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PII: S0039-6028(21)00193-X
DOI: <https://doi.org/10.1016/j.susc.2021.121990>
Reference: SUSC 121990



To appear in: *Surface Science*

Received date: 22 August 2021
Revised date: 8 November 2021
Accepted date: 11 November 2021

Please cite this article as: Ryan T. Hannagan , Yicheng Wang , Romain Réocreux , Julia Schumann , Michail Stamatakis , E. Charles H. Sykes , PORATAL Tuning the Product Selectivity of Single-Atom Alloys by Active Site Modification, *Surface Science* (2021), doi: <https://doi.org/10.1016/j.susc.2021.121990>

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Tuning the Product Selectivity of Single-Atom Alloys by Active Site Modification

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Highlights

- RhCu single-atom alloys catalyze both ethyl hydrogenation and dehydrogenation
- Isolated Rh atoms in the single-atom alloy can be selectively populated with CO
- The amount of adsorbed CO can be used to control product selectivity towards ethene

Abstract

There is widespread interest in developing catalysts with uniform active sites that consist of single atoms, thereby simplifying the reaction mechanism and improving product selectivity. We examine experimentally how CO can be used to modify the active sites on a strong binding single-atom alloy and examine how this in turn impacts product selectivity for a reaction that has two different pathways. Specifically, we find that CO can be used to selectively block isolated Rh atom active sites in a RhCu(111) model single-atom alloy catalyst surface and promote the dehydrogenation pathway for adsorbed ethyl groups by suppressing the hydrogenation pathway.

1. Introduction

Improving and controlling product selectivity are key aims in heterogenous catalysis research. One strategy that has recently been implemented involves reducing the structural complexity of the active site to a single supported atom. The presence of such uniform, isolated

active sites in single-atom catalysts can enable high selectivity by virtue of the single atom catalyzing just one reaction pathway.¹⁻³ Single-atom alloys (SAAs) are a subset of single-atom catalysts.⁴ These materials are generally comprised of a reactive dopant metal atomically dispersed in a more inert but selective host metal.⁵ SAAs have been shown to catalyze a wide range of industrially relevant reactions, and display many interesting and useful properties such as deviations from traditional scaling relationships, unique “free-atom” like electronic states, bifunctional reaction mechanisms, and resistance to catalyst poisons.⁵⁻¹¹ For example, Sykes and coworkers have shown that PtCu SAAs are resistant to the effect of CO poisoning during hydrogenation reactions.¹¹ This is important because even trace amounts of CO often present in hydrogen streams can poison the Pt-based materials common in hydrogen fuel cells.¹² Specifically, they found the addition of 200 part-per-million CO to the reaction stream resulted in a >90% reduction in the hydrogenation rate of acetylene for pure Pt catalysts, as opposed to only a ~50% reduction for PtCu SAA nanoparticles.¹¹ This result was rationalized based on the weaker binding of CO to isolated Pt atoms in Cu compared to extended Pt surfaces. Furthermore, this CO-tolerance appears to extend to other SAAs as recent theory papers have identified SAA bimetallic combinations that display weakened binding of CO as compared to the pure dopant metal surface.^{13,14}

The RhCu SAA has recently been shown to be a promising C-H activation catalyst.¹⁵ However, unlike most other SAAs which have been tested experimentally such as PdCu, PdAu, PtCu, NiCu, and PtAg that bind CO more weakly than the dopant metal – isolated Rh atoms in Cu bind CO quite strongly.^{11,16-20} In fact, the binding strength of CO to isolated Rh atoms in Cu is close to CO bound to Rh(111).²⁰ This is somewhat unique amongst the experimentally demonstrated SAAs which tend to bind CO weaker than the pure dopant metal and raises an important question: how does this strongly bound CO influence reactivity and selectivity? Herein, we examine the chemistry of surface-bound ethyl groups which have two distinct reaction pathways – hydrogenation to ethane and dehydrogenation to ethene – and show how selective blocking of the Rh sites with CO can be used to change the preferred pathway. This effect can not only be used to understand the role of the dopant atom by turning on and off its reactivity, but also to tune the relative amounts of each product at intermediate CO coverages.

