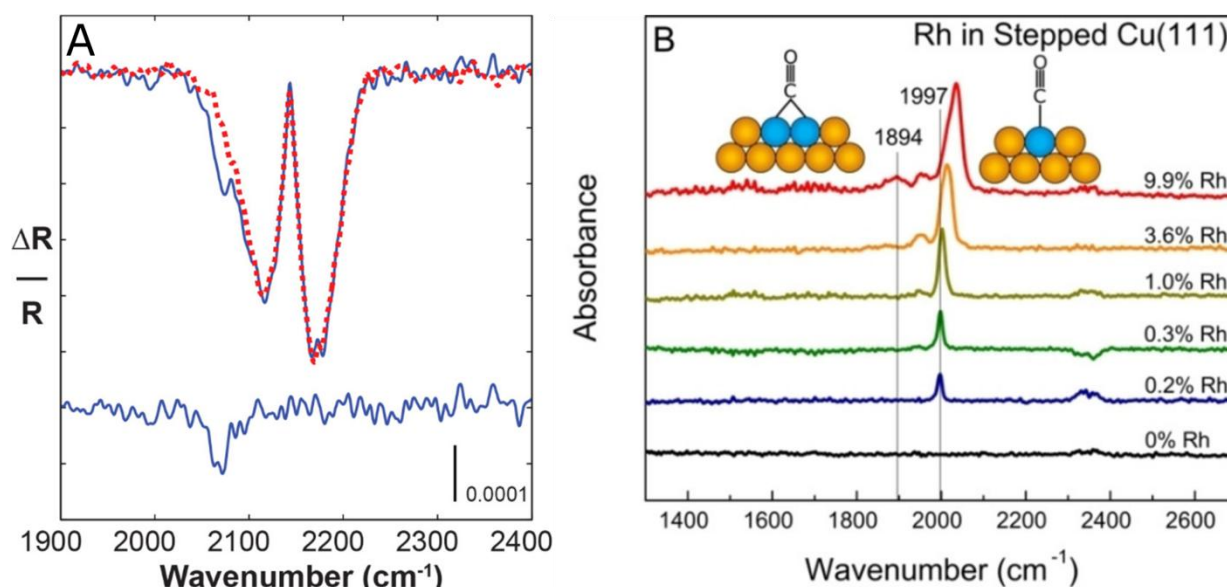


**Figure A1.10.** (A) PD-RAIR spectra of  $1 \times 10^{-2}$  Torr of CO over Cu(111). An overlay of p- (blue) and s- (red dotted) polarized spectra (top) and their difference (bottom). The difference represents a surface-phase only spectrum. The results reveal that there is a slight contribution (0.0015 ML) at  $2070 \text{ cm}^{-1}$  from CO stabilized on the Pd-free Cu(111). Reproduced with permission from ref 86. Copyright 2017 American Chemical Society. (B) RAIR spectra of CO on Rh in a stepped Cu(111) surface with increasing coverage of Rh. Surfaces were held at 250 K to saturate only the Rh sites,

leaving Cu free from CO. Atop CO on isolated Rh Sites is seen around  $2000\text{ cm}^{-1}$ . Formation of Rh ensemble sites is evident at higher coverages due to the appearance of bridge-bound CO at  $\sim 1900\text{ cm}^{-1}$ . Adapted with permission from ref 33. Copyright 2019 Wiley-VCH Verlag GmbH & Co.

Similar to nanoparticle catalyst characterization, the behavior of probe molecules such as CO which is common to both the catalysis and surface science communities can be examined on model catalysts using infrared experiments. The IR technique most widely used for model surface science experiments is reflection adsorption infrared spectroscopy (RAIRS). The most valuable characteristic of using RAIRS for surface analysis is its ability to be used in both UHV and at ambient pressures. This versatility enables it to be used as a bridge over the pressure gap between studies done in UHV and those performed at more catalytically relevant pressures/conditions. Furthermore, probe molecule IR studies can be effectively cross compared across different pressure and material regimes which allows active sites to be characterized on both model and actual high surface area catalysts. Probe molecule vibrational frequencies and desorption energetics also provide useful benchmarks for theoretical modelling of the experiments, the most common of which are DFT calculations.<sup>25,33,34,86</sup>

One limitation of RAIRS and other IR techniques is that they are unable to yield direct information on the dopant atom-host metal bonding or the dopant-adsorbate bond.<sup>87</sup> Surface IR techniques generally only produce spectra of bonds within the adsorbates themselves. As a result, RAIRS on its own is not able to fully characterize the surface structure of SAA catalysts, and we must rely on other techniques like STM and TEM to fill in this gap. Furthermore, at high pressures, CO can induce surface restructuring which is an important consideration when using RAIRS in ambient conditions on molecules like CO that are known to restructure metal surfaces.

Another important characterization technique for these model catalysts is X-Ray photoelectron spectroscopy (XPS). XPS is based on the photoelectric effect that arises when high energy photons (keV range) hit a material and emit electrons (photoelectrons) from the material. If the incident photon has enough energy, many different energy levels of atoms in the sample can be ionized. This process produces a spectrum displaying all accessible energy levels as a distribution of photoelectrons with kinetic energies ( $E_k$ ) dictated by Einstein's law  $E_k = h\nu - E_b - \phi_{\text{spec}}$ , where  $h\nu$  is the energy of the radiation,  $E_b$  is the binding energy of the electron in a particular orbital/level, and  $\phi_{\text{spec}}$  is the work function of the spectrometer.<sup>88</sup> This spectrum contains information on all orbitals/energy states for the sample being analyzed, so the specific peaks to be analyzed are chosen in accordance with what atom(s) or orbitals are of interest to the particular research question. Because XPS spectra are graphed as a function of binding energy, the different chemical binding energies of different electronic states provides insight into the identities and concentration of elements present, their charge/oxidations states among other features. The ability to use XPS to obtain information of the surface and near subsurface of a catalyst by adjusting the photon energy is another highly valuable aspect to this technique.

It is also important to note that XPS is another technique that can be performed across different pressure regimes. It is usually done under UHV conditions, but it can be used at ambient, or near-ambient pressures (AP-XPS or NAP-XPS). Similar to IR techniques, this functional pressure range is highly valuable for model studies as it allows for cross comparison of reaction environments in UHV or at ambient pressures. This comparison across pressure regimes provides information on the effects that higher gas pressures have on the structure of the surface of the catalyst, such as adsorbate-induced segregation effects, as seen in the below example, Figure 11.

