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Project Goals

During the past several years some of our major goals involved contributing to the understanding of issues related to gold catalysis through the study of specific surface chemical reactions on gold model catalysts in vacuum, including: What is the origin of the gold particle size effect? What is the nature and structure of the active site? What mechanisms drive the reaction [e.g., what is the role of moisture, which seems to be required for so many gold-catalyzed reactions]? What is the role of a metal oxide support?

DOE Interest

Catalysis by metal-oxide supported gold is of interest to the Department of Energy since this catalytic system holds some promise for low-temperature one-step chemical conversions (e.g., epoxidation of propylene). Additionally, fundamental catalysis science is of interest to the DOE.

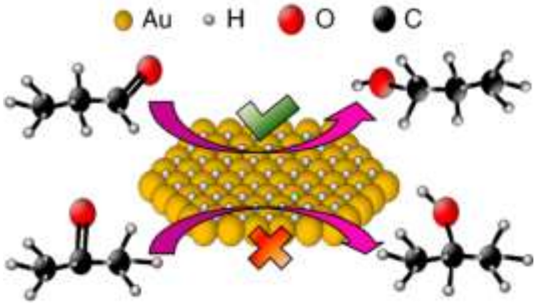
Products of the Research

Several archival journal articles have been published that present and discuss the results that were discovered through this DOE grant. Over the following pages these papers are briefly discussed and a url is provided as a link to the full paper and all of the results and further discussion of these findings.

Archival Papers Published Via DOE Grant # DE-FG02-04ER15587

1. Ming Pan, Z. D. Pozun, A. J. Brush, G. Henkelman, and C. Buddie Mullins, "Low-temperature chemoselective gold-surface-mediated hydrogenation of acetone and propionaldehyde," *ChemCatChem* **4**,1241-1244 (2012). http://dx.doi.org/10.1002/cctc.201200311

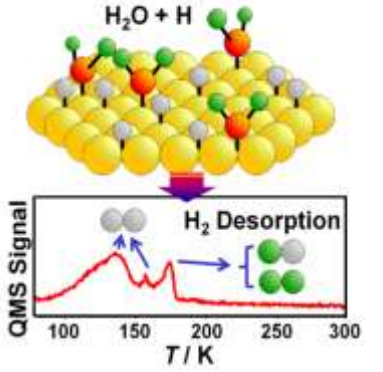
In this paper, employing acetone and propionaldehyde as probe molecules, we investigated hydrogenation chemistry of C=O bonds on a H pre-covered model Au(111) catalyst to make a contribution to a better holistic understanding for chemoselective hydrogenation of α,β-unsaturated carbonyls. H atoms were used in this study due to the high energetic barrier of H_2 dissociation on gold. Temperature programmed desorption (TPD) measurements indicated different activities for hydrogenation on gold; propionaldehyde hydrogenates to 1-propanol on H-covered gold but acetone does not form 2-propanol. Density functional theory (DFT) calculations reveal dissimilar activation energies for the reactions between a single carbonyl moiety an H atom.



A chemoselective reactivity for hydrogenation of acetone and propionaldehyde on H-covered gold. Propionaldehyde forms 1-propanol, whereas no hydrogenated product has been detected from the interaction of acetone and H. Dissimilar energetic barriers and the polymerization of CH_3CH_2CHO are the basis of the chemoselective activity. The production of di-n-propyl ether from propionaldehyde is also noted.

2. Ming Pan, Zachary D. Pozun, Wen-Yueh Yu, Graeme Henkelman, and C. Buddie Mullins, "Structure revealing H/D exchange with co-adsorbed hydrogen and water on gold," *J. Phys. Chem. Lett.* **3**, 1894-1899 (2012). http://dx.doi.org/10.1021/jz3007707

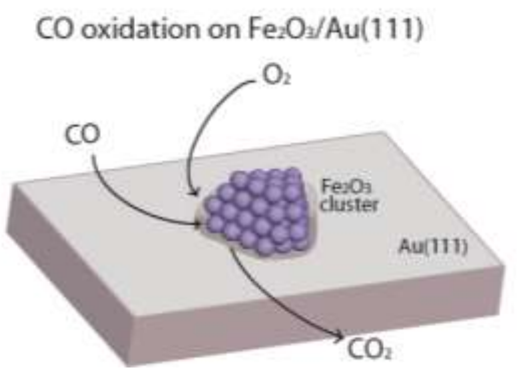
A fundamental understanding of the interactions between co-adsorbed water and hydrogen on metallic surfaces is critical to many chemical processes including catalysis and electrochemistry. Here, we reported on the strong and intricate interactions between co-adsorbed H/D and water on the close-packed (111) surface of gold. Deuterium isotopic labeling shows H-D exchange in H-D_2O and D-H_2O systems, indicating water dissociation and suggesting a non-random scrambling process by revealing the origin of hydrogen evolution (from surface H atoms or from water molecules) during annealing. In this reaction, the protonation of the H-bonding ice network (i.e., the formation of $(H_2O)_nH^+$) is energetically favorable and is responsible for water dissociation. Density functional theory (DFT) modeling suggests that the thermodynamics and structure of the protonated clusters are predominant factors for yielding the traceable H_2 desorption features from the surface interaction with H atoms, providing insights into reaction mechanisms.



Schematic of co-adsorbed water and hydrogen on Au(111 and temperature programmed desorption spectra.