2. Experimental Methods

Temperature programmed desorption (TPD) experiments were performed in a home built ultra-high vacuum (UHV) chamber with a base pressure of $< 1 \times 10^{-10}$ mbar pumped with a turbomolecular pump (HiPace 300) and a titanium sublimation pump. The chamber was equipped with a Hiden mass-spectrometer (HAL 201) capable of being advanced to within 1 mm of the crystal face for TPD measurements. All TPDs were run with a 2 K/s heating rate. Cu(111) crystals from Princeton-Scientific (99.999%, $< 1^\circ$) were used for all experiments and cleaned with repeated cycles of argon ion bombardment (RBD sputter gun, 5×10^{-5} argon pressure, $\sim 2 \mu\text{A}$ drain current, 1.5 keV beam energy) and thermal annealing to ~ 720 K. Ethyl iodide (99%

purity) was purchased from MilliporeSigma and further purified by repeated cycles of free-pump-thawing. Argon and CO gases were purchased from Airgas and used as received. To prepare the RhCu(111) surfaces, Rh was deposited on Cu(111) using a flux monitored electron bombardment evaporator (EFM 3, Scienta Omicron) at ~420 K to promote alloying and prepare RhCu(111) SAAs as previously described.²⁰ Scanning-tunneling microscopy (STM) experiments were conducted in a separate low-temperature STM chamber (Scienta Omicron) pumped with a series of ion, turbomolecular, and titanium sublimation pumps. The base pressure of the preparation chamber was $\sim 2 \times 10^{-10}$ mbar and that of the STM chamber was $< 1 \times 10^{-11}$ mbar. TPD data for each desorbing species were corrected for the ionization cross section, fragmentation pattern, and mass spectrometer quadrupole m/z sensitivity using values from NIST or previous experimental calibration.²¹ The TPD traces were then compared to a saturation coverage of CO on Cu(111), which has a known packing density of 0.52 CO molecules per Cu atom,²² to convert the TPD desorption traces to ML/s (monolayer per s). The ML is defined as the number of molecules per Cu atom in the Cu(111) surface. The m/z traces presented are as follows: hydrogen (m/z 2), ethene (m/z 27), carbon monoxide (m/z 28), and ethane (m/z 30). As ethane has a significant fragment at 27, we subtracted this component from the ethene desorption traces. Specifically, the ratio of m/z 30 to m/z 27 for pure ethane is ~ 1.5 as experimentally measured by mass spectroscopy of neat ethane (Matheson Tri-Gas). Reaction selectivity was calculated by dividing the TPD trace area of the product of interest (either ethane or ethene) by the total amount of ethane plus ethene. For instance, the ethene selectivity is calculated by: $S_{\text{Ethene}} = \frac{A_{\text{Ethene}}}{A_{\text{Ethene}} + A_{\text{Ethane}}} \times 100$, where S is the selectivity in %, and A is the corrected TPD trace areas.

3. Results and Discussion

In order to first examine the energetics of CO binding to both the Cu host and the RhCu SAA we performed CO TPD experiments. As seen in Fig. 1, CO desorption from Cu(111) occurs below 220 K due to the weak binding of CO to Cu.^{20,23} However, when a small amount of Rh is deposited on Cu(111), a new desorption feature at ~470 K is observed which corresponds to CO bound to isolated Rh atoms.²⁰ The left inset in Fig. 1 displays a 5 K STM image of isolated Rh atoms in Cu(111) which are covered by adsorbed CO. This is directly visualized by experiments in which we use the STM tip to provide localized high-voltage pulses that removes the CO. As seen in the insets, we start with 5 isolated Rh atoms bound to CO (which appear in the STM image as depressions), and then remove the CO by applying 8 V pulses to reveal the Rh atoms underneath which appear as protrusions. Together, these results demonstrate that low coverages of CO can be used to selectively bind to and block isolated Rh atoms.

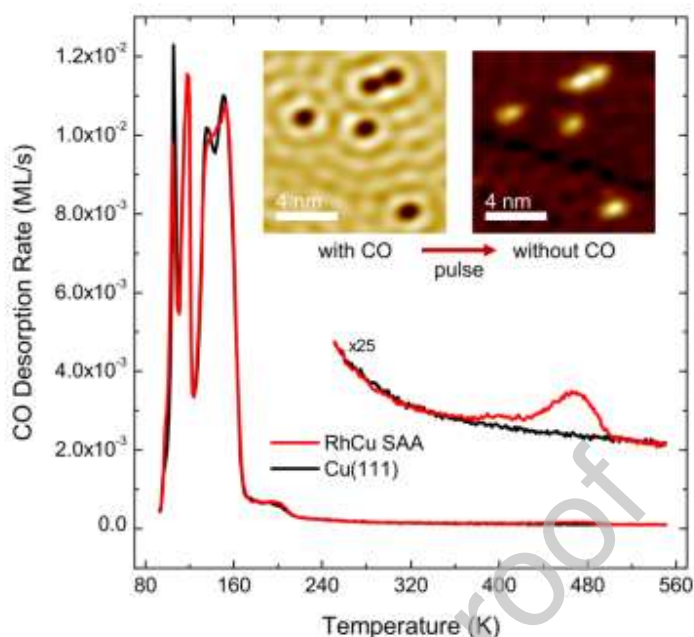


Fig. 1. TPD and STM results showing selective occupation of Rh atom sites with CO molecules. Black and red traces show TPD of saturation CO on Cu(111) and a 0.2% RhCu(111) SAA surface. Insets show STM experiments where 8 V pulses (before and after) were used to remove CO from the isolated Rh atoms. Imaging conditions were 30 mV and 30 pA in both cases.

To understand how this selective blocking of isolated Rh sites with CO molecules influences a chemical reaction, we chose a reaction with two divergent and well-defined pathways. Specifically, we studied the reaction of surface-bound ethyl groups which has been shown on other SAAs to proceed via two pathways; dehydrogenation to ethene and hydrogenation to ethane.²⁴ Here, we examine the same reaction on a RhCu(111) SAA and study how blocking the active sites with CO impacts the relative amounts of the reaction products, ethene and ethane. Fig. 2 shows a comparison of the reactivity of Cu(111), a 0.2% RhCu(111) SAA, and a RhCu(111) SAA that has been covered with saturation CO and annealed to 250 K (so that each Rh site is blocked with CO, but the Cu surface is free of CO). First, let us focus on the behavior of Cu(111). In agreement with previous reports, ethyl groups undergo β -dehydrogenation on Cu(111) at \sim 240 K to form ethene and hydrogen with high selectivity.^{25–27} In contrast, the RhCu(111) SAA not only liberates ethene at lower temperatures than Cu(111), but also dramatically changes the product selectivity. While Cu(111) produces only \sim 6% ethane, the RhCu SAA also catalyzes the hydrogenation pathway yielding \sim 50% ethane and \sim 50% ethene. Furthermore, the considerably lower ethene evolution temperature (200 K on RhCu vs 235 K on Cu) is consistent with low C-H action barriers exhibited by RhCu SAAs.^{15,24,28}