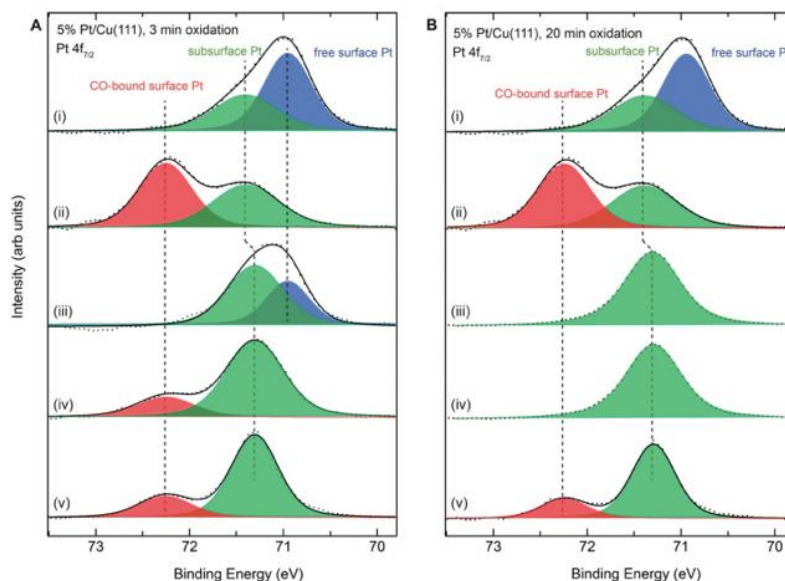


**Figure A1.11.** Pt  $4f_{7/2}$  XPS spectra of 5% PtCu(111) SAA before and after oxidation (A) 3 min, and (B) 20 min: (i) as-deposited surface, measured under UHV at 300 K; (ii) as-deposited surface under  $1 \times 10^{-4}$  Torr of CO at 300 K; (iii) after oxidation under  $5 \times 10^{-6}$  Torr of  $O_2$  at 400 K, measured under UHV; (iv) oxidized sample, under  $1 \times 10^{-4}$  of CO at 300 K; (v) after reduction of the oxide by  $H_2$ , measured under  $1 \times 10^{-4}$  Torr of CO at 300 K. Reproduced with permission from ref 89. Copyright 2020 American Chemical Society.

With regard to SAAs, the majority of work done on dilute bimetallic systems with XPS has been done by the Waluyo and Schlögl groups.<sup>28,89–91</sup> For instance, Greiner coworkers used synchrotron XPS to show that the isolated Cu atoms in a CuAg SAA exhibit a free-atom-like electronic structure even under reaction conditions, and predict that these free-atom-like electronics also exist in other Ag based SAAs.<sup>28</sup> In a different study, Schilling and coworkers used NAP-XPS (Near-ambient Pressure XPS) to demonstrate the effect of Pt on the reduction of oxidized Cu(111) surfaces.<sup>89</sup> Their XPS data showed that oxidized PtCu(111) SAA surfaces are reduced in  $H_2$  much faster than oxidized Cu(111). After an initial induction period the Pt atoms of

the SAA became exposed, which allowed them to dissociate  $\text{H}_2$  and therefore speed up the reduction of the oxide.

## **A1.4 General Properties**

In this section, we will examine the important general properties common to many SAA catalysts which have been discovered in the past ~10 years. These properties include structural stability, increased reactivity without compromised product selectivity, spillover of reaction intermediates leading to bifunctionality, opportunities to break linear scaling relationships, and unique electronic properties. First, we will discuss the thermodynamic stability of SAA catalysts at a fundamental level and then describe how this is influenced by the presence of reaction intermediates present on the catalyst surface under operating conditions. Next, we will discuss the high selectivity and activity observed for many of these SAA catalysts, which in many cases, is aided by spillover pathways leading to bifunctional reaction mechanisms. Lastly, we will look at the free-atom-like electronic properties of SAAs and how SAAs can escape linear scaling relationships that limit the efficiency of traditional catalysts. In these sections, we focus on the catalytic studies which first reported these properties, but there has also been considerable work done on SAAs for a diverse range of thermal, photo-, and electro-catalytic reactions. The interested reader is pointed to reference <sup>15</sup> for a more exhaustive description of these studies.

### **4.1 Structural Stability**

The stability of a SAA depends on two parameters: the aggregation energy and the segregation energy of the dopant atoms in the host metal. The aggregation energy is a thermodynamic value indicative of the relative stability of isolated dopant atoms versus clusters of such atoms in the host metal.<sup>25,92</sup> The segregation energy is a thermodynamic value indicative

of the relative stability of the isolated dopant atoms in the surface layer of the host versus the bulk.<sup>25,92</sup> In most SAAs, the dopant metal generally has a higher reactivity, and hence a higher surface free energy than the host. This relationship leads to the dopant having a negative segregation energy, which means that the dopant atoms are more stable in the bulk of the host metal than in the surface layer under vacuum conditions.<sup>25,92,93</sup> However, adsorbates can stabilize the dopant atom at the surface if the strength of adsorbate-dopant bond is sufficient, which will be discussed later in this section.<sup>25,92</sup> In terms of aggregation energy, if the dopant and host metal have a positive aggregation energy, it is thermodynamically unfavorable to form small clusters, such as dimers and trimers, from monomers. Conversely, if the two metals have a negative aggregation energy, the formation of such clusters will be thermodynamically favored. Therefore, metal combinations in which the dopant has positive segregation and aggregation energies under reaction conditions is conducive to the SAA catalysts being stable for extended periods.

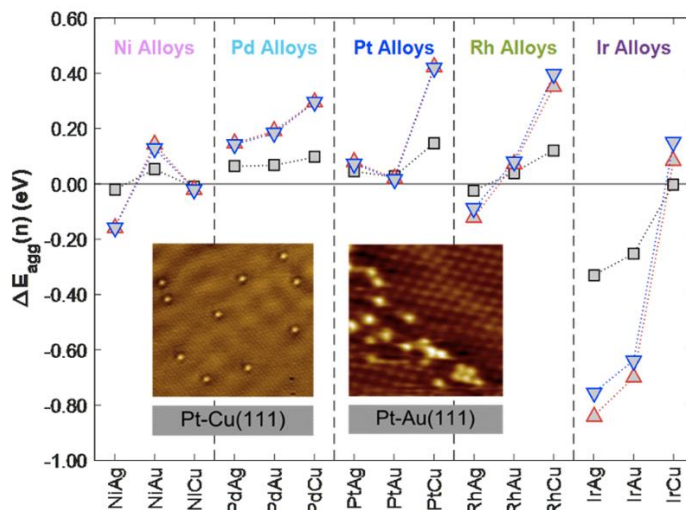


**Figure A1.12.** DFT results predicting which metal combinations thermodynamically favor SAA formation. Aggregation energy,  $\Delta E_{\text{agg}}(n)$ , is shown relative to the SAA phase for the clustering of dopant atoms (Ni, Pd, Pt, Rh, Ir) in the (111) surface of host metals (Cu, Ag, Au) into dimers (denoted by black squares) and trimers where dopant atoms surround face-centered cubic (fcc)

(red up-triangles) and hexagonal close-packed (hcp) (blue down-triangles) sites. Negative values of  $\Delta E_{\text{agg}}(n)$  correspond to preference for surface aggregation, while positive values correspond to a preference for the dopant atom to disperse and form the SAA structure. The insets show STM images of examples when aggregation is not favored (PtCu) versus when aggregation energy is  $\sim 0$  (PtAu) and both single atoms and small clusters of Pt are seen in the surface. Adapted with permission from ref 7. Copyright 2018 American Chemical Society.

Many theoretical studies have examined the thermodynamic tendency for reactive dopant metals to disperse in less reactive coinage metal hosts and thereby form a SAA. Some of the most extensive studies up to this point have been conducted by Stamatakis and coworkers who have investigated Pt, Pd, Rh and Ir atoms alloyed into (111), (100) and (211) facets of Cu, Ag and Au hosts.<sup>25,94</sup> Their results showed that under vacuum conditions most of the dopant atoms are more stable in the bulk rather than in the surface of the host. Stamatakis and coworkers also studied the aggregation energy (the thermodynamic driving force to keep monomers from agglomerating into dimers or trimers). They found that most of the metal combinations they looked at showed a thermodynamic tendency for the dopant atom to isolate and therefore form an SAA.<sup>25,94</sup> Some of their results are shown in Figure 12. For instance, PtCu(111) has a positive aggregation energy which gives rise to isolated Pt sites in Cu, while PtAu(111) has near zero aggregation energy which gives rise to a mixture of isolated sites and small ensembles in the system as shown by the inset STM images in Figure 12. It must be noted that these calculations neglect entropic contributions to the aggregation tendencies of these systems. Entropically, the dispersion of the dopant atom is favored, so as a result, SAA combinations with aggregations energies close to zero may still be accessible experimentally in catalysts operating at, or prepared at, elevated temperatures. An

example of this is the successful preparation of NiCu SAA in model surface science studies and in nanoparticle and nanoporous form.<sup>34,51</sup>

There have been several other DFT studies that screened the structural stability of SAAs. For instance, Fu and Luo looked at aggregation tendencies for a number of other dopant atoms with Cu as the host metal.<sup>92</sup> However, the dopants they investigated that were not screened by Stamatakis and coworkers (Fe, Co, Ru and Os) show a thermodynamic tendency to form ensembles rather than the desired isolated sites. Zhang and coworkers also studied the mixing and segregation energies of a variety of dopants (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn) in a silver host.<sup>95</sup> They found that of these dopant metals, only Sc and Zn showed a tendency for site isolation in the surface layer of the silver host. The other major finding of both these papers was further evidence that the majority of dopant metals prefer to be subsurface in the absence of adsorbates/reaction intermediates.

Recently, machine learning has been increasingly employed to accelerate the screening of new SAA combinations.<sup>96–99</sup> Rao and coworkers looked at the stability of the SAA configuration relative to subsurface, dimer, and adatom configurations using a machine learning approach.<sup>97</sup> They examined 26 d-block metals as well as Al and Pb to form a 28 x 28 database and found that for 250 of these metal combinations, the SAA configuration is the most stable phase. Dasgupta and coworkers used machine learning techniques to predict reaction and adsorption energies for 300 bimetallic d-block compounds in order to identify which of these compounds do not follow known scaling laws.<sup>98</sup> These machine learning based methods may prove especially useful in identifying novel SAAs considering the large phase space of possible combinations of elements.

An important point to note is that the trends discussed in this section, regarding surface aggregation and segregation of bimetallic catalysts, can be strongly influenced by interactions with

adsorbates present under reaction conditions. Adsorbates such CO and H<sub>2</sub> are capable of keeping certain reactive dopant atoms in the surface layer versus the bulk of the host metal.<sup>100</sup> Stamatakis and coworkers examined CO induced restructuring on a wide range of single-atom alloys.<sup>25,67,94</sup> First and foremost, they showed CO adsorption is capable of stabilizing the dopant atom in the surface layer. This phenomenon, known as reverse segregation, is due to the strong CO-dopant bond that can overcome the negative segregation energy of a SAA in the absence of adsorbates.

This has also been confirmed experimentally by NAP-XPS for the case of CO on PtCu SAAs. In addition to these segregation effects, adsorbates can also influence the aggregation of SAAs.<sup>25,92,94,101</sup> While vacuum conditions may favor a certain alloy structure, CO,<sup>25,68,94,102</sup> acetylene,<sup>101</sup> ethanol,<sup>53</sup> oxygen,<sup>103</sup> and other such adsorbates have been predicted to drive aggregation and dispersion of isolated sites as a function of surface coverage of the adsorbate.

This phenomena of adsorbate-induced surface restructuring was confirmed by Ouyang et al. who used DFT calculations to predict that the pressure of CO and temperature affect the stability of the dopant ensembles in a variety of SAA combinations. These calculations indicated that if there is less than one CO per dopant atom then the dopant atoms are stabilized as dimers, whereas if there is one or more CO per dopant atom then the dopant atoms are more stable as isolated atoms. These predictions were then verified using DRIFTS of supported PdAu catalysts which showed that by controlling the surface coverage of CO a PdAu alloy catalyst can be transitioned in situ between a SAA and a Pd cluster structure, and that these two structures of the catalyst exhibited different activity and selectivity for the dehydrogenation of ethanol reaction.<sup>68</sup>

In-situ studies of model SAA systems at elevated pressures were performed by Waluyo and coworkers. Using X-ray photoelectron spectroscopy (XPS) on PtCu model SAAs, they found that CO prevents segregation of the Pt to the bulk, while H<sub>2</sub> has little effect.<sup>90,102</sup> These higher

pressure studies are important as they demonstrate how active sites change at more catalytically relevant reaction conditions. They also found that an standing pressure of CO causes surface segregation of the Pt atoms even at room temperature.

Segregation and aggregation effects can also be caused by the catalyst support. For instance, Christopher and coworkers looked at support effects on the aggregation and segregation of bimetallic NiCu catalysts for the conversion of furfural to 2-methylfuran.<sup>104,105</sup> They found that NiCu particle formation on a titania ( $\text{TiO}_2$ ) support promotes the formation of isolated Ni sites. Conversely, NiCu particles synthesized on alumina ( $\text{Al}_2\text{O}_3$ ) exhibited Ni ensembles. This difference in dopant ensemble size on different supports is due to the strong interactions between Ni and  $\text{TiO}_2$  which results in a lower abundance of Ni at the Cu surface.<sup>104</sup> This is an important result as it shows that choice of support can also affect aggregation and segregation of dopant atoms in nanoparticle SAAs.

To summarize, the aggregation energy of SAAs is a key descriptor of how the dopant atoms mix in the host metal surface, while the segregation energy indicates the preference of the dopant atom to be in or below the surface of the host metal. Importantly, these findings described in this section demonstrate that the site isolation that defines SAAs is in most cases driven by thermodynamics in terms of SAA combinations that have positive aggregation energies, and not merely by dilution. Various theoretical investigations have screened hundreds of bimetallic alloy combinations to provide insight into aggregation and segregation effects thereby providing important guidance for future SAA studies. Furthermore, adsorbates like CO have been shown experimentally and theoretically to also affect both aggregation and segregation of the dopant atoms, but more experimental work is still needed to systematically understand all these adsorbate-induced restructuring effects and to fully test theoretical predictions.

## 4.2 Selectivity and Catalytic Stability

A guiding principle in the field of single-site catalysts is that high reaction selectivity can be achieved if there is only one type of active site present on the catalyst which leads to a single reaction pathway being favored. In contrast, most traditional heterogenous catalysts expose an array of active sites on the metal nanoparticles which can lead to undesirable side reactions being catalyzed.<sup>106,107</sup> SAAs also benefit from the single-site effect as the dopant metal site typically dominates the overall reactivity over the less active host metal nanoparticles on which even the undercoordinated step edges or kinks are less active than the dopant element itself.

SAA catalysts have exhibited high selectivity to desirable products as well as resistance to deactivation for a variety of reactions.<sup>15</sup> These properties are the result of a combination of ligand and ensemble effects as well as bifunctionality that many SAAs exhibit. Ligand effects refer to changes in electronic structure of metals due to alloying, and ensemble effects refer to changes in the number of atoms that make up an active site.<sup>108</sup> It is well accepted in catalysis that the best catalysts bind molecules with an intermediate strength that is strong enough to activate the desired bonds, but weak enough to desorb the desired products without further reaction to undesirable products. This trade-off is the basis of the century-old Sabatier principle and gives rise to volcano plots where the metals exhibiting the best catalytic performance bind molecules with an intermediate strength and are located at the top of the volcano.

SAAs are generally comprised of highly selective host metals such as Cu, Ag or Au doped with individual atoms of a more reactive metal such as Pd, Pt Rh, Ru or Ni. The reactive metals themselves are often at the top of the volcano plot for many reactions, but they are still afflicted by issues such as catalyst deactivation and non-ideal selectivity. These issues arise because while these reactive metals activate reactants, they also promote unfavorable steps such as C-C bond

activation which leads to side product formation, and they bind C strongly which commonly leads to coking.

Many SAAs are resistant to this deactivation pathway as the atomic dispersion of the active elements generally prevents reactions that result in coke formation such as C-C bond scission. The ultimate extreme of the ensemble effect, the single atom, allows the reactive dopant metal to perform selective chemical reactions without deactivating due to for example, coking. Additionally, the host metals are chosen for their resilience to coking to further enhance this catalytic stability. Furthermore, the spatial location of the transition and final states for bond breaking steps on SAAs are often separated which can enable both low reaction barriers and weak binding of reaction intermediates, which are the two key requirements for active and selective reaction chemistry.<sup>27</sup>

The SAA geometry also gives rise to important ligand effects i.e. electronic structure changes of the dopant atoms and surrounding host that can affect chemical reactivity. For most SAAs, ligand and ensemble effects induced by the substitution of a host metal atom with a reactive dopant atom led to considerably weaker binding of adsorbates to the dopant metal. For instance, CO desorbs from a single Pd atom in a Cu(111) surface at 270 K whereas it doesn't desorb until ~500 K for pure Pd(111) meaning that the electronic structure of isolated Pd atoms in Cu is very different to pure Pd.<sup>109</sup> Surface strain has been used to explain some of these effects, but it cannot account for all observations, such as CO having near identical desorption temperatures from PdCu (270 K) and PdAu (260 K) despite the lattice difference of Cu (0.256 nm) and Au (0.288 nm) being significantly different.<sup>109–111</sup>

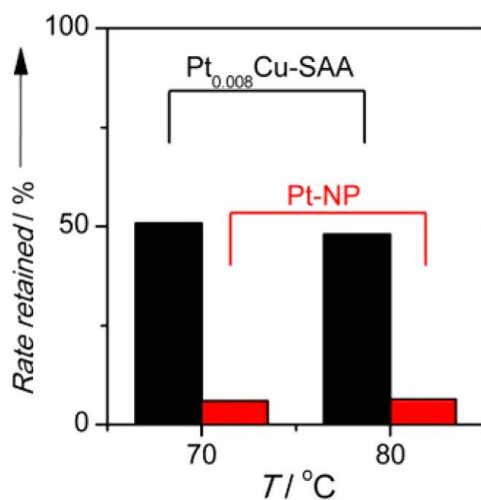


**Figure A1.13.** Ratio of retained reaction rate of acetylene hydrogenation in CO over PtCu SAA and Pt nanoparticles at different temperatures. Rate retained is equal to reaction rate with CO divided by reaction rate without CO in the reaction gas. Gas composition was 20% H<sub>2</sub>, 2.2% C<sub>2</sub>H<sub>2</sub>, 200 ppm CO, 10% Ar and the rest He. Reproduced with permission from ref 23. Copyright 2016 American Chemical Society.

In fact, many SAAs display CO tolerance due to weaker binding of CO to isolated sites compared to the pure dopant metals.<sup>25</sup> This weaker CO binding leads to favorable properties. For example, Liu and coworkers showed that the introduction of 200 ppm CO to the reactant stream in the hydrogenation of acetylene to ethene led to a 90% loss of activity of Pt nanoparticles vs only a 50% drop for PtCu SAA nanoparticles as seen in Figure 13.<sup>23</sup> This CO tolerance illustrated for the selective hydrogenation of acetylene to ethene is predicted to be a somewhat general property for many SAAs.<sup>94</sup>

Another considerable advantage SAAs hold over many other single-site catalysts is their impressive thermal stability under reducing conditions. This thermal stability arises due to the fact that for many SAA combinations, isolated single atom sites are thermodynamically preferred

relative to ensembles.<sup>25</sup> The preference to form single atom sites allows SAAs to overcome a major issue in the field of single-atom catalysts which is the sintering of the single atom sites into ensembles.<sup>112</sup> For example, Sun and coworkers demonstrated remarkable stability of PtCu SAAs for propane dehydrogenation at 520 °C for 120 h on steam.<sup>59</sup> The catalyst was analyzed post reaction, revealing that the Pt sites remained isolated even after reaction under relatively harsh conditions. When Sun and coworkers heated the catalyst to 600 °C, they observed sintering of the Cu host nanoparticles themselves, resulting in catalyst deactivation. However, HAADF-STEM images revealed that the Pt atoms in the sintered Cu nanoparticles were still present as isolated sites. This finding does highlight that one current limitation of SAAs is the stability of the host nanoparticles themselves, rather than the isolated sites, leading to high temperature deactivation via sintering and loss of surface area. In fact, some SAAs are more thermally stable than the pure host metal nanoparticles, for example, Giannakakis et al. demonstrated that NiAu nanoparticles exhibit stability with respect sintering compared to pure Au nanoparticles, but the reason behind this stability has not been fully understood.<sup>53</sup> Despite this improvement in sintering, coinage metal-based SAAs are still not capable of stable operation at temperatures > ~400°C such where some industrial reactions take place. As a result, more work must be done to increase the thermal stabilities of SAAs to allow them to function under even the harshest industrial reaction conditions. One approach to further improve the thermal stability under harsh conditions may be to stabilize the host nanoparticles against sintering by overcoating the NPs with thin layers of a metal oxide using atomic layer deposition and related techniques.<sup>113–115</sup>

### 4.3 Spillover and Bifunctionality

A significant advantage of bifunctional catalysts is their ability to deviate from linear scaling relationships that can limit catalytic performance via the fact that different reaction steps can occur at different sites.<sup>6,7,116</sup> SAAs are good candidates for bifunctional chemistry as they have two distinct sites; the reactive dopant atom and the less active but more selective host. Tierney et al. examined hydrogen activation and spillover on PdCu SAAs, and they found H<sub>2</sub> activation was facile on individual isolated Pd atom sites and H atoms spilled over to the weaker binding Cu host.<sup>21</sup> Subsequently, Sykes and coworkers studied the effect of spillover on reactivity using the hydrogenation of styrene and acetylene on PdCu SAAs.<sup>5,21</sup> When hydrogen pre-covered PdCu and SAAs were exposed to alkenes or alkynes, 100% selective hydrogenation was observed. Specifically, the Pd sites dissociate the hydrogen which spills over onto the Cu where selective hydrogenation is able to occur via a bifunctional mechanism.

Another example of this SAA bifunctionality from Liu et al. is shown in Figure 14b, where H atoms have spilled over from isolated Pt sites to Cu as seen in the STM images.<sup>23</sup> The H atoms appear in STM images as depressions which can be removed from the scan area via imaging at 200 mV. The depressions that remain behind are CO molecules which can be removed with 5 V pulses after which the Pt sites beneath each CO molecule are observed. This set of STM experiments definitively demonstrates that the individual Pt atoms are preferred sites for CO adsorption and that H occupies the Cu surface. Unlike PdCu and PtCu SAAs which exhibit spontaneous H atom spillover, PdAu SAAs did not show H spillover from Pd to Au due to the weaker binding of H to Au. However the adsorption of CO or hexyne could be used to force dissociated H atoms at the Pd site onto the Au surface.<sup>22,110,111,117</sup> These adsorbates bound preferentially to the Pd atoms which induced the spillover of H to Au. Furthermore, Jiang et al.

suggested in a recent paper that while hydrogen spillover from Pd atoms occurs on different facets of Cu, the degree of hydrogenation by spillover hydrogen is facet dependent.<sup>118</sup>

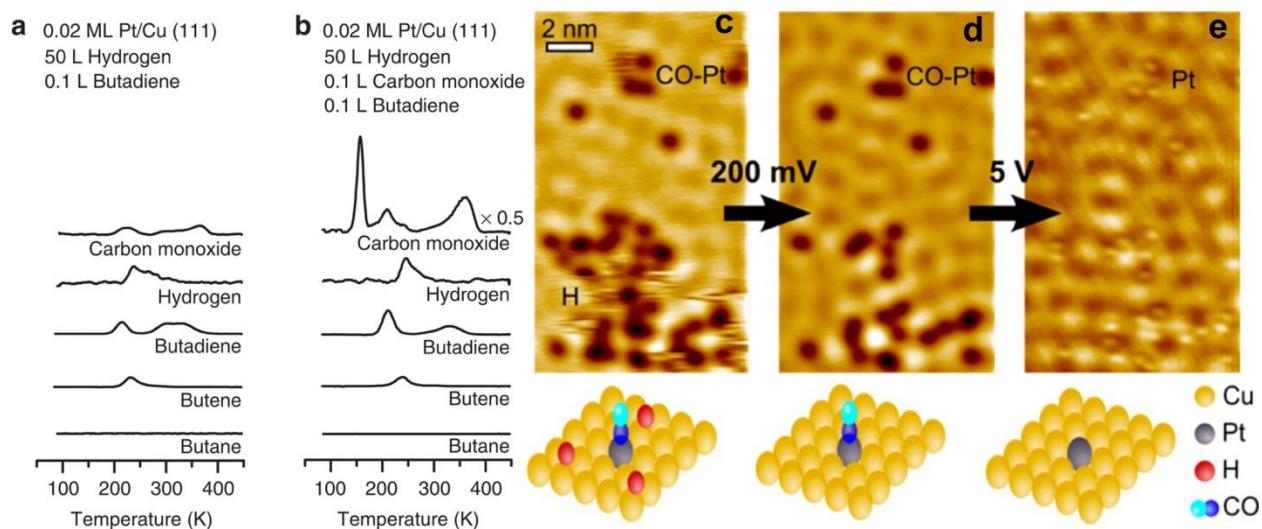


**Figure A1.14.** Demonstration of bifunctional reaction mechanisms on SAAs. The left figure shows a bifunctional reaction mechanism for the hydrogenation of butadiene to butene. TPD traces for the coadsorption of H<sub>2</sub> and butadiene (a) without and (b) with CO on 2% PtCu(111) revealing identical product distributions which indicates that the hydrogenation step occurs on Cu sites. H<sub>2</sub> was adsorbed on the surface before adsorption of CO. Reproduced with permission from ref 49. Copyright 2015 Springer Nature. The right images show STM images of the coadsorption of H and CO on a PtCu(111) SAA surface and STM tip-induced adsorbate removal which reveals the binding sites underneath. (C) H and CO adsorbed on the PtCu(111) SAA. (D) Image of the same area following scanning at 200 mV to remove adsorbed H. (E) 5 V pulses removed adsorbed CO revealing individual Pt atoms underneath each removed CO molecule. Reproduced with permission from ref 23. Copyright 2016 American Chemical Society.

To add to the understanding of these types of bifunctional reaction mechanisms, Sykes and coworkers performed experiments on the hydrogenation of butadiene to butene on PtCu SAAs as shown in Figure 14a and b.<sup>49</sup> They utilized the “molecular cork effect” to selectively block sites and study the effect on reactivity.<sup>109,119</sup> When hydrogen is exposed to clean PtCu SAAs, the hydrogen desorbs around 230 K. However, if the Pt sites are selectively titrated by CO post hydrogen adsorption (similar to the process shown in Figure 14C - E), the hydrogen desorbs ~55 K hotter due to the CO blocking the Pt sites and the H being trapped on the surface due to the high H<sub>2</sub> recombination barrier on Cu(111). This phenomenon has been termed the molecular cork effect as CO is acting as a molecular cork to keep hydrogen on the surface beyond its normal desorption temperature.