3. Ting Yan, Daniel W. Redman, Wen-Yueh Yu, David W. Flaherty, Jose A. Rodriguez, and C. Buddie Mullins, "CO oxidation on inverse Fe_2O_3/Au(111) model catalysts," *J. Catal.* **294**, 216-222 (2012). http://dx.doi.org/10.1016/j.jcat.2012.07.024

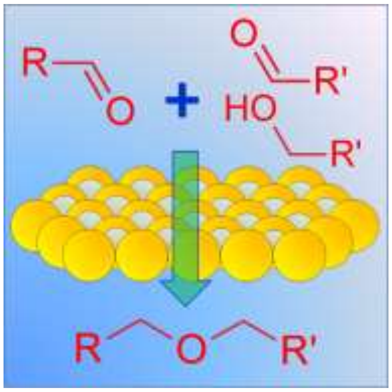
In this paper CO oxidation was studied at pressures between 4 to 100 Torr and temperatures from 400 K to 670 K on inverse model catalysts made of Fe_2O_3 nanoclusters grown on a Au(111) single crystal surface. The addition of Fe_2O_3 nanoclusters transformed the inert Au(111) single crystal into an active catalyst for CO oxidation. The catalytic activity increases with iron oxide coverage initially, and then decreases when the iron oxide coverage is greater than 0.5 monolayers. Additionally, when the iron oxide particles form a continuous film on Au(111) there is no catalytic activity. These experimental results strongly suggest that the active sites for CO oxidation are located at the iron oxide/gold perimeter. Kinetics measurements suggest that CO oxidation by chemisorbed oxygen at the Fe_2O_3/Au perimeter is likely to be the rate limiting step. C-O bond cleavage observed via a post-reaction Auger electron spectrum suggests that multiple reaction pathways are involved in CO oxidation over Fe_2O_3/Au(111).



Schematic of iron oxide clusters supported on Au(111) for study of CO oxidation.

4. Ming Pan, Adrian J. Brush, Guangbin Dong, and C. Buddie Mullins, "Tunable ether production via coupling of aldehydes or aldehyde/alcohol over hydrogen-modified gold catalysts at low temperature," *J. Phys. Chem. Lett.* **3**, 2512-2516 (2012). http://dx.doi.org/10.1021/jz301105e

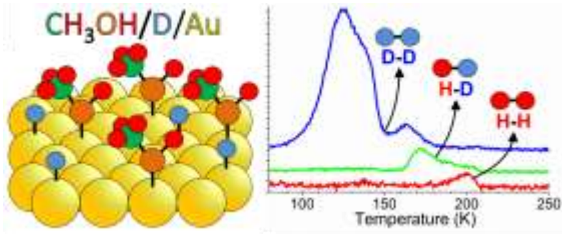
Here we studied ethers since they are an important group of organic compounds that are primarily prepared via homogeneous catalysis, which can lead to operational and environmental issues. In this paper we demonstrated the production of ethers via heterogeneous-catalysis over H adatom-covered gold at temperatures lower than 250 K. Symmetrical ethers can be formed via a self-coupling reaction of corresponding aldehydes, for example, homo-coupling of acetaldehyde and propionaldehyde yields diethyl ether and di-n-propyl ether, respectively. In addition, coupling reactions between alcohols and aldehydes, with different carbon chain lengths, are observed via the production of the corresponding unsymmetrical ethers. A reaction mechanism was proposed suggesting that an alcohol-like intermediate via



Schematic of ether formation from alcohols and aldehydes on Au(111) at low temperature.

partial hydrogenation of aldehydes on the surface plays a key role in these reactions. These surface chemical reactions suggest possible heterogeneous routes to low temperature production of ethers.

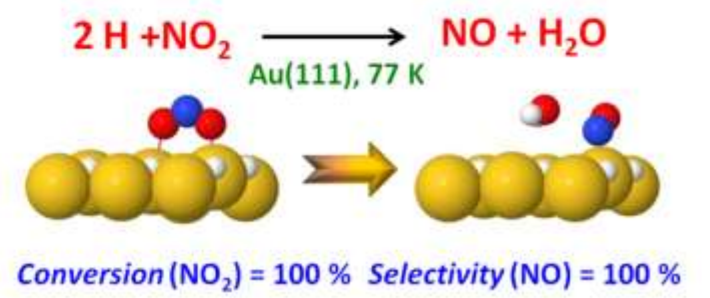
5. Adrian J. Brush, Ming Pan, and C. Buddie Mullins, "Methanol O-H bond dissociation on H-precovered gold originating from a structure with a wide range of surface stability," *J. Phys. Chem. C* **116**, 20982-20989 (2012). http://dx.doi.org/10.1021/jp308099y



Influence of adsorbed methanol on Au(111) on hydrogen desorption.

In this paper, we reported that the adsorption of methanol onto a H-precovered Au(111) surface induces an adsorbate structure, or set of structures, on the surface involving both methanol and hydrogen adatoms with a wide range of stability on the surface. Coadsorption of H/MeOD or D/MeOH indicates H/D exchange between the two surface species, providing evidence that the H-precovered gold surface can dissociate the methanol O-H bond at low temperature (<120 K). These isotopic experiments also demonstrate that hydrogen/deuterium atoms released from a methanol molecule desorb at higher temperatures than hydrogen/deuterium atoms originating from the surface, providing insight into the adsorbate structure(s) present. Additionally, the presence of MeOH on the surface is shown to inhibit the ability of adsorbed MeOD to undergo hydrogen exchange, providing additional clues regarding the exchange reaction mechanism. These phenomena are also shown to exist for ethanol on H-precovered Au(111), suggesting that this behavior may be common to alcohols or species with an O-H functional group in general. These observations give insight into the behavior of the O-H group on a gold surface, which can aid in determining reaction mechanisms and directing future catalytic research.

6. Ming Pan, Hyung Chul Ham, Wen-Yueh Yu, Gyeong S. Hwang, and C. Buddie Mullins, "Highly selective, facile NO_2 reduction to NO at cryogenic temperatures on H pre-covered gold," *J. Am. Chem.* Soc. **135**, 436-442 (2013). http://dx.doi.org/10.1021/ja3096575

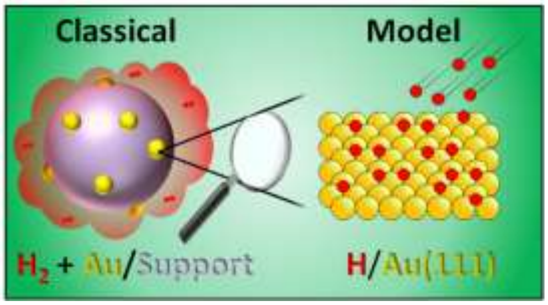


Schematic of the conversion of NO_2 into NO and H_2O on hydrogen precovered Au(111).

In this study we discovered that NO_2 is reduced to NO at 77 K by hydrogen pre-covered gold in vacuum. NO_x reduction is crucial to control and abatement of transportation emissions and air pollution. Here, we investigated NO_2 reduction on an atomic-hydrogen populated model gold catalyst for a more fundamental understanding of the surface chemistry of hydrogenation. Gold-based catalysts have been found to be active for many hydrogenation reactions but few related fundamental studies have been conducted. Our experimental results reveal a high catalytic activity for gold: indeed, NO_2 is reduced to NO with 100% conversion and 100% selectivity at temperatures lower than 120 K. Density functional theory (DFT) calculations and reflection-absorption infrared spectroscopy measurements (RAIRS) indicate that HNO_2 and N_2O_3 are intermediates which are highly dependent on surface hydrogen concentrations; subsequent hydrogenation of HNO_2 and dissociation of N_2O_3 upon annealing induces the production of NO and H_2O.

7. Ming Pan, Adrian Brush, Zachary D. Pozun, Hyung Chul Ham, Wen-Yueh Yu, Graeme Henkelman, Gyeong S. Hwang, and C. Buddie Mullins, "Model studies of heterogeneous catalytic hydrogenation reactions with gold," *Chem. Soc. Rev.* **42**, 5002-5013(2013). http://dx.doi.org/10.1039/c3cs35523c

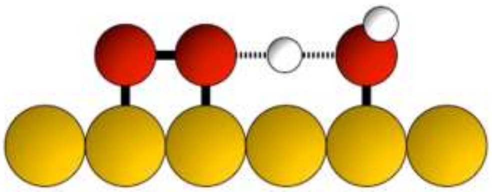
Supported gold nanoparticles have recently been shown to possess intriguing catalytic activity for hydrogenation reactions, particularly for selective hydrogenation reactions. However, fundamental studies that can provide insight into the reaction mechanisms responsible for this activity were largely lacking. In this tutorial review, we highlighted several recent model experiments and theoretical calculations on a well-structured gold surface that provide some insights. In addition to the behavior of hydrogen on a model gold surface, we review the reactivity of hydrogen on a model gold surface in regards to NO_2 reduction, chemoselective C=O bond hydrogenation, ether formation, and O-H bond dissociation in water and alcohols. Those studies indicate that atomic hydrogen has a weak interaction with gold surfaces which likely plays a key role in the unique hydrogenative chemistry of classical gold catalysts.



This review summarized our model studies of hydrogenation on gold, indicating the importance of weakly-absorbed H atoms for selective hydrogenation processes.

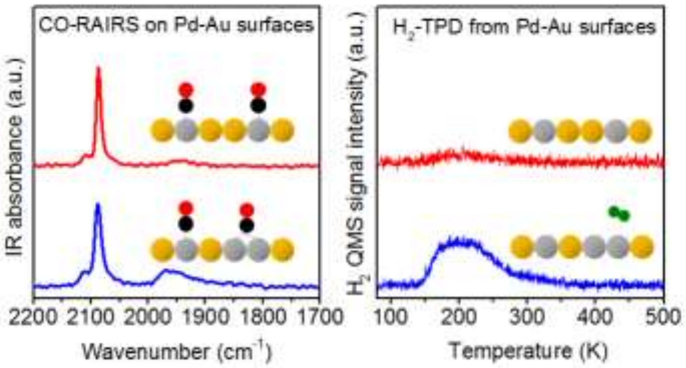
8. Gregory M. Mullen, Jinlong Gong, Ting Yan, Ming Pan, and C. Buddie Mullins, "The effects of adsorbed water on gold catalysis and surface chemistry," *Top. Catal.* **56**, 1499-1511 (2013). http://dx.doi.org/10.1007/s11244-013-0143-x

Water has important effects on several reactions occurring over gold catalysts. In this work, we review studies demonstrating the interactions of water in surface chemistry and catalysis over gold, with specific emphasis on the ability of water to enhance activity for the CO oxidation reaction and the role water plays in the mechanism of the water-gas shift reaction. Water significantly influences these and other catalytic reactions over gold catalysts.



Schematic representation of hydroperoxyl-like complex generated from the interaction of O_2 with H_2O. Red = O, white = H, yellow = Au.

9. Wen-Yueh Yu, Gregory M. Mullen, C. Buddie Mullins, "Hydrogen adsorption and absorption with Pd-Au bimetallic surfaces," *J. Phys. Chem. C.* **117**, 19535-19543 (2013).http://dx.doi.org/10.1021/jp406736b



RAIRS and hydrogen desorption from a Pd-Au surface.

Pd-Au bimetallic catalysts have shown promising performance in numerous reactions that involve hydrogen. Fundamental studies of hydrogen interactions with Pd-Au surfaces could provide useful insights into the reaction mechanisms over Pd-Au catalysts, which may, in turn, guide future catalyst design. In this study, the interactions of hydrogen (*i.e.*, adsorption, absorption, diffusion and desorption) with Pd/Au(111) model surfaces were studied using temperature-programmed desorption (TPD) under ultrahigh vacuum conditions. Our experimental results reveal Pd-Au bimetallic surfaces readily dissociate H_2 and yet also weakly bind H adatoms, properties that could be beneficial for catalytic reactions involving hydrogen. The presence of contiguous Pd sites, characterized by reflection-absorption infrared spectroscopy using CO as a probe molecule (CO-RAIRS), was found to be vital for the dissociative adsorption of H_2 at 77 K. The H adatom binds to Pd-Au alloy sites more strongly than to Au(111) but more weakly than to Pd(111) as indicated by its desorption temperature (~200 K). With hydrogen exposure at slightly higher temperatures (i.e., 100 - 150 K), extension of a low temperature desorption feature was observed, suggesting the formation of subsurface H atoms (or H absorption). Experiments using deuterium indicate that H-D exchange over the Pd-Au bimetallic surface obeys Langmuir-Hinshelwood kinetics and that H/D adatoms are mobile on the surface at low temperatures.

10. Ming Pan, Jinlong Gong, Guangbin Dong, and C. Buddie Mullins, "Model studies with gold: A versatile oxidation and hydrogenation catalyst," *Acc. Chem. Res.* **47**, 750-760 (2014).http://dx.doi.org/10.1021/ar400172u

Historically, gold has been considered as an inert catalyst constituent. However, in recent decades, it has been discovered that nano-scale gold shows exceptional activity for many chemical reactions. Model gold surfaces have been investigated in order to obtain fundamental understanding of catalytic properties. In this account, we provide our current understanding of oxidation and hydrogenation reactions on the Au(111) single crystal as a planar representative of gold catalysts, revealing the interesting surface chemistry of gold.

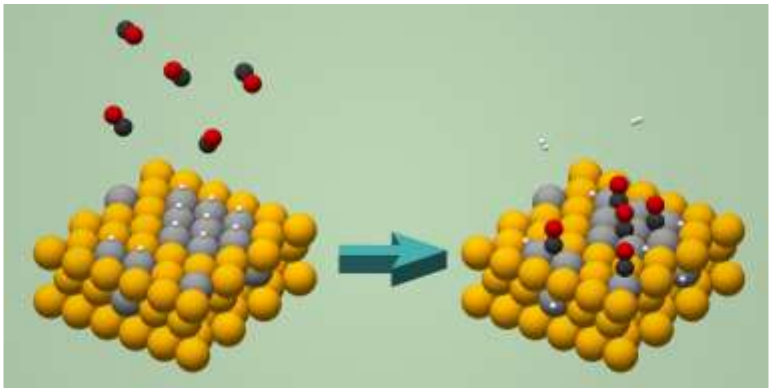
In this short review paper we compared two inverse reactions, alcohol oxidation and aldehyde hydrogenation, on a Au(111) surface. Beyond the expected different chemistry, there are intriguing similarities observed since the same surface is employed. First, both molecular oxygen and hydrogen have high barriers to dissociation on Au(111) and frequently atomic O and H are employed to populate surfaces for the study of chemical reactions. Recombinative desorption features of oxygen and hydrogen are apparent at ~500 K and ~110 K, lower temperatures compared to other transition metals. These results indicate that oxygen and hydrogen have low desorption activation energies and weakly chemisorb on the surface, likely leading to selective reactions. On the oxygen-pre-covered Au(111) surface, alcohols are selectively oxidized to aldehydes. Similarly, weakly bound hydrogen atoms on Au(111) also show chemoselective reactivity for hydrogenation of propionaldehyde and acetone. The second similarity is that the gold surface activates self-coupling of alcohol or aldehyde with oxygen or hydrogen, resulting in the formation of esters and ethers, respectively in alcohol oxidation and aldehyde hydrogenation. During these two reactions, the different reaction intermediates, alkoxy groups and alcohol-like species, are produced, which likely play a key role in the formation of coupling products. In addition, the cross coupling reaction between alcohol and aldehyde occurs on both O- and H-modified surfaces, yielding the production of esters and ethers, respectively. Thus, the synthesis of ester and ether can be tuned regarding the molecular structure via selecting the corresponding aldehyde and alcohol for the coupling reaction.

Schematic of potential oxidation and hydrogenation reactions on oxygen or hydrogen precovered Au(111).