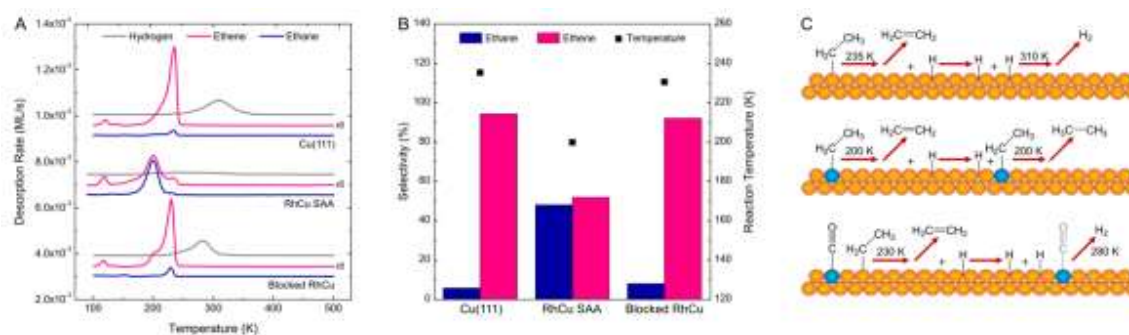


Fig. 2. TPD experiments showing product selectivity and ethene evolution temperatures on Cu(111), 0.2% RhCu(111), and CO blocked 0.2% RhCu(111) SAA. (A) TPD results following a 2 L (1 L = 10^{-6} Torr · s) ethyl iodide exposure at 90 K. (B) Quantification of product selectivity and formation temperature derived from the TPD results in panel (A). (C) Schematic of the proposed reaction pathways. Blue circles represent Rh atoms and orange circles represent Cu.

Exposure of the Rh atoms to saturation amounts of CO followed by a 250 K anneal to remove the CO from the Cu sites left the Rh sites selectively blocked with CO. After all the Rh atoms are blocked with CO, the selectivity and desorption temperatures of ethene returned to Cu-like values (ethene evolution occurred at 235 K on Cu with a selectivity of 94% vs 231 K with 92% selectivity on fully CO-blocked RhCu SAA). This demonstrates that CO adsorption deactivates the Rh atom active sites and prevents them from catalyzing the C-H cleavage required to evolve low temperature ethene, and also prevents the hydrogenation reaction which does not readily take place on Cu(111) as shown schematically in Fig. 2C. Interestingly, despite the ethane production being nearly totally suppressed and the ethene evolution occurring very close to 235 K (as would be expected for pure Cu surfaces), the hydrogen evolution on the CO-blocked SAA occurs at a lower temperature than Cu(111). Specifically, on Cu(111), hydrogen from ethyl decomposition is evolved at ~310 K. However, on the fully CO-blocked RhCu SAA, hydrogen evolves well below this temperature at ~280 K. This is not because the CO has desorbed from the Rh sites (which does not occur until temperatures above ~375 K as seen in Fig. 1). Instead, it may be because the CO has become mobile enough that hydrogen adatoms are able to diffuse to and recombine at a transiently free Rh atom. Alternatively, it may be because there is a pathway available to hydrogen which involved two H adatoms and a CO bound to the same Rh sites (which is able to liberate hydrogen at a hotter temperature than CO-free Rh, but a lower temperature than Cu). A previous study has looked at these pathways on PtCu SAAs and similar DFT calculations could be used to examine the pathways here.²⁹

To further explore the effect of CO on reaction selectivity, we conducted experiments in which we blocked different fractions of the Rh atoms by varying the CO exposure. As shown in Fig. 3, the reaction selectivity is dictated by the relative amount of CO present on the Rh atoms. At low CO coverages, selectivity to the hydrogenation product is close to 50% and increasing the

CO coverages leads to a gradual shift to higher dehydrogenation selectivity. Interestingly, it does not appear that the selectivity varies linearly with the CO coverage as low coverages of CO have a much smaller impact on the selectivity than higher ones. This suggests that the ethyl groups are mobile on the surface and only when all their local Rh sites are blocked by CO do they react at Cu sites. Overall, these results demonstrate that the ethyl hydrogenation/dehydrogenation reaction selectivity can be continuously varied by selective blocking of the Rh sites with CO.