This effect can also be used to selectively block single atom dopant sites to examine which reaction steps involve which surface sites. Specifically, if the Pt sites are selectively blocked with CO before hydrogen exposure, no hydrogen is observed/detected on the sample. The lack of adsorbed hydrogen indicates that the Pt sites are responsible for H<sub>2</sub> activation. If hydrogen is adsorbed, and then the Pt sites are blocked with CO, subsequent exposure to butadiene and heating results in the hydrogenation of butadiene to butene with the same conversion and selectivity as the CO-free SAA. This important result provides definitive evidence for the bifunctionality of the PtCu SAA for selective butadiene hydrogenation in demonstrating that the Pt atom sites supply the hydrogen, but the hydrogenation itself occurs solely on Cu because the butene yield is the same regardless if the Pt sites are blocked with CO.<sup>6,49</sup>

#### **4.4 Electronic Structure & Deviations from Linear Scaling**

Linear scaling relationships that correlate the energy of the transition state to the binding energy of key intermediates have been well established in the heterogenous catalysis field.<sup>120</sup> As

these scaling relationships often limit catalyst performance, there has been significant interest in discovering methods for deviating from the established scaling relationships in order to improve catalyst performance. Many approaches to this problem have been taken including metal doping, near-surface alloys and engineering strain effects.<sup>116</sup> Both experimental and theoretical work from multiple groups has shown SAAs are capable of breaking traditional linear scaling in several important reaction steps.<sup>7,27,59</sup> One such study, from Darby et al. looked at the scaling relationships for five elementary reactions on twelve different SAAs and compared them to reactions on the pure metals.<sup>27</sup> They found that CH<sub>4</sub>, H<sub>2</sub>, and NH<sub>3</sub> dissociation steps display different scaling behavior on SAAs compared to the pure metal surfaces, while CO<sub>2</sub> and CH<sub>3</sub>OH did not exhibit such a difference. They explained this trend by considering the aforementioned distinct differences between the transition state and final state geometries for each reaction. Some of these scaling behaviors are represented in Figure 15.

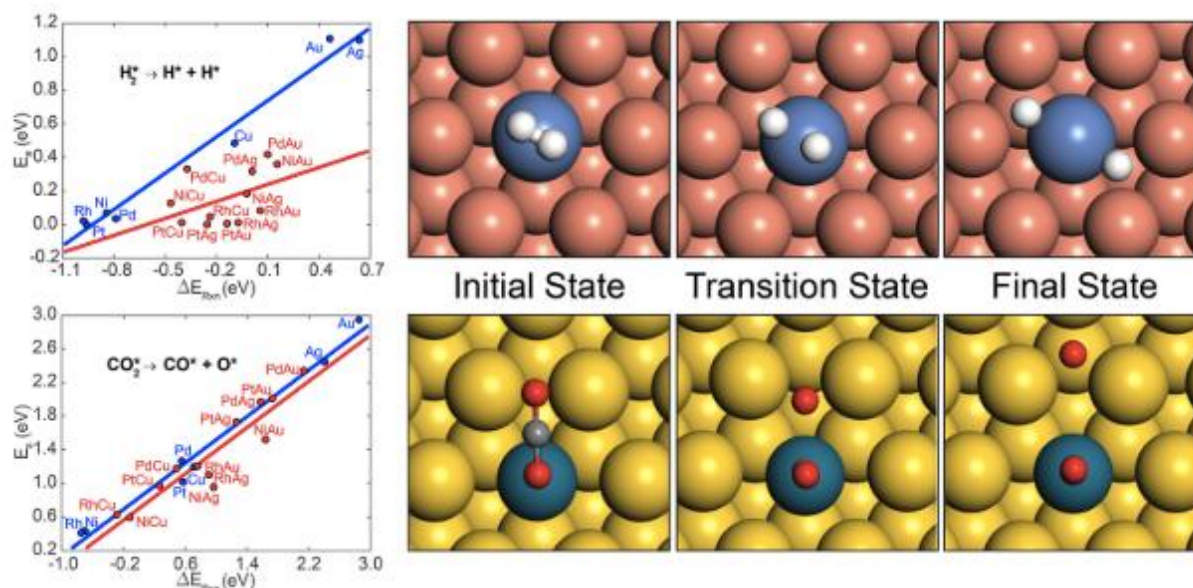


**Figure A.15.**  $H_2$  and  $CO_2$  dissociation on SAAs. Brønsted-Evans-Polanyi relationships for simple catalytic bond scissions on pure metal (111) surfaces (blue) and SAA surfaces (red). Activation energy ( $E_a$ ) is plotted as a function of the reaction energy ( $\Delta E_{rxn}$ ). The panel graphics on the right show initial state (left), transition state (middle), and final state (right) for  $H_2$  dissociation on NiCu(111) SAA and  $CO_2$  dissociation on PdAu(111) SAA. Adapted with permission from ref 27. Copyright 2018 American Chemical Society.

For instance, with  $H_2$  dissociation, the transition state is atop and stabilized by the isolated dopant, while in the final state, the H atoms are coordinated more with the weaker binding host metal in three-fold hollow sites as seen in Figure 15. Spillover of hydrogen from the dopant site to the host metal increases the deviations from linear scaling even further. In contrast, the  $CO_2$  dissociation transition state has the dissociating O coordinated to the host in a hollow-like configuration that is similar to the final state. This arrangement leads to little net stabilization of the transition state compared to the final state, and therefore no significant deviations from linear scaling would be expected for this elementary step. In a related study, Dasgupta et al. used machine

learning to study an even wider range of metal combinations.<sup>121</sup> They used this approach to highlight SAA combinations that have the highest potential for deviating from traditional scaling relationships.

Thirumalai and Kitchin also demonstrated that the d-band center, a common and normally apt descriptor of the binding strength of metal surfaces, is not a good descriptor of the dopant atoms' binding energy in SAAs. Work has also been performed to examine the electronic structure of SAAs from both a theoretical and experimental standpoint. Most notably, Thirumalai and Kitchin carried out a screening of 15 SAAs and found many of these SAA combinations showed sharp electronic features of the dopant atom near the Fermi edge.<sup>26</sup> These sharp density of states features correspond to the isolated dopant atom's d-orbitals. In general, the Ag and Au SAAs displayed the narrowest electronic states that closely resembled the d-states of the gas phase dopant atoms, so called "free-atom-like" electronic states. They conclude that this deviation from the d-band theory bodes well for breaking linear scaling relationships.<sup>122,123</sup> However, studies where more reactive metals such as Ni or Pt were used as host metals for forming SAAs appeared to follow the d-band model, i.e. the d-band center is a good descriptor of binding energy.<sup>124,125</sup> Together, these two sets of work suggest that there may be something unique about the coinage metal SAA combinations.

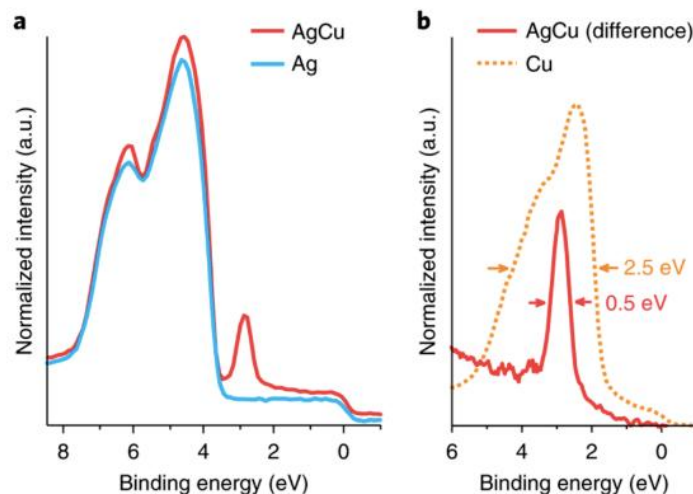


**Figure A1.16.** Density of states plots demonstrating the free-atom-like nature of dilute Cu atom 3d states in a Ag host. (a) The measured valence photoemission spectra ( $h\nu = 150$  eV) of an AgCu alloy that contained 0.3% Cu and metallic Ag reveal the narrow Cu 3d states at a binding energy of  $\sim 2.5$  eV. (b) The difference spectrum of AgCu and Ag plotted with a reference Cu spectrum. The spectrum shows that the Cu 3d states in AgCu are five times narrower than those of bulk Cu. (Note: in this figure Greiner et al. refer to isolated Cu atoms in Ag as AgCu which is opposite of the naming convention we use for this chapter where the dopant metal is followed by the host metal). Adapted with permission from ref 28. Copyright 2018 Springer Nature.

Greiner et al. were the first to demonstrate this concept of isolated free-atom like electronic states experimentally.<sup>28</sup> Specifically, they looked at CuAg SAA catalysts with Cu loadings low enough such that the Cu atoms were isolated in the Ag host surface. The XPS results show a narrow electronic state close to the Fermi level which corresponds to the isolated Cu atom in Ag (see Figure 16). These results are important as they demonstrate that the electronic structure of SAAs can be “atom-like” which is common in homogenous catalysts in which ligands are used to tune the electron density and hence reactivity of the metal center. In this regard, the dopants of some

SAA catalysts that display these narrow electronic states can be thought of analogously as the metal centers in homogeneous catalysts.

#### **A1.4 Industrial Scale-up**

The most significant challenge for the industrial adoption of promising new catalyst formulations is the scale-up to pilot and industrial scale use. The potential issues of industrial scale-up fall into one of two areas. First, the complexity of how the catalyst is synthesized e.g., those that involve multiple synthesis steps, expensive materials, or the incompatibility with current industrial processes makes industrial adoption unlikely. Secondly, the lack of long-term catalyst stability under the dynamic environment of an industrial scale reactor in terms of e.g., heat losses or temperature runaway along the bed, both of which can deactivate the catalyst poses another challenge. However, SAA catalysts appear well poised to overcome such challenges as discussed below.

As described in Section 2.2, a wide variety of methods can be employed for the synthesis of SAAs in nanoparticle form. Some of these synthesis processes, such as controlled surface reaction or galvanic replacement, involve a high level of complexity. However, alternative techniques, such as impregnation or sequential reduction offer precise control over the alloying through simple steps and are therefore considered ideal for the large-scale production of SAA catalysts. Furthermore, as also mentioned in Section 2.2, Gan et al. have successfully implemented a ball milling procedure for kilogram-scale production of SAAs.<sup>11</sup>

Regarding the thermal stability of SAAs as discussed in Section 3.2, high temperature catalytic studies have demonstrated that active site isolation persists to high temperature.<sup>25,59,115</sup> This is because many SAAs have negative mixing enthalpies which favors isolation over

aggregation, and in addition, the entropic stabilization of the isolated atom active sites is larger at higher temperatures. Furthermore, the issue of single atom active sites segregating to the bulk of the host metal is not a major concern in many SAA catalysts because the reactants and intermediates themselves generally bind more strongly to the dopant atoms which helps to stabilize them in the surface.<sup>25,68,92</sup> While site isolation is not generally a concern, the SAA nanoparticles themselves can be prone to sintering as it is well known that Cu, Ag, and Au nanoparticles suffer from significant sintering at elevated temperature. However, alloying low concentrations of dopants into these metals can significantly increase their thermal stability. An example of this approach already used in industry is the addition of small amounts of Cr to stabilize Cu particles for ethanol dehydrogenation.<sup>126</sup> A similar effect has been demonstrated for small amounts of Ni added to Cu to form a SAA. These NiCu SAAs were not only stable for prolonged periods, but the Ni also aided in the ethanol dehydrogenation reaction itself.<sup>38</sup> These NiCu SAAs are inexpensive and more environmentally friendly catalysts that exhibit increased reactivity and stability compared to pure Cu while retaining the desired high selectivity of Cu. As a result, NiCu SAAs are promising catalyst materials for use in industry for dry alcohol dehydrogenation reactions.

This valuable effect of suppressed sintering is not fully understood yet, and it is not always significant enough to fully stabilize the catalyst at the desired reaction temperatures. This is especially important for alkane dehydrogenation reactions which operate at ~600 °C. For example, alkane dehydrogenation on PtCu SAAs was limited to ~400 °C due to the sintering of the host particles.<sup>24</sup> While this is a considerable improvement over pure Cu, it is still not stable enough to run at industrially desired temperatures. However, Sun et al. used coimpregnation instead of galvanic replacement as the synthesis method for PtCu SAA catalysts and found that the resulting particles were partially encapsulated in the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support, which enabled propane

dehydrogenation to be performed up to 520 °C.<sup>59</sup> Another method that has been shown to stabilize SAAs is the use of reverse colloid templates which have been used for the partial encapsulation of PdAu SAA nanoparticles in silica, allowing for their operation at high temperatures while avoiding sintering.<sup>113–115</sup> Atomic layer deposition over Cu nanoparticles has also been used for the preparation of sinter-resistant catalysts, and should be able to be successfully applied to SAAs which would enable the synthesis of very thermally robust catalysts.<sup>127,128</sup> Many other methods for stabilizing metal catalysts have been described at length in other literature. For more information on such methods see references <sup>129–133</sup>.

Some SAAs have already been shown to be effective for operation under industrially relevant conditions. For instance, PtCu SAAs were shown to be highly stable, active and selective for the hydrogenation of butadiene to butene under industrial process conditions.<sup>49</sup> Specifically, butadiene hydrogenation is an industrially important process as one must remove butadiene impurities from propylene feedstocks prior to polymerization because butadiene poisons the polymerization catalyst.<sup>134</sup> PtCu SAAs have been shown to selectively hydrogenate 1,3-butadiene to butenes at mild temperatures in excess propylene without reducing the propylene itself.<sup>49</sup> Importantly, this selectivity was maintained even at high conversion which is an important criterion for an industrial process.<sup>49</sup> In another example, the extensive study of Pd doped Au, Ag, and Cu nanoparticles performed by the Zhang group for the partial hydrogenation of acetylene demonstrated the successful synthesis of active, selective and stable SAA catalysts that are capable at operating at industrially relevant conditions.<sup>57,135</sup>

Overall, there are existing synthesis methods that can be used to produce large quantities of SAA catalysts, methods to stabilize the SAA particles against sintering, and great promise for their successful operation under industrially relevant conditions. Moreover, the fact that many

SAA combinations bind CO (a common catalyst poison) weakly and do not suffer from coking that plagues some current industrial catalysts, bodes well for their application in both large-scale industrial and distributed processes such as three-way catalysts. Thus far, there appears to be no intrinsic limitations on the widespread use of SAA catalysts in the chemical, energy and automotive sectors, and some current industrial processes may serendipitously benefit from SAA geometries in the working phase of bimetallic catalysts. For example, small amounts of Pd in industrial Cu-based catalysts have been shown to benefit the methanol synthesis reaction by keeping the Cu in a more reduced and active state.<sup>136</sup>

## **A1.5. Conclusion and Future Directions**

SAA catalysts are a new class of heterogeneous catalyst that exhibit many novel and desirable properties. SAA catalysts consist of an active dopant metal atomically dispersed in a less active host metal. This atomic dispersion is essential to the function of SAA catalysts as it results in well-defined active sites, which is a significant advantage over other heterogeneous catalysts as it allows relationships between the SAA structure and reactivity to be elucidated. These structure-function relationships underpin the rational design of next generation heterogeneous catalysts. Thus far, a lot of the work on SAA catalysts has been focused on dehydrogenation and hydrogenation reactions. While performing these studies on both model and nanoparticle catalysts, many unique properties of SAA catalysts were discovered. These properties include high selectivity to desirable products, resistance to deactivation by typical catalyst poisons, novel electronic structures, spillover pathways that lead to bifunctionality, the ability to break traditional linear scaling relationships, and lastly, and perhaps most importantly, opportunities for rational catalyst design. SAA catalysts are still a relatively young field, and although a significant amount of work has been performed in this area since 2012,

more research is needed to fully understand the properties of SAAs made from a wider range of metal combinations and for a different reactions.

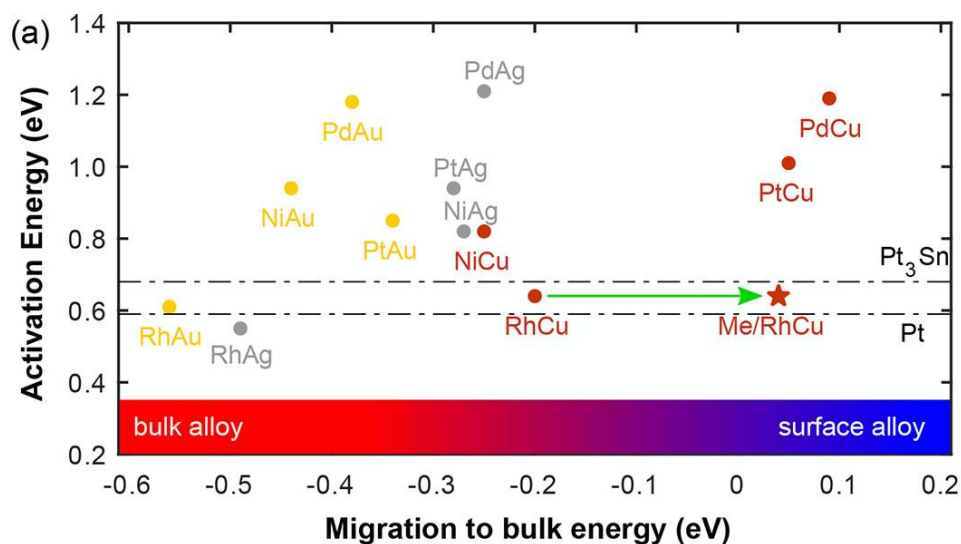


**Figure A1.17.** Theoretical screening of SAA catalysts for C-H activation. Activation energy of the first C-H cleavage in CH<sub>4</sub> is plotted against segregation energy of each SAA. RhCu maximizes resistance to bulk segregation and minimizes the activation energy for methane activation. The star shows how the RhCu SAA point shifts its preference to be a surface alloy when methyl is adsorbed on the surface. Adapted with permission from ref 29. Copyright 2021 Science.

Computational screening has been demonstrated to be a promising route for guiding future SAA studies into a wider range of reactions by identifying SAA combinations which are as active, or even more active, than the parent metal, thus optimizing metal combination choices for future studies and new reactions. Theory-led design can thereby inform the design of new catalysts, as illustrated in Figure 17. Theoretical screening predicted that the RhCu SAA is a promising catalyst for C-H activation in terms of the alloy stability, weak binding of intermediates, and a low C-H activation barrier. Surface science experiments supported these calculations, and reactor results

demonstrated the successful rational design of a new propane dehydrogenation catalyst from first principle calculations.<sup>29</sup>

While we have predominantly discussed thermal catalysis in this chapter, there is also emerging work in both photo- and electro-catalysis as these approaches have shown promise in catalyzing reactions that are difficult under thermal conditions. For example, Zhou et al. demonstrated that RuCu SAAs were effective at facilitating the dry reforming of CH<sub>4</sub> with CO<sub>2</sub> to yield syngas (CO and H<sub>2</sub>).<sup>10</sup> They found that the SAA particles were both more selective and active under illumination by white light compared to thermal catalysis conditions. Other groups have also reported similar results where photocatalytic conditions sped up reactions on SAAs.<sup>137,138</sup> There has also been progress on SAAs studied in the field of electrocatalysis. One of the first reports from Behm and coworkers demonstrated, using a combination of cyclic voltammetry and in situ STM, that Pd monomers in Au promoted CO oxidation.<sup>45</sup> Other studies on electrocatalysis on SAAs demonstrated PtPd SAAs outperform commercial catalysts for hydrogen evolution and oxygen reduction reactions,<sup>12</sup> PtAu SAAs have been shown to be highly active for formic acid decomposition,<sup>139</sup> and RuPt SAAs outperform commercial catalysts for methanol oxidation.<sup>14</sup> Lastly, there has also been theoretical screening work performed on SAA electrocatalysts that used first-principles calculations to guide future studies in this area.<sup>140–142</sup>

Looking ahead, there are many new opportunities for the development of SAA catalysts. The biggest area for further exploration is to expand both the number of metal combinations and reactions examined on SAAs. Another exciting direction involves trimetallic SAAs where small amounts of two active dopant metals are alloyed into a more inert host. Trimetallics offer an even larger design space than SAAs and may offer solutions for challenging multi step reactions.

Overall, SAAs combine the uniform active sites, typical in homogenous catalysts, with the robust thermal stability common in heterogeneous catalysts. This thermal stability, combined with the excellent catalytic activity and the facile, low-cost synthesis methods, renders SAAs as ideal candidates for scale-up and use in industrial chemical conversions. As such, SAAs have a promising future ahead in thermal catalysis as well as their rapid adoption by other fields such as photo- and electro-catalysis.

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