These studies indicate that gold is a versatile active catalyst for various reactions including oxidation and hydrogenation transformations. Despite the very different chemistry for these two reactions, an intrinsic relationship can be established due to the distinct catalytic properties of gold - showing activity for selective reactions on both O- and H-covered Au(111) and further inducing the coupling reaction between surface reactants and adsorbed O/H to produce esters and ethers. This comparison demonstrates the unique surface chemistry of gold and enhances understanding of its' catalytic properties.

11. Wen-Yueh Yu, Gregory M. Mullen, C. Buddie Mullins, "Interactions of hydrogen and carbon monoxide on Pd-Au bimetallic surfaces," *J. Phys. Chem. C*. **118**, 2129-2137 (2014). http://dx.doi.org/10.1021/jp411299e

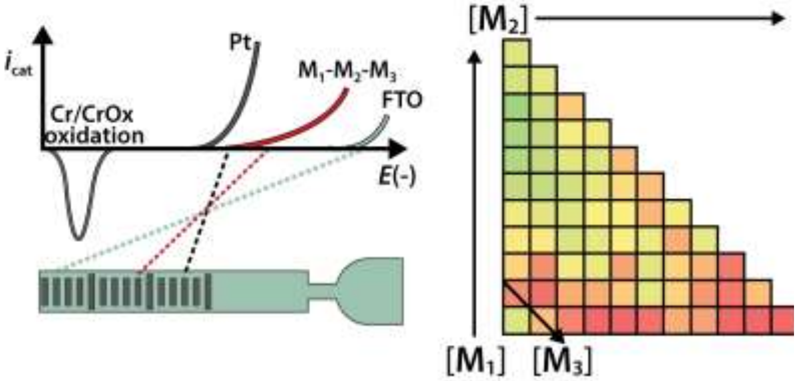
In this study, the interactions of hydrogen and CO with Pd/Au(111) model surfaces were investigated by temperature-programmed desorption (TPD) and molecular beam scattering (MBS) experiments, carried out under ultrahigh vacuum conditions. Our results revealed that CO adsorbs competitively on the hydrogen-precovered Pd-Au surface, causing surface H adatoms to diffuse away from stronger-binding sites (e.g., Pd(111)-like islands) to weaker-binding sites (e.g., Pd-Au alloy sites and subsurface) as evidenced by a shift of the H_2 desorption feature to lower temperatures in TPD measurements. Additionally, evolution of H_2 was observed when a CO molecular beam was impinged onto the H-precovered Pd-Au surface, providing direct evidence that CO induces recombinative desorption of H adatoms. The presence of H adatoms on the Pd-Au surface was found to decrease the initial sticking probability of CO during MBS experiments but had little influence on CO desorption during subsequent TPD measurements.



Schematic of the interactions of carbon monoxide and hydrogen on a Pd-Au surface.

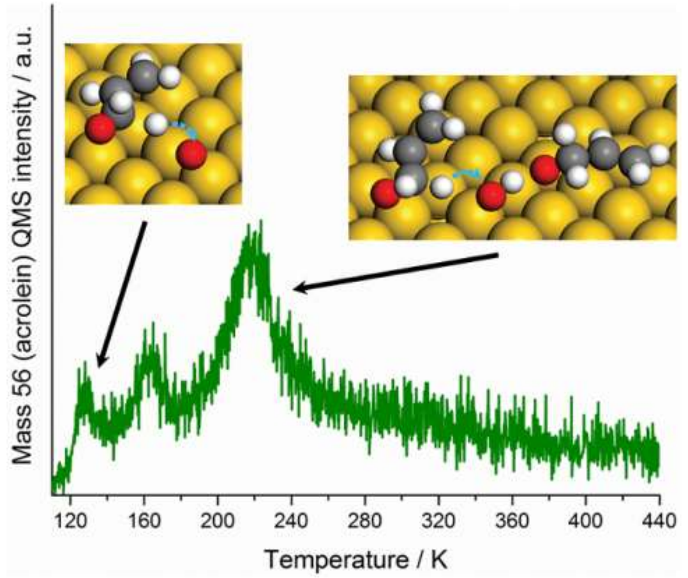
12. Stephen E. Fosdick, Sean P. Berglund, C. Buddie Mullins, and Richard M. Crooks, "Evaluating electrocatalysts for the hydrogen evolution reaction using bipolar electrode arrays: Bi- and trimetallic combinations of Co, Fe, Ni, Mo, and W," *ACS Catal.* **4**, 1332-1339 (2014). http://dx.doi.org/10.1021/cs500168t

Here we reported on the development of a parallel electrocatalyst screening platform for the hydrogen evolution reaction (HER) using bipolar electrodes (BPEs) through a collaboration with Professor Dick Crooks and his research group. Electrocatalyst candidates were subjected to screening in a N_2-purged bipolar electrochemical cell where a pair of driving electrodes produce an electric field in the electrolyte solution. The HER occurring at the BPE cathodes is electrically coupled to the electrodissolution of an array of Cr microbands present at the BPE anodes. The readout of this device is simple, where the species that dissolve the most Cr microbands are identified as the most promising electrocatalyst candidates for further evaluation. We demonstrate the utility of this technique by comparing several bi- and trimetallic systems involving Co, Fe, Ni, Mo, and W, which are compared directly to pure Pt. Of all the compositions tested, Ni_8-Mo_2 is demonstrated to be the most active for the HER in a neutral electrolyte solution.



Schematic of the set-up for testing mixed metal HER electrocatalysts employing a bipolar electrode strategy.

13. Gregory M. Mullen, Liang Zhang, Edward J. Evans Jr., Ting Yan, Graeme Henkelman, and C. Buddie Mullins, "Oxygen and hydroxyl species induce multiple reaction pathways for the partial oxidation of allyl alcohol on gold," *J. Am. Chem. Soc.* **136**, 6489-6498 (2014). http://dx.doi.org/10.1021/ja502347d

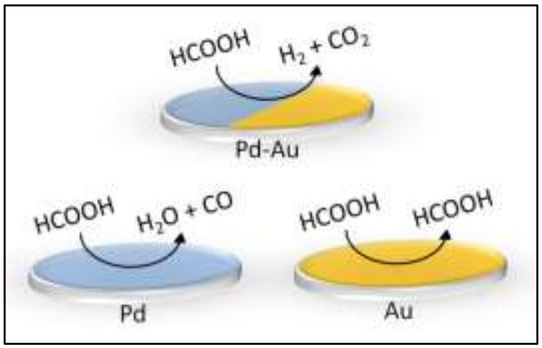


Schematic of the partial oxidation of allyl alcohol via oxygen and hydroxyl on Au(111).

Partial oxidation of alcohols is a topic of great interest in the field of gold catalysis. In this work, we provide evidence that the partial oxidation of allyl alcohol to its corresponding aldehyde, acrolein, over oxygen precovered gold surfaces occurs via multiple reaction pathways. Utilizing temperature programmed desorption (TPD) with isotopically-labeled water and oxygen species, reactive molecular beam scattering, and density functional theory (DFT) calculations, we demonstrate that the reaction mechanism for allyl alcohol oxidation is influenced by the relative proportions of atomic oxygen and hydroxyl species on the gold surface. Both atomic oxygen and hydroxyl species are shown to be active for allyl alcohol oxidation but each displays a different pathway of oxidation as indicated by TPD measurements and DFT calculations. The hydroxyl hydrogen of allyl alcohol is readily abstracted by either oxygen adatoms or adsorbed hydroxyl species on the gold surface to generate a surface bound allyloxide intermediate, which then undergoes α-dehydrogenation via interaction with an oxygen adatom or surface hydroxyl species to generate acrolein. Mediation of a second allyloxide with the hydroxyl species lowers the activation barrier for the α-dehydrogenation process. A third pathway exists in which two hydroxyl species recombine to generate water and an oxygen adatom, which subsequently dehydrogenates allyloxide. This work may aid in the understanding of oxidative catalysis over gold and the effect of water therein.

14. Wen-Yueh Yu, Gregory M. Mullen, David W. Flaherty, and C. Buddie Mullins, "Selective hydrogen production from formic acid decomposition on Pd-Au bimetallic surfaces," *J. Am. Chem. Soc.* **136**, 11070-11078 (2014). http://dx.doi.org/10.1021/ja505192v

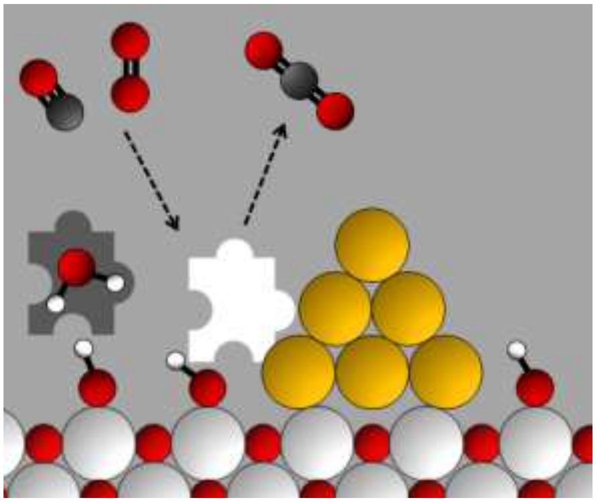
Pd-Au catalysts have shown exceptional performance for selective hydrogen production via HCOOH decomposition, a promising alternative to solve issues associated with hydrogen storage and distribution. In this study, we have utilized temperature-programmed desorption (TPD) and reactive molecular beam scattering (RMBS) in an attempt to unravel the factors governing the catalytic properties of Pd-Au bimetallic surfaces for HCOOH decomposition. Our results show that Pd atoms at the Pd-Au surface are responsible for activating HCOOH molecules; however, the selectivity of the reaction is dictated by the identity of the surface metal atoms adjacent to the Pd atoms. Pd atoms that reside at Pd-Au interface sites tend to favor dehydrogenation of HCOOH; whereas, Pd atoms in Pd(111)-like sites, which lack neighboring Au atoms, favor dehydration of HCOOH. These observations suggest that the reactivity and selectivity of HCOOH decomposition on Pd-Au catalysts can be tailored by controlling the arrangement of surface Pd and Au atoms. The findings in this study may prove informative for the rational design of Pd-Au catalysts for associated reactions including selective HCOOH decomposition for hydrogen production and electro-oxidation of HCOOH in the direct formic acid fuel cell.



Schematic of the conversion of formic acid into products as a function of surface composition.

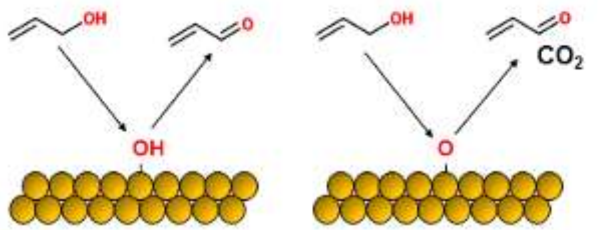
15. Gregory M. Mullen and C. Buddie Mullins, "Water's place in Au catalysis," a "perspective" written for *Science* **345**, 1564-1565 (2014). http://www.sciencemag.org/content/345/6204/1564

In this short perspective for *Science* we provided highlights concerning an important paper from the group of Bert Chandler at Trinity University [J. Saavedra et al., *Science* **345**, 1599 (2014)] involving the effects of adsorbed water on CO oxidation catalysis over a titania supported gold catalyst. The mechanism presented by Saavedra *et al.* suggests that both hydroperoxyl and hydroxyl species are involved in the water-enhanced CO oxidation reaction. Hydroxyl species associated with both the support and the gold surface play roles in the process. Furthermore, water helps to both activate O_2 and decompose reactive intermediates associated with CO_2 generation. This mechanism not only ties together observations made in a number of previous studies of the water-enhanced CO oxidation reaction but also lends credence to many of their seemingly conflicting claims. The work by the Chandler group represents a significant stride in the understanding of gold catalysis and the important effects of water therein. In this respect, we believe that the study by Saavedra *et al.* may prove key to solving many of the puzzles of gold catalysis.



Solving the puzzle of water-enhanced CO oxidation on gold.

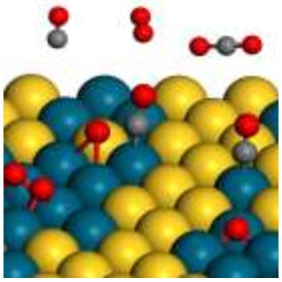
16. Gregory M. Mullen, Liang Zhang, Edward J. Evans Jr., Ting Yan, Graeme Henkelman, and C. Buddie Mullins, "Control of selectivity in allylic alcohol oxidation on gold surfaces: The role of oxygen adatoms and hydroxyl species," *PhysChemChemPhys* **17**, 4730-4738 (2015). http://dx.doi.org/10.1039/C4CP04739G



Schematic of the partial oxidation of allyl alcohol over hydroxyl pre-covered versus oxygen precovered Au(111).

As discussed earlier, gold catalysts display high activity and good selectivity for partial oxidation of a number of alcohol species. In this work, we discussed the effects of oxygen adatoms and surface hydroxyls on the selectivity for oxidation of allylic alcohols (allyl alcohol and crotyl alcohol) on gold surfaces. Utilizing temperature programmed desorption (TPD), reactive molecular beam scattering (RMBS), and density functional theory (DFT) techniques, we provided evidence to suggest that the selectivity displayed towards partial oxidation versus combustion pathways is dependent on the type of oxidant species present on the gold surface. TPD and RMBS results suggest that surface hydroxyls promote partial oxidation of allylic alcohols to their corresponding aldehydes with very high selectivity, while oxygen adatoms promote both partial oxidation and combustion pathways. DFT calculations indicate that oxygen adatoms can react with acrolein to promote the formation of a bidentate surface intermediate, similar to structures that have been shown to decompose to generate combustion products over other transition metal surfaces. Surface hydroxyls do not readily promote such a process. Our results help explain phenomena observed in previous studies and may prove useful in the design of future catalysts for partial oxidation of alcohols.

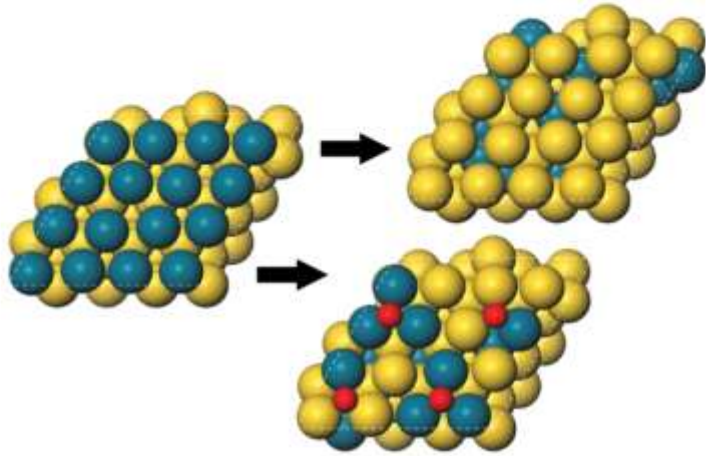
17. Wen-Yueh Yu, Liang Zhang, Gregory M. Mullen, Graeme Henkelman and C. Buddie Mullins, "Oxygen Activation and Reaction on Pd−Au Bimetallic Surfaces," *J. Phys. Chem. C*. **119**, 11754-11762 (2015). http://dx.doi.org/10.1021/acs.jpcc.5b02970



Schematic of the reaction of CO and O_2 on a partially Pd-covered Au(111) surface.

Pd−Au bimetallic catalysts have shown promising performance for a number of oxidative reactions. This study utilized reactive molecular beam scattering (RMBS), reflection-absorption infrared spectroscopy (RAIRS), temperature-programmed desorption (TPD) and density functional theory (DFT) techniques in an attempt to enhance fundamental understanding of oxygen activation and reaction with CO on Pd−Au surfaces. Our results revealed that the presence of contiguous Pd sites is crucial for adsorption of oxygen molecules on Pd/Au(111) surfaces at 77 K. Upon heating, oxygen admolecules desorbed molecularly without detectable dissociation in O_2-TPD measurements. CO-RMBS experiments indicate that at lower temperatures (77-150 K), oxygen admolecules were readily displaced by CO due to competitive adsorption. Oxygen admolecules can be thermally activated at higher temperatures (180-250 K) to react with CO to form CO_2. DFT calculations show that the Pd−Au surface containing larger Pd ensembles favors dissociative CO oxidation, whereas associative CO oxidation and O_2 desorption are the two main competing processes for the Pd−Au surface containing small Pd ensembles. An associative CO oxidation pathway was not experimentally observed, which is likely due to facile CO-induced O_2 desorption. These results provide mechanistic insights into the interaction of oxygen with Pd−Au surfaces, which may prove informative for the rational design of Pd-Au catalysts for associated reactions involving O_2 as a reactant.

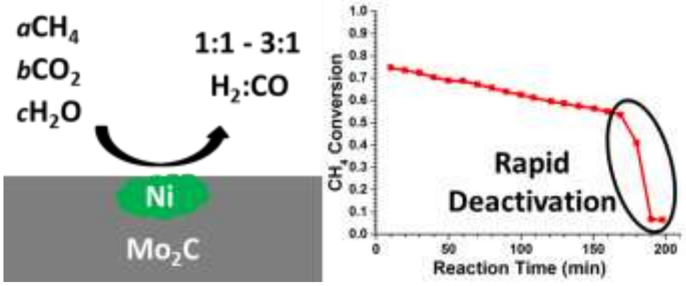
18. Wen-Yueh Yu, Liang Zhang, Gregory M. Mullen, Edward J. Evans Jr., Graeme Henkelman, and C. Buddie Mullins, "Effect of annealing in oxygen on alloy structures of Pd−Au bimetallic model catalysts," *Phys. Chem. Chem. Phys.* **17**, 20588-20596 (2015). http://dx.doi.org/10.1039/C5CP03515E



Annealing the Pd-Au surface in an oxygen ambient stabilizes Pd atoms on Pd-Au surfaces, resulting in higher oxygen uptake and CO oxidation activity.

It has been reported that Pd−Au bimetallic catalysts frequently display improved catalytic performance after calcination. In this study, a model catalyst study was conducted to investigate the effects of annealing in oxygen on the surface structures of Pd−Au alloys by comparing the physicochemical properties of Pd/Au(111) surfaces that were annealed in ultrahigh vacuum (UHV) versus in an oxygen ambient. Auger electron spectroscopy (AES) and Basin hopping simulations reveal that the presence of oxygen can inhibit the diffusion of surface Pd atoms into the subsurface of the Au(111) sample. Reflection-absorption infrared spectroscopy using CO as a probe molecule (CO-RAIRS) and King−Wells measurements of O_2 uptake suggest that surfaces annealed in an oxygen ambient possess more contiguous Pd sites than surfaces annealed under UHV conditions. The oxygen-annealed Pd/Au(111) surface also exhibited a higher activity for CO oxidation in reactive molecular beam scattering (RMBS) experiments. This enhanced activity likely results from the higher oxygen uptake and relatively facile dissociation of oxygen admolecules due to stronger adsorbate-surface interactions as suggested by temperature-programmed desorption (TPD) measurements. These observations provide fundamental insights into the surface phenomena of Pd−Au alloys, which may prove beneficial in the design of future Pd−Au catalysts.

19. Adrianne Brush, Edward J. Evans, Jr., Gregory M. Mullen, Karalee Jarvis, and C. Buddie Mullins, “Tunable Syn Gas Ratio via Bireforming over Coke-Resistant Ni/Mo_2C Catalyst,” *Fuel Process. Technol.* **153**, 111-120 (2016). http://dx.doi.org/10.1016/j.fuproc.2016.07.012



Schematic of Ni/Mo_2C to catalyze the Methane Bireforming Reaction.

This study demonstrated the ability of Ni/Mo_2C to catalyze the Methane Bireforming Reaction (combined Dry Methane Reforming Reaction, $CH_4 + CO_2 \rightarrow 2H_2 + 2CO$, and Steam Methane Reforming Reaction, $CH_4 + H_2O \rightarrow 3H_2 + CO$). By varying the ratio of CO_2:H_2O, the resulting H_2:CO ratio could be tuned from 0.91 to 3.0, covering a wide range of Syn Gas (H_2 + CO) ratios relevant to various hydrocarbon syntheses. We also document the unusual deactivation behavior of Ni/Mo_2C in this system. The catalytic activity would change from very high (greater than 50% conversion) to very low (less than 10% conversion) within 10 minutes. Despite running under conditions typically favorable for coking with a Ni catalyst (high temperature, 950°C, and excess methane), XRD, TGA, TEM, SEM, and EDX results clearly show no evidence of coking during the reaction or after deactivation. In addition, the changes to the Ni/Mo_2C catalyst seen after deactivation (oxidation of Mo_2C to MoO_2, Ni-phase changes, and catalyst morphology changes) could not be seen in the catalyst subjected to reaction conditions that were halted before deactivation could occur. This suggests a sudden, rapid deactivation “event” occurs in this catalytic system as opposed to gradual catalyst deactivation, a behavior more typically seen with catalysts.