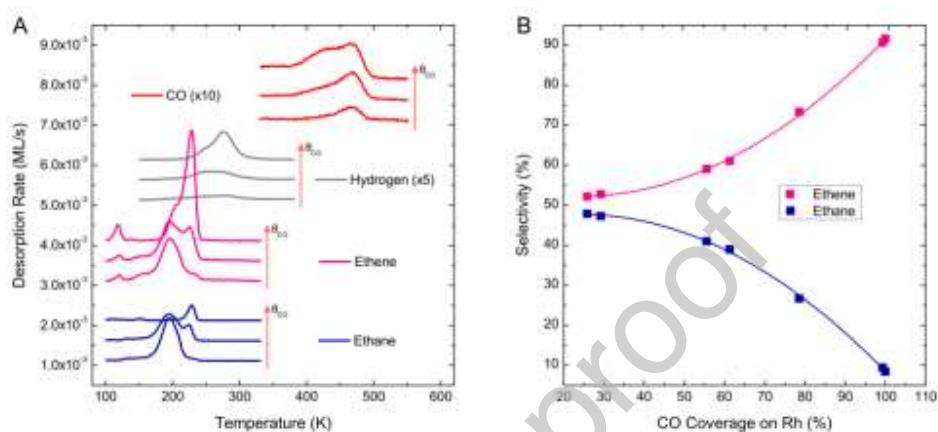


Fig. 3. TPD experiments showing the amount of CO covering the Rh sites dictates the relative dehydrogenation/hydrogenation selectivity. (a) Representative TPD results showing the evolution of CO, hydrogen, ethene, and ethane from a 0.5% RhCu(111) surface as a function of increasing CO coverage of the Rh sites (θ_{CO}). Note, Cu(111) which constitutes >99% of the surface sites of the SAA is free of CO in these experiments. (b) Product selectivity as a function of CO coverage on the Rh atoms. Fits are intended to guide the eye.

4. Conclusions

We have demonstrated for the first time how selective blocking of the dopant sites in a model SAA catalyst surface enables control over the selectivity of a reaction with two-well defined pathways. Our results demonstrate that the amount of adsorbed CO on the Rh atom sites in a RhCu SAA dictates the relative amounts of ethene (product of the dehydrogenation pathway) and ethane (product of the hydrogenation pathway) formed. While this effect is quite pronounced for ethyl dehydrogenation/hydrogenation chemistry, it is much less prominent for hydrogen evolution, and hydrogen formed during the dehydrogenation process is liberated from blocked Rh surfaces below the expected desorption temperature from Cu. This points to the important role CO plays in moderating the reaction energetics of different species and provides benchmark data for future DFT-parameterized kinetic Monte Carlo simulations that should further elucidate these complex adsorbate-adsorbate interactions and how they affect the reaction mechanism. Overall, we expect that this new effect whereby CO can be used to block the dopant site and control the selectivity of a reaction should be somewhat general for systems in which CO binds strongly to the isolated dopant atoms.^{13,14} Moving forward, it would be interesting to

test this effect in working nanoparticle SAA catalysts by co-flowing CO in order to selectivity block the active dopant metal atom sites active sites and study how this effects reaction chemistry.

Author Contributions

R.T.H. performed the surface science experiments, analyzed the results, and wrote the initial draft. Y.W. did the microscopy experiments. R. R., J. S., and M. S. discussed and aided in analysis of the results. E.C.H.S. was responsible for supervision, analysis, and funding acquisition. All authors reviewed and edited the manuscript

5. Declaration of Competing Interests

The authors declare no competing interests.

6. Acknowledgements

R.T.H., Y.W., and E.C.H.S. acknowledge funding from the Division of Chemical Science, Office of Basic Energy Science, CPIMS Program, US Department of Energy, under grant DE-SC 0004738. R.R. and M.S. acknowledge funding from the Leverhulme Trust, grant ref. RPG-2018-209. J.S. is supported by a Feodor Lynen Fellowship of the Alexander von Humboldt Foundation.

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