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Dilute alloys based on Au, Ag or Cu for efficient catalysis: from synthesis to active sites

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ABSTRACT: The development of new catalyst materials for energy-efficient chemical synthesis is critical as over 80% of industrial processes rely on catalysts, with many of the most energy-intensive processes specifically using heterogeneous catalysis. Catalytic performance is a complex interplay of phenomena involving temperature, pressure, gas composition, surface composition and structure over multiple length and time scales. In response to this complexity, the integrated approach to heterogeneous dilute-alloy catalysis reviewed here brings together materials synthesis, mechanistic surface chemistry, reaction kinetics, in-situ and operando characterization, and theoretical calculations in a coordinated effort to develop design principles to predict and improve catalytic selectivity. Dilute alloy catalysts—in which isolated atoms or small ensembles of the minority metal on the host metal lead to enhanced reactivity while retaining selectivity—are particularly promising as selective catalysts. Several dilute alloy materials using Au, Ag and Cu as the majority host element, including more recently introduced support-free nanoporous metals and oxide-supported nanoparticle "raspberry colloid templated (RCT)" materials, are reviewed for selective oxidation and hydrogenation reactions. Progress in understanding how such dilute alloy catalysts can be used to enhance selectivity of key synthetic reactions is reviewed, including quantitative scaling from model studies to catalytic conditions. The dynamic evolution of catalyst structure and composition studied in surface science and catalytic conditions and their relationship to catalytic function are also discussed, followed by advanced characterization and theoretical modeling that have been developed to determine the distribution of minority metal atoms at or near the surface. The integrated approach demonstrates the success of bridging the divide between fundamental knowledge and design of catalytic processes in complex catalytic systems, which can accelerate the development of new and efficient catalytic processes.

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1 Introduction

1.1 Background

Chemical production, which relies heavily on heterogeneous catalysis, now accounts for nearly 30% of industrial energy use.[1] Forecasts for global energy demand project this number will rise to 45% by 2040. Current trends in energy supply and use are unsustainable—economically, environmentally, and socially. Due to the potential for substantial energy savings, building a foundation of fundamental principles that can guide the development of new materials and new catalytic processes is a high priority around the world.[2]

Heterogeneous catalytic processes are extremely complex. Not only do they require optimization of factors across multiple length, time, pressure, and temperature scales, but development of efficient catalytic processes also mandates team science and an interdisciplinary approach, inclusive of materials synthesis, mechanistic surface chemistry, reaction kinetics, and in-situ and operando characterization. Numerous studies show that complex metal/oxide interfaces, generally present in catalysts, appear to play an important synergistic role in determining reactivity. Further, since materials are often affected by the reaction environment, pre- and on-stream activation and optimization of performance is necessary.

Historically, heterogeneous catalytic processes have been designed empirically, with broad guidelines informed by prior experience in organic and organometallic chemistry. Recent advances in theory and experiments provide tools with the potential to move beyond the traditional "trial-and-error" approach to design principles that predict and develop highly efficient heterogeneous catalysis materials systems.

This review provides a multidisciplinary view of heterogeneous catalysis (Figure 1), wherein a combination of theory and fundamental studies together with advanced materials synthesis and characterization informs general principles towards the design of more efficient and stable, heterogeneous catalysts, with a vision to advance the fundamental science necessary to reduce the carbon footprint of the chemical industries sector. This is, naturally, a broad topic, spanning numerous materials classes and reactions. From this large range of materials, this review specifically focuses on dilute metal alloy catalysts where the majority element host is Au, Ag or Cu, a class of heterogeneous catalysts which are particularly promising as industrial catalysts as they present a multitude of advantageous properties, including a significantly reduced use of ultra-rare metals as Pt, Pd or Rh, the possibility of a reduced carbon footprint, increased atom efficiency,[3] and resistance to poisoning.[4–6] This is due to the unique dual functionality they provide, in which a more reactive minority metal is key for bond activation in elementary steps and initiates the catalytic cycle while the less reactive majority metal imparts selectivity by providing a different environment, coordination and electronic properties to the active element.[7–14]

Importantly, dilute alloy catalysts are a particularly valuable system for a fully integrated theoretical-computational-experimental approach to bridge the divide between fundamental knowledge and design of catalytic processes, specifically by quantitatively scaling from model studies to catalytic conditions due to the relatively simple arrangement of atoms on the surface and the obtained low coverage of intermediates. Experimentally, isolated clusters or atoms (in the case of single atom alloys) of minority species facilitate imaging and interpretation of data in model surface science studies compared to other bimetallic heterogeneous catalysts. Meanwhile, the orbitals of isolated small clusters ensembles or individual atoms of minority species are tractable for theoretical calculations.[15,16]

Dilute alloy catalysts facilitate scaling between model and catalytic studies. It is often challenging to scale between model and catalytic studies due to the typical orders of magnitude difference in temperature and pressure: e.g., ~10^{-8}–10^{1} Pa in surface science studies, where the state of the surface is well-defined due to the low number of adsorbates, *vs.* ~0.1–100 atm in catalytic conditions. Surface science studies typically employ low temperatures to increase the surface lifetime of reactants and products as the relatively non-reactive metal host of dilute alloy catalysts is less likely to accumulate strongly-bound species, while higher temperatures and high pressure are typically used in catalytic processes to increase the reaction rates. Ideally, the reactions investigated would not be sensitive to the surface structure; however, if the rates of reaction depend on surface structure, single crystals with different crystallographic orientation can be investigated using both theory and experiment to model the more complex catalytic materials that expose surfaces with a variety of crystallographic faces.

The elementary steps determined from fundamental studies provides a means of predicting and modeling reactivity and selectivity under catalytic conditions.[17] To scale between model systems and catalytic studies, the state of the surface must be similar for the two cases; this challenge is well-met by dilute Au-, Ag-, and Cu-based catalysts because accumulation at high coverage of strongly-bound species that can modify the surface is less likely on these relatively low-reactivity host metals. For example, pure Au has an extremely low reactivity; hence, the state of the surface is readily controlled over widely varying conditions encountered during catalytic processes. The consequence is the successful bridging of a wide pressure range[18] and prediction of catalytic selectivity for oxidation reactions based on fundamental studies. Because Au has low reactivity, a second metal is required to initiate the catalytic cycle in the catalyst; for example, small amounts of Ag are used to activate O_2, the first step in selective oxidation reactions.[19–22] Similar approaches have been used with materials in which Ag or Cu are the majority elements. Both of these metals are somewhat more reactive than Au, so that scaling between model and catalytic studies are somewhat more challenging, yet possible. For example, Pd doping of Cu is used to initiate hydrogenation catalysis via H_2 dissociation which does not readily occur on Cu.[23]

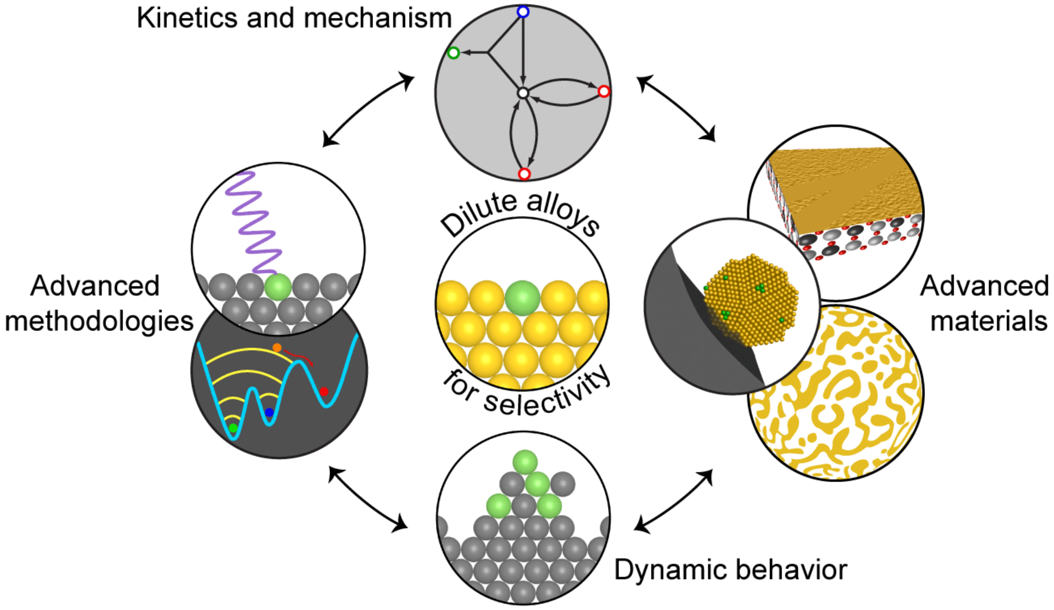


Figure 1. Graphical overview of the integrated theoretical-computational-experimental approach needed to bridge the divide between fundamental knowledge and design of catalytic processes in complex dilute alloy systems.

Distribution of minority species. The underlying principle governing the design of dilute alloy catalysts is that the reactive minority metal, e.g., Pd, Ni, Pt, or Ag, initiates the catalytic cycle, whereas the abundant and more "noble" host, e.g., Au, Ag or Cu, imparts selectivity, either by performing part of the catalytic cycle itself or by electronically modifying the dilute dopant, compared to its bulk state (Figure 2). This simple paradigm requires that intermediates formed from bond activation on the reactive site, migrate ("spillover") across the less reactive majority site.[16] While simple in principle, design of the catalytic system is complex in practice due to (1) variations in the structure and distribution of the reactive minority component in and on the catalyst, (2) differences in the reaction conditions, which can themselves affect this distribution, and (3) influence of the support both in terms of macroscopic transport phenomena and participation in the catalytic reaction.

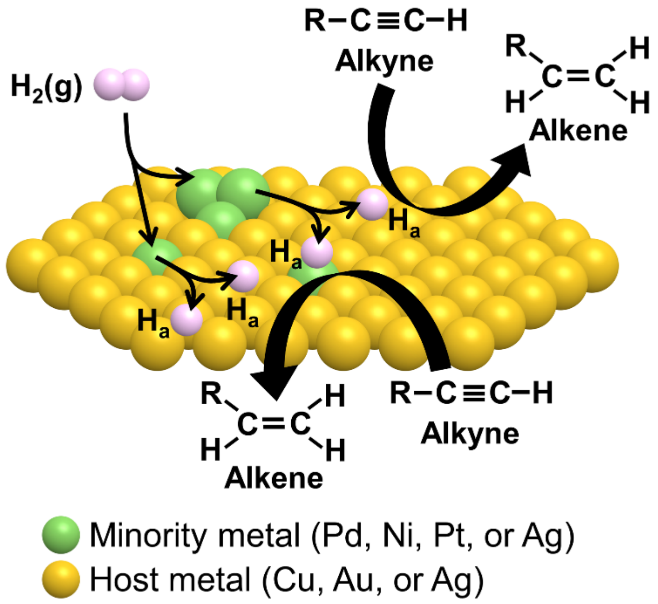


Figure 2. Schematic of the underlying design principle of dilute alloy catalysts using selective hydrogenation of alkynes to alkenes as an example. The catalytic cycle is initiated by the reaction minority metal (e.g., Pd, Ni, Pt, or Ag) where H_2 dissociates and followed by spillover across the abundant host metal (e.g., Au, Ag or Cu) that imparts selectivity.

The distribution of the minority metal has three important effects. First, the minority metal must be on or near the surface of the catalyst to impart reactivity. Second, the ensemble size of the minority metal on the catalyst surface is important—for example, single atoms, small ensembles, and larger islands of the minority metal will all have different chemical properties. Third, the distribution and structure of the minority metal in the catalyst is dynamic and depends on the pretreatment and reaction conditions, including temperature and the composition of the reactant gas phase. The effect of adsorbates on surface composition and catalytic function is a key aspect of the research reviewed here. Indeed, reactive species such as CO, O_2, and others, are known to alter the distribution of minority species as adsorbates may impart additional thermodynamic stabilization of the minority atom at the surface.[24] For example, adsorbed CO provides a thermodynamic driving force for Pd to reside at the surface of a model Pd/Ag(111) alloy at room temperature.[25]

Temperature is another important variable that can alter the composition and distribution of the reactive metal on and near the surface.[4,7] In general, higher temperatures lead to higher activity and lower selectivity for any given chemical process because of the exponential dependence of reactivity on temperature. For dilute alloy catalysts, temperature affects the steady state concentration of adsorbed species at a given pressure, which in turn may alter the thermodynamic stability of the minority atom at the surface. In addition, the rate of exchange of surface atoms and those in the bulk are affected by the temperature as diffusion rates increase with temperature. All-in-all, there is a complex interplay among temperature, pressure, gas composition, surface composition and structure. We will show in this review how all these aspects affect the dynamics, surface composition and catalytic reactivity of dilute alloys.

Materials to test concepts from catalytic studies. A challenge in testing heterogeneous catalyst is often the non-uniformity and dynamic structure at the atomic or nanoscale level. There is thus an impetus to develop well-defined materials with controlled structure and composition. Heterogeneous catalysts come in the form of (1) model systems for ultrahigh vacuum studies (UHV) as well as (2) support-free and (3) supported materials for reactor studies (Figure 3). The synthesis of single or polycrystal dilute alloy catalysts for UHV studies as well as supported and unsupported nanoparticles (NPs) has been discussed in several review articles.[7,26,27] The current review provides illustrative examples from those works in Section 2—but is by no means exhaustive—and highlights more recent materials developments in dilute alloy catalysts, namely support-free nanoporous materials (Section 2.3), which provide high surface-to-volume ratio, high surface curvature, and confinement with properties of extended 3D materials, including high thermal and electrical conductivity; and supported NPs, including the raspberry colloid templating (RCT) approach to prepare sinter-resistant supported dilute metal alloy NPs partially embedded in nanoporous oxide supports (Section 2.4). The consistent nature of these materials in terms of composition and morphology throughout numerous catalysis and treatment conditions makes them amenable to a variety of characterization techniques and aids the connection to theoretical investigations, allowing for feedback between the fundamental surface science studies, calculations, and catalytic processes.

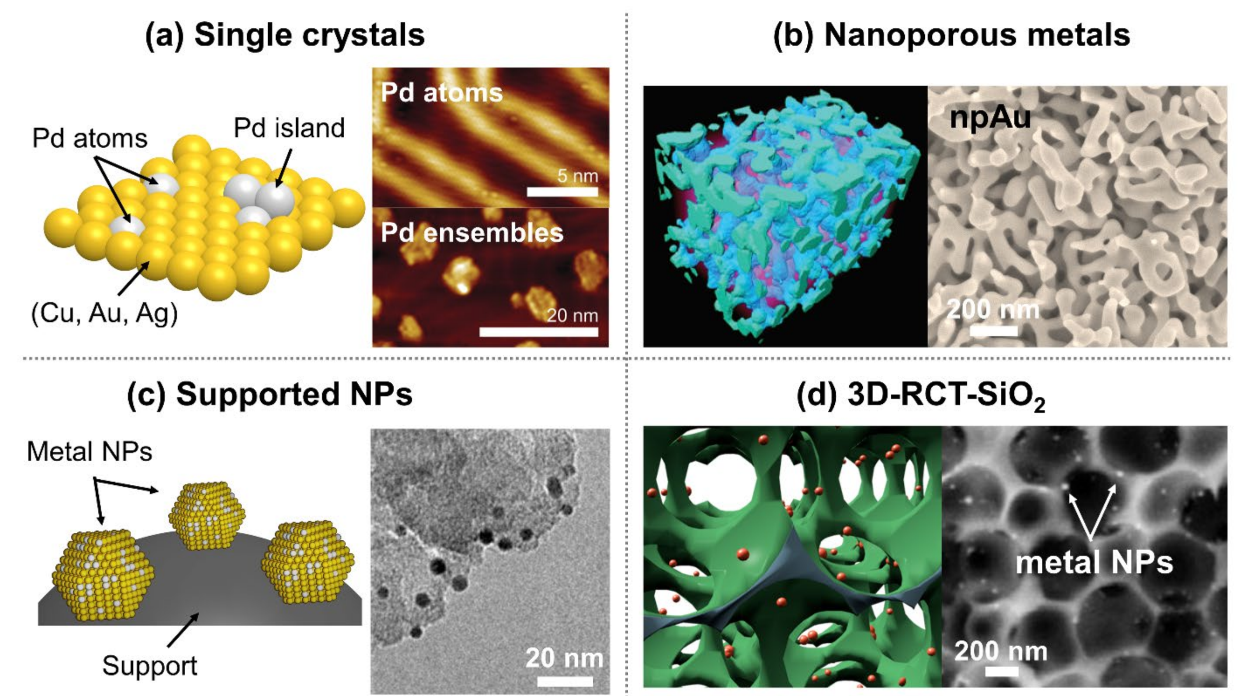


Figure 3. Examples of dilute alloy catalysts employed in fundamental studies and catalytic applications. Schematics (left) and example microscopy images (right) of (a) single crystals, (b) nanoporous metals, supported alloy NPs produced by (c) colloidal synthesis, and (d) RCT approach. The corresponding microscopy images includes (a) scanning tunneling microscope (STM) image showing single Pd atoms and extended Pd ensembles on an Au(111) surface, (b) scanning electron microscopy (SEM) images of support-free, npAu, (c) transmission electron microscope (TEM) image of $Pd_{0.15}Au_{0.85}$ NPs supported on carbon, and (d) SEM image of an RCT material consisting of Au NPs partially embedded in nanoporous SiO_2 support. The schematic of npAu in (b) is generated by fully atomistic molecular dynamic (MD) simulations, adapted with permission from reference 28. Copyright 2008, Springer Nature. Images in (a), (c), and (d) are adapted with permission from references: (a)29, (c)30 and (c) 31, respectively. Copyrights 2019 Royal Society of Chemistry, 2020 American Chemical Society and 2018 John Wiley and Sons.

Reactions, their mechanisms and kinetics, and dynamic behavior during catalysis. By correlating surface science studies with density functional theory (DFT) of well-defined systems, strong, fundamental insights into mechanisms, energetics, and the role of structure towards understanding the selected oxidation and hydrogenation reactions can be obtained (Section 3). The success of relating model studies to catalytic performance over dilute alloy catalysts has advanced the paradigm for control of a wide range of reactions, examples including CO and alcohol oxidation over Au-based dilute alloy materials (Section 3.2) and non-oxidative dehydrogenation over Cu-based catalysts (Section 3.3) are emphasized in this review due to the wealth of information acquired through fundamental and catalytic studies as well as their industrial relevance. The importance of introducing minority reactive metals in coinage metals is also reviewed for selective hydrogenation of carbon-carbon multiple bonds (Section 3.4), where the difference in adsorption energy of reactant and product governs the high selectivity towards alkene. The dynamic changes in the surface structure and composition as well as adsorbate migration between reactive ensembles can have profound effects on the catalytic behavior of dilute alloys (Section 4). This includes determining dynamic behavior in response to gas-phase composition and temperature and identifying reaction conditions that retain the optimal catalyst structure (Section 4.2). The mechanisms for adsorbate migration between co-existing surface phases and their influence on reaction kinetics and surface restructuring can be demonstrated using model bimetallic surfaces (Section 4.3).

The need for development of methodologies. A major challenge in studying catalytic processes involving dilute alloys is tracking the minority component in the catalyst, including the amount and the sizes of reactive metal ensembles on the surface. Even more challenging is the fact that the surface composition and ensemble size will fluctuate because of temperature effects or the binding of reactants and products to the surface, creating the need for understanding kinetics and dynamics of materials rearrangement and the relationship to reaction kinetics.

A concerted effort has been made to advance experimental tools to understand the state of the surface under different conditions (Section 5). This requires a combination of spectroscopy, imaging and simulation. One area of focus has been the advancement of analysis of extended X-ray absorption fine structure (EXAFS) data using machine learning (ML) methods to map out the atomic distribution of the metal atoms (Section 5.2). Atomic-scale imaging complements the spectroscopic data, and together with in-situ capabilities, materials under reaction conditions can be characterized (Section 5.3). In both cases, the highly dilute nature of the alloys reviewed here push the boundaries of the methods. Theoretical tools include ML methods and automation that accelerate Molecular Dynamics (MD) simulations are also under development to model the atomic-scale events that lead to rearrangement of the alloy surfaces and thus understand changes in materials properties, migration of reactants across boundaries in the material, and to model reaction pathways (Section 5.4).

The development of these and other methods are broadly useful in the field of heterogeneous catalysis and can also be applied to other materials and processes involving complex materials. Hence, considerable effort has been made by researchers in this area to both develop new methods and push the boundaries of existing tools.

1.2 Summary

The foundational concept underlying the research reviewed here is that fundamental surface chemistry studies combined with advanced materials synthesis and characterization provides a means of understanding and predicting catalyst function, opening the door to “catalysis by design,” with a special focus on materials consisting of an Au, Ag, or Cu host and Pd, Pt, Ag, or Ni minority species due to their importance in a broad range of catalytic reactions. This review strives to provide an overview of how a highly interdisciplinary approach, inclusive of materials synthesis, mechanistic surface chemistry, reaction kinetics, and in-situ and operando characterization, can be used to understand catalytic processes. Each of the subtopics discussed cannot be covered exhaustively; rather, the value of combining various methods is articulated, referring the reader to more complete reviews of those topics.

2 Advanced Materials

2.1 Overview

The ability to reproducibly fabricate customizable and robust catalysts is critical to improve catalytic performance by quantitatively scaling from model studies to reaction conditions. A variety of dilute alloy materials have been developed to address these complexities (Figure 3).

UHV surface science studies on single crystal surfaces in the presence of low concentrations of reactants and other adsorbates are used to gain a fundamental understanding of the reaction pathways and surface restructuring, which can be directly correlated to DFT calculations. Adding a level of complexity in materials design, support-free nanoporous metals have been introduced to bridge between surface science and catalytic reactor studies without the confounding effects introduced by a support. At the highest level of complexity are supported NPs, the structure of most heterogeneous catalysts currently employed in industry but the most challenging to characterize due to the complex interplay of phenomenon such as mass and thermal transport, accessibility of active sites, direct participation of the support in reactions, and metal-support interactions. As part of the multi-pronged approach to understanding dilute alloy catalysts, it is imperative to synthesize well-defined supported catalysts to be able to relate materials studies to catalytic activity in order to facilitate their further design. RCT has recently emerged as an approach to prepare supported NP catalysts with highly stable NPs that are uniform in size and distribution throughout the macroporous metal oxide support, allowing correlations between bulk materials characterization techniques and local electron microscopy techniques.

This section discusses the most common synthetic routes for preparing the materials presented in Figure 3 and the corresponding characterization techniques, highlighting the systems that will be commented later on in the review. The ability to precisely synthesize and characterize these materials is critical to understand changes that occur in the dynamic environments experienced by catalysts and to guide materials optimization.

2.2 *Metal foils for UHV studies*

Fundamental surface science studies of single atoms deposited on well-defined single crystal metal surfaces led to the discovery of single and dilute atom alloy catalysts, a rare instance of fundamental studies initiating the development of a class of heterogeneous catalysts, as opposed to the more traditional approach of testing various catalysts and then turning to fundamental studies to gain mechanistic understanding and further optimize the catalyst.[7,26] Samples for UHV studies can be prepared by melting a quantitative amount of the two metals (e.g., Au slugs together with Pd granules) above their alloying temperature, followed by cold-rolling into a foil and annealing (e.g., ~1100 K) for grain growth; the samples are then cycled between thermal treatments and Ar ion sputtering to remove impurities, with a final step of thermal treatment under UHV conditions for recrystallization.[32] A more ubiquitous strategy is to introduce the minority species by physical vapor or electron beam deposition onto the surface of a pristine metal substrate, which has a well-defined crystalline orientation and an exceptionally low defect and impurity density (often commercially obtained), e.g., Pd/Au(111), Pt/Ag(100), Pt/Cu(111), etc. During the deposition process, the substrate should be held at an appropriate temperature (typically ~400 K), high enough to allow for diffusion of the minority species and its substitution onto surface sites but low enough to limit diffusion into the bulk.[7,33] Cycles of sputtering with non-reactive Ar ions followed by annealing (~800–1000 K) under UHV conditions is a standard method of cleaning the surface prior to deposition of the minority species.

As these structures are planar, their surface is easily accessed by STM, allowing an atomic-scale view of the arrangement of minority species before, during, and after exposure to various reactants, adsorbates, and conditions. Figure 4a shows an example STM image of Pt deposited on a Cu(111) surface. STM has been employed, for example, to visual the distribution minority species deposited onto a host surface as a function of substrate temperature, identifying general principles regarding atom exchange at step edges vs. terraces and the formation of isolated atoms vs. clusters.[33] Such phenomena can then be modeled with DFT to aid the development of a mechanistic understanding of the alloying process.[33,34] The alloying processes involve minority species that either bind strongly (Figure 4b) or weakly (Figure 4c) to step edges of the host metal. STM images can be correlated with other experimental techniques; for example, temperature programmed desorption (TPD) of CO and other probe molecules in a UHV system.[4]

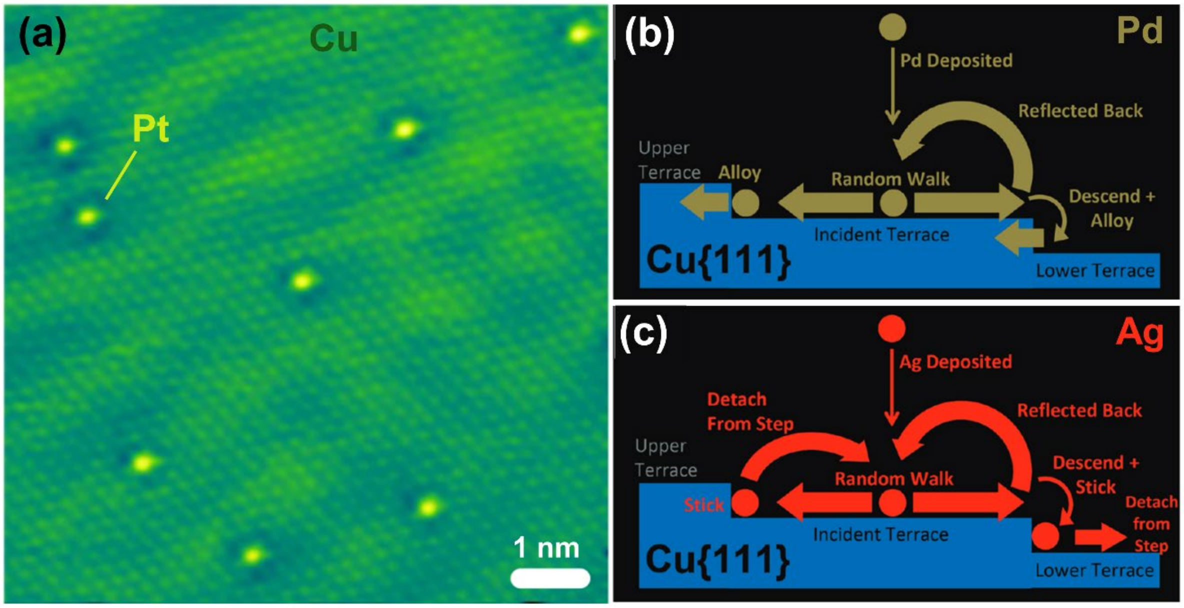


Figure 4. (a) STM image of a 0.02 ML Pt/Cu(111) surface. The bright spots correspond to Pt atoms substituted on the Cu(111) surface. Proposed mechanisms for alloying of (b) Pd and (c) Ag on Cu(111) surfaces, where the thickness of the arrows represents the relative prevalence of the events. The difference between the two minority species are attributed to their different binding strengths at ascending step edges, e.g., weakly binding for Ag and strongly (irreversible) for Pd. Adapted with permission from references (a) 35 and (b and c) 34. Copyrights 2015 Macmillan Publishers and 2009 American Chemical Society.

2.3 Support-free nanoporous alloys

Support-free nanoporous materials readily connect results from surface science studies to catalytic conditions due to their highly ordered character and low density of grain boundaries, as well as their amenability to both UHV surface science tools and reactor studies.[36] Nanoporous alloys consist of metals with feature sizes on the order of tens of nanometers with morphology, uniformity, purity, and density controlled through the choice of synthetic route and parameters therein[37,38] (see examples produced by dealloying and selective leaching in Figure 5). The extended connected network provides beneficial properties such as high thermal and electrical conductivities. High thermal conductivity is of critical importance for process intensification in highly exothermic or endothermic reactions where the catalyst utilization becomes limited by thermal gradients;[39] high electrical conductivity is a prerequisite for electrochemical transformations such as electrochemical CO_2 reduction.[40–42] The electrical conductivity of monolithic nanoporous metals also facilitates fundamental surface science studies that rely heavily on electron spectroscopies (e.g., Auger electron spectroscopy and X-ray photoelectron spectroscopy (XPS)). At the same time, the highly curved surfaces of nanoporous metals mimic those of metal NPs, including a high density of undercoordinated surface sites, though they exhibit many saddle points where the principal radii of curvature are of opposite sign in contrast to NPs which are exclusively convex.[43]

Numerous approaches towards fabrication of monolithic nanoporous metals have been developed, and several review articles[44–46] provide an overview over the different synthesis techniques ranging from bottom-up approaches based on assembly of nanoscale objects such as metal NPs and nanowires to corrosion-based top-down approaches, templating, nanosmelting and combustion. The various bottom-up approaches[44] offer different degrees of control over morphology, uniformity, purity, and density. Compositional tuning is generally performed in the preassembly stage, for example, by controlling the composition of the primary NPs to be assembled through electroless plating or galvanic exchange reactions.[47] The most common and universal top-down approach is dealloying, via a corrosion-based process starting with binary (M_1M_2) or ternary ($M_{1a}M_{1b}M_2$) alloys where M_1 represents the more noble alloy component(s) and M_2 is a less noble alloy component. The process generates a unique bicontinuous ligament pore morphology with unimodal nanoscale ligament/pore size distribution at a length scale of 10–100 nm depending on the details of the alloy composition and dealloying conditions (Figure 5).[48,49] Nanoporosity is generated by selective removal (leaching) of the less noble alloy component M_2 from the starting alloy and the composition is controlled by the starting alloy and the specifics of the dealloying process; for example, nanoporous $Ag_{0.03}Au_{0.97}$ (npAgAu) is readily formed from a bulk AuAg alloy. A coherent nanoporous morphology, where the grain structure of the starting alloy is preserved, is produced from starting alloys in which components form a solid solution and both the starting alloy and the remaining more noble alloy component share the same crystal lattice and lattice constant.[36,50] The resulting crystallite size is orders of magnitude larger than the characteristic length scale of the ligaments and pores.

Combinations of bottom-up and top-down approaches typically include fabrication and assembly of larger particles made, for example, by templating[51] or ball milling[40] followed by dealloying. Dealloying is in fact a universal process: it can be performed with a variety of different starting alloys in the form of bulk materials (Figure 5a),[52] thin films,[53] or particles (Figure 5b)[54,55] as long as the alloy components have a sufficiently different corrosion behavior. Furthermore, various dealloying environments have been established with or without applied electrochemical potential, in aqueous or ionic liquid electrolytes or even in molten metal[56] and vapor phase.[57]

Further tuning the structure, the feature size of both pores and ligaments can be adjusted from a few nanometers to a few microns by thermal annealing (Figure 5c).[58] The coarsening is self-similar, that is, the number of connections in a representative volume element remains constant, independent of the ligament size, thus providing an ideal platform to study size effects.[59] The coarsening kinetics depends strongly on alloy composition and surface chemistry, with both high melting point alloy components[60,61] and surface oxides[58] strongly suppressing coarsening (Figure 5c).

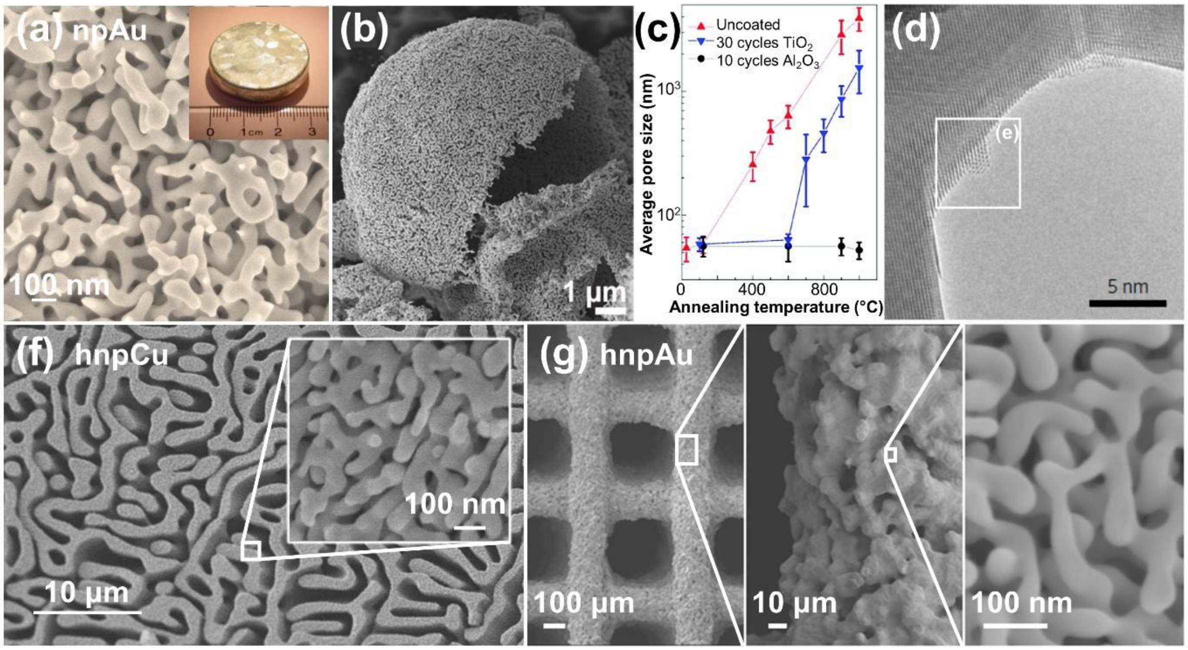


Figure 5. A variety of nanoporous metal catalyst architectures have been synthesized to suit specific applications. SEM images of npAu in the form of (a) a monolithic bulk sample and (b) hollow shells. Inset in (a) is a photograph of the starting alloy $Au_{0.3}Ag_{0.7}$*. (c) Inhibition of coarsening of npAu when nanometer-scale* Al_2O_3 *and* TiO_2 *coatings are present. (d) TEM image of npAu demonstrating its single-crystalline character. Boxed area in (e) indicates the formation of highly crystalline metallic NPs after reduction by 0.1 Torr methanol at 423 K for 30 min. SEM images of (f) hierarchical npCu (hnpCu) made from a Cu-*$CuAl_2$ *starting alloy and (g) hierarchical npAu (hnpAu) with residual Ag fabricated by direct ink printing with increasing magnifications going from left to right. Images in (b), (c) and (d) are adapted with permission from references: (b)[55], (c)[58] and (d)[62]. Copyrights 2015, 2011 American Chemical Society and 2016 Springer Nature.*

The classical example for a monolithic nanoporous metal made by dealloying is npAu prepared by selective corrosion dealloying of Ag from $Au_{1-x}Ag_x$ alloys ($x = 0.65$–0.75). npAu is an Au-rich AuAg alloy where the residual Ag reflects the dealloying process is never 100% complete (Figure 5d).[63] The same dealloying process can be applied to many other alloy systems, including Ag-free npAu prepared by dealloying AuAl starting alloys;[64] npCu generated from CuMn,[50] CuAl[65] and CuZn[52] alloys, and npAg prepared from AgAl alloys.[66] While dealloying single-phase starting alloys generally generates a unimodal nanometer-scale pore size distribution, more complex, hierarchical pore size distributions can be obtained by dealloying multi-phase starting alloys such as the two-phase Al-$CuAl_2$ eutectic alloy (Figure 5f). The presence of larger pores in these hierarchical nanoporous metals helps overcome mass transport limitations to improve the efficiency of nanoporous catalyst materials in the case where chemical reactions are fast compared to mass transport.[67] Besides the traditional metallurgical techniques, 3D metal printing can be used to create hierarchical nanoporous architectures where the macro-pore (~0.1–1 mm in diameter) morphology is defined (and limited) by the resolution of the 3D-printing process (Figure 5g).[68] This, for example, can be used to realize engineered pore architectures that are designed to improve mass transport properties.

In the case of bottom-up approaches, more reactive minority alloy components can be added after dealloying by a variety of methods including galvanic exchange, liquid impregnation, and atomic layer deposition.[47,60,69,70] For example, Ni has been added to npAu and npCu by using a liquid impregnation technique.[47,67] Alternatively, more complex ternary starting alloys can be used to directly generate nanoporous dilute alloys if both the majority and minority components are more noble than the porosity forming alloy component. Examples include Pd-doped npAg and npAu fabricated from ternary AgPdAl and AuPdAl alloys, respectively. However, many of the ternary alloy systems are not thermodynamically stable at room temperature and thus require metallurgy techniques like melt spinning that realize extremely high cooling to keep the alloy system homogenous. Catalytic studies employing such nanoporous materials are presented in Table 1 and discussed in more detail in Sections 3.2.1, 3.2.2, and 3.3.1.

Table 1. Support-free dilute alloy catalysts and the corresponding catalytic reactions summarized in this review.

Target reactions	**Support-free materials**
CO oxidation	$Ag_{0.007}Au_{0.093}$,[71] $Cu_{0.12}Au_{0.88}$[72]
Oxidative self-coupling	$Ag_{0.03}Au_{0.97}$[55,68,73–75]
Oxidative cross-coupling	$Ag_{0.03}Au_{0.97}$[76–78]
Anhydrous aldehyde production	$Ni_xZn_{0.04}Cu_{0.96-x}$ (x = 0.003, 0.01)[47,69,a] $Ni_{0.01}Cu_{0.99}$[60] $Ni_xAg_{0.03}Au_{1-x}$ (x = 0.0001, 0.001, 0.002, 0.01)[60]

[a] Residual Zn content depends on the dealloying conditions, with HCl resulting in lower Zn concentrations, and H_3PO_4 resulting in higher Zn concentrations.

2.4 *Supported dilute alloy catalysts*

Supported heterogeneous catalysts are used in a wide range of industrial applications, thus the integration of dilute alloys with a support is an important step in advancing the field of dilute alloys catalysis towards industrial applications. Although the NPs often function as the catalytically active site, the support can play an important role in the performance of the catalyst as well, affecting the overall activity, selectivity and stability. Among others, the support determines the internal mass transport, accessibility of active sites, stability of the incorporated metal NPs, and can even directly participate in the catalytic cycle. Strategies for controlling metal-support interactions have been reviewed previously.[79]

Over the past decade, synthesis and material science efforts have enabled the preparation of dilute alloy NPs with well-defined size, shape, composition, and distribution of minority species, as well as their incorporation on and in a variety of supports for catalytic studies under reaction conditions. The variety of synthetic methods have been extensively discussed previously[7] and a brief summary is provided here.

A wide range of traditional catalyst preparation approaches have been applied to the synthesis of dilute alloy catalysts, including deposition precipitation[80,81] and impregnation[3,81–84] of the metal precursors on a support materials, or wet-chemical approaches such as colloidal synthesis[9,30,35,85–89] and/or galvanic replacement. In deposition precipitation, metal salt precursors are deposited on a support by reducing their solubility in solution, followed by drying and calcination to decompose the salt and form NPs. Impregnation involves infiltrating the support with metal precursor solution followed by drying and calcination. These two methods have been applied to producing dilute alloy NPs with sizes typically below 10 nm and consisting of a variety of metals combinations, including PdAu,[83,85] PdAg,[3] PdCu,[80] to PtCu.[90] The TEM image in Figure 6 shows an example of dilute $Pd_{0.025}Ag_{0.975}$ NP alloys synthesized via co-impregnation of $Pd(NO_3)_2$ and $AgNO_3$ on a SiO_2 support. A class of dilute alloy NPs containing singly dispersed active metal atoms embedded into a less active host metal are often referred to as single-atom alloys (SAAs).

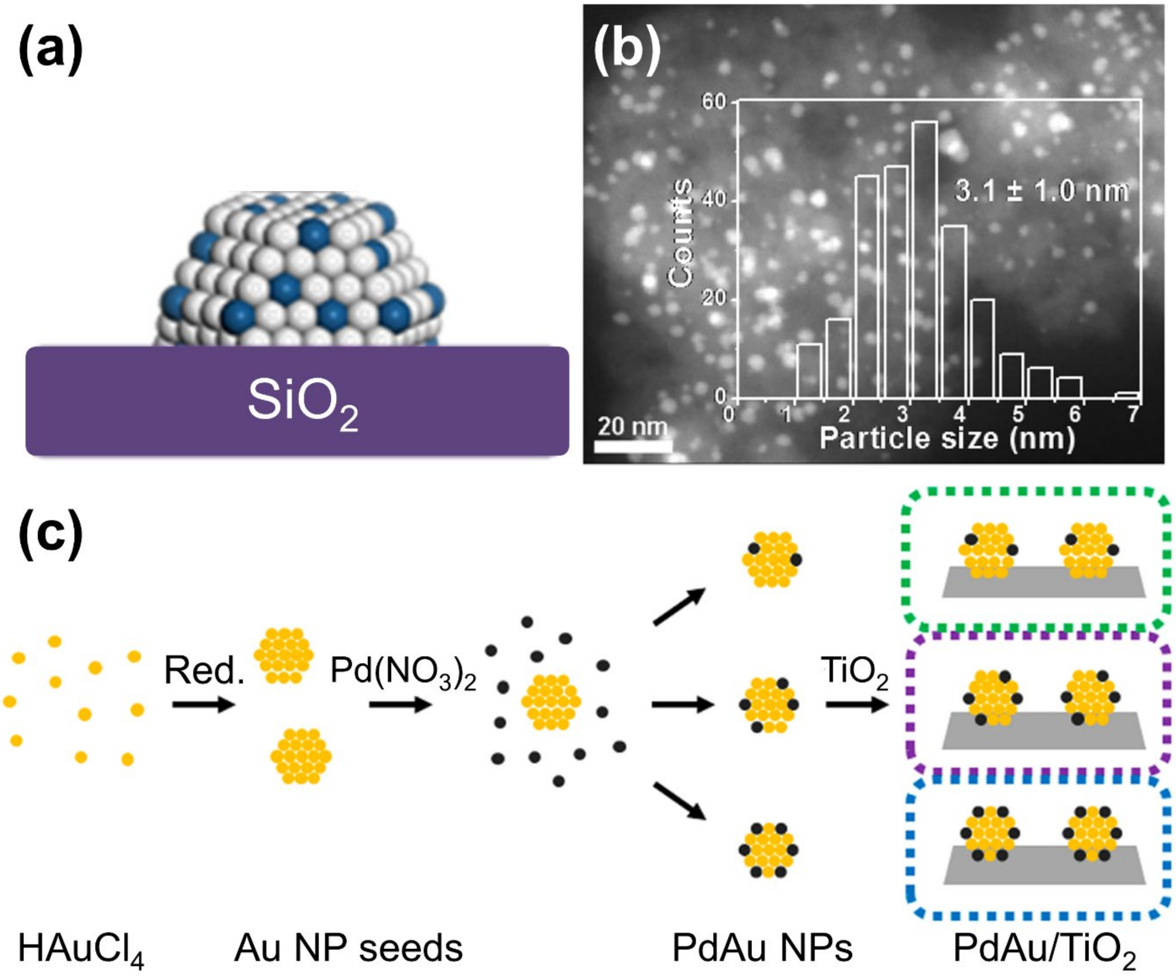


Figure 6. (a) Schematic and (b) TEM image of $Pd_{0.025}Ag_{0.975}$ NP catalyst supported on SiO_2 formed by wetness incipient co-impregnation of $Pd(NO_3)_2$ and $AgNO_3$ in a silica gel. The histogram in (b) shows the particle size distribution. (c) Schematic of a 2-step colloidal synthesis of PdAu NPs followed by deposition onto TiO_2 support. Here, Au NP seeds were synthesized in the first step with particle size determined by the reaction temperature. Pd is incorporated in the second step with the concentration depending on the Pd precursor concentration. The as-prepared PdAu NPs were then deposited onto a calcined TiO_2 support. Images are adapted with permission from references: (a and b) 3, (c) 9. Copyrights 2015 and 2018 American Chemical Society.

The advantage of deposition precipitation and impregnation are the large quantity of catalysts that can be prepared in a single batch (typically several grams of material are obtained). However, ensuring homogeneity in particle size, metal composition, and distribution can be challenging. Recent advances in material science have enabled the synthesis of alloy NPs with well-controlled size, shape and composition via colloid methods. Briefly, the alloy NPs are grown in solution prior to being deposited on a support (Figure 6c); the metal composition is tuned via the metal precursor concentrations in solution and the size and shape are controlled via the reaction conditions (e.g., temperature, pH) and the type of organic ligands used to direct the particle growth. After depositing the NPs on the support, the ligands are removed via thermal treatment[91,92]or chemical washing[93] to ensure that the metal surface is accessible for catalysis. A wide range of dilute alloy catalysts have been prepared, including PdAu,[9] PdAg, PtCu,[35,94] PdCu,[87,88] NiAu[95] NPs with sizes between 2 and 5 nm, supported on various metal oxide supports (e.g., SiO_2, TiO_2, Al_2O_3). Finally, it is possible to introduce a dilute amount of the second metal onto an already existing metal NP via galvanic replacement.[7,95] This methodology can be applied if the metal host consists of a less noble metal (i.e., lower electrode potential) than the second/dopant metal, and is therefore suitable for Ag and Cu host materials but not for Au.

A well-known deactivation mechanism of supported catalysts is NP migration and sintering, especially during reactions at elevated temperatures and pressures, although the support does substantially improve NP thermal stability compared to their unsupported counterparts.[96] In addition to reducing catalytic efficiency, variations in NP accessibility and size complicate the materials characterization and understanding. Both the dopant distribution on the surfaces of dilute alloy NPs as well as the NPs themselves can suffer from metal redistribution and NP sintering, respectively, at the temperatures required to remove the stabilizing ligands from the NP surface (~573–673 K), or under the reaction conditions used.[7,97] Various strategies have been developed to stabilize the host NPs at high temperature and pressure, including confining NPs in pores or cavities of inorganic supports where encapsulation in porous materials allows for facile reactant and product transport but precludes NP migration. Encapsulating materials include zeolites[98] and metal oxides such as mesoporous SiO_2[97,99,100] or ZrO_2.[97]

Precise control over the materials composition, support architecture, and NPs distribution are desirable to perform fundamental studies and optimize catalyst design. A particularly promising route to substantially improve the thermal stability of dilute alloy NPs is to employ the recently developed RCT approach, wherein NPs are anchored in the 3D microporous metal oxide (MOx) support at the pore interfaces, ensuring that every NP is accessible to the reactant stream.[101] Importantly, anchoring of the NPs gives rise to the high sinter-resistance of RCT materials, which has been demonstrated through extensive TEM studies, and more recently 3D TEM imaging.[102] The NPs thus maintain a uniform spatial distribution and size throughout the microporous structure as shown for a variety of treatment conditions and after multiple reaction cycles.[102–105] This exceptional uniformity allows for the application of bulk materials characterization techniques in addition to more localized characterization techniques such as electron microscopy.

The synthetic route to RCT catalysts (Figure 7) entails self-assembly of sacrificial templating polymeric colloidal particles decorated with pre-synthesized NPs either together with (co-assembly) or followed by infiltration with a MO_x precursor. Once the template is removed─typically by calcination in oxidative conditions─a highly interconnected network of spherical voids results, where the void size is determined by the templating colloid (anywhere from 50–1000 nm, with ~300–400 nm being the most common in the catalytic studies to date) and the windows (or necks) connecting them of ~80–100 nm width are the result of MO_x precursor not being able to fill the regions where the templating spheres had been in contact.

The RCT strategy is highly modular, enabling screening through various structural and compositional features independently or quasi-independently. Features that can be varied include the composition, phase, and microporosity of the MO_x support; the composition, size, loading, and placement of the single- or multi-metallic NPs; and the pore size and organization of the 3D MO_x framework. RCT has been demonstrated for various combinations of mono- and multi-metallic NPs (e.g., Au, Pt, Pd, Ag_xAu_{1-x}, Pd_xAu_{1-x}) and MO_x (e.g., SiO_2, TiO_2, CeO_2).[101] Catalytic studies based on supported dilute alloy catalysts are summarized in Table 2 and discussed in more detail in Sections 3.2.1, 3.2.2, 3.3.1 and 3.4.1.

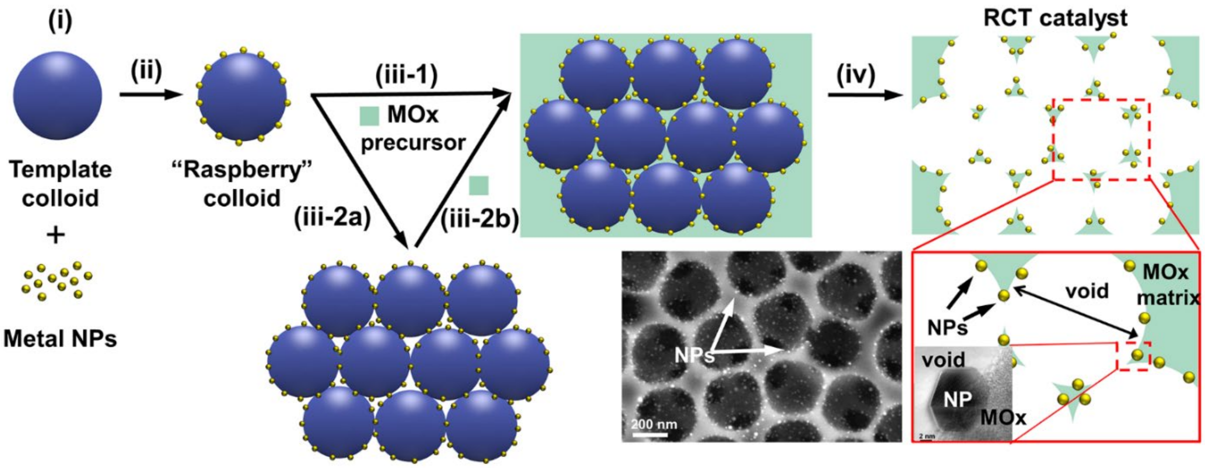


Figure 7. Schematic of the synthetic procedure to produce RCT materials. The procedure consists of (i) synthesis of ligand-capped polymeric template colloids and metal NPs of well-defined size and shape, (ii) attachment of NPs onto the colloid surface, and (iii) assembly of the resulting raspberry colloids either (iii-1) together with the MO_x precursor in a process known as co-assembly or without (iii-2a), followed by (iii-2b) infiltration by the MO_x precursor. Once (iv) the template is removed, typically through calcination at 773 K in oxidative conditions, a porous RCT catalyst is formed, featuring interconnected voids with metal NPs at the air-MO_x interface. The inset is a TEM image of a Ag_xAu_{1-x} RCT-SiO_2 catalyst. The SEM image to the left is taken over the same catalyst. Adapted with permission from reference 31. Copyright 2018 John Wiley and Sons.

Table 2. Dilute alloy NPs on metal oxide supports and the corresponding catalytic reactions discussed in this review.

Target reactions	Supported dilute NPs
CO oxidation	Pd_xAu_{1-x} RCT-SiO_2 (x = 0.02, 0.04, 0.09)[105]
Oxidative coupling	Ag_xAu_{1-x} RCT-SiO_2 (x = 0.1, 0.2, 0.5)[31] Pd_xAu_{1-x} NPs/TiO_2 (x = 0.014, 0.048, 0.071, 0.15)[9,30]
Anhydrous aldehyde production	Ni_xCu_{1-x} NP/SiO_2 (x = 0.001,[47] 0.01,[106] 0.04,[89] 0.18[89]) Pt_xCu_{1-x} NP/SiO_2 (x = 0.003,[107] 0.01[106,107]) $Pd_{0.01}Cu_{0.99}$ NP/SiO_2[106,107] Ni_xAu_{1-x} NP/SiO_2 (x = 0.001, 0.002, 0.005, 0.01)[60]
Selective hydrogenation of alkynes	Pd_xAg_{1-x} NP/SiO_2 (x = 0.005,[3] 0.01,[3,108] 0.15,[80] 0.025[3]) Pd_xAu_{1-x} NP/SiO_2 (x = 0.004,[109,110] 0.025,[3,108,111] 0.01,[111] 0.1[111]) Pd_xAu_{1-x} RCT-SiO_2 (x = 0.02, 0.04, 0.09)[104,112] Pd_xCu_{1-x} NP/SiO_2 (x = 0.006, 0.015, 0.025, 0.09)[80,108] Pd_xCu_{1-x} NP/TiO_2 (x = 0.02, 0.08)[80] $Pd_{0.18}Cu_{0.82}$ NP/Al_2O_3 (x = 0.013,[113,114] 0.02,f 0.04, [113,114] 0.1, [113,114] 0.18[87])

3 Mechanisms and Kinetics

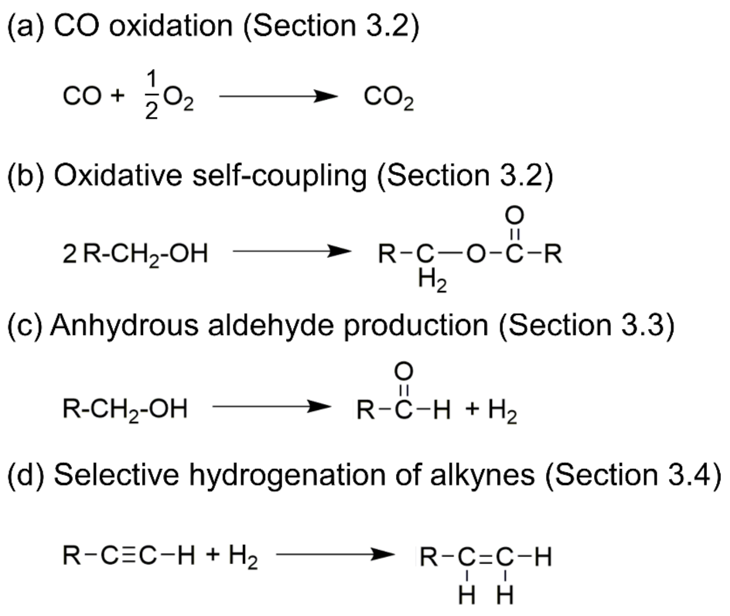
3.1 Overview

A central goal in the rational design of dilute alloy catalysts is to predict reaction selectivity under catalytic conditions based on reaction mechanisms and kinetics determined from fundamental studies on metallic single crystals. The design principle for dilute alloy catalysts involves a small amount of reactive metal atom (minority species) activating one key reactant and the selective reactions followed on the less reactive host metal (majority species). Catalytic behavior is studied under flow and batch conditions, often using operando spectroscopy. Remarkable progress has been made on the research objective to advance the paradigm for control of selective oxidation and hydrogenation on dilute alloy catalysts and to quantitatively model their kinetics.

The mechanisms and kinetics are determined for model systems using experimental studies on well-defined single crystal materials at low pressure and complemented by theoretical studies of bonding and activation barriers. This fundamental information of specific elementary steps is used to model and understand the behavior of catalysts. In selected cases, the reactions and kinetics are analyzed and refined using advanced transient pulse techniques at intermediate pressures and temperatures used in catalytic operation on the actual catalysts.

Thus far, dilute alloy catalysts based on Au, Ag, or Cu with Pd, Ni, Pt, or Ag as the minority species have been employed in a several reactions, some of which have been described in previous review papers.[7,26] Here, the reactions have been intentionally selected to show how model studies and catalyst performance can be related in an integrative approach that employs the feedback between a combination of rationally-designed materials, advanced characterization methodologies, and theoretical approaches. This section will focus on three main reactions (Scheme 1): 1) CO oxidation and oxygen-assisted coupling of alcohols, 2) non-oxidative dehydrogenation of alcohols for aldehyde and hydrogen production, and 3) selective hydrogenation of alkynes to alkenes.

Scheme 1. Selected reactions reported on Au-, Ag-, and Cu-based dilute alloys reviewed in Section 3.



3.2 *Oxidation reactions on Au-based materials*

3.2.1 CO oxidation

The catalytic converter is a critical technology in automotive emission control for reducing air pollution to meet air quality regulations. The oxidation of CO is also often used as a prototype reaction to understand key steps in oxidation reactions. The general reaction mechanism of CO oxidation involves O_2 activation followed by the removal of adsorbed O by CO to produce CO_2. Hence, this process probes the efficacy of the critical O_2 activation step and provides insight into catalyst stability. Using CO oxidation as a probe reaction, it can provide insights into the catalytically optimal composition and structure of catalyst design that leads to enhanced activity, selectivity and stability.

3.2.1.1 CO oxidation over supported Au-based materials

CO oxidation over supported Au-based materials has been studied extensively, starting with the discovery of high activity at or below room temperature over monometallic Au.[115] The CO oxidation activity correlates with the Au NP size,[115] the metal oxidation state,[116] and the choice of oxide support.[117,118] For instance, the earliest report has pointed to the interface between Au and the TiO_2 support as the active site for O_2 activation in CO oxidation based on comparing the catalytic behavior under different pretreatment conditions.[115,117] In this case, the turnover frequency increases as the Au particle size decreases, with 3.5 nm being the optimum size for CO oxidation.[115] The optimum Au cluster size was also confirmed by surface science studies of different thickness of Au on $TiO_2(110)$.[119] The structure sensitivity is the result of quantum size effect, where islands with two-atom-thick Au clusters being most effective for catalyzing CO oxidation.[119]

Microscopy study has revealed the unique Au bilayer (BL) nanoclusters that contain ~10 Au atoms to be the origin of CO oxidation activity in FeO_x-supported Au catalysts.[120] The presence of both metallic and cationic Au in MgO-supported catalysts reported based on spectroscopy evidence directs the catalytic activity, with CO acting as both a reactant and a reducing agent.[116] In contrast, CO oxidation has been reported to be more facile on metallic Au than oxidized Au clusters supported on Fe_2O_3 and CeO_2 supports.[118] The CeO_2-supported Au catalysts treated under H_2 at 673 K showed a 2-fold enhancement in CO oxidation reaction rate than the pristine catalysts. This enhancement is correlated with the change in Au oxidation states probed by UV-Vis, X-ray absorption near edge structure (XANES) and XPS. In the proposed reaction pathway, weakly bound CO on metallic Au reacts with O_2 adsorbed on undercoordinated Au sites or O_2 from the support.[121]

3.2.1.2 CO oxidation over support-free Au-based catalysts

Introducing a minority component to Au-based catalysts has improved the catalyst design for CO oxidation. As introduced in Section 2.3, the high surface-to-volume ratio and surface curvature of hierarchical nanoporous metals makes them good candidates for catalytic studies. Minority alloy components can be present as residual from selective corrosion dealloying process[63] or introduced after dealloying by various methods.[47,60,69,70] For example, npAu prepared by dealloying a AuAg alloy showed low-temperature CO oxidation activities similar to supported Au, without the contribution of Au-oxide interfaces.[21,71,122,123] The spongelike morphology of npAu consists of polycrystalline ligaments with diameters on the order of tens of nanometers (Figure 8a).[71] Based on the XPS spectrum (Figure 8b), 4.4% metallic Ag is present at the surface of the sample, where the total Ag content in the bulk is only 0.7% as determined by atomic absorption spectroscopy. High catalytic activity for CO oxidation was found in the temperature range of 273–323 K (Figure 8c). Even at 253 K, the turnover at CO concentrations up to 2 vol% is close to total conversion. Similarly, npAu containing 12% Cu prepared via leaching of ordered AuCu showed comparable activity to Au/TiO_2 catalysts.[72]

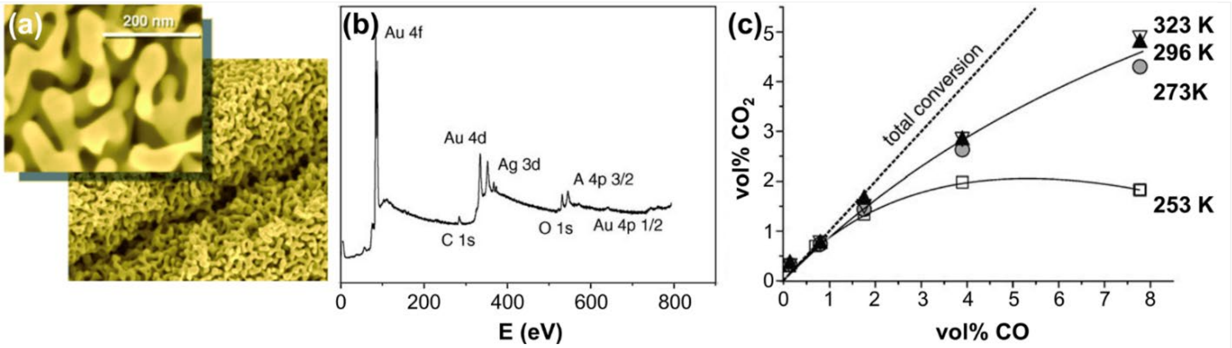


Figure 8. Characterization of the morphology and Ag content in npAu and its temperature-dependent CO oxidation activity. (a) SEM images of a npAu catalyst reveal a spongelike morphology consisting of ligaments with diameters in the order of several tens of nanometers and (b) the corresponding XPS spectrum showing a Ag content of 4.4%. (c) The dependence of CO_2 concentration on CO concentration at temperature ranges between 253 to 323 K. Below 2 vol% CO, nearly total conversion to CO_2 is attained. Adapted with permission from reference 71.Copyright 2006 John Wiley and Sons.

The low-coordination Au sites from the curved shape of ligaments in npAu adsorb CO while residual impurities (e.g., Ag or Cu) facilitate O_2 activation, which has been supported by both experimental observations and theoretical studies.[124] The surface structure of npAu with ~2% of Ag predicted by theoretical calculations suggests the presence of Ag-rich step sites and only these sites will facilitate O_2 dissociation (see Section 3.2.3).[125] The contribution of impurities is evident by the poor activity towards CO oxidation over extremely pure npAu[122] and by varying the amount of residual Ag.[20] In-situ TEM observations further reveal the stabilization of steps and kinks on the Au ligaments by residual Ag suppressing the surface reconstruction dynamics.[123,124,126] However, deactivation due to the coarsening of the porous structure often leads to reduced catalytic activity.[58,123,127] The faceting and coarsening of the nanopores after exposure to reaction gas mixture observed via environmental high resolution transmission electron microscopy (HRTEM) is the result of increased mobility of the Au-containing species.[127] Introducing oxides onto npAu is an efficient way to improve the thermal stability of porous materials and improve CO oxidation activity.[20,58] For instance, depositing a thin TiO_2 layer via atomic layer deposition followed by annealing at high temperature demonstrates improved CO oxidation activity compared to uncoated npAu.[58]

Because of the nanostructured nature of npAu, reactants may be hindered from accessing regions deep inside the material. By combining npAu structures measured with STM, Lattice-Boltzmann fluid dynamics simulations, and DFT-based thermodynamic predictions, it was shown that this hindrance can have significant consequences for the surface structure and reactivity of npAu.[128] Specifically, O_2 partial pressures can be quite low for internal regions of npAu, leading to a lack of Ag at the surface and a consequent lack of catalytic activity for oxidation reactions. Hence, npAu samples are often crushed into fine powders for reactor studies to avoid these transport limitations. As the temperature increases, Ag is predicted to increasingly prefer the subsurface or bulk, consistent with studies that show that high temperatures can lead to lower activity for AgAu alloys.[129,130].

The pretreatment condition of npAu can also affect its CO oxidation activity. For instance, npAu can be activated via reactant gases (CO and O_2) at ~348 K for CO oxidation but remains inactive after O_3 treatment.[55] No CO_2 production was observed under standard operation conditions over O_3-activated npAu catalysts. On the other hand, O_3 activates npAu for oxygen-assisted alcohol coupling by removing carbonaceous residuals resulting from synthesis and thus increases accessible surface area. As a result, the activity and selectivity for alcohol coupling are different for O_3-activated materials. Therefore, it is important to understand adsorbate-triggered dynamic changes of morphology and surface composition, which will be discussed further in Section 4.2.

3.2.1.3 CO oxidation over supported Au-based catalysts

Alloying Pd with Au to increase O_2 dissociation activity and improve catalyst stability has been shown as an efficient catalyst design for CO oxidation.[131,132] Higher turnover rates were observed for PdAu NPs at 473 K compared to the parent monometallic NPs, where high Pd content was present (25–75%).[133] The enhanced CO oxidation activity was attributed to the charge transfer between Pd and Au due to alloying based on CO diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and XPS studies.[131] However, the same electronic effect was also reported to have little effect on CO oxidation in PdAu alloys with lower Pd content.[134] The CO oxidation activity is also affected by the Pd cluster size in PdAu NPs.[81] By exploring different Au:Pd molar ratios in PdAu alloys, it was shown that only contiguous Pd atoms are capable of catalyzing CO oxidation while isolated Pd atoms are not.

Other studies reveal the correlation between Pd surface segregation with CO oxidation activity. Pd preferentially segregates to the surface of PdAu NPs due to a stronger binding to CO under reaction conditions.[134–136] This was demonstrated by a combined X-ray absorption fine structure (XAFS)/DRIFTS approach to characterize the restructuring.[135] The pristine catalysts exhibit surface PdO islands, which are reduced to metallic Pd under reaction conditions and followed by the formation of a Pd-rich shell. A similar restructuring was observed in Pd-doped Au nanoclusters supported on TiO_2, where Pd migration from the core to the surface was supported by operando DRIFTS spectroscopy.[136] This is consistent with surface science studies of PdAu bimetallic model catalysts, where at elevated CO pressure, Pd segregates to the surface and forms contiguous Pd sites to catalyze CO oxidation.[137] The PdAu alloy shows superior reactivity compared with monometallic Pd as a result of reduced CO inhibition. The structural changes were supported by in-situ polarization-modulation infrared reflection absorption spectroscopy (PM-IRAS) studies during CO oxidation conditions.[137]

Despite the success in introducing Pd to Au to increase O_2 dissociation activity for CO oxidation, there are limited reports on PdAu with low Pd concentration. As described in Section 2.4, the recent development of RCT materials improves the thermal stability of NPs by embedding them in an interconnected 3D microporous MO_x support. The tunability in the composition, size and loading of metallic NPs as well as the MO_x support composition, phase and microporosity offer opportunities for the design of dilute alloy catalysts. Pd_xAu_{1-x} RCT-SiO_2 catalysts with low Pd concentrations (<10 at%) activate O_2 and catalyze CO oxidation with long-term stability via atomically distributed Pd atoms at the surface.[105] CO oxidation was chosen here as a probe reaction to provide insights into the catalytically optimal composition and structure of catalyst design that leads to enhanced CO oxidation activity. The apparent activation energies observed for PdAu ($Pd_{0.02}Au_{0.98}$ and $Pd_{0.09}Au_{0.91}$) RCT-SiO_2 catalysts are close to those observed for pure Pd and thus the reaction on Pd sites appears to drive the kinetics for the oxidation of CO (Figure 9a). Pd K-edge EXAFS data indicates that Pd distribution within Au host for $Pd_{0.09}Au_{0.91}$ is mostly uniform with N_{PdAu} = 12.0±0.9. However, it is difficult to obtain the N_{AuPd} values because Au-Au contribution dominates the Au L_3-edge EXAFS data, especially for low Pd concentration ($Pd_{0.02}Au_{0.98}$). This limitation is common for analyzing the EXAFS of dilute metal component, which has inspired the development of a ML aided analysis method (See section 5.2.3). Minor amounts of Pd atoms are stabilized on the surface by interaction with CO and varies with the bulk concentration. Based on CO-DRIFTS measurements (Figure 9b) correlated with DFT-calculated CO adsorption structures, it was concluded that atomically distributed Pd exists at the surface of $Pd_{0.02}Au_{0.98}$ RCT-SiO_2 after CO exposure while both isolated and clustered Pd appear to be present in $Pd_{0.09}Au_{0.91}$ RCT-SiO_2. No deactivation was observed for $Pd_{0.09}Au_{0.91}$ RCT-SiO_2 catalysts for more than 20 hours under CO oxidation reaction conditions at 523 K (Figure 9c). The resistance to sintering is the result of NPs partially anchored in the matrix as well as the RCT architecture of the MO_x support.[138]

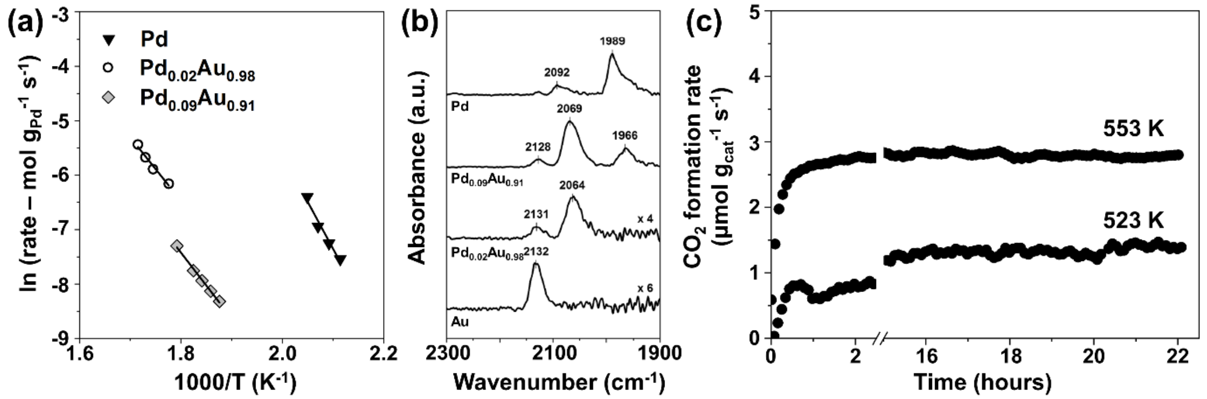


Figure 9. Catalytic performance of Pd_xAu_{1-x} RCT-SiO_2 catalysts for CO oxidation and the characterization of its surface Pd distribution. (a) Apparent activation energies for Pd, $Pd_{0.02}Au_{0.98}$, and $Pd_{0.09}Au_{0.91}$ RCT-SiO_2. (b) CO-DRIFTS spectra of Au, $Pd_{0.02}Au_{0.98}$, $Pd_{0.09}Au_{0.91}$, and Pd RCT-SiO_2 after reduction at 523 K for 1 hour and exposure to CO for 20 minutes at room temperature. (c) Time-on-stream measurements for CO oxidation over $Pd_{0.09}Au_{0.91}$ RCT-SiO_2. Adapted with permission from reference 105.Copyright 2019 American Chemical Society.

3.2.1.4 Reaction pathway over reducible oxide supports: Mars-van Krevelen

An alternative reaction pathway of CO oxidation proceeds via the Mars-van Krevelen mechanism,[139] which involves the release of lattice oxygen from reducible oxide supports during oxidation reaction to generate oxygen vacancies, which are then filled by molecular oxygen. The mobility of lattice oxygen in the oxide support has a positive effect on the CO oxidation activity of Au and Pd catalysts.[140–143] Similarly, the surface lattice oxygen at the perimeter of Au NPs supported on TiO_2 serves as the active oxygen species to react with CO and is later replenished by gas-phase O_2. This is demonstrated in both temporal analysis of products (TAP) reactor measurements and microreactors operated at atmospheric pressure.[144,145] An Mars-van Krevelen-type mechanism has also been reported for single-atom Au catalysts supported on reducible oxides, including Au_1/FeO_x and Au_1/CeO_2.[146,147] Adsorption of O_2 on an oxygen vacancy near the single-atom catalyst forms an intermediate with CO, which facilitates O_2 dissociation and improves CO oxidation activity. On the contrary, single-atom Pd_1/CeO_2 goes through a Langmuir-Hinshelwood type mechanism where the reaction only proceeds when CO and O_2 are co-adsorbed.[148] In this case, single Pd atoms stabilized in the form of PdO and PdO_2 give very low activation barriers for CO oxidation, where metallic Pd is inactive due to CO poisoning.

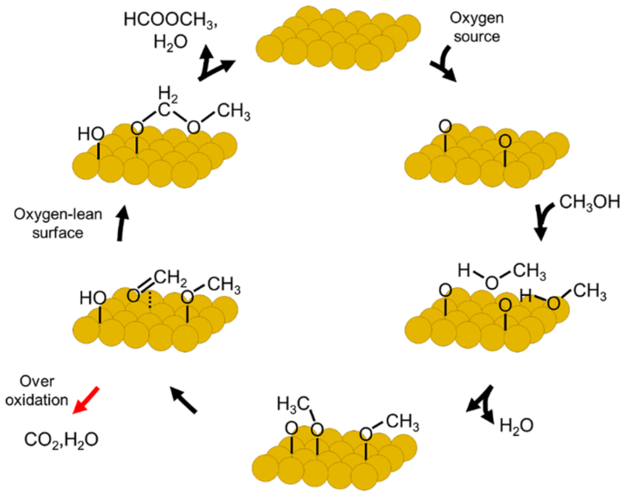
3.2.2 Alcohol oxidation

Au-based catalysts have been shown to be highly selective for oxygen-assisted self and cross coupling of alcohols, as well as cross coupling of amines with alcohols or aldehydes. Although Au surfaces are active for selective oxidation reactions, pure Au does not activate molecular O_2 efficiently. This could be improved via the addition of a dopant metal to facilitate O_2 dissociation or with the presence of a MO_x support. The general mechanism for oxidative coupling of alcohols involves the activation of the O-H bond in the alcohol by adsorbed atomic oxygen to form an adsorbed alkoxy intermediate and the subsequent C-H bond activation to yield an aldehyde, which reacts further with the adsorbed alkoxy. Fundamental understanding of these processes provides an insight into optimizing the cross-coupling selectivity/yield on Au-based catalysts.

3.2.2.1 Alcohol oxidation mechanism

A major inspiration for the work described in this review originated from the discovery that O atoms adsorbed on the surfaces of Cu, Ag and Au promote novel, selective reactions of gas phase acids, meaning molecules with reasonably acidic C-H, N-H or O-H bonds.[19] These unique, single atom O sites behave as a Brønsted base and extract acidic protons from such molecules to create the conjugate base of the acid bound to the surface (Scheme 2). Typical examples are the creation of adsorbed alkoxy from alcohols, adsorbed amides from amines and adsorbed alkylidynes from alkynes. Because neither Cu, Ag nor Au is otherwise particularly reactive, these molecules are initially selectively activated by the adsorbed O atom via reactions with low energy barriers.[149] Further, due to the limited reactivity of these surfaces, the surface-bound intermediates typically react selectively by C-H bond cleavage from the carbon atom adjacent to the atom bound to the surface (e.g., the O, N or C originally bound the acidic H) and selectively yield dehydrogenation products, such as aldehydes or imines.

Scheme 2. Elementary steps in the catalytic cycle for oxygen-assisted self-coupling methanol to methyl formate. Adsorbed oxygen atoms initiate the reaction cycle, which is propagated by dehydrogenation of adsorbed methoxy and the nucleophilic reaction between formaldehyde and methoxy to form the adsorbed hemiacetal alcoholate. Reprinted with permission from reference 150. Copyright 2021 Elsevier, Inc.



To make matters even more interesting, these surface bound intermediates are themselves nucleophilic because they bear a negative charge at the O, N or C atom. Consequently, they readily attack electron deficient centers, such as the carbonyl carbon of the coadsorbed aldehydes or imines that formed, leading to coupling and cross-coupling reactions that can be utilized to produce mono or mixed esters (from mixed alcohols) and amides (from alcohols and amines) (Scheme 2).[19] These coupling reactions are indeed fascinating in themselves, but because Au does not dissociate O_2, they cannot be effectively carried out catalytically with pure Au catalysts. Moreover, for other reasons, neither Cu nor Ag is suitable for selective production of these coupled products. Thus, a catalytic material that preserves the selectivity of pure Au but provides adsorbed atomic O is ideal for promoting these oxidative coupling reactions.

3.2.2.2 Alcohol oxidation over support-free Au-based materials

As described earlier in this review (Section 2.3), npAu is produced by leaching excess Ag from a bulk AuAg alloy. The process results in the inclusion of a low percentage of Ag in the npAu. Although the ability of pure Ag to activate O_2 is low, it is *finite*, so the possibility of creating atomic oxygen on the surfaces of npAu at high pressures of O_2 appeared possible.

In a breakout experiment, pursuant to the principles described in Section 3.2.2.1, npAu was shown to produce methyl formate in a flowing stream of methanol and O_2 below 373 K with 60% conversion and above 90% selectivity.[73] The activation of O_2 was attributed to the presence of Ag,[125] and the selectivity was assigned to the surface chemistry of Au (Scheme 1). The hypothesis was then born that one could, in principle, use a binary combination of metal atoms to effect selective reactions, where the more reactive metal atom activates one key reactant and the selective reactions followed on the less reactive metal.

Subsequently, a variety of oxygen-assisted coupling and cross-coupling reactions on npAu and other Au-based dilute alloy catalysts were studied in catalytic flow reactors[76–78] and on single crystal Au surfaces, and shown to form coupled products with high selectivity. For example, the oxygen-assisted reaction of mixtures of methanol and ethanol on the single crystal Au surfaces show preferential self-coupling of the ethanol at low concentration of methanol, progressing to increasing amounts of cross coupling as the methanol concentration in the reactant mixture is increased (Figure 10a). The veritable absence of methyl formate in even a modest excess of the higher molecular weight species is due to the significantly higher thermal stability of the ethoxy intermediate than the adsorbed methoxy, so the dominant coupling pathway in the mixture is the reaction of acetaldehyde with adsorbed ethoxy (Scheme 2). An analogous pattern of reactivity is seen with coupling of methanol and allyl alcohol (Figure 10c). These patterns of selectivity were also observed for reactions of methanol and ethanol over the npAu catalyst under flow reactor conditions at 425 K (Figure 10b and d).[77] Quite notably, the optimal concentration of methanol in the reactant mixture necessary to maximize the yield of cross-coupling product is not 50%, which would be expected if the relative surface concentrations of the two alkoxy species were reflective of the relative reactant concentrations. The origin of this effect is discussed in Section 3.2.3. This general pattern is typical of these types of coupling reactions catalyzed in the vapor phase.[151]

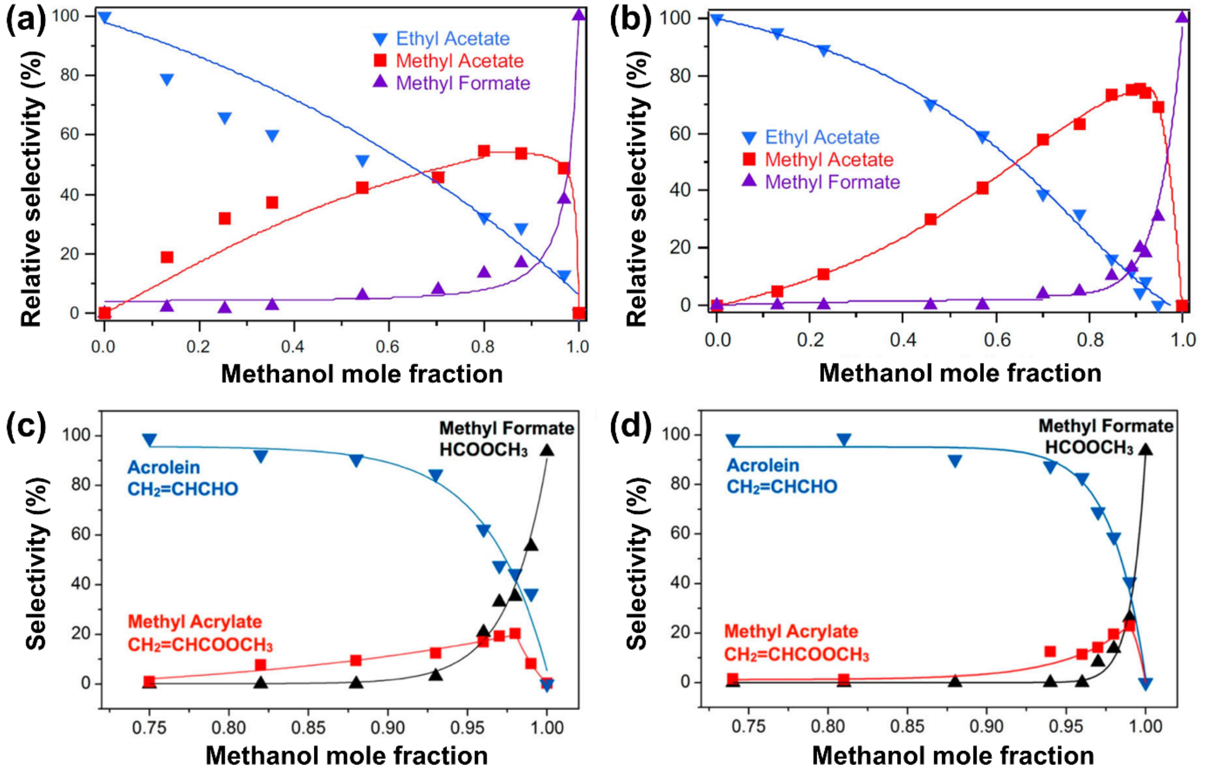


Figure 10. The selectivity of the products of oxygen-assisted cross coupling of alcohols on Au varies asymmetrically with the concentrations of the reactants. The distribution of esters formed by oxygen-assisted reactions of methanol with ethanol (a and b) and allyl alcohol (c and d) on Au(110) (a and c) and under flow reactor conditions (b and d). The optimal concentration for cross coupling to form the mixed ester greatly exceeds equimolar due to the greater stability of the adsorbed alkoxy of the higher molecular weight species. Adapted with permission from references: (a and b) 77, (c and d) 78. Copyrights 2015 Elsevier Inc. and 2016 American Chemical Society.

Since the extent of these coupling reactions is directly related to the rate of activation of O_2 by the more reactive minority metal, replacement of Ag in the binary alloy catalyst with a more reactive metal could conceivably increase the activity of the catalyst. Furthermore, in general, these nanoporous metals do not make the best use of the precious metals, since much of the Au in the nanoporous material resides in the bulk of the material. Unfortunately, supported NPs of Au tends to sinter under reaction conditions, and, as dilute alloys of Au are needed for these reactions, they would be expected to sinter as well. In order to avoid this issue, supported, dilute binary alloy NP catalysts were synthesized using a special templating procedure, as reviewed in Section 2.4.

3.2.2.3 Alcohol oxidation over supported Au-based materials

More recently, Ag_xAu_{1-x} and Pd_xAu_{1-x} NPs anchored in the RCT-SiO_2 have been examined for methanol self-coupling.[31,150] The catalysts do not sinter appreciably, even after extended use. These new catalyst architectures make significantly better use of the metal than npAgAu alloy catalysts, while retaining a clear predictive relationship between their surface reactivity with that of single crystal Au surfaces. Furthermore, the activity of the $Pd_{0.03}Au_{0.97}$ RCT-SiO_2 catalyst per unit weight of active metal exceeded that of a $Ag_{0.10}Au_{0.90}$ RCT-SiO_2 catalyst by nearly 10-fold (Table 3). The indication is that the Pd-based catalyst is significantly more effective in activating O_2 than the Ag-based catalyst, thus promoting a higher turnover rate.

Table 3. Reaction rates over the $Pd_{0.03}Au_{0.97}$ RCT-SiO_2,[150] $Ag_{0.1}Au_{0.9}$ RCT-SiO_2, and np$Ag_{0.03}Au_{0.97}$[31] under oxidative reaction conditions. Conversion of methanol (CH_3OH) and selectivity to methyl formate ($HCOOCH_3$) over the $Pd_{0.03}Au_{0.97}$ RCT-SiO_2 catalyst was found to be 94.2% and 71.4%, respectively. Reaction conditions: 6% methanol, 20% O_2, balanced in He, 50 sccm total, at 423 K.

Catalysts	**$HCOOCH_3$ distribution**	**Selectivity to $HCOOCH_3$**	**Consumption rate of CH_3OH**		**Production rate of $HCOOCH_3$**	
	(%)	**(%)**	**(µmoles mg^{-1} s^{-1})**	**(µmoles $mg_{minority}^{-1}$ s^{-1})**	**(µmoles mg^{-1} s^{-1})**	**(µmoles $mg_{minority}^{-1}$ s^{-1})**
$Pd_{0.03}Au_{0.97}$	55.5	71.4	0.54	29	0.19	10
$Ag_{0.1}Au_{0.9}$	90.0	94.7	0.23	3.9	0.11	1.8
np$Ag_{0.03}Au_{0.97}$	98.0	99.0	0.06	3.3	0.03	1.6

Dilute PdAu alloys supported on TiO_2 synthesized via colloidal methods have shown improved hydro-oxidation of 2-propanol to acetone (Figure 11).[9] Selective oxidation activity on Au can be enhanced under hydro-oxidation conditions with H_2 assisting the formation of oxidizing species, similar to the case of propylene epoxidation.[152,153] Here, the presence of isolated Pd facilitates H_2 dissociation while Au/oxide interface promotes the formation of hydroperoxy intermediates. The formation of selective oxidizing species is probed by measuring the difference in acetone yield between oxidation and hydro-oxidation conditions (Figure 11a). The $Pd_{0.014}Au_{0.986}/TiO_2$ catalyst showed the greatest increase in activity due to its lower activity under oxidizing conditions, whereas high-Pd content alloys behave similarly to pure Pd with a less active hydro-oxidation pathway (Figure 11b). A follow-up study further demonstrates the mobility of H_2O_2 intermediates formed under hydro-oxidation reactions and that metal PdAu NPs are capable of producing the same species without the presence of metal oxide interface (Figure 11c).[30] PdAu/TiO_2 catalysts remained active for hydro-oxidation of 2-propanol to acetone regardless of the choice of support, either on TiO_2 or carbon diluted with TiO_2 supports, indicating that similar reactive species are formed without the presence of metal oxide interface. In the case of $Pd_{0.15}Au_{0.85}$/C diluted with

TiO_2, H_2O_2 is generated on PdAu NPs and travels through the gas phase to TiO_2, where selective alcohol oxidation occurs.

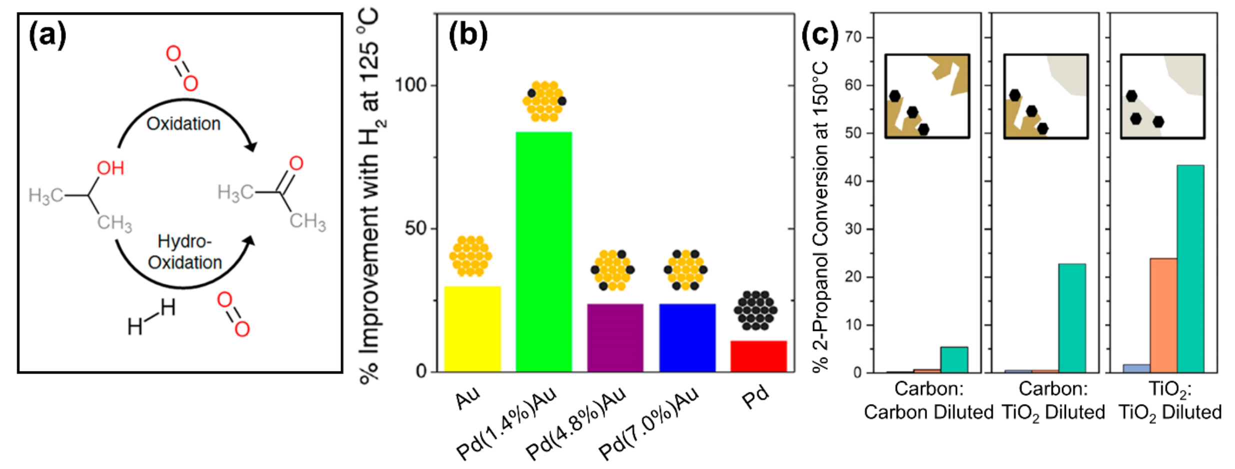


Figure 11. (a) Oxidation pathways of 2-propanol to acetone with reaction conditions involving only O_2 (oxidation, top path) or a combination of H_2 and O_2 (hydro-oxidation, bottom path). (b) Comparison of percent improvement in acetone yield between hydro-oxidation and oxidation conditions at 398 K over TiO_2-supported catalysts. (c) Comparison of 2-propanol conversion over catalysts containing no particles (blue), Au NPs (orange), and $Pd_{0.15}Au_{0.85}$ NPs (green) on different supports at 423 K. Adapted with permission from references: (a and b) 9, (c) 30. Copyrights 2018 and 2020 American Chemical Society.

A very critical issue in catalysis research is how to link the knowledge of kinetics and mechanism obtained on single crystal surfaces with the performance of real catalysts under flow reactor conditions.[18] In principle, a direct connection can be obtained using the rate constants for each elementary step in the mechanism determined on the single crystal model surfaces in a microkinetic model of the functioning catalyst in the reactor.[154] This connection requires that the functional state of the catalyst surface be very similar under operating conditions. Au single crystals and dilute binary alloy Au catalysts satisfy this criterion, so it is possible to use the elementary steps and rate constants determined for Scheme 2 to bridge the gap between low pressure, single crystal studies and the reactor performance of npAu catalysts.[155]

Most of the rate constants for the elementary steps pictured in Scheme 2 were determined in the single crystal studies.[156,157] Two key rate constants, those for O_2 dissociation and for reaction of methanol with adsorbed O to form methoxy and water, were measured directly on the actual npAu catalyst with a Knudsen pulse, low-pressure technique over a temperature range that spanned the temperature used in the catalytic reactor.[158] The remainder of the rate constants could be estimated by a combination of DFT and elementary transition state theory (TST).[18] With these rate constants it was possible to make semiquantitative predictions of both the selectivity and conversion of the npAu catalyst under reactor conditions using microkinetic analysis. Indeed, such results yielded generally correct trends in the selectivity with changes in reactant partial pressures and temperature, but quantitative agreement was not achieved.[159]

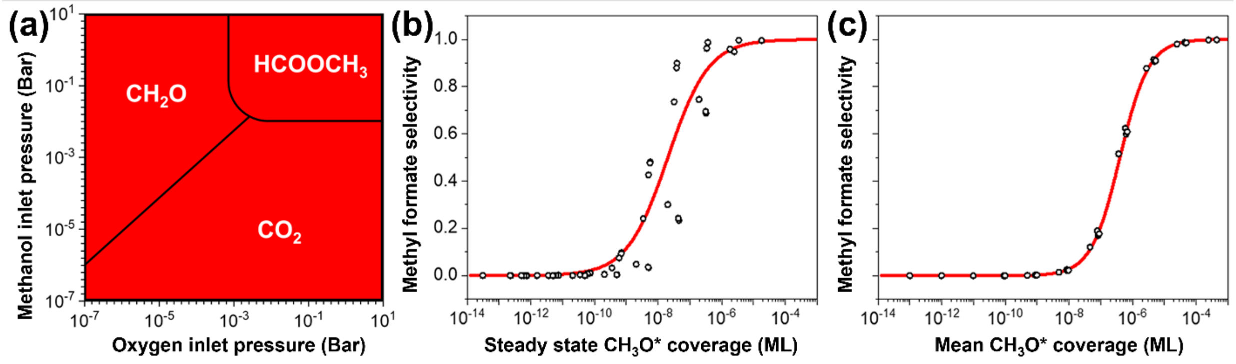


Figure 12. (a) Selectivity phase diagram for the methanol self-coupling reaction at 383 K indicating the regions where either formaldehyde (CH_2O), methyl formate ($HCOOCH_3$), or CO_2 is the major product (>50% selectivity). Reactor conditions were approximately 0.1 bar of both methanol and O_2; the microkinetic analysis based on single crystal source date accurately predicted reactor selectivity. (b and c) The surface concentration of adsorbed methoxy determines the selectivity for methyl formate production from the self-coupling of methanol over a wide range of reactant conditions. (b) Steady-state methoxy coverage vs selectivity to methyl formate from plug flow cofeed simulation, with O_2 and methanol pressures varied from 10^{-5} to 10^{-1} bar, at 423 K. (c) Mean methoxy (CH_3O^*) coverage recorded during Knudsen pulses vs selectivity to methyl formate taken from simulation of the Knudsen pulse data with mean methanol pressure varying between 10^{-7} and 10 bar, with fixed oxygen coverages of 10^{-1} to 10^{-7} monolayers at 423 K. Solid red lines represent the best fit. Adapted with permission from reference 155. Copyright 2019 American Chemical Society.

In order to attain *predictive* accuracy, the rate constants determined in the single crystal surfaces were adjusted to fit the performance of the npAu catalyst by reacting small Knudsen pulses of methanol with O atoms preadsorbed on the npAu catalyst itself, monitoring the time evolution of products as the O was reacted away.[18] The resultant information allowed regression of the rate constants determined from the single crystal experiments to yield an adjusted set of values for the catalytic material itself. When these regressed rate constants were used in the microkinetic analysis, excellent quantitative agreement with the conversion and selectivities observed under reactor conditions was achieved. In short, scaling of the reactivity from single crystal studies in ultrahigh vacuum to reactor conditions at atmospheric pressure was accomplished. Further analysis revealed separated regions of reactant partial pressures favoring methyl formate, formaldehyde and CO_2 (Figure 12a).[155] Significantly, high selectivity to methyl formate was predicted under reactor conditions, whereas high selectivity to formaldehyde was predicted under the conditions of the low pressure Knudsen pulse flow, in agreement with experiment. Furthermore, the analysis showed that reaction conditions which favored a high surface concentration of adsorbed methoxy was key intermediate to determining the high selectivity for methyl formate production (Figure 12b and c).

3.2.3 Fundamental studies of oxidation reactions on Au- and Cu-based materials

Au-based materials can catalyze a variety of selective oxidation reactions[160] and Section 3.2.1 and 3.2.2 have provided several examples of reactor studies of CO and alcohol oxidation reactions. As a complement to reactor studies of nanostructured catalysts, surface science and DFT studies can provide strong, fundamental insights on these reactions. The correspondence between reactor studies and fundamental studies can be particularly strong for Au-based materials because Au surfaces are relatively inert and therefore may be less crowded under reaction conditions than more reactive materials. This can allow a close correspondence in the state of the surface between fundamental studies and catalytic reactor studies.

3.2.3.1 Fundamental studies of the effect of van der Waals interactions on intermediate stability and reaction selectivity

For oxidative coupling on Au, the highest amounts of cross-coupling products do not necessarily occur at a 1:1 molar ratio of the two reactants as described in Section 3.2.2. For example, the highest yield of the cross-coupling product between methanol and ethanol on Au(111) occurs at roughly 80% methanol and 20% ethanol, qualitatively similar to the result on npAu catalysts (Figure 10).[151] In fact, selectivity in cross-coupling reactions is controlled by surface coverage of the relevant intermediates, not by the gas-phase concentration of the reactants, and the ratio of surface coverages often differs from the gas-phase molar ratio (Figure 13),[77] due to differences in surface stability. To carefully probe the factors that control surface stability of crucial intermediates on metal surfaces, several studies measured relative stabilities using competition and displacement experiments on well-defined surfaces as well as DFT calculations, as will be discussed in the next few paragraphs. For Au surfaces, O was first dosed onto the surface at a low coverage (0.05 ML), and then two alcohol species were dosed either sequentially or together. By subsequently measuring signature desorption products, the coverage of each species can be determined. Comparison to DFT calculations allows further understanding of trends and atomic-scale details. However, a detailed, quantitative comparison of energetics can be difficult due to entropic effects, such that qualitative trends are generally the focus of comparison.

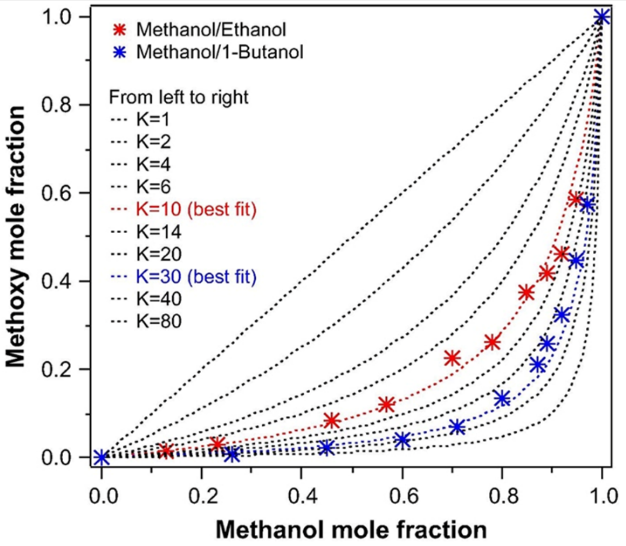


Figure 13. The surface coverage of methoxy as a function of the methanol mole fraction in the gas-phase when Au(110) is exposed to a mixture of methanol and ethanol or 1-butanol. The points are data from experiments while the lines represent ratios derived from different equilibrium constants. The surface coverage ratio is not the same as the gas-phase molar ratio, due to differences in surface stability between alkoxy groups. Adapted with permission from reference 77. Copyright 2015 Elsevier Inc.

For alcohol cross coupling on Au surfaces, the surface coverage is controlled by the stability of the alkoxy intermediates, which is influenced by van der Waals interactions. Indeed, DFT calculations that do not include van der Waals interactions predict nearly identical binding strength for most alkoxy groups, in clear disagreement with experiment.[151] When the calculations do include van der Waals interactions, the correct stability hierarchy is reproduced (Table 4). Therefore, van der Waals interactions—though often considered weak—can strongly influence overall catalytic selectivity.[151,161,162] Van der Waals interactions can also somewhat influence the adsorption geometry of adsorbed species.[151] Based on the hierarchy of stability, it was determined that longer alkyl chains, unsaturated C=C bonds, aromatic rings, and bidentate adsorption lead to stronger binding of alkoxy groups.[151] Changing H to F in a molecule tends to make adsorption weaker or have no effect, depending on the surface structure.[162] Both experiment and theory show similar trends for Au(111) and Au(110), suggesting that there is little structure sensitivity, although absolute binding energies differ between these two surfaces.[151,162]

Table 4. Experimental and computational binding hierarchy on Au surfaces.[151]

Experimental binding hierarchy[a]	**DFT reaction energy (eV)**[b]			
	Au(111), PBE	**Au(111), PBE+vdW^{surf}**	**Au(110), PBE**	**Au(110), PBE+vdW^{surf}**
Methoxy	0.18	0.28	0.18	0.40
Ethoxy	0.21	0.44	0.21	0.50
1-Propoxy	0.22	0.55	0.22	0.58
2-Propoxy	0.21	0.59	0.21	0.66
Allyloxy	0.22	0.66	0.24	0.68
Methallyloxy	0.22	0.73	0.27	0.75
Benzyl alkoxy	0.20	0.84	0.20	0.92

[a] *Least stable to most stable.*

[b] *Calculated as the negative of* $2XH_{(g)} + O_{(ads)} \rightarrow 2X_{(ads)} + H_2O_{(g)}$*, such that a higher absolute value is more stable.*

A combined computational and experimental study of alkoxy groups on Cu(110) found similar trends as the Au studies.[161] On Cu(110), pre-adsorbed O is not needed for the experiments, as alcohols are activated at defect sites. Similar to the Au surfaces, on Cu(110) van der Waals interactions are crucial in controlling the relative stability of alkoxy groups, and on both Au and Cu surfaces each CH_2 group adds roughly 0.1 eV of stability.

For carboxylates on Au, adsorbate-surface van der Waals interactions are not as important. There is some stabilization of longer alkyl chains, but the effect is small.[163] Instead, stability depends on the group that binds to the surface and adsorbate-adsorbate interactions.[163] Specifically, carboxylates form dense islands on Au(110), which lifts the 1x2 reconstruction that occurs on pristine Au(110).[163,164] In these islands, adsorbate-adsorbate van der Waals interactions increasingly stabilize larger carboxylates. Indeed, DFT calculations of isolated carboxylates without van der Waals interactions do not obtain the correct stability hierarchy, but calculations of close-packed molecules that include van der Waals interactions reproduce most of the experimental trends.

For some sets of homologous molecules, gas-phase acidities correlate with binding strengths, likely because polarizability correlates with the gas-phase acidity and the strength of van der Waals interactions.[151,163] This can provide a simple, useful predictor for binding strength in these cases. However, the correlation between acidity and binding can break down when considering a wider array of molecules altogether.[162] For example, this correlation does not hold when considering molecules where H has been replaced by F.[163]

Even for small molecules like CO_2, van der Waals interactions can be important. DFT calculations that do not include van der Waals interactions predict that CO_2 has an adsorption energy of approximately 0 eV on Cu(111), at variance with TPD experiments suggest an adsorption energy of approximately 0.25 eV (Figure 14).[165] DFT calculations that include van der Waals interactions predict a similar adsorption energy as that found from TPD, with particularly close agreement for PBE-D2 and optB86b-vdW. More generally, different methods for correcting DFT calculations for van der Waals interactions can give fairly different energetics.[166]

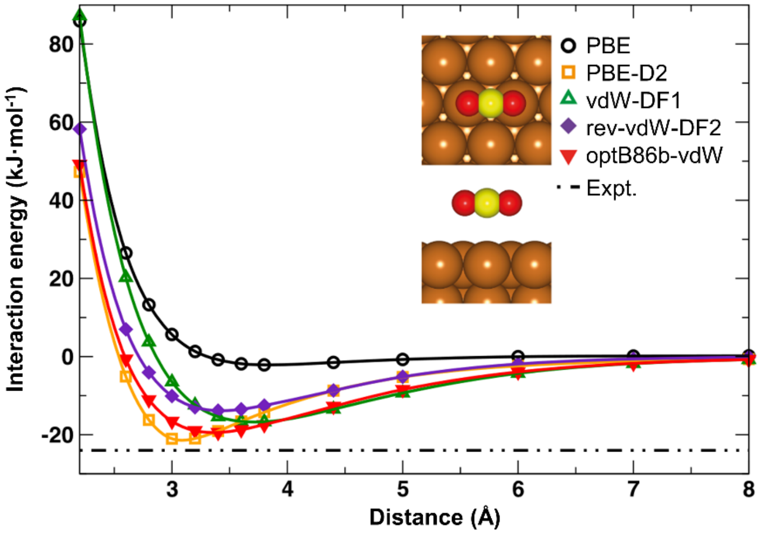


Figure 14. DFT-calculated interaction energy of CO_2 on Cu(111) as a function of the surface-molecule distance, using different functionals. The experimentally derived adsorption energy from TPD is shown as the dot-dash line. Adapted from reference 165 with the permission of AIP publishing. Copyright 2017 American Institute of Physics.

While van der Waals interactions will have the largest fractional contribution to adsorption on more inert metals, such as coinage metals, these interactions can still be critical on more reactive metals. For example, DFT calculations suggest that van der Waals interactions can be important for formic acid dehydrogenation on Pt(111).[167,168] DFT calculations also suggest that van der Waals interactions can have significantly different effects on different reaction pathways—specifically, O-H vs. C-H bond breaking in methanol.[169] However, careful comparison using many functionals suggests that this is an artifact of optimized van der Waals functionals.[168]

In addition to the extended surfaces discussed above, van der Waals interactions have also been studied on small clusters. Propene adsorption has been studied on pure and Y-doped Au clusters with 9 to 15 atoms, where the van der Waals interactions ranged from 0.08 to 0.22 eV without a clear dependence on the size of the cluster.[167] This contribution is somewhat smaller than what has been observed for similarly sized molecules on extended Au surfaces. Whether this is due to the binding through the double bond or the small cluster size is unclear as of yet.

Therefore, van der Waals interactions can play a crucial role in catalytic reactions, especially for cases that involve chemically similar species of varying sizes. Related work in other fields, such as tribology, has also highlighted the importance of van der Waals interactions.[166,170,171]

3.2.3.2 Fundamental studies of the surface structure and active site of Au-based materials

Metallic Au cannot dissociate O_2 except under extreme conditions;[172] however, Au-based materials can be effective oxidation catalysts using O_2. As discussed in section 3.2.2, npAu can catalyze methanol oxidative coupling with high activity and 100% selectivity.[73] Reactor studies suggest that residual Ag (typically 1–3%) in the material[62,74,127] and the step sites on the surface may be important,[127] but the specific role of each in O_2 dissociation, and the structure of the active site, is difficult to elucidate using reactor studies of nanostructured materials. Therefore, fundamental studies have been performed to gain some insight into the active site for O_2 dissociation on AgAu alloys such as npAgAu. Studies on stepped pure Au surfaces were also performed to specifically show the role of the surface structure.

To shed light into the nature of the active site for O_2 dissociation on dilute AgAu alloys, DFT-based thermodynamic studies were performed to predict the surface structure of dilute AgAu alloys in the presence of O_2.[125] These studies predicted that terraces are Au-terminated, with Ag in the subsurface. In contrast, step sites are predicted to have Ag at the surface—specifically, the atoms next to the step atoms are predicted to be Ag, while all other atoms are Au (Figure 15a). These AgAu step sites have a low O_2 dissociation barrier (Figure 15b), in qualitative agreement with the experimentally measured barrier on npAu.[158] Subsequent experimental studies have supported the finding that reaction conditions induce Ag segregation to the surface,[173] and have shown that adding Ag to Au(111) results in no oxidation activity, but adding Ag to curved Au surfaces with steps results in activity.[174] DFT studies also suggest that subsequent oxidation steps after O_2 dissociation occur on or near step sites, primarily because O spillover onto pure Au terraces is unfavorable.[175]

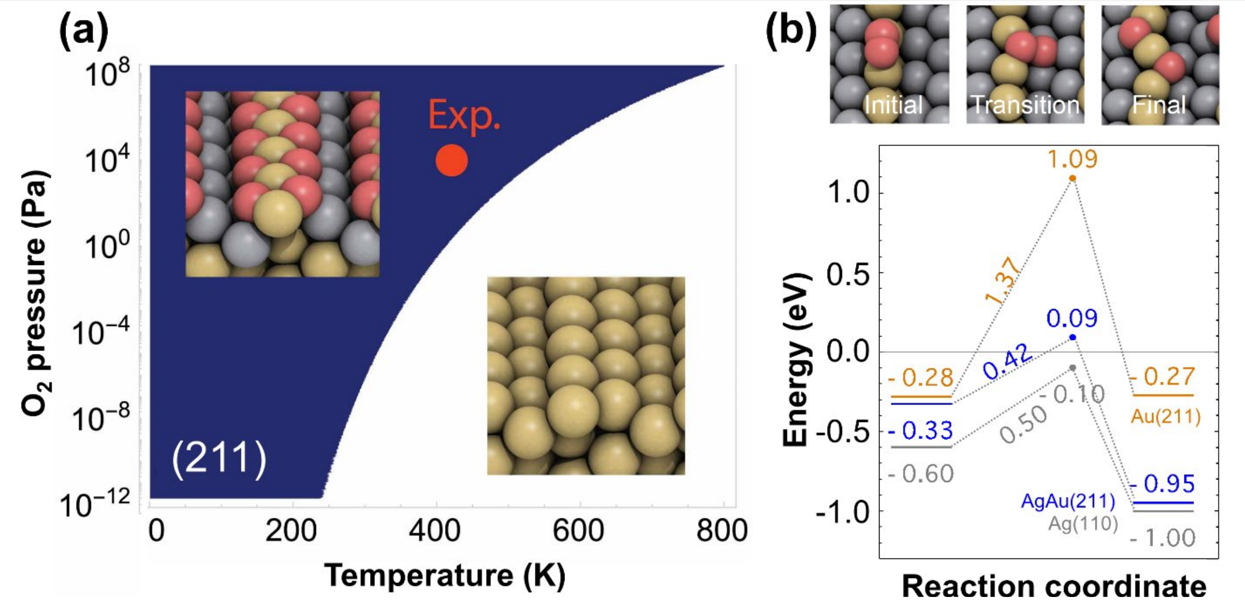


Figure 15. DFT calculations for predicting the surface structure of dilute AgAu alloys in the presence of O_2. (a) Phase diagram of the surface structure of dilute AgAu alloys for the (211) facet. The red dot marks typical experimental conditions for catalytic studies on npAgAu. (b) O_2 dissociation pathway and energetics on the thermodynamically stable AgAu(211) structure, as compared to Au(211) and Ag(110). Adapted with permission from reference 125.Copyright 2016 American Chemical Society.

Comprehensive computational studies employing DFT, cluster expansion, and ab initio MD have found similar conclusions for AgAu(321) as were found for AgAu(211).[176] Without O, the surface is predicted to be pure Au. Adsorbed O forms zig-zag chains, and when these chains are present the most stable surface structures generally have Ag in the surface next to the step atoms, while the step atoms typically remain Au (Figure 16).

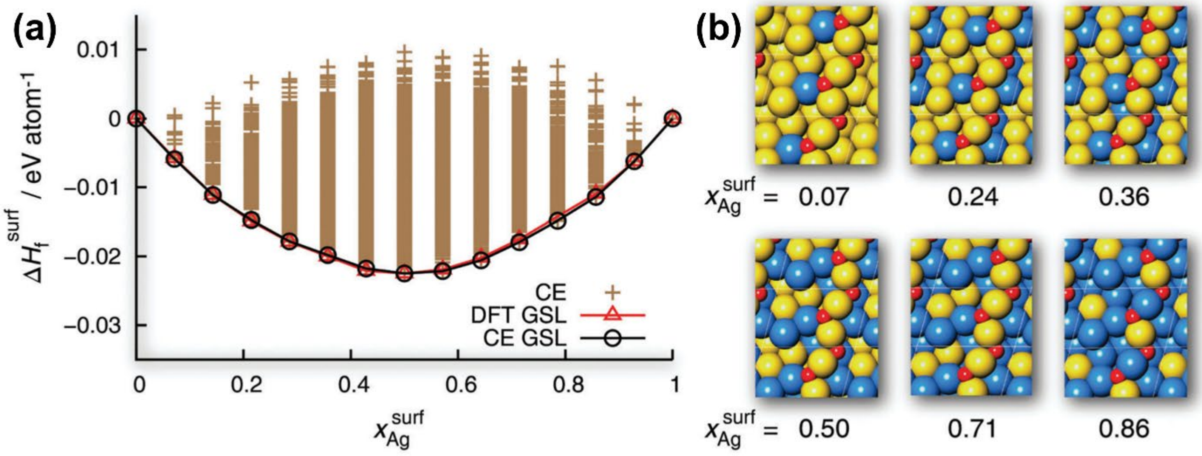


Figure 16. (a) Surface stability of many AgAu(321) structures at different Ag concentrations. (b) The most stable structures at several different Ag concentrations. Adapted from reference 176. Copyright 2016 Royal Society of Chemistry.

A crucial difference between steps and terraces for Au-based materials is the structure and energetics of adsorbed O. On terraces at low and moderate coverage, O occupies fcc hollow sites, and O-O interactions are generally repulsive. On step sites, O forms zig-zag chains, with attractive interactions between the O atoms. These chains have been observed directly using STM on Au(110)[177] and Au(511)[178]. On Au(110), which exhibits a missing-row reconstruction, oxidation happens preferentially along the step direction and the reaction rate increases significantly at a low overall O coverage.[179] Both of these effects are due to the specific structure and stability of O chains, including strain effects. The more strongly bound and more tightly packed O at steps also stabilizes Ag there, based on DFT calculations.[125] As a more extreme example of oxygen-induced segregation, a $Ag_{0.7}Au_{0.3}$ alloy exposed to O_3 results in dramatic Ag segregation, leaving an Ag-depleted nanoporous region.[180]

Taking the major findings together, there appears to be an interplay for AgAu oxidation catalysts under steady-state conditions: surface O is needed to stabilize Ag on the surface, and surface Ag is needed to dissociate O_2. This appears to also require step sites.[125,181] This is consistent with catalytic studies that show that as-prepared npAu is not always active for oxidation catalysis, but samples pretreated with O_3 are consistently active for alcohol coupling reactions.[55]

However, there is some potentially conflicting evidence concerning the behavior of Ag in dilute AgAu alloys under various conditions. For example, transient reactor experiments find that as-prepared np$Ag_{0.01}Au_{0.99}$ can dissociate O_2 at a limited number of localized sites, without first exposing the material to oxidizing species.[158] These sites may be metastable, or may be stabilized by other species present during sample preparation. Further, some studies of np$Ag_{0.03}Au_{0.97}$

suggest that Ag is present in the near-surface region under reducing conditions, although in much lower amounts than under oxidizing conditions.[62] This may indicate Ag prefers to reside in the second layer in the absence of adsorbates, which is what DFT calculations predict, or that kinetic limitations prevent Ag from diffusing away from the near-surface region. Additionally, some work has suggested that alcohols may be able to facilitate O_2 dissociation such that O_2 activation could occur on some pure Au steps.[182] Overall, the atomically precise structure of Ag in these materials under oxidation conditions has not been directly confirmed by experiment.

Au alloys can also be used for oxidative C-C coupling, based on surface science studies.[29] Specifically, when methyl iodide is exposed to a Au(111) surface embedded with Pd, ethane is formed. DFT studies suggest that Pd atoms at undercoordinated sites on the surface are needed for the coupling to occur, again highlighting the importance of undercoordinated sites (such as step sites).

3.3 Anhydrous aldehyde production

3.3.1 Ethanol to acetaldehyde on Cu-based and Au-based catalysts

The current industrial process for aldehyde production from alcohols relies on oxidative dehydrogenation of the alcohols; however, the formation of water-aldehyde mixtures poses separation problems and thus reduces the energy efficiency of this process.[183,184] For non-oxidative dehydrogenation of alcohols, H_2 gas is produced as a by-product and is valuable as an energy carrier. The oxygen-free condition will also suppress over-oxidation to form carboxylic acids.[185] Moreover, as ethanol can be produced from biomass fermentation with increased availability and reduced cost, it serves as an alternative and renewable feedstock for the production of fine chemicals.[186,187]

3.3.1.1 Ethanol to acetaldehyde on Cu-based catalysts

Ethanol dehydrogenation to acetaldehyde can be achieved over copper chromite ($CuO{\cdot}CuCr_2O_4$) catalysts with selectivity above 95%.[188] The reaction steps involve initial cleavage of the O-H bond to form alkoxide and hydrogen intermediates, followed by C-H bond scission to produce an aldehyde and by hydrogen recombination to form H_2. This was revealed by a combination of surface science experiments and DFT calculations performed on oxygen-free, highly defective Cu surfaces.[189] Because Cu is more reactive than Ag and Au, but less reactive than most other transition metals, Cu-based materials can often activate alcohols without adsorbed oxygen atoms, without decomposing or combusting them beyond the desired aldehydes. Cu supported on SiO_2 and Al_2O_3 prepared by incipient wetness impregnation showed above 85% selectivity towards acetaldehyde for the ethanol dehydrogenation reaction occurring at 473–523 K.[190,191] A mixture of Cu^+/Cu^0 that is formed on the catalyst surface during reduction pretreatment is proposed to be the active site, based on CO-DRIFTS analysis and time-resolved XANES studies. On the other hand, Cu supported on high surface area graphite has also shown close to 100% selectivity to acetaldehyde for ethanol dehydrogenation reaction performed at 423–573 K.[192] However, Cu-based catalysts are often unstable and tend to sinter extensively under reaction conditions.[193] More recently, a 4-fold enhancement in ethanol dehydrogenation activity with above 95% selectivity to acetaldehyde at 473 K over Cu NPs was closely correlated with the appearance of surface defect sites.[194] This enhancement was extended to the dehydrogenation of longer chain alcohols. The oxygen-induced surface reconstruction and roughening without altering Cu dispersion and oxidation state was observed via in-situ TEM and XAFS measurements. This is consistent with temperature programmed reaction spectroscopy (TPRS) and STM studies that showed the step sites on a roughened Cu(111) surface are the active sites for alcohol dehydrogenation.[189] Reactor studies summarized here have shown that dehydrogenation of ethanol (or longer chain alcohols) for aldehyde formation over Cu catalysts occurs at around 423 to 573 K; however, it is important to note that dehydrogenating a C_1 alcohol (methanol) to formaldehyde often requires a promotor or extremely high temperatures.[183] This difference is further discussed in Section 3.3.2 by taking into account the effect of van der Waals interactions.

It has been demonstrated that the presence of atomically dispersed Ni in Cu-based materials could lead to 100% selectivity of acetaldehyde and H_2 in non-oxidative ethanol dehydrogenation while greatly suppressing catalyst sintering (Figure 17).[47,106] For instance, a low loading of Ni (0.1–3%) can be introduced to SiO_2-supported Cu NPs by galvanic exchange,[47] where atomically dispersed Ni appears on the near surface layer of Cu (Figure 17a). Reduction pretreatment of $Ni_{0.01}Cu_{0.99}$ SAAs/SiO_2 at 623 K brings Ni atoms to the subsurface, which was confirmed by the decrease in surface atomic ratio of Ni/Cu from XPS, and remained in place during reaction conditions. A nearly 100% selectivity for ethanol dehydrogenation to acetaldehyde up to 623 K was observed based on TPRS measurements over $Ni_{0.01}Cu_{0.99}$ SAAs/SiO_2 (Figure 17b). The catalysts are stable after 8 hours in ethanol dehydrogenation reaction conditions at 523 K and 573 K, whereas monometallic Cu NPs deactivates quickly (Figure 17c). This clearly demonstrates that the addition of Ni atoms into the Cu surfaces prevented the Cu NPs from coarsening.

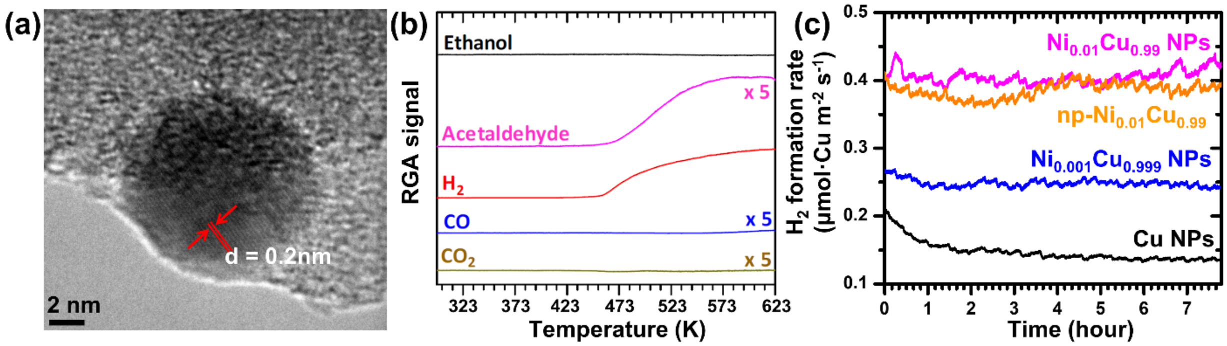


Figure 17. Selective non-oxidative dehydrogenation of ethanol to acetaldehyde and H_2 on highly dilute NiCu alloys. (a) HRTEM image of $Ni_{0.01}Cu_{0.99}$ SAAs/SiO_2. (b) TPRS of ethanol on $Ni_{0.01}Cu_{0.99}$ SAAs/SiO_2. Reaction conditions: 100 mg catalyst, 6% ethanol balanced in He, He flow rate 10 sccm. (c) Stability tests of Cu NPs, np$Ni_{0.01}Cu_{0.99}$, and SiO_2-supported Ni_xCu_{1-x} SAAs (x = 0.001–0.01) in ethanol dehydrogenation reaction at 523 K. The reaction rates are normalized by the surface area of Cu in the catalyst. Adapted with permission from reference 47. Copyright 2017 Elsevier B.V.

Unsupported npNiCu materials were also compared in the study mentioned above and showed similar intrinsic catalytic activity to the $Ni_{0.01}Cu_{0.99}$ SAAs/SiO_2. The rate-limiting step for ethanol dehydrogenation over dilute NiCu catalysts has been identified as a C-H bond cleavage step via in-situ DRIFTS observations of ethoxy and acetaldehyde species, which is the same as the rate-limiting step on pure npCu.[106] The reaction mechanism is also consistent with surface science experiments and DFT calculations performed on Cu step sites (Section 3.3.2). In the current study, isolated Ni atoms lower the activation barrier for C-H bond scission and thus promote ethanol dehydrogenation. The high activity and near-100% selectivity of $npNi_{0.01}Cu_{0.99}$ is independent of catalyst pretreatment conditions (O_2 or H_2).[69] However, H_2-treated $npNi_{0.01}Cu_{0.99}$ suffers from deactivation within ~40 hours on stream as a result of the formation of Ni-rich metallic particles on the surface under reduction conditions and carbon deposition during ethanol exposure. In contrast, O_2 treatment stabilizes the catalyst by keeping it in a metastable Ni^{2+} state covered by a surface overlayer of copper oxide, where most of the Ni is trapped in its oxidized state and thus improved long-term stability. A more recent example of ethanol dehydrogenation over NiCu dilute alloy catalysts with 0.04–0.18% of Ni is to drive the reaction by focused solar light and achieve a high solar-to-fuel conversion efficiency as a result of the synergistic effects of photothermal heating and hot carrier generation through the excitation of surface plasmon resonance of Cu followed by migration to Ni atoms.[89]

Other minority metals have also shown a positive impact on the ethanol dehydrogenation performance. For instance, the presence of isolated Pd and Pt in $Pd_{0.01}Cu_{0.99}$ and $Pt_{0.01}Cu_{0.99}$ SAAs/SiO_2 lowers the reaction barrier for hydrogen atom recombination and desorption but has a negligible promotion effect on its activity compared with monometallic Cu NPs based on DRIFTS measurements. This is different from $Ni_{0.01}Cu_{0.99}$ SAAs/SiO_2 where the addition of Ni improves the reactivity of Cu.[106] Comparing the three different Cu-based SAAs discussed so far, the trend in apparent activation energy for Cu-based SAAs/SiO_2 decreases in the order of Pd to Pt to Ni (Figure 18). The role of Pt proposed for $Pt_{0.01}Cu_{0.99}$ SAAs/SiO_2 is in good agreement with a separate flow reactor study based on TPRS measurements of water-catalyzed methanol dehydrogenation. Both SiO_2-supported $Pt_{0.01}Cu_{0.99}$ SAAs and Cu NPs are not active in methanol dehydrogenation to formaldehyde unless there is water present, and the addition of isolated Pt atoms promotes the reactivity of Cu.[107] The study of $Pt_{0.01}Cu_{0.99}$ SAAs/SiO_2 for alcohol dehydrogenation also suggests that ethanol dehydrogenation can proceed without the presence of water while methanol remains inactive.[106,107] This is consistent with surface science experiments and DFT calculations as describe in Section 3.3.2. With water facilitating the formation of methoxy species, it further promotes C-H bond activation and thus formaldehyde formation.

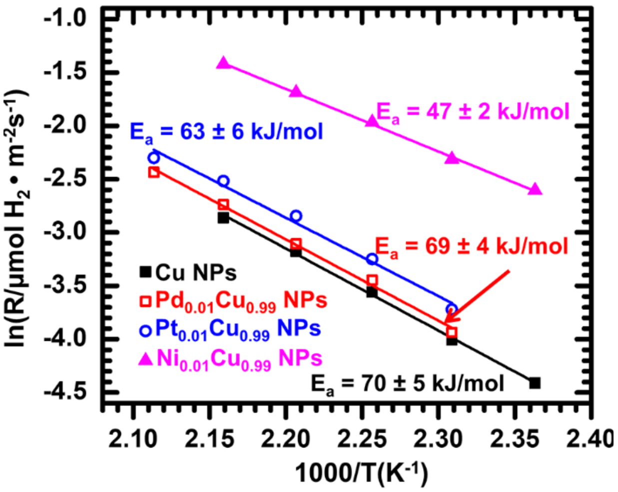


Figure 18. Comparison of Cu-based SAAs with different minority metals for anhydrous acetaldehyde production. Arrhenius-type plots of the reaction rate in ethanol dehydrogenation, normalized by the surface area of Cu over metallic Cu NPs, $Pd_{0.01}Cu_{0.99}$, $Pt_{0.01}Cu_{0.99}$, and $Ni_{0.01}Cu_{0.99}$ SAAs/SiO_2. Adapted with permission from reference 106. Copyright 2017 Elsevier B.V.

However, the minority component does not always have a significant impact on the catalytic performance. For instance, npCu prepared by different etching solutions allows control of the morphology, and more specifically, the step-edge densities. Typically, the residual impurities left behind during the dealloying process contribute to the catalytic performance, as in the case of npNiCu for ethanol dehydrogenation and npAgAu for CO oxidation[122] However, for the ethanol dehydrogenation reaction over npZnCu occurring at 453–503 K, it was not sensitive to residual Zn amount or the nanoscale ligament morphology in npCu based on the comparison of apparent activation energies calculated under steady-state conditions.[52]

3.3.1.2 Ethanol to acetaldehyde on Au-based catalysts

Supported Au materials have also been studied for non-oxidative dehydrogenation of ethanol to acetaldehyde. For instance, a size-dependency study of Au/SiO_2 revealed an optimum conversion of 90% and above 95% acetaldehyde selectivity over ~6 nm Au NPs.[195] The surface step sites are proposed to be the active sites for non-oxidative dehydrogenation, where the rate-limiting step involves C-H bond scission.[195] The activity and selectivity of C_2–C_4 alcohol dehydrogenation over Au NPs on various oxide supports showed a strong dependency on the support acidity.[185] The most promising result is with amphoteric supports, such as hydrotalcite (HT), and the activity of Au/HT increases in the order of ethanol to 1-propanol to 1-butanol with selectivity all above 80%.[185] It was proposed that an alkoxide intermediate forms over the basic support and the rate-limiting step involving C-H bond scission occurs over coordinately unsaturated Au sites based on kinetic isotope effect studies.[185] The presence of isolated Ni atoms in SiO_2-supported npNiAu increases the catalyst activity for alcohol dehydrogenation while preserving the selectivity of monometallic Au, which activates O-H and C-H bonds but not the C-C bond.[60] The apparent activation energy for non-oxidative dehydrogenation of ethanol decreased from 96 ± 3 kJ/mol for SiO_2-supported Au NPs to 59 ± 5 kJ/mol for np$Ni_{0.001}Au_{0.999}$. Atomically dispersed Ni in $Ni_{0.005}Au_{0.995}$ SAAs/SiO_2 showed 100% selectivity to acetaldehyde and H_2, which behaves similarly to the $Ni_{0.01}Cu_{0.99}$ SAAs discussed previously. Although both catalysts showed similar catalytic performance, the active structure is different. In $Ni_{0.005}Au_{0.995}$ SAAs/SiO_2, the catalyst is activated by the reactant where reduction pretreatment brings Ni atoms to the subsurface and the presence of ethanol brings Ni back to the surface. This is different from $Ni_{0.01}Cu_{0.99}$ SAAs/SiO_2 where Ni was brought to the subsurface by catalyst pretreatment and remained there during reaction. The presence of Ni also slows down the coarsening kinetics of the NiAu catalyst, allowing for prolonged use under reaction conditions without any apparent drop in activity. The dynamic behavior of NiCu and NiAu catalyst surfaces are further discussed in Section 4.2

3.3.2 Fundamental studies of anhydrous aldehyde production

As a complement to the reactor studies of anhydrous aldehyde production discussed in Section 3.3.1, surface science and DFT studies of well-defined model systems can bring more detailed insight into mechanisms, energetics, and the role of structure. These studies have elucidated differences between steps and terraces, the role of alloy sites, and differences between alcohols.

3.3.2.1 Effect of surface structure and alloy sites

Fundamental studies strongly suggest that Cu terraces are essentially inactive for alcohol dehydrogenation.[189,196] DFT studies of alcohols on Cu(111) terraces predict that alcohol desorption is favored over reaction by 0.39 eV for methanol and 0.26 eV for ethanol. Ethanol-ethanol interactions do not facilitate dehydrogenation on flat Cu(111), so higher alcohol coverages will not change this conclusion. A possible confounding factor is the fact that water can act as a co-catalyst for alcohol dehydrogenation on Cu(111) (see 3.3.2.2), but for the experimental work described here, conditions were carefully controlled such that water has no impact on the activity.

In contrast to Cu terraces, Cu steps can be active for alcohol dehydrogenation.[189,196,197] For example, a significant fraction of methanol dosed at high coverage on Cu(210) at 100 K is converted to formaldehyde.[197] On Cu(111) single crystals, the density of active sites for alcohol activation is similar to the density of step sites. Similarly, STM studies show that step sites on Cu(111) are the active site for alcohol dehydrogenation. Sputtering Cu(111) and Cu(110) single crystals results in much higher activity towards alcohol dehydrogenation than is observed on flatter, annealed surfaces (Figure 19).[189] These experiments showed 100% selectivity towards aldehydes and the same yields for several cycles. Cu(110) steps had higher activity than Cu(110), perhaps due to the more open structure of this surface.[189] The higher yields on sputtered surfaces are attributed to the lower initial alcohol coverages, as adsorbed clusters of alcohols do not fit as well on sputtered surfaces.

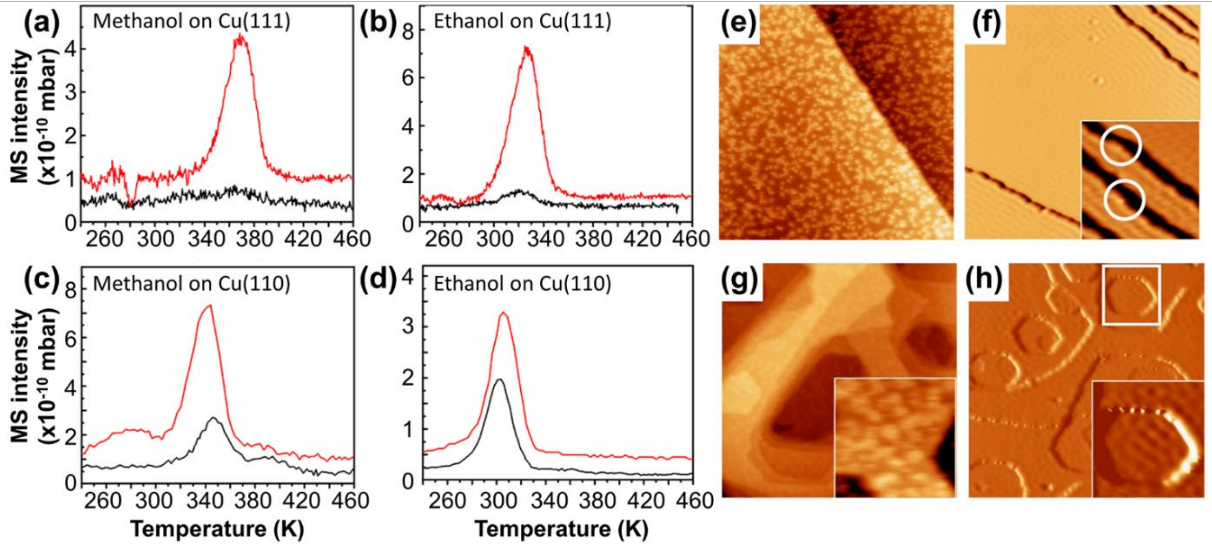


Figure 19. Surface structure dependence of the dry dehydrogenation of alcohols on Cu single crystals. (a-d) TPD traces of aldehyde desorption from alcohols dosed onto flat (black) and sputtered (red) Cu surfaces. Roughened surfaces produce a much greater yield of aldehydes. (a) Methanol and (b) ethanol on Cu(111), dosed at 180 K for saturation. (c) Methanol and (d) ethanol on Cu(110), dosed at 200 K for saturation. (e-h) STM images (50 nm x 50 nm) of Cu(111) surface exposed to ethanol. White circles in (f) highlights ethoxy adsorbed at Cu(111) steps. The inset in (g) shows ethanol adsorbed on a small terrace of Cu(111). The inset in (h) highlights adsorbed ethoxy intermediates on Cu steps and kinks. Adapted with permission from reference 189. Copyright 2017 American Chemical Society.

Steps are more active than terraces due to both stronger binding and lower reaction barriers. For step sites on Cu(111),[196] DFT studies show that it is more favorable for alcohols to react than desorb by roughly -0.25 to -0.5 eV. Both STM and DFT studies show that alcohols are more strongly bound at steps than terraces, with DFT calculations showing a difference of roughly -0.3 eV.[189,196] These DFT calculations also show that the O-H activation energy decreases from roughly 0.9 eV on terraces to roughly 0.5 to 0.6 eV on steps. Therefore, the alcohols are more strongly bound and have lower reaction barriers on steps. Indeed, all adsorbates in the reaction are more stable at steps than terraces. Alcohols are more stable at kink sites than step sites, but DFT calculations suggest that these sites do not facilitate reaction due to higher barriers.[189,196]

Through a combination of surface science experiments and DFT calculations, strong insight was gained into the reaction mechanism and energetics of alcohol dehydrogenation on Cu step sites. The first step is rupture of the O-H bond, while the reactivity is controlled by the subsequent C-H bond breaking step.[189] More specifically, DFT results suggest that the reaction rate is controlled by the energy difference between the adsorbed alkoxy (the most stable state) and the gas-phase aldehyde.[196] While aldehyde desorption has the largest single barrier along the pathway, this step alone cannot explain the observed kinetics. Using the energy difference between the alkoxy and the aldehyde with a simple kinetic model in the Redhead formalism gives a predicted desorption temperature of roughly 350 K for desorption of formaldehyde when ethanol is exposed to Cu(111), in good agreement with the experimental value of roughly 325 K.[189] This kinetic scheme also allowed comparison between DFT-calculated (or extrapolated) energetics and experimental desorption temperatures for several C_1 to C_4 alcohols on Cu surfaces.[196] A strong correlation was found, where the DFT tended to predict desorption temperatures around 41 K higher than the experimental values.

The DFT studies gave further insights that are not directly testable with current experiments.[196] First, van der Waals interactions and zero-point energies were found to be important for correctly calculating the energetics. Based on the DFT results, it was hypothesized that Cu(111) terraces can dehydrogenate 1-butanol and longer alcohols because they will be bound strongly enough to the surface to allow reaction. Furthermore, recombining H* to H_2 would force aldehydes to stay as aldehydes instead of allowing them to rehydrogenate, which would make them desorb at a lower temperature.

Introducing Pt as a minority metal that binds alcohols stronger than Cu(111) can have a positive impact on its ethanol dehydrogenation reactivity. The Pt site interacts more strongly with ethanol and lowers the barrier for O-H scission, promoting activation of the alcohol, which occurs below 160 K. Importantly, Cu sites interact more strongly with ethoxy than the Pt site, which promotes spillover of the ethoxy intermediate.[107,198] DFT calculations show that O-H bond scission is favored over ethanol desorption on the PtCu site, but desorption is favored on a Cu site.

Fundamental studies of PdAu(111) alloys for ethanol conversion have found that these alloys can also form acetaldehyde.[199,200] These studies also showed the critical importance of ensemble size. While smaller Pd concentrations can produce acetaldehyde, ethanol decomposition becomes more prevalent at higher surface concentrations of Pd. DFT calculations suggest that the $Pd_2Au(111)$ surface is particularly active because reaction barriers are fairly low, but H and C are not too strongly bound, which leads to fast H_2 evolution and prevents coking.

Additionally, other Cu-, Ag-, and Au-based alloys have been suggested as effective catalysts for alcohol dehydrogenation, especially dilute alloys, based on computational studies.[201,202] Many of these alloys promote dehydrogenation of the α C-H bond over the O-H bond. For the (211) facet of Cu_3M alloys (M=Ni, Pd, Pt, Rh), Pt and Rh were found to give the lowest dehydrogenation barriers (Figure 20), and Cu_3Pt was predicted to be the most active based on microkinetic modeling.[202]

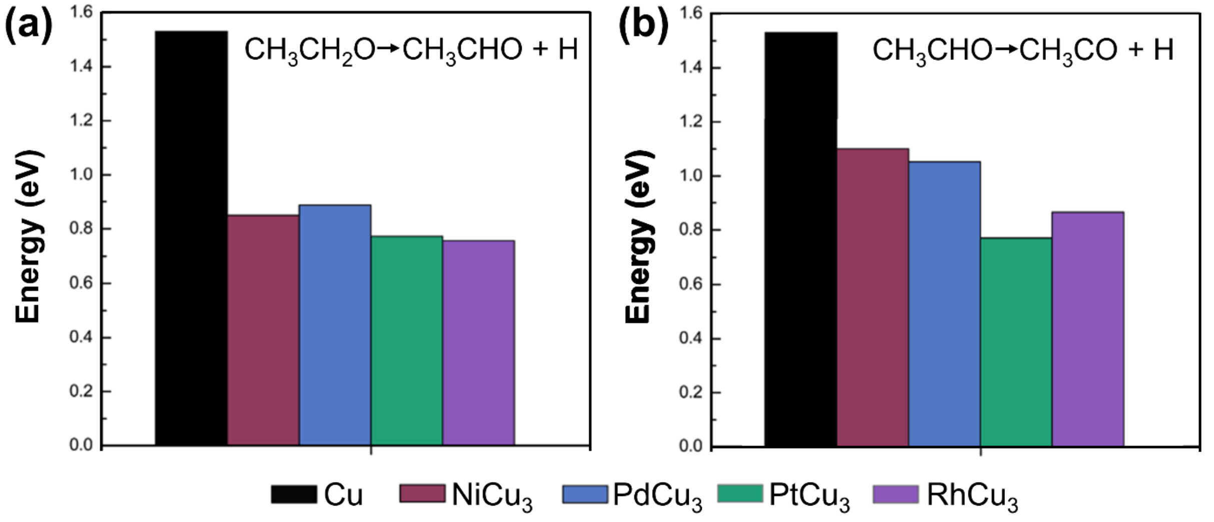


Figure 20. DFT-calculated activation barriers for a) ethoxy dehydrogenation and b) acetaldehyde dehydrogenation on the (211) facet of different Cu alloys. Taken from reference 202. Copyright 2018 Springer New York LLC.

TPD and DFT studies of ethanol on Ag surfaces have also shown that adsorption is slightly stronger at steps and kinks than on terraces[203]. The measured differences for Ag are 0.03 and 0.07 eV for steps and kinks respectively, which appears to be somewhat smaller than the differences on Cu.

3.3.2.2 Effects of chain length and adsorbate-adsorbate interactions

Reactor experiments have shown that Cu catalysts can dehydrogenate ethanol to acetaldehyde at around 473 to 573 K (Section 3.3.1),[204] but dehydrogenating methanol to formaldehyde requires a promotor or extremely high temperatures.[183,205] To shed insight into this difference, DFT studies with van der Waals corrections were performed to compare dehydrogenation of C_1–C_4 alcohols on Cu(110).[206] These studies found that the initial O-H activation barrier was similar for all alcohols. However, the subsequent C-H activation barrier was found to be 0.93 eV for methoxy, much higher than the barrier of 0.55 to 0.58 eV for the other alcohols. As a result, these barriers suggest that methoxy groups prefer to reform methanol and desorb, rather than forming formaldehyde, while aldehyde formation is kinetically favored for longer chain alcohols. The calculated barrier for methanol is quite similar to the experimentally measured barrier of 0.91 eV, and similarly close agreement is found for the methanol adsorption energy.

Kinetic modeling confirmed that formaldehyde production is much slower than production of longer chain alcohols. The longer alcohols have similar rates, with 1-butanol having a somewhat lower rate due to stronger adsorption of butyraldehyde. Based on the kinetic model, stabilizing the transition state (TS) and/or final state for C-H bond scission should increase the rate. On Cu(111) single crystals, experiments show that ethanol dehydrogenates more easily than methanol.[189] The estimated barrier was roughly 0.1 eV lower for ethanol than methanol, while DFT calculations on a stepped Cu(111) surface found a somewhat smaller difference of around 0.06 eV for the rate-controlling energy difference.[196]

Water can greatly increase the rate of anhydrous methanol dehydrogenation on Cu-based materials, such as dilute PtCu alloys.[107] At low temperature, steam reforming does not occur on these materials. Relatedly, ethanol-ethanol interactions can be stabilizing on Cu surfaces,[107,196] where ethanol-ethanol hydrogen bonding is roughly -0.3 eV on a Cu(111) terrace and roughly -0.1 eV on steps. Ethanol-ethoxy hydrogen bonding is weaker with -0.06 eV on terraces and +0.02 to +0.05 eV on steps. For an ethanol-ethoxy pair at a (111) step, an H atom is shared between the two molecules, hopping between the two O atoms approximately every 150 fs. This may have consequences for alcohol-alkoxy replacement reactions.

3.4 Selective hydrogenation of alkynes

3.4.1 Selective hydrogenation of alkynes on Pd catalysts

Selective hydrogenation of carbon-carbon multiple bonds is a key step for purification in upgrading light alkanes via steam cracking processes as trace amounts of alkynes can be detrimental to the downstream polymerization processes.[207,208] In large-scale applications, hydrogenation of acetylene and diene impurities in alkene feedstocks is achieved via Pd-based catalysts.[209] The reaction mechanism for the hydrogenation of alkynes is often referred to as the Horiuti−Polanyi mechanism, where H_2 is dissociated and added sequentially to molecularly adsorbed alkyne followed by desorption of the product. Typically, the difference in the heat of adsorption of alkyne versus alkene governs the selectivity. Weakening the alkene adsorption will turn the selectivity to favor its formation while binding alkynes strongly will result in higher activity.[210] Pd is active for hydrogenation but often suffers from over-hydrogenation of alkynes to alkanes, especially at high conversions. It is, however, possible to achieve selective hydrogenation of alkynes to alkenes over Pd catalysts where the population of hydrogen or carbon on the subsurface Pd sites governs the selectivity.[211–213] The catalyst support also plays a role in tuning the selectivity. For instance, carbon-supported Pd has been reported to be more selective than oxide supports towards ethylene formation for the hydrogenation of acetylene in excess ethylene, due to an increased electron density on Pd that results from the presence of Pd-C bonding as evidenced by XANES and EXAFS characterizations.[214]

3.4.2 Alkyne hydrogenation on Ag and Au-based materials

The addition of a second metal is another strategy to modify the electronic structure of Pd atoms and reduce the binding energies of adsorbates to Pd surface, thereby improving the selectivity towards alkenes.[210] PdAg alloy is widely used for industrial alkyne partial hydrogenation with the addition of Ag changing the stability of adsorbed acetylene and ethylene; this effect is comparable to that of subsurface carbon on Pd based on theoretical studies.[3,215] The improvements in selectivity of acetylene to ethylene have been attributed to both geometric and electronic effects between Pd and Ag in dilute PdAg alloys.[3,80] For example, high activity and selectivity in partial hydrogenation of acetylene was demonstrated over a wide range of temperatures for a series of Ag-alloyed Pd single atom catalysts.[3] The selectivity further increased with increasing reduction temperature, and under optimum conditions, long-term stability of over 24 hours time-on-stream was achieved over $Pd_{0.01}Ag/SiO_2$ catalysts. Isolated, electron-rich Pd atoms formed via charge transfer from Ag to Pd was observed from XPS and XANES and proposed to be the reason for enhancement in ethylene selectivity.[3] In a separate study, acetylene hydrogenation reaction over PdAg catalysts was compared to PdCu alloys supported on SiO_2 and TiO_2.[80] While $Pd_{0.64}Ag/TiO_2$ catalysts give the highest turnover frequency (TOF) with 97% selectivity to ethylene, $Pd_{0.02}Cu$ TiO_2 catalysts show the highest rate per Pd basis with more than 99% selectivity measured. Although the Pd concentrations are very different in these two catalysts, CO-FTIR showed the presence of primarily isolated Pd species in both cases, which have been reported to be the active sites for high ethylene selectivity.[216,217] The choice of support also affects the distribution of Pd, characterized by CO chemisorption, EXAFS, and IR. For PdAg, the stronger interaction between Pd and TiO_2 results in subsurface Pd while on SiO_2 support Pd remained on the surface.[80]

Au catalysts are another example where over-hydrogenation reaction is limited.[218,219] However, they are often not active at low temperatures and suffer from deactivation.[219–221] Promoting Au catalysts with Pd by forming PdAu alloys has shown improved selectivity with similar activity as monometallic Pd.[111,219,222] This is the result of improved hydrogen activation kinetics – often the rate-determining step – by the formation of surface Pd on PdAu under reaction condition, which was characterized by the DRIFTS studies.[82,134] A similar conclusion was reported based on the increase in ethylene selectivity over Au@Pd core-shell structure with a high dispersion of Pd.[223]

Efforts have been made to introduce single-atom Pd on Au to enhance activity while maintaining the high selectivity to alkenes. For instance, single-atom Pd in PdAu/SiO_2 catalysts showed higher selectivity in the hydrogenation of acetylene to ethylene compared to catalysts containing higher Pd loadings.[111] The presence of isolated Pd sites promotes the formation of adsorbed π-species over dissociation adsorption of ethylene and thus a superior selectivity to ethylene, which is confirmed by in-situ DRIFTS and EXAFS combined with microcalorimetry results.[111]

PdAu RCT-SiO_2 catalysts with a dilute ratio of Pd (2–9 %) in Au showed 90% selectivity to 1-hexene at 80% conversion of 1-hexyne for gas-phase reaction.[104,112] The $Pd_{0.04}Au_{0.96}$ RCT-SiO_2 catalysts yielded the highest rate of 1-hexyne hydrogenation than any other Pd compositions with above 97% selectivity to 1-hexene (Figure 21a). The catalytic performance remains stable after more than 30 hours of operation at 363 K (Figure 21b) with no change in the average particle size based on post-reaction TEM analysis (Figure 21c), demonstrating the high stability and resistance to sintering of the RCT catalysts. The long-term stability is also achievable under CO oxidation reaction conditions.[105]

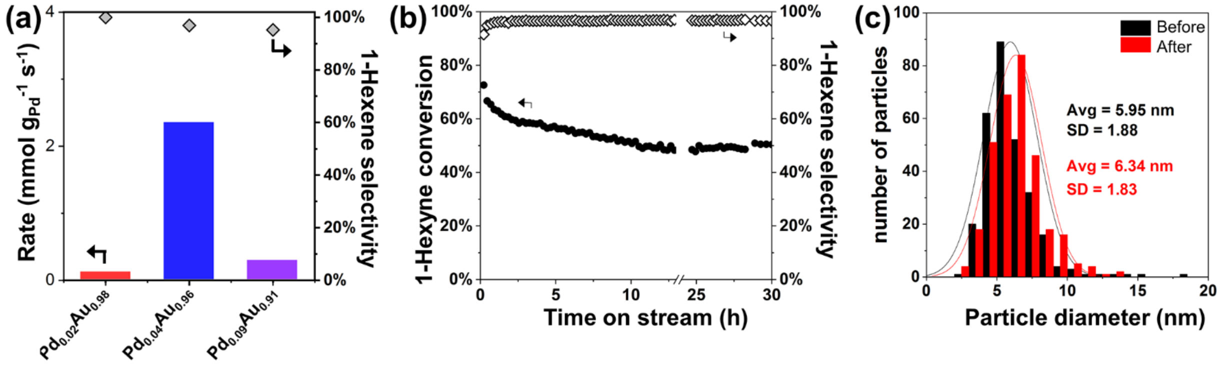


Figure 21. Catalytic performance and characterization of Pd_xAu_{1-x} RCT-SiO_2 catalysts for selectivity hydrogenation of 1-hexyne. (a) The rate of 1-hexyne conversion (box) and the selectivity for 1-hexene (diamond open) over Pd_xAu_{1-x} (x = 0.02, 0.04, 0.09) RCT-SiO_2 catalysts at 323 K. (b) Time-on-stream of 1-hexyne conversion (circle solid) and 1-hexene selectivity (diamond open) over $Pd_{0.04}Au_{0.96}$ RCT-SiO_2 catalysts. (c) The average particle size of $Pd_{0.04}Au_{0.96}$ RCT-SiO_2 catalysts calculated based on TEM analysis before and after 1-hexyne hydrogenation reaction. Adapted with permission from reference 112. Copyright 2019 American Chemical Society.

The structures of $Pd_{0.04}Au_{0.96}$ RCT-SiO_2 catalysts are sensitive to pretreatment conditions, which results in changes in its catalytic performance.[104] For instance, the activity of $Pd_{0.04}Au_{0.96}$ RCT-SiO_2 catalysts for 1-hexyne hydrogenation increased from 20 to 30% with increasing O_2 pretreatment temperature from 323 to 673 K while selectivity to 1-hexene maintained around 96% over all temperatures. The increase in activity is attributed to the stabilization of Pd on the surface by Pd-O bond formation, based on the EXAFS spectra collected after O_2 pretreatment at 673 K. Pretreating the same catalyst in H_2 at high temperature facilitates Pd dissolution into the bulk and thus diminishes catalyst activity to <5% 1-hexyne conversion. The catalyst can be partially reactivated by pretreatment in CO even at room temperature, which is attributed to adsorbate-induced stabilization of surface Pd. The dynamic restructuring of the catalyst surface in response to the pretreatments are concluded from correlations between theoretical calculations and experimental results. Specifically, a shorter Pd-Pd distance in EXAFS fitting of samples after O_2 or CO pretreatment was observed compared to those treated in H_2 pretreatment. No change in NP size and morphology based on in-situ TEM characterization in O_2 or H_2 further supports the redistribution of Pd atoms within single particles. With the rate-limiting step being the addition of the second hydrogen to the half-hydrogenated intermediate, the high selectivity is the result of higher stability of the half-hydrogenated intermediate of alkyne over the half-hydrogenated alkene. The reaction mechanism was determined based on experimentally calculated reaction order and DFT calculations.[112] Based on DFT calculations of adsorption energies, it was shown that acetylene and ethylene bind more strongly on Pd(111) than on dilute Pd/Au(111).[112] A similar mechanism has also been reported for hydrogenation of acetylene to ethylene over single-atom Pd on Au or Ag NPs, where the presence of alloyed Pd single-atom structure successfully weakens the adsorption of ethylene.[3,111]

A different mechanism for improved alkene selectivity was proposed in the study of PdAu NPs for liquid-phase hydrogenation reaction.[100,110] $Pd_{0.004}Au_{0.996}$ NP/SiO_2 showed a 10 times higher activity for hydrogenating 1-hexyne compared to monometallic Au in liquid phase reaction (Figure 22a).[100] This was achieved by facilitating H_2 dissociation with isolated Pd atoms, where the rate-limiting step being H_2 activation. $Pd_{0.004}Au_{0.996}$ NP/SiO_2 showed much higher HD production rate than Au/SiO_2 in H_2-D_2 exchange experiments, which supports the presence of single Pd atoms on the surface of Au NPs effectively catalyze the H_2 activation (Figure 22b). The similar apparent activation energy observed for PdAu NPs and monometallic Au also indicates the reaction pathways are identical and qualitatively different from monometallic Pd.[110] The atomistic insight provided by DFT calculations suggests that the selectivity was governed by the second step of hydrogenation and a high selectivity can be achieved by $Pd_{0.004}Au_{0.996}$ NP/SiO_2 where the reactive surface atom attracts both the hydrogen atom and the most reactive atom in the intermediate (Figure 22c and d).[110] In TPD studies over PdAu(111) SAA surface, both reactant and product have almost identical binding strengths. This led to favoring the selective over non-selective reaction pathway and provides clear evidence supporting the proposed mechanism. Different from $Pd_{0.04}Au_{0.96}$ RCT-SiO_2 catalysts, where differential binding strength of the reactant and products governs selectivity, product and reactant have almost identical binding strengths on $Pd_{0.004}Au_{0.996}$ NP/SiO_2. This suggests the selectivity of $Pd_{0.004}Au_{0.996}$ NP/SiO_2 is the result of changes in the favorability of the selective versus non-selective reaction pathway.

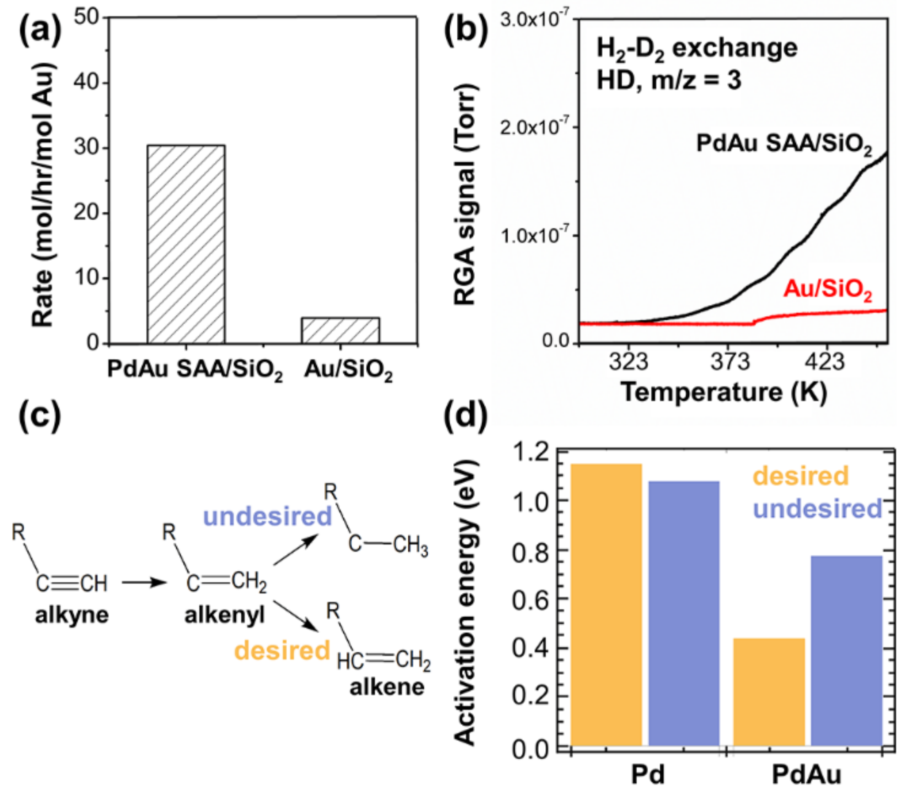


Figure 22. $Pd_{0.004}Au_{0.996}$ NP/SiO_2 catalysts for liquid phase selective hydrogenation of 1-hexyne. (a) Initial reaction for hydrogenation of 1-hexyne normalized by the amount of Au and (b) H_2-D_2 exchange over Au/SiO_2 and $Pd_{0.004}Au_{0.996}$ NP/SiO_2 catalysts. (c) Schematic of alkyne hydrogenation pathways and (d) DFT calculations of the activation energy of desired and undesired hydrogenation pathways over Pd(111) and PdAu(111) SAA surfaces. Adapted with permission from references: (a and b) 109, (c and d) 110. Copyrights 2017 Royal Society of Chemistry and 2019 American Chemical Society.

3.4.3 Alkyne hydrogenation on Cu-based materials

Different from the PdAu SAAs introduced previously, high selectivity of partial hydrogenation of alkynes and dienes has also been reported in PdCu and PtCu SAAs where a bifunctional mechanism dominates.[5,35,87,224] One of the earliest example was demonstrated over PdCu and PtCu model SAA surfaces via STM and H_2-TPD experiments for facile H_2 dissociation and recombination, even at cryogenic temperatures.[14,224] Hydrogen spillover onto Cu, where Cu imparts selective hydrogenation of acetylene on 0.01 ML PtCu(111) alloy surface.[23] Cu is intrinsically selective for hydrogenation reactions because of the relatively low energy barrier of alkene desorption compared to the hydrogenation barrier of alkenes. Substituting Au with Cu also provides a route to reduce catalysts cost. Based on TPRS results, the low-temperature pathway for ethene formation showed >95% selectivity on 0.01 ML PtCu(111), whereas extensive decomposition happens on 1 ML Pd/Cu(111).[23] In addition to the model systems, the bifunctional concept has been translated to NP catalysts. For example, PdCu SAAs/Al_2O_3 with 0.18 at% Pd are active for the hydrogenation of phenylacetylene to styrene at ambient temperature with 94% selectivity at all conversions.[87] H_2 dissociates on single-atom Pd sites followed by spillover onto the Cu host metal where selective product forms and desorbs prior to complete hydrogenation. The incorporation of Pd atoms into the subsurface layer of Cu(111) has also been proposed as the active site that can effectively reduce the H_2 dissociation barrier based on simulated XPS and theoretical calculations.[225] In this case, the high catalytic activity is the result of enhanced surface-adsorbate interactions by subsurface Pd atoms modifying the Pd-doped Cu surfaces.

Another example of single-atom Pd on Cu (Pd/Cu = 0.006) supported on SiO_2 showed 85% selectivity to ethylene at 100% acetylene conversion with the same bifunctional nature.[108] By exploring different Pd/Cu atomic ratios (Figure 23a), the decrease in Pd/Cu ratio results in increased isolated Pd atom sites and thus the improved selectivity to ethylene. This improvement is mainly the result of weakened adsorption of ethylene, which was confirmed via microcalorimetric measurements and DFT calculations. This work also compared across Cu, Ag, and Au as the host metal with single-atom Pd dopant and all three showed similar apparent activation energies and ethylene adsorption strengths, suggesting the ability for acetylene activation was almost equal among the group IB metals.[108] The selectivity to ethylene decreased going from $Pd_{0.006}Cu$ to $Pd_{0.01}Ag$ to $Pd_{0.025}Au/SiO_2$ (Figure 23b), which correlates well with the amount of electron transfer from group IB metals to Pd based on DFT calculations, XANES and XPS results.[3,108] Electron transfers from host metal to Pd for PdCu or PdAg catalysts, whereas it's the opposite direction for PdAu (Figure 23c), this is consistent with the order of their electronegativity.

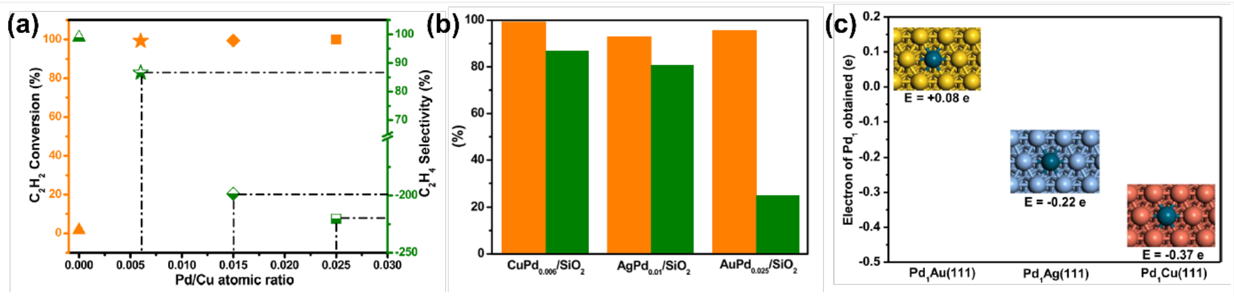


Figure 23. Acetylene conversion (orange) and ethylene selectivity (green) at 433 K (a) as a function of the Pd/Cu atomic ratio and (b) over SiO_2 *supported* $Pd_{0.006}Cu$, $Pd_{0.01}Ag$, *and* $Pd_{0.025}Au$. *(c) DFT calculations of electron states of isolated Pd atoms alloying into Au(111), Ag(111), and Cu(111) surfaces. Adapted with permission from reference 108. Copyright 2017 American Chemical Society.*

Evidence of hydrogen spillover has been demonstrated in PdCu dilute alloy catalysts.[114,226,227] PdCu alloys with dilute Pd in Cu showed combined intrinsic properties of its monometallic components for the hydrogenation of acetylene and propyne. The catalyst can be activated and used at moderate temperatures (~373 K) with performance strongly dependent on the Pd:Cu ratio.[114,226,227] At close to 100% conversion of acetylene, over 80 % selectivity to ethylene over $Pd_{0.02}Cu_{0.98}/Al_2O_3$ was attributed to small Pd clusters formed at both the surface and sub-surface region over a Cu-rich surface, which promotes H_2 dissociation as shown via CO-Fourier-transform infrared spectroscopy (CO-FTIR) characterization.[226] Furthermore, the hydrogenation activity can be improved by CO-induced Pd surface segregation; however, at a higher Pd:Cu atomic ratio ($Pd_{0.1}Cu_{0.9}/Al_2O_3$), the increase in surface Pd dimers due to CO-induced segregation shifted selectivity towards ethane production.[113]

4 Dynamic Behavior During Catalysis

4.1 Overview

Dynamic changes in the surface structure and composition as well as adsorbate migration between reactive ensembles are fundamental to the catalytic behavior of dilute alloys. The atomic-scale arrangement of an alloy surface depends on the reactant composition and temperature and can thus be modified through pretreatment and reaction conditions. The reactive minority metal(s) can be substantially enriched at the surface by pretreatment conditions to provide a thermodynamic driving force for surface segregation. Once at the surface, the reactive metal can be trapped in metastable states even in absence of the original trigger, thereby providing sites needed to initiate catalytic chemistry. Reactive intermediates must then migrate between the minority and host metals to undergo selective transformations. Recent research has provided fundamental insights for understanding the dynamic behavior of dilute alloy catalysts and its role in mediating catalytic chemistry.

This section will focus on two main themes of dynamic behavior during catalysis: 1) determining how alloy surface structure and composition change in response to gas-phase composition and temperature and identifying reaction conditions that retain the optimal catalyst structure, and 2) elucidating the mechanisms for adsorbate migration between co-existing surface phases and its coupling to reaction kinetics and surface restructuring.

4.2 Dynamic materials behavior - support-free nanoporous materials

Adsorbate triggered dynamic changes of morphology and surface composition can dramatically affect activity and selectivity as well as long-term stability of catalyst materials. For instance, the high surface area morphology of nanoporous metals is not thermodynamically stable with respect to coarsening.[228] Adsorbate induced changes of the surface mobility can thus directly affect the coarsening kinetics and long-term stability of nanoporous alloy catalysts. The actual surface composition, on the other hand, can reflect the thermodynamically stable surface composition or, at low enough temperatures, be kinetically trapped in a metastable state. Thus, adsorbate induced changes in both the thermodynamically stable surface composition and the diffusion kinetics can trigger compositional changes ranging from local place exchange between different surface and subsurface alloy components to large scale mass transport leading to the formation of thick surface oxide layers or large-scale surface segregation phenomena. An extreme example is the dry oxidation of $npAg_{0.7}Au_{0.3}$ alloys by O_3 at 423 K (Figure 24a and b) that dramatically changes both the morphology and surface composition by oxygen-triggered Ag outward diffusion to the gas/alloy interface and consequent formation of nanoporosity in the Ag depleted near-surface volume.[180] Adsorbate induced changes in surface stress can further contribute to changes in the catalytic properties of nanometer-sized ligaments as they can trigger lattice strain up to several permille.[28]

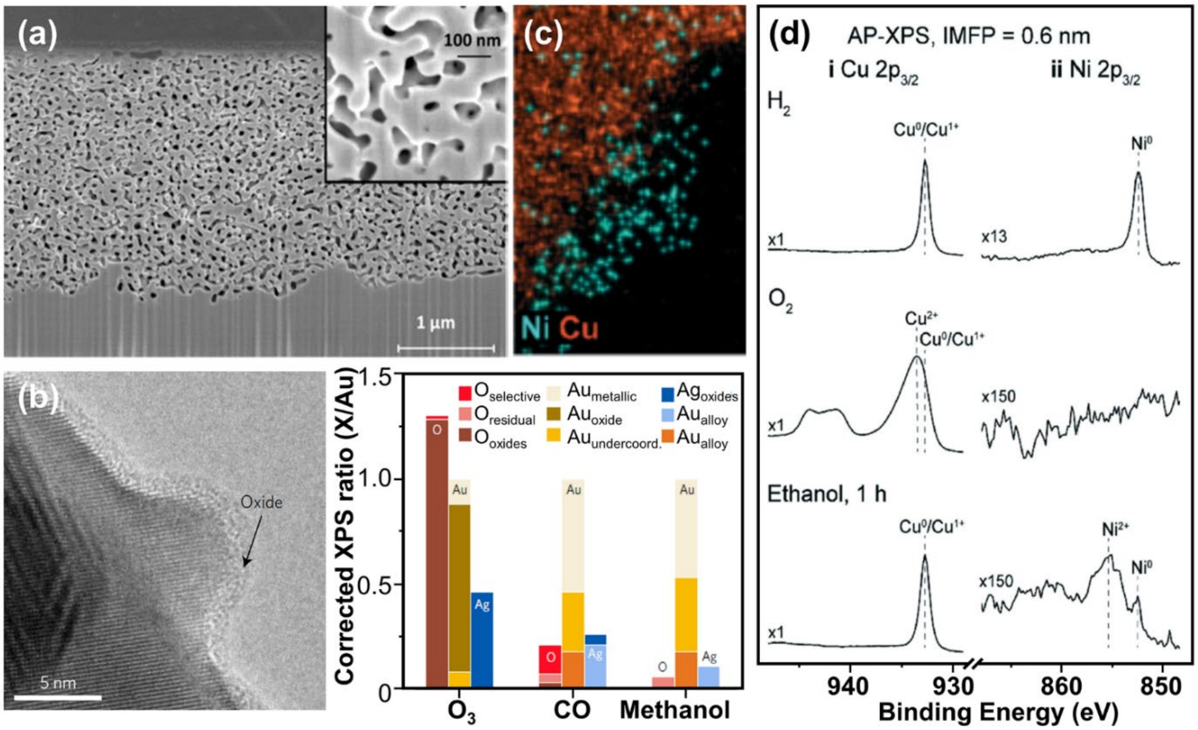


Figure 24. (a) FIB/X-SEM showing O_3 induced 3D nanoporosity formation in npAg$_{0.7}$Au$_{0.3}$. Inset in (a) shows a higher magnification image. (b) Formation of a 1-2 nm thick Ag rich surface oxide layer on npAu upon O_3 exposure (left), and changes of the surface composition upon O_3 exposure as well as consequent reduction with CO and methanol (right). (c) STEM-EDS map of an O_2-stabilized npNiCu catalyst confirming that Ni is also present in the form of a dilute NiCu alloy in addition to oxidized Ni-rich particles at the surface, and (d) ambient pressure XPS (AP-XPS) data revealing the compositional and chemical-state changes of npNiCu during H_2 and O_2 pretreatments as well as during ethanol-to-acetaldehyde conversion. Adapted with permission from references: (a)180, (b) 62, (c and d)69. Copyrights 2017 American Chemical Society, 2016 Springer Nature and 2020 Royal Society of Chemistry.

In most cases the morphological and compositional changes induced by surface chemistry are subtle but nevertheless of critical importance for catalyst activity and selectivity. For example, while as-dealloyed npAu (with dilute amount of Ag) is highly active toward CO oxidation, it is only after activation with O_3 that npAu shows high selectivity towards oxidative coupling of alcohols while becoming inactive for CO oxidation (catalytic studies over npAu is reviewed in Section 3.2).[55] Advanced in-situ environmental TEM (ETEM) and AP-XPS have been used to explore the complex restructuring and compositional changes that occur along the path to catalytic activity for selective alcohol oxidation.[62,74] In short, O_3 exposure at 423 K leads to the formation of a 1 nm thick Ag-rich surface oxide layer with about 10 times the average Ag concentration of npAu (Figure 24a). In contrast to the npAg$_{0.7}$Au$_{0.3}$ alloy example discussed above, npAu no longer reacts with O_3 once the 1 nm thick Ag-rich surface oxide layer has been formed. The oxygen of this oxide layer is highly reactive toward both CO oxidation and alcohol combustion. While some of the Ag re-alloys into the bulk of the ligaments during reduction of the Ag-rich surface oxide layer by either CO or alcohol exposure, the surface of the npAu ligaments remains enriched in Ag and becomes covered with disordered Ag-containing NPs which crystalize upon further alcohol exposure. The formation of the AgAu surface alloy together with the increase in the concentration of undercoordinated Ag and Au surface atoms caused by the formation and growth of the crystalline NPs seem to be responsible for stabilization of a distinct oxygen species which provides the high selectivity towards partial oxidation of alcohols. Similar effects have been observed during the oxidation of PdAg single crystal model surfaces whereby oxygen exposure at ~373 K leads to Pd dewetting and formation of ~1 nm tall Pd particles on the planar Ag surface.[229]

No specific activation procedure is necessary for the more reactive NiAu dilute alloy catalysts for non-oxidative dehydrogenation of ethanol as this catalyst is activated by the interaction with the reactant ethanol at temperatures as low as 423 K. Ni segregation to the surface is induced by ethanol while it prefers to occupy subsurface sites on the clean surface under H_2-rich conditions.[60] The presence of Ni also slows down the coarsening kinetics of the NiAu catalyst allowing for prolonged use under reaction conditions without an apparent drop in activity.

While npNiCu dilute alloys show good long-term stability for non-oxidative ethanol dehydrogenation at lower reactant flow (conversion) rates,[47] O_2 pretreatment is necessary to stabilize the catalyst activity at higher reactant flow rates.[69] Here, O_2 pretreatment at 523 K leads to the formation of a Cu^{2+} oxide surface layer that completely buries the more reactive Ni component. Subsequent ethanol exposure under reaction conditions (523 K) reduces the copper oxide overlayer while Ni remains in a kinetically trapped Ni^{2+} subsurface state thus preventing the Ni cluster formation which has been linked to catalyst deactivation through carbon deposition. Using H_2 pretreatment instead leads to rapid deactivation (Figure 24c and d). The catalytic studies of NiAu and NiCu dilute catalysts can be found in Section 3.3.1. It is important to note that similar, but more localized compositional changes have been observed in $Pd_{0.04}Au_{0.96}$ RCT-SiO_2 catalysts[104] where exposure to H_2, O_2, and CO alters the Pd content in the NP surface and thus the hydrogenation activity of the catalyst.

4.3 *Dynamic behavior of catalyst surfaces: Fundamental studies of Au- and Ag- based bimetallic surfaces.*

Surface science and theoretical models can provide unparalleled fundamental insights into dynamic phenomena that occur on dilute alloy surfaces and their effects on surface reactivity. Material rearrangement and reactive species migration at bimetallic surfaces have been examined in detail using model PdAu, PdAg and PtAg surfaces. Bimetallic surfaces were among the first to establish fundamental understanding of dynamic behavior and the principles established generally translate to dilute alloy systems of interest. The composition and structure of bimetallic surfaces under reaction conditions are a result of a balance between the surface free energy of the system and the kinetics for material rearrangement. Further, the structure and coverages of reactive species can mediate the migration of intermediates across phase interfaces and directly contribute to the surface reactions. Material rearrangement and reactive species migration were demonstrated to not only occur concurrently but to directly impact one another thus highlighting the need for fundamental model studies to understand complex catalyst behavior towards improving catalyst design.

4.3.1 Material rearrangement at bimetallic surfaces

Surface segregation can play a decisive role in the performance of dilute alloy catalysts based on coinage metals. Under vacuum conditions, thermodynamics favors surface enrichment by the coinage metal component because their surface free energies are lower than those of the late transition metals typically utilized in these catalysts, including Pd, Pt, Rh, Ir, Ru and Ni.[230] In contrast, surface segregation of the transition metal dopant is thermodynamically preferred in the presence of reactive gases due to the stronger adsorbate bonding that can be achieved. Although kinetic barriers can hinder surface segregation, coinage metals have high atomic mobility that enable their surfaces to efficiently restructure at the moderate temperatures at which these dilute alloy catalysts are employed.

Model studies with PdAu alloys were among the first to establish fundamental principles for understanding surface segregation in other dilute alloys of coinage metals. The exposure of strongly interacting species, such as CO[231–233] and O_2,[234] on PdAu bulk alloys drives the segregation of Pd to the surface when there are no kinetic limitations for restructuring. At room temperature, the partial pressure of CO impingent on AuPd(100) controls the segregation of Pd to the surface, with higher CO pressures enhancing the Pd enrichment of the surface.[231] The surface segregation of Pd by CO is not observed below ~200 K, suggesting that Pd diffusion to the surface becomes kinetically limited at sufficiently low temperature.[232] The surface site distribution of Pd in PdAu bulk alloys is dependent on both the CO pressure (10^{-7}─10 Torr) and temperature (100─650 K) as determined by IR spectroscopy and STM measurements, where low pressure and temperature predominantly induce the formation of isolated Pd atoms while ensembles with contiguous Pd sites develop at higher pressure and temperature.[232,233] Isolated Pd atoms also tend to distribute randomly on clean PdAu(111), with larger Pd_n ensembles developing at higher Pd coverages.[235,236] More facile H_2 activation and greater stabilization of adsorbed H-atoms is achieved with increasing Pd_n ensemble size; Pd tetramers are the smallest ensemble capable of activating H_2 in UHV.[236] The presence of contiguous Pd sites is also necessary for the dissociation of O_2, which directly controls the rate of CO oxidation.[232,237] This is evident in both reactor and surface science studies of the CO oxidation reaction (Section 3.2.1). The exposure of O_2 to $Au_{0.3}Pd_{0.7}$(110) at room temperature also can induce the segregation of Pd to the surface.[234] The demonstration of these surface phenomena on PdAu surfaces provides a foundation for understanding structural rearrangements on PdAg and PtAg surfaces.

In the absence of adsorbates, there is a strong thermodynamic driving force for PdAg alloys to form a Ag-terminated surface although metastable structures can exist when there is insufficient thermal energy for rearrangement.[25,238] The energetic driving force for Ag-termination is to minimize the surface free energy of the system, where bare Pd and Ag have surface free energies of 2.05 J m^{-2} and 1.25 J m^{-2}, respectively.[230] Investigations with PdAg surfaces confirm the tendency for Ag to enrich the surface of crystalline PdAg alloys and further demonstrate that the Pd and Ag atoms tend to disperse within the surface layer.[239–242] The formation of well-mixed PdAg surface alloys is thermodynamically favored but requires thermal energy to overcome kinetic barriers for intermixing, enabling metastable structures to be formed at low temperature. For instance, the deposition of submonolayer coverages of Pd on Ag(111) at 300 K predominantly forms single-layer Pd islands as determined by a combination of surface science experiments and DFT calculations.[25,238] A mild thermal treatment provides sufficient energy to form Ag-terminated double-layer structures and neighboring Ag vacancy pits, as predicted by DFT calculations.[25,238]

Similar to PdAu introduced above, exposure of the Ag-terminated double-layer PdAg structure to both CO and O_2 induces the segregation of Pd to the surface.[25] DFT calculations predict phase diagrams of the most stable structures in CO and O_2 gas environments, where increasing gas pressure favors Pd-terminated structures while increasing temperature favors Ag-terminated structures (Figure 25a).[25,242,243] In fact, under sufficiently O_2-rich conditions, a single-layer Pd oxide becomes thermodynamically favored on PdAg(111) surfaces and forms under relatively mild conditions.[242,243] Likewise, surface oxidation of the $Pd_{75}Ag_{25}$(100) bulk alloy generates an ordered, single-layer Pd oxide in addition to an Ag-rich interfacial region in the subsurface.[242,243] The partial pressure of CO can also drive the segregation of Pt in a PtCu alloy surface.[244] However, the thermodynamically preferred structures may not be accessible under experimentally relevant timescales due to kinetic limitations for structural rearrangement as demonstrated by the gradual surface segregation of Pd in a PdAg alloy observed during exposure to O_2 (Figure 25b).[25] Therefore, it is critical to understand the kinetics for structural changes in addition to the thermodynamically preferred structures.

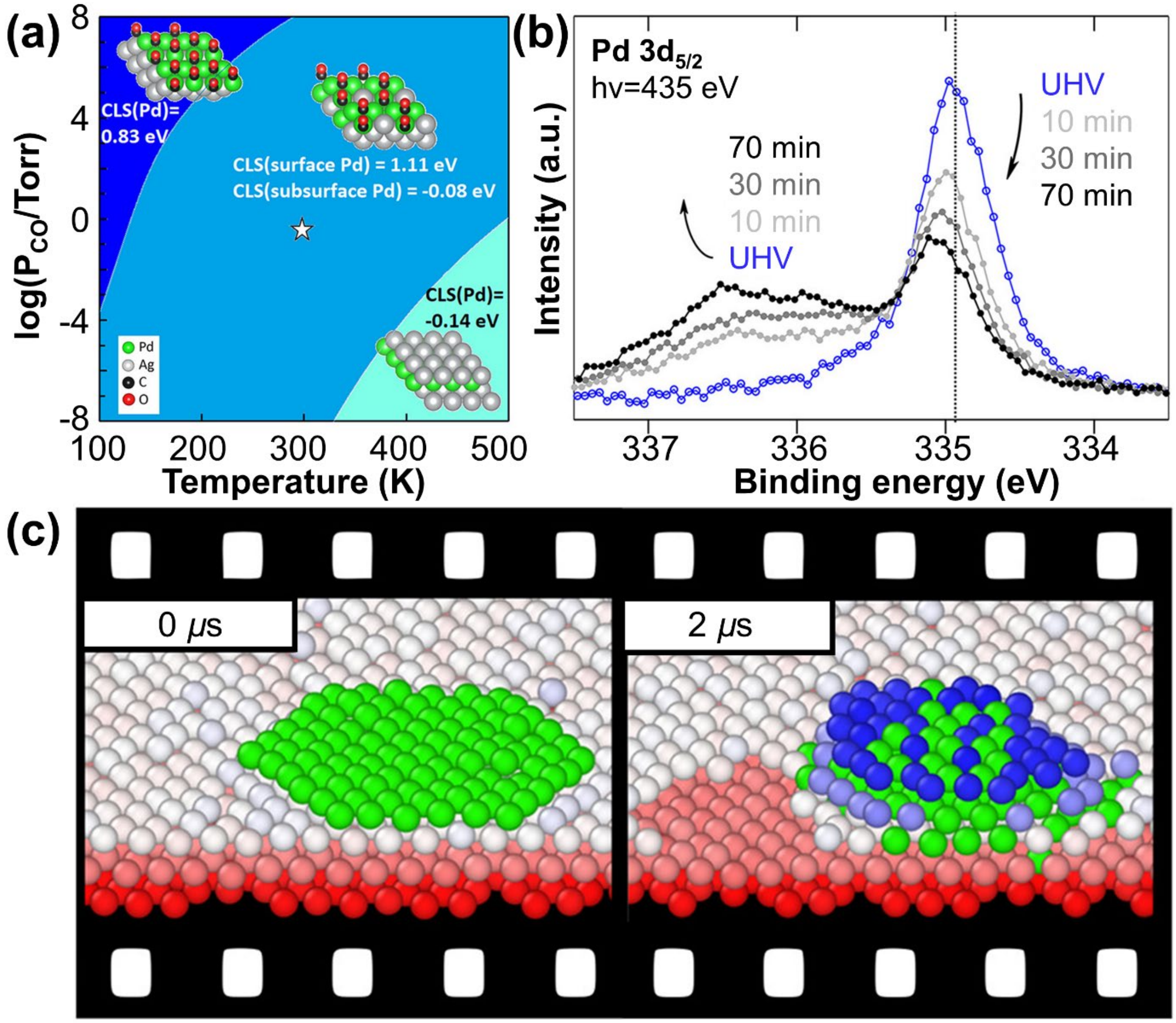


Figure 25. (a) DFT was used to generate a surface stability diagram of Pd/Ag(111) as a function of CO pressure and temperature. (b) Surface-sensitive Pd 3d$_{5/2}$ photoelectron spectra acquired as a function of exposure time to 1 Torr O$_2$ at 400 K show the development of a broad shoulder at higher binding energy assigned to oxidized Pd that has been segregated to the surface. (c) Frames of MD simulation showing the evolution of a Pd$_{91}$ island on Ag(111) at 500 K over 2 μs. Adapted with permission from references (a and b) 25 and (c) 238. Copyrights 2018 and 2020 American Chemical Society.

The kinetics of elementary restructuring events control whether thermodynamic minimum energy structures or kinetically trapped metastable structures are observed under reaction conditions.[238,245] Advanced MD simulations of a single-layer Pd$_{91}$ island on Ag(111) at 500 K demonstrate that the system rapidly reaches an apparent quasi-equilibrium structure composed of a double-layer island that has a Ag-rich surface, in agreement with experiments (Figure 25c).[238] However, at elevated temperatures, layer-by-layer dissolution of Pd into the bulk occurs while Pd atoms periodically visit the surface as single-atom Pd sites.[238] The evolution of thermodynamically stable and sufficiently long-lived metastable structures can be understood by advanced dynamics simulations coupled with experiments which inform the most relevant structures under reaction conditions.

Surface temperature can also contribute to the kinetics of dilute alloy surfaces. For instance, the surface structure of PtAg alloys can be modulated by the surface temperature during alloying, which controls the dispersion of Pt in Ag by tuning the kinetics for Pt-Ag direct exchange on terraces and at step edges.[4] Near-room temperature deposition of dilute Pt on Ag(111) leads to the preferential formation of Pt aggregates as islands due to insufficient thermal energy for surface alloying. Depositing Pt at elevated temperatures enhances the dispersion of Pt in Ag as well as the concentration of isolated Pt alloy sites. Surface alloying at elevated temperatures occurs primarily by widening the PtAg alloy brim at the step edges; however, at 480 K, extensive alloying occurs directly into the Ag terraces. The kinetics for Pt-Ag exchange can be tuned by surface temperature to control the dispersion of Pt in Ag for kinetically trapped surface configurations.

4.3.2 Reactive species migration across bimetallic interfaces

The surface migration of reactive species is critical to realizing unique reactivity and selectivity in bimetallic alloy materials. Hydrogen atom migration between the host and dopant sites of dilute alloy surfaces and across domain interfaces (metal/metal, metal/oxide) is particularly important due to its role in supplying hydrogen atoms for selective hydrogenation reactions.[14,87,252,224,229,246–251] For example, on dilute alloys, selective hydrogenation can be accomplished by hydrogen atom spillover onto the host metal surface to enable the activation and subsequent hydrogenation of the co-reactant on a dopant site.[7] Employing surface science and theoretical models can provide a detailed understanding of the energetics and kinetics of reactive species migration on alloy surfaces. These investigations establish fundamental principles to guide the understanding and prediction of phenomena in dilute alloy catalyst systems.

Hydrogen spillover on dilute alloys generally requires a mechanism by which hydrogen atoms can overcome a thermochemical energy barrier that arises from stronger binding of hydrogen on the dopant site compared with the coinage metal surface. In the absence of other adsorbates, hydrogen migration away from isolated dopant sites can be driven by the entropic gain that results from dispersion onto the host surface. Indeed, hydrogen atom spillover is facile on several dilute alloys employed in catalytic applications (see examples reviewed in Section 3.4.3), suggesting that the differences in H binding energy on the dopant vs. host metal in these systems are small enough to allow hydrogen release onto to the host surface.[253]

The co-adsorption of hydrogen with a more strongly-binding species can also induce hydrogen spillover onto the host surface.[249,251] In this case, thermodynamics favors configurations in which the strongly-binding species adsorbs on dopant sites while hydrogen atoms disperse onto the host surface. Lastly, hydrogen spillover can also be mediated by the local H-coverage. On PdAg surfaces, hydrogen migration away from isolated Pd sites is inefficient below ~200 K,[254] suggesting that entropic gain is insufficient to overcome the reaction endothermicity. However, hydrogen migration from contiguous Pd domains to Ag becomes accessible when a dense phase of hydrogen atoms forms on Pd and a substantial hydrogen atom concentration can accumulate on both metals.[255] DFT shows that increasing the H-coverage on the Pd lowers the hydrogen binding energy and renders hydrogen migration to the Ag surface thermodynamically and kinetically feasible. These studies establish fundamental mechanisms governing hydrogen spillover on dilute alloys and reveal a sensitive dependence on reaction conditions and surface structure.

Species that bind strongly to the dopant metal can undergo reverse spillover, wherein adsorbates migrate from the host surface to the dopant and typically induce aggregation of the dopant atoms.

The reverse spillover of oxygen can be particularly important in oxidation reactions promoted by Ag and Au-based alloys. Recent work demonstrates that oxygen atom migration from Ag to Pd occurs efficiently,[254] which is driven by the greater oxophilicity of Pd.[256–258] Auto-oxidation of Pd clusters occurs facilely during Pd deposition onto oxidized Ag(111) surfaces at 300 K, generating local O-coverages on Pd that depend on the Pd domain size and the properties of the initial AgO_x layer.[256–258] Further, the oxidation of large, single-layer Pd islands on metallic Ag(111) with near-ambient pressure of O_2 at elevated temperature causes Pd to dewet the surface forming multilayer Pd particles with a surface PdO_x termination while Ag forms a surface AgO_x.[229,258] The oxidation and structure of Pd and Ag domains of a PdAg oxide surface are intimately connected as a result of facile oxygen transport between the two metals. This illustrates the importance of understanding the complex interplay between reactive species migration and the structure and concentration of surface species and their impact on catalytic chemistry.

4.3.3 Dynamic coupling of material evolution and species migration and its effect on reactivity

The dynamical coupling of material evolution and reactive species migration is rarely considered; however, the concomitance of these phenomena can significantly influence surface reactivity. A clear demonstration of the coupling of material evolution and reactive species migration is observed by examining the reaction of both H_2 and CO with oxidized PdAg surfaces. In both cases, the reactivity is significantly modified, highlighting the need to understand the co-existence of these phenomena and inclusion of these effects when modeling surface chemistry on bimetallic surfaces.

The reactivity of AgO_x with H_2 at 300 K is dramatically enhanced on PdAg oxide surfaces by reactive species migration that involves Pd-Ag intermixing.[229,258,259] PdO_x readily dissociates H_2 which reacts with oxygen atoms to evolve water,[260] while Ag surfaces have a significant barrier which prevents H_2 dissociation and the accumulation of hydrogen atoms.[261,262] The AgO_x structure that forms during oxidation of a PdAg surface reacts with H_2 at a rate that is 10^4 times larger than the reaction rate on pure AgO_x, due to hydrogen atom migration from Pd to Ag as well as oxygen atom migration from Ag to Pd (Figure 26a).[229] Similarly, an enhancement in the reaction rate of a CuO_x phase with H_2 on a PtCu oxide surface compared with pure CuO_x has been observed.[263] The surface reaction is accompanied by Pd-Ag intermixing which slows the reduction rate of PdO_x for the PdAg oxide surface compared to pure PdO_x (Figure 26b).[229] Smaller, well-distributed Pd domains have a higher rate of AgO_x reduction due to 1) an increased Pd-Ag interface for enhanced reactive species migration, 2) lower spatial requirement for species migration, and 3) higher concentration of undercoordinated Pd sites for H_2 dissociation, possibly at the Pd island edges.[258] Alternating between oxidizing and reaction conditions causes drastic composition changes by Pd dewetting and PdAg alloying which slightly affects the reactivity of PdO_x while maintaining a nearly constant reactivity of AgO_x with H_2.[259] These studies demonstrate that the migration of reactive species across a Pd-Ag interface leads to a dramatic change in surface reactivity and that the evolution of the structure of the PdAg surface is affected by the surface reaction. The overall reaction rate is highly sensitive to the nature of the Pd-Ag interface and the structure and dispersion of Pd domains.

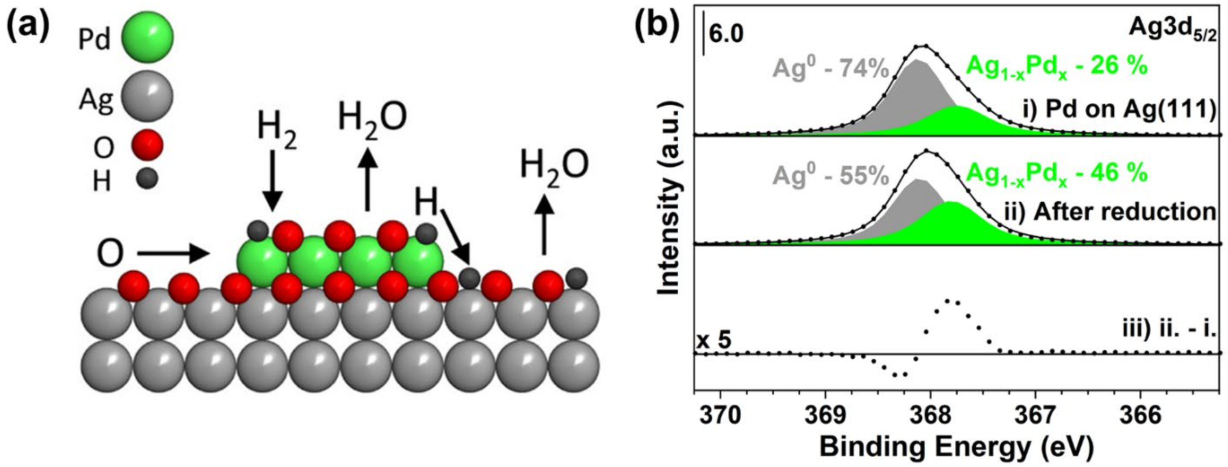


Figure 26. (a) Representation of cooperative mechanisms for reduction of an oxidized Pd/Ag(111) surface by H_2, including hydrogen and oxygen atom migration. (b) Pd-Ag intermixing occurs after reduction of PdO_x on Ag(111) as evidenced by the increased $Ag_{1-x}Pd_x$ alloy peak in the Ag $3d_{5/2}$ region (green) using AP-XPS. Adapted with permission from references (a) 229 and (b) 258. Copyrights 2020 The Authors and 2020 American Chemical Society.

The reactivity of PdAg oxide surfaces with CO is significantly affected by oxygen atom migration from AgO_x to Pd which is controlled by the structure and contact of the Pd and Ag phases.[257] Pure PdO_x as well as oxygen-covered, metallic Pd readily oxidize CO to CO_2 at mild temperatures (~100–500 K), where oxygen transport from less reactive PdO_x phases can enhance the reactivity of a more reactive metallic phase.[264–267] A similar mechanism is reported on AgO_x.[268] Reduction of a Pd_5O_4 layer by CO occurs more slowly on $Pd_{0.75}Ag_{0.25}$(100) compared with Pd(100) because the reemergence of surface Ag atoms during reduction suppresses CO adsorption as well as diffusion to oxidized domains.[243] Understanding the interaction of the metallic and oxide phases for a catalyst surface with minority reactive metal dispersed on a selective metal is important for bimetallic catalyst design for CO oxidation (see Section 3.2.1 for catalytic studies). The reaction of CO adsorbed at 100 K with a partially oxidized, PdAg surface yields efficient production of CO_2, whereas minimal reactivity is observed for the AgO_x surface in the absence of Pd.[257] Oxygen atom transfer occurs via both the buried PdAg oxide interface and diffusion across the AgO_x surface to the Pd domains.[257] A heterogeneous distribution of oxygen atoms on Pd is generated, where preferential oxygen binding to the edges of Pd islands enhances the CO oxidation activity of Pd clusters of decreasing size. The interplay between the oxygen-rich Pd edges and the CO-enriched Pd interior facilitates efficient CO oxidation. In summary, the initial oxygen transfer determines the local distribution of oxygen on the Pd phases which in turn controls the CO oxidation activity of the PdAg surface. Similar oxygen-transfer processes may be broadly important in oxidation catalysis by dilute alloys.

5 Advances in Methodology

5.1 Overview

Understanding the evolution of structure and composition of catalysts and their relationship to catalytic function is the key and central challenge to advance the understanding of dilute alloy catalysts. The challenges stem from the dilute nature of the minor species in the metal alloys, the restricted geometry of the nanostructures, and the multi-lengthscale- and multi-timescale-evolution on the surface of catalysts. To overcome these challenges and to investigate the catalyst structures and compositions, including their evolution under reactive conditions, new tools and advanced methods are required.

In this section, new experimental and theoretical techniques developed for dilute alloy catalysts are reviewed. Experimental tools include in-situ atomic-scale imaging using electron microscopy and structural determination using X-ray absorption spectroscopy combined with ML. Theoretical tools include ML methods and automation that accelerate MD simulations and enable the modeling of catalyst restructuring over microsecond time scales.

5.2 Novel strategies of X-ray absorption spectroscopy for dilute alloy catalysts

XAFS spectroscopy is an element-specific technique for probing local structural, electronic, and dynamic properties in a wide range of materials,[269] from crystalline to amorphous to liquids.[270–279] It is common to extract bond lengths, coordination numbers, and electronic states (e.g., metal oxidation states) from XAFS data. These local structural parameters provide rich information pertaining to the geometry and chemistry of nanoporous or NP catalysts, such as particle sizes, shapes (sometimes) as well as compositional motifs.[280–282] Following the changes of these parameters over pretreatments and reactions can elucidate the important local structures for highly active and selective catalysts.

However, it can be challenging to extract structural parameters for the dilute minority species from XAFS data because the measured signal is an ensemble average, and hence all contributions are lumped into one total spectrum. For example, as described in Section 2.4, one prominent method to synthesize high surface area dilute alloy catalysts employs RCT-SiO_2 materials, where dilute alloy NPs are supported and stabilized within a porous silicate matrix. The element of interest, the dilute minority metal, has an atomic fraction less than 5 at% in the NPs, and the weight loading of the NPs in the RCT matrix can be as low as 2.5–10 wt%. The significant heterogeneity stemming from diverse configurational motifs as well as static and dynamic disorder poses a very significant challenge to structural refinement due to the ensemble-averaging nature of XAFS, making active site characterization impossible with conventional analytical techniques.

This challenge can be addressed by several routes. This section briefly reviews several novel solutions that are particularly suitable for dilute alloys. Because of the challenges and these recently developed solutions are common for a large class of mixed systems, examples from other dilute systems such as molten salts with metal impurities and doped ceramic oxides are also reviewed.

5.2.1 MD-EXAFS for resolving unique metal complexes in dilute systems

One route to reduce the degeneracy of different heterogeneous structural motifs is to seek guidance from first-principle calculations that can describe different structural motifs, such as using MD simulations. *Ab initio* molecular dynamics (AIMD) is a common method for modeling materials evolution.[283] The resulted trajectories for each motif (if their numbers can be limited to just a few unique local structural units) can then be used to construct theoretical time-resolved EXAFS spectra. The spectra of the entire simulation box are then averaged to simulate the ensemble average done in experiments. By comparing the so obtained MD-EXAFS theoretical spectrum with experiments, the heterogeneity in local motifs can be resolved using their theoretically calculated structure and dynamics information.

One example uses this method to resolve the possible metal impurities in the molten salts[284,285], which is a multi-component system with multiple MX_n (where M is the metal (Ni or Co), X is a halogen, $n = 3-6$) complexes coexisting. To ultimately deconvolute the experimental EXAFS signal, which is the sum of the signals coming from multiple species, AIMD was used to generate simulation trajectories and reveal the highly disordered coordination environments of dilute ions. The experimental data were then fitted to a linear combination of the theoretical spectra that are constructed from these AIMD trajectories. This analysis was able to provide accurate quantification on the heterogeneous distributions of ions with different coordination states at various temperatures and melt compositions[284,285].

5.2.2 RMC-EXAFS for modeling local environment in dilute alloys

Reverse Monte Carlo (RMC) modeling, similar to the MD-EXAFS method described in the previous section, offers another way to disentangle partial contributions to the total EXAFS spectrum. During the RMC simulation, the coordinates of all atoms in the computational model are varied until the best agreement between the experimental and calculated EXAFS spectra is reached. This method was used in trivalent cation doped CeO_2[286]. In this example, dopant cations and oxygen vacancies are distributed in several motifs throughout the lattice, which can be hard to distinguish by conventional EXAFS fitting. RMC was used to find the most likely motif for each dopant and doping concentration whose computed spectra matches experimental EXAFS well. The optimized coordinates were used to extract detailed information about the local structure of multiple cation and anion sites, including oxygen vacancies.

5.2.3 Neural network analysis for unlocking structural information

In the two methods described above, theoretical spectra that were constructed with the aid of atomistic simulations are directly used to compare with or fit to the experimental EXAFS data. ML replaces these comparison/fitting processes with more sophisticated learning frameworks. The ML methods used for XAFS analysis can be from supervised, semi-supervised, and unsupervised learning categories. In most cases, a model is designed to take input spectra (either XANES or EXAFS) and predict structural descriptors or, in general, problem-specific descriptors. An inversion approach was developed by utilizing the neural network (NN) as a function that directly "inverts" the XANES spectrum to structure descriptors, including coordination numbers and distances.[287] The same method was used to invert EXAFS to the radial pair distribution function.[287] Recently, a similar inversion approach but with the more advanced self-organizing map (SOM) NNs was used to decompose and interpret the EXAFS of various technetium species as they interact with chukanovite in terms of problem-specific descriptors such as pH, redox potential, Tc loading, carbonate concentration, and contact time.[288] ML methods are also applied to enhance conventional EXAFS fitting procedures. In addition to NN- based methods, other ML methods were also explored. For example, an Extra Trees regressor algorithm was applied to enhance the ability to fit EXAFS spectra with multiple scattering paths;[289] and an evolutionary algorithm method was employed to automate EXAFS analysis, with a goal of enhancing reliability and reproducibility of results.[290]

These ML methods can provide statistical correlation among diverse configurations, more flexible analysis, and better interpretability, which is suitable for analyzing XAFS data for dilute alloys. Here, two examples are elaborated on how NN-based methods can significantly improve the analysis of XAFS data for Pd_xAu_{1-x} NPs (x = 0.02─0.09).

Considering a dilute alloy system composed of AB components, an ML method was developed to predict partial radial distribution function (PRDF), $\boldsymbol{g_{AB}(R)}$ for A-B pairs and $\boldsymbol{g_{AA}(R)}$ for A-A pairs directly from EXAFS signal of A; similarly, $\boldsymbol{g_{BA}(R)}$ for the B-A and $\boldsymbol{g_{BB}(R)}$ for B-B pairs can be predicted from the EXAFS signal of B. [287,291] Absorber-specific NNs were trained to predict all 4 PRDFs with 250 computational PdAu NP models with different sizes, shapes, packing motifs (cuboctahedral and icosahedral), and Pd distributions. These NP structures were all equilibrated using MD simulations at different temperatures. The NNs were deployed on EXAFS data collected from the $Pd_{0.02}Au_{0.98}$ RCT-SiO_2 and $Pd_{0.09}Au_{0.91}$ RCT-SiO_2.[105] The NN-assisted EXAFS (NN-EXAFS) analysis is able to obtain the PRDF in four coordination shells, whereas this was not possible with conventional analysis. With this new information, a more detailed model was constructed, which helps to conclude the presence of surface segregation of Pd atoms in these NPs.[292]

Similarly, another NN method was developed to predict partial first coordination numbers using XANES spectra of PdAu alloy as input (Figure 27).[293] Because high quality XANES data is easier to measure than high quality EXAFS data in challenging conditions of high temperature, low weight loading, and reactor configuration constraints, this NN method has been used to analyze the structural information of $Pd_{0.03}Au_{0.97}$ RCT-SiO_2 catalyst using XANES spectra collected in situ under different gas treatments. The analysis results are consistent with the previous hypothesis that the H_2 treatment induces Pd dissolution into the subsurface, decreasing the number of Pd atoms on the surface.[104,245,294] The PdAu RCT-SiO_2 studied here is reviewed in Section 3.4.2 for its catalytic performance.

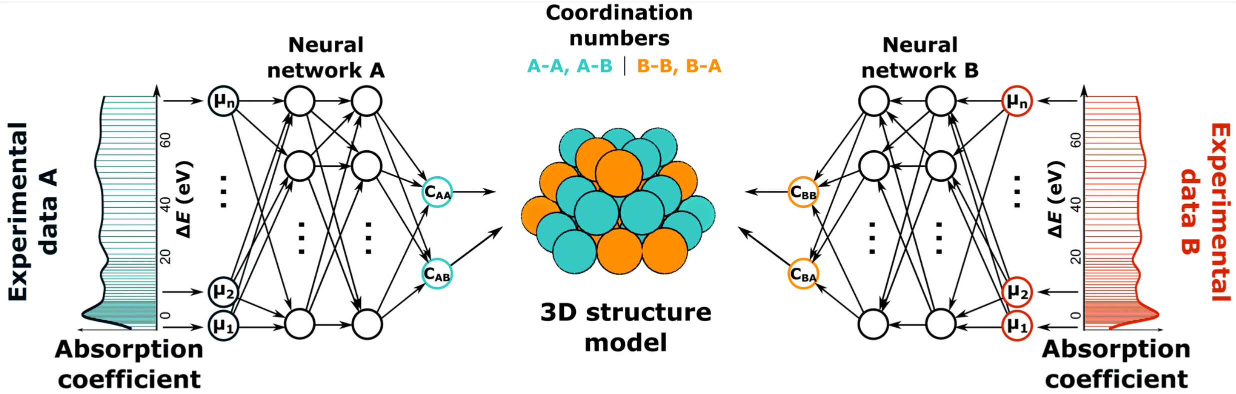


Figure 27. A schematic that represents the application of NN-XANES to an A_xB_{1-x} bimetallic system. Partial first coordination numbers are extracted from the XANES of A and B absorbing components. The partial coordination numbers (A–A, A–B, B–B, and B–A) are used to deduce the average NP structure. Adapted with permission from reference 293. Copyright 2020 The Royal Society of Chemistry.

5.2.4 Novel detection method of contiguous Pd regions in PdAu alloys

For alloys containing Pd as one component, it is possible to discriminate between different structural motifs, notably, those in which Pd segregates to form contiguous, Pd-rich regions or homogeneously disperses in Au.[103] The key idea is that bulk Pd[295] and Pd NPs[296–298] are known to form a β-phase hydride under H_2 treatment. Previous EXAFS studies showed that Pd-Pd bond length increased as the octahedral fcc sites were occupied by hydrogen.[297,298] In PdAu NPs, Pd hydride also forms under H_2 treatment.[103] Importantly, the bond length expansion between Pd and its nearest neighbors can occur only at contiguous, 3D Pd regions but not the alloyed PdAu regions nor the low dimensional (e.g., 2D) Pd regions. Furthermore, the EXAFS measurement of Pd-Pd distance can probe contiguous Pd regions quantitatively by measuring the relative interatomic distance (R) change upon H_2 treatment compared to the baseline value under He, $(\mathrm{R}_{\mathrm{H}_2} - R_{\mathrm{He}})/R_{\mathrm{He}}$.[103]

EXAFS data were measured for Pd NPs and a $Pd_{0.25}Au_{0.75}$ RCT-SiO_2 system under He and H_2 treatment. The Pd-Pd interatomic distance in Pd NPs is consistent with the hydride formation observed in the literature.[297,298] The spectra of $Pd_{0.25}Au_{0.75}$ NPs varied upon H_2 treatment (Figure 28) and the quantitative fitting shows a slight increase in Pd-Pd interatomic distances. Even though the change in interatomic distance was near the limit of detectability by the conventional EXAFS fitting, the existence of contiguous Pd regions was confirmed, which is also corroborated with other experimental evidence from STEM-energy-dispersive X-ray spectroscopy (STEM-EDS) and CO-DRIFTS measurements. In conclusion, this EXAFS-based method could be used as a probe of Pd hydride formation in Pd alloys with other metals and, as a result, provide insights into the nature of the distribution (homogeneous or heterogeneous) of Pd within the host metal structure.

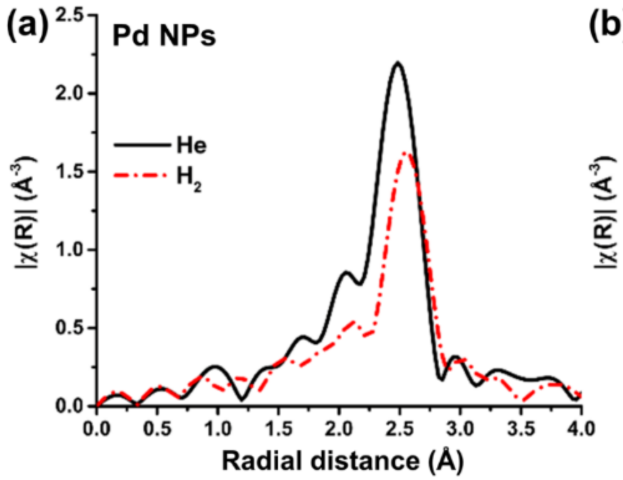


Figure 28. Fourier transform magnitudes of k2-weighted EXAFS spectra of (a) Pd NPs and (b) $Pd_{0.25}Au_{0.75}$ RCT-SiO_2 under flowing He or H_2 at 298 K and 1 bar. Adapted with permission from reference 103. Copyright 2020 John Wiley and Sons.

5.3 Transmission electron microscopy technique for bimetallic catalysts

TEM is particularly suitable to characterize metallic nanostructures for catalysis.[299] Combined with spectroscopy methods such as EDS or EELS, high-resolution images obtained with TEM can provide an insight into the chemistry of materials at the atomic level. Additionally, in-situ TEM studies can complement traditional ex-situ TEM studies to analyze materials under reaction conditions, which can image and chemically characterize a metallic catalyst in contact with reactants such as H_2, O_2, or N_2 under a range of temperatures. This is critical to elucidate the crucial localized features for the control and design of highly active and selective catalysts.

5.3.1 Ex-situ transmission electron microscopy for bimetallic catalysts

Dark field imaging and EDS can be used to elucidate the compositional profile of bimetallic alloy NPs. For example, dark-field STEM images of Pd_xAu_{1-x} NPs[104] can show the Pd segregation zones, which are less bright. The brightness contrast is the result of the signal detected by a dark-field detector being proportional to $Z^{1.6}$ (Z=46 for Pd and 79 for Au). The quantification analysis of the EDS data can also reveal whether the Pd segregated zone is constituted of 100 %. For $Pd_{0.25}Au_{0.75}$ NPs (Figure 29), Pd segregates to the edge of the particle with a Pd content of 40–45 at%, higher than the bulk composition of 25 at%. Similar segregation is also observed for $Pd_{0.09}Au_{0.91}$ NPs. For $Pd_{0.04}Au_{0.96}$ NPs, no Pd-rich regions were detected. However, Pd-rich regions may still exist, even though they are not detectable due to insufficient signal. The absence of large Pd clusters in $Pd_{0.04}Au_{0.96}$ NPs suggests that Pd atoms are better dispersed across the surface, which contributes to the high activity and selectivity of these samples.

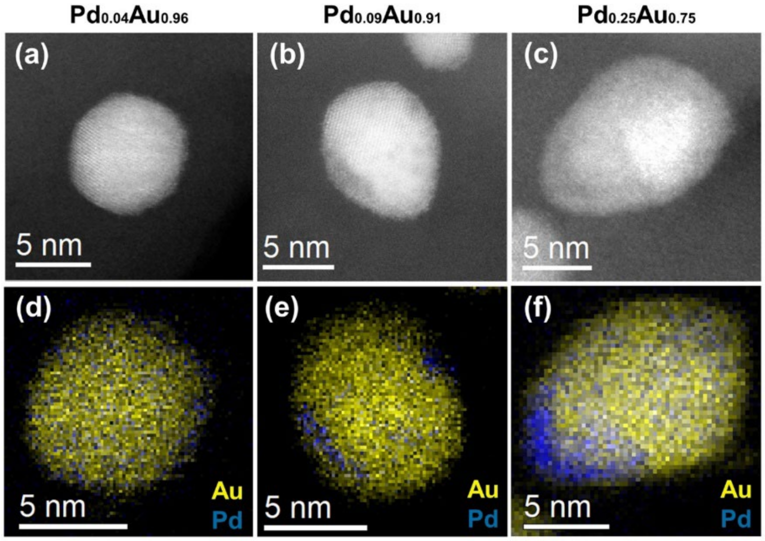


Figure 29. The presence of Pd-rich regions in Pd_xAu_{1-x} RCT-SiO_2 was observed for $Pd_{0.25}Au_{0.75}$ and $Pd_{0.09}Au_{0.91}$ NPs, but not in $Pd_{0.04}Au_{0.96}$ NPs. The control of the Pd distribution within individual particles is crucial to optimize the selectivity and the activity of the particles. (a-c) Dark-field STEM images of $Pd_{0.04}Au_{0.96}$, $Pd_{0.09}Au_{0.91}$ and $Pd_{0.25}Au_{0.75}$ NPs and (d-f) the corresponding EDS maps, respectively.

5.3.2 In-situ transmission electron microscopy for bimetallic catalysts

In-situ studies of bimetallic catalysts can complement ex-situ ones to understand dynamical phenomena during reactions, such as restructuring.[103,300,301] Indeed, restructuring events can occur during reactions where an ex-situ measurement cannot detect.[302]

Two methods are available to perform in-situ TEM analysis: First is a dedicated ETEM where the part of the column surrounding the sample is kept under pressure, while the rest of the column is maintained under normal vacuum conditions with differential pumping. The typical maximum pressure available with an ETEM is 1 Torr but can be higher, depending on the number of pumps in the system.[303] With this setup, ETEM can be used to directly observe catalyst restructuring, such as oxidation of Cu and reduction of Cu_2O[304] as well as oxidation of dilute alloys of $Ni_{0.05}Cr_{0.95}$ NPs.[305] The second option is an ETEM holder (Figure 30).[302] This holder contains samples enclosed in a small microreactor, with electron-transparent windows, multiple gas inlets, and an outlet. The 50-nm electron transparent windows made of amorphous Si_3N_4 can sustain the pressure difference between the inside of the microreactor and the surrounding vacuum of the TEM column. The temperature can be controlled up to 1273 K and the pressure inside the microreactor can go up to 2 atm. Examples of using the ETEM holder include studies of the crystal growth of NiCr NPs with 5-15% of Cr,[306] and NP oxidation of NiFe[307] and Ni_2Co[308] bulk alloys.

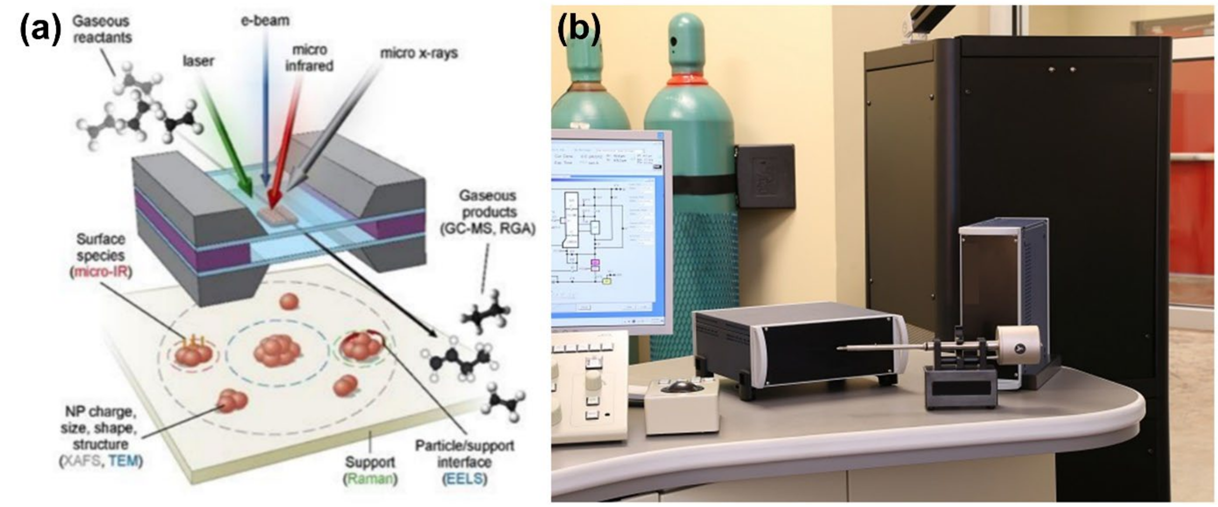


Figure 30. General principles of ETEM holders for in-situ studies. (a) Cartoon showing how the sample is sandwiched between two electron-transparent windows and can be heated with an integrated micro-coil. Small inlets and an outlet make the flow of gas possible. This approach is feasible for electron-based characterization techniques such as TEM, but can also be applied to bulk approaches such as X-ray absorption spectroscopy. (b) Picture of a dedicated in-situ holder for a gas-heating experiment. A software and a gas system regulate the flow of gases going through the holder. The inlet and outlet are at the bottom of the holder and can be connected to gas lines. Image in (a) is reprinted with permission from reference 309, image in (b) used with permission from Hummingbird Scientific. Copyrights 2015 The Authors and 2022 Hummingbird Scientific.

In-situ TEM with an environmental holder was used to characterize $Pd_{0.04}Au_{0.96}$ RCT-SiO_2 catalysts, as this specific system showed excellent catalytic properties (also reviewed in Sections3.2.1 and 3.4.1). The catalyst was treated with O_2 at 673 K, then H_2 at 773 K, and finally O_2 at 673 K. TEM images (Figure 31) show that the particle morphology did not change during the experiment. Only several particles initially very close to each other merged at the end of the process via the center of mass migration, but the amount of merged particles is negligible. The interaction between particles and the RCT support prevents particle migration and coalescence. Because of the unchanged particle morphology, internal restructuring, i.e., Pd atoms redistribute within particles, can be the only cause of the catalytic performance drop after H_2 treatment. However, EDS analysis performed in situ did not reveal dramatic shifts, indicating a very subtle change of the Pd distribution.

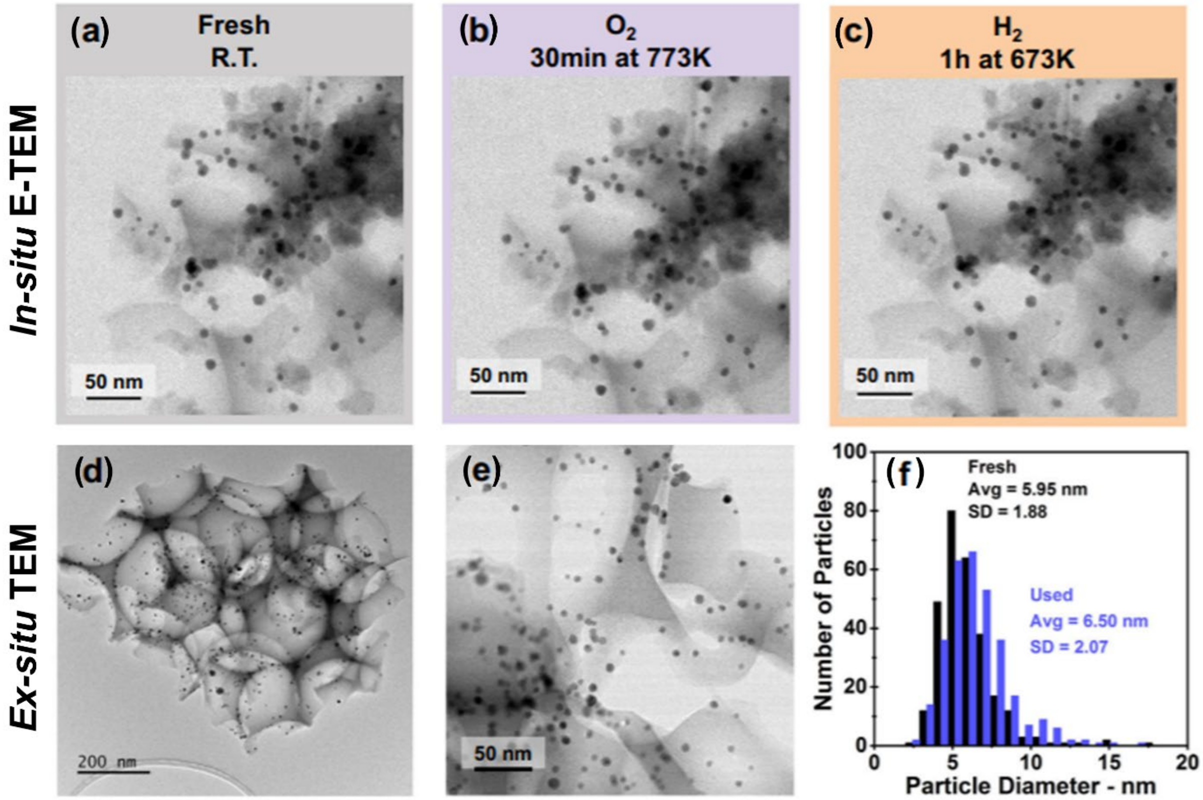


Figure 31. In-situ TEM results compared with ex-situ results, all images were taken in bright-field STEM mode. (a) Fresh $Pd_{0.04}Au_{0.96}$ RCT-SiO_2 at room temperature. (b) Sample after a 30-minute exposure to H_2 at 773 K with a flow rate of 4 sccm. (c) Sample after 1-hour exposure to O_2 at 673 K with a flow rate of 4 sccm. (d and e) Images of samples analyzed for ex-situ studies. (f) The size distribution of $Pd_{0.04}Au_{0.96}$ NPs before and after treatment was obtained using images collected with ex-situ TEM: The results are consistent with those collected with in-situ analysis, showing the particle migration and coalescence is happening at a smaller scale. Adapted with permission from reference 104. Copyright 2020 The Authors.

5.4 Machine learning accelerated molecular dynamics

Computational modeling techniques have advanced the atomistic understanding of heterogenous catalysis, correlating electronic structure to surface reactivity,[310,311] interpreting microscopic and spectroscopic observations,[312] and predicting kinetics of reaction networks.[18,313,314] Methods based on the explicit quantum mechanical treatment of electronic structures, such as DFT calculations, are critically important since they can accurately describe the forming and breaking of bonds in catalytic reactions.

However, modeling dilute alloy catalysts is still an untrivial task due to the complexity of these systems. As discussed in Section 2.4, typical dilute alloy catalysts are supported NPs, where catalytically active structural motifs, such as edges, corners, and surface islands, are several nanometers in extent. At the same time, as discussed in Section 4, the catalytic activity can be altered by slow surface restructuring under different pretreatments and chemical reaction conditions. Directly modeling these larger structures and slow events with AIMD is prohibitive due to AIMD's poor scaling and high computational cost. For this reason, AIMD simulations are often limited to fast reactions on small periodic surfaces[315,316] or small nanoclusters[317–319] at high temperatures.

5.4.1 Cluster expansions and classical interatomic potentials

Initially, cluster expansions (CE) and classical interatomic potentials were used to replace DFT for faster calculations. Both methods rely only on the information about atomic positions and do not directly consider the electronic structure. Due to their local nature, the cost of these methods scales linearly with the number of atoms, as opposed to the cubic scaling of DFT, resulting in an overall acceleration of several orders of magnitude. For example, combined with Monte Carlo, CE predicted oxygen-induced Ag segregation on AgAu surfaces[176] (also discussed in Section 3.2.3), CO-induced Pd segregation on PdAu surfaces[320], and acetylene-induced reverse segregation on PdAg surfaces[321]. Reactive force fields, such as ReaxFF[322] and COMB[323], can model some catalytic reactions, including oxidation and dissociation of small molecules on Pt,[324,325] Cu,[326,327] Pd,[328] Ni,[329] and Fe[330] metals and their oxide surfaces.

However, the accuracy and transferability of these parametric models are limited due to their restricted analytical expressiveness. Unlike DFT, which treats electronic degrees of freedom explicitly and is thus transferable across different systems, there is no guarantee that a CE model or an interatomic potential developed for one set of reaction intermediates and bonding chemistry can work well in other scenarios that are not considered in the model construction.

5.4.2 Machine-learned interatomic potentials

The advent of ML for developing interatomic potentials opens new possibilities in the realm of catalysis. Machine-learned interatomic potentials (MLIPs) are much more flexible than classical interatomic potentials. Additionally, they can model complex reaction pathways with many distinct bonding chemistries. With over a decade of development, noteworthy examples of MLIPs include the High Dimensional Neural Network (HDNN),[331–334] Gaussian Approximation Potential (GAP),[335] Schnet,[336] Moment Tensor Potential (MTP),[337] Spectral Neighbor Analysis Potential (SNAP),[338] Mapped Force Field (MFF),[339] and DeepMD,[340] in addition to recently developed Fast Learning of Atomistic Rare Events (FLARE)[341–343] and Neural Equivariant Interatomic Potential (NequIP).[344]

A growing number of MLIPs have been developed to model Au-, Ag- and Cu-based alloys. Table 5 lists several alloys discussed in Section 2─4. It is worth noting that MLIPs also have transferability issues: MLIPs that do not incorporate physical information are usually limited to specific compositions and phases. For example, potentials trained on bulk alloy data may not model NPs accurately, nor *vice versa*. This transferability challenge is exacerbated by the need to include the reactant and product molecules as well as the rare and often *a priori* unknown intermediate configuration in the training set to ensure accuracy across the catalytically relevant reaction path. Except for the CuAu potential[345], which can model CuAu NPs in water, all MLIPs in Table 5 focus on predicting NPs or bulk alloys in vacuum, while most MLIPs that can study chemical reactions at gas/solid or liquid/solid interfaces are often limited to a single metal instead of metal alloys.[334,344,346–352]

Table 5. A list of ML potentials developed for alloys.

Alloys	**Year**	**Type of MLIP**[a]	**Training Set**
CuZn	2021[353]	HDNN	Bulk, surface and cluster structures @ up to 1400 K
CuNi	2019[354]	MTP[a]	FCC, BCC, and HCP bulk
CuPd	2019[355]	MTP	BCC, HCP, and FCC bulk
CuPt	2019[356]	MFF	Active learning on NPs
CuAu	2014[357], 2015[345]	HDNN	FCC bulk, surface, and clusters in vacuum and in water
PdAg	2018[358]	NN-EA	Clusters
	2020[238]	FLARE	Active learning on melted surface
	2021[359]	GAP, MTP	FCC and BCC bulk structures and liquid-like structures @ up to 3360 K
AgAu	2017[360]	ANN	NPs
	2021[361]	DeepMD	FCC bulk, low index surfaces, amorphous and nanoparticle @ 100-1500 K
PdAu	2017[235]	HDNN	FCC(111) surface
CuPdAg	2019[362]	HDNN	Bulk FCC and NPs
PtNiCu	2018[363]	HDNN	NPs

[a] This study includes multiple MLIPs including MBTR +KRR, MBTR +DNN, SOAP +GP, MTP (+ polynomial reg), and it also trained on 9 other alloys (AgCu, AlFe, AlMg, AlNi, AlTi, CoNi, CuFe, CuNi, FeV, and NbNi).

Training a robust MLIP requires DFT calculations that are representative of the reaction pathways of interest. However, efficiently exploring the landscape of these pathways and selecting configurations that are relevant for training and benchmarking the ML model accuracy is difficult. Among the examples listed in Table 5, the training data were obtained from: (1) enumeration by automated workflow or evolutionary algorithms,[346,353–355,358] (2) AIMD trajectories[359,361] and (3) active learning.[238,356] One example of an MLIP that uses active learning is FLARE.[341–343,364] Its prediction of forces for each atomic configuration is accompanied by the variance, or uncertainty of the model prediction, which enables active learning of the potential energy surface on the fly during the time evolution of the MD simulation. When the model encounters a configuration outside its training set, such as a rare transition event, causing uncertainty to exceed a certain threshold, DFT calculations are autonomously performed to acquire accurate forces and augment its training set. This approach was successfully employed to train models and perform large-scale MD of the restructuring of PdAg dilute alloy catalysts[238] reviewed in Section 4.3.1, as well as the reactive simulation of H_2 splitting and recombination of the Pt (111) surface.[365] For the former example of active learning on PdAg, this model uses only two- and three-body terms to compare atomic environments and can be turned into a very efficient model that can simulate a million atoms on a single GPU.[342]

5.4.3 Automated mechanism extraction from molecular dynamics

MLIPs are beginning to enable quantum-accurate simulations of reactive dynamics over μs, long enough to capture catalyst restructuring at gas-solid or liquid-solid interfaces and to understand microscopic mechanisms governing catalysis and material degradation. The large amount of data captured by long MD trajectories brings additional challenges to data management and post-processing, especially automated extraction of rare events and reaction mechanisms.

Unambiguously determining the initial and final states of rare transition events and categorizing them is a research frontier.[366] In the example of surface segregation in binary alloys discussed in Section 4.3.1, high-temperature MD simulations were used to explore the energy landscape and restructuring events of bimetallic PdAg surfaces. By isolating restructuring events in classical force field simulations of a single-component Ag surface and estimating the reaction barriers using DFT, new predominant classes of mechanisms controlling rearrangement at step edges were found.[245] A more complex bimetallic system was later modeled with more accurate GP MLIPs, and reactive events were analyzed by an automated workflow.[238] Furthermore, Ag encapsulation of the Pd island, prior to the layer-by-layer Pd dissolution, was observed in a µs-long simulation of thousands of atoms (Figure 32).

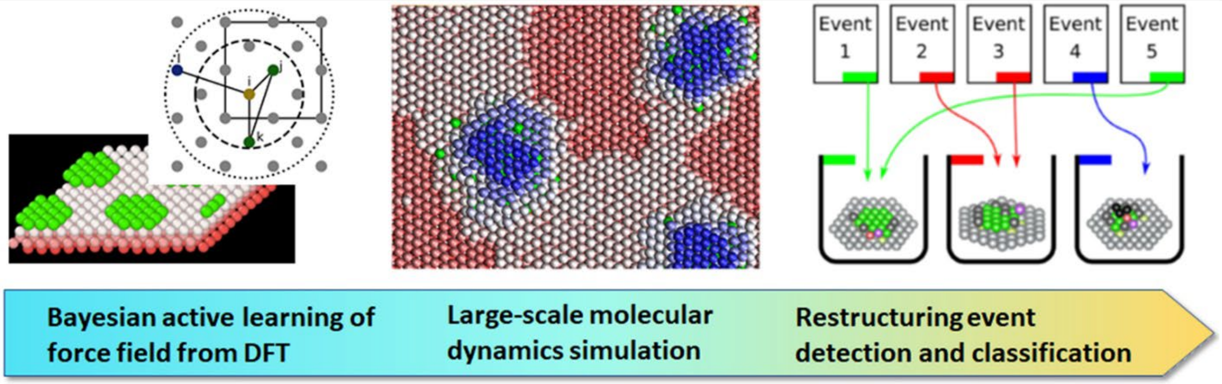


Figure 32. Automated workflow to discover restructuring events on surfaces of PdAg dilute metal alloy from MD with MLIPs.

6 Conclusion and Outlook

Bridging between model systems and catalytic systems. The research described herein is sharply focused on the development of design principles for dilute alloy catalysts that can be used in more energy-efficient chemical synthesis. Because of the complexity of heterogeneous catalytic processes, a comprehensive approach that integrates experiment and theory is required. The approach described in this review integrates fundamental studies at low pressure using well-defined single crystals, first-principles theory on model systems, and kinetic studies of dilute alloy catalysts under catalytic conditions. The ability to advance understanding of other catalytic processes by using fundamental theoretical and experimental studies has been exemplified by several groups,[367,368] further establishing the validity of this approach. This methodology provides valuable insights into the key factors that determine reaction selectivity, as demonstrated for several different dilute alloy systems. For example, the mechanisms and rate constants determined for selective alcohol oxidation on Au single crystals and anhydrous aldehyde production on Cu single crystals provided a framework for predicting performance of Au- and Cu-based dilute alloy catalysts.

A major breakthrough was the ability to quantitatively model changes in the selectivity for alcohol oxidation over npAgAu alloys.[159] Transient kinetic measurements performed for methanol oxidation catalyzed by npAgAu at operational temperatures provided a critical bridge to the model studies at low pressure and low temperature, enabling prediction of changes in selectivity over several orders of magnitude of pressure and several hundred degrees of temperature. Furthermore, scaling relationships obtained from DFT measurements successfully predicted selectivity for oxidation of higher chain alcohols.[17] This set of studies clearly illustrates the predictive power of molecular-level understanding of the reaction network for catalytic processes.

The ability to accurately model selective oxidation reactions on Au-based materials relied on several important factors. Firstly, the surface concentrations of reactants must be similar under lower pressure and temperature to those achieved under catalytic conditions. Hence, the reactions of interest must occur at sufficiently low temperature (with a low enough barrier) that reactants have a sufficient surface lifetime for reaction to occur. Selective hydrogenation reactions on the PdAu and PdAg alloys are an example of a more challenging system because the binding of hydrogen atoms on these materials is relatively weak, leading to desorption below room temperature at low pressure. Nevertheless, DFT models provide insight into reaction mechanisms and key kinetic steps as a complement to reactor studies, which can guide the understanding and prediction of the function of dilute alloy catalysts.

A second critical factor that is important for connecting fundamental studies to catalytic performance is that the state of the surfaces must be the same both for the models and the working catalysts. Thus, if spectator species accumulate under catalytic conditions, they must also be included in any experimental or theoretical models. The fact that Au is itself relatively unreactive renders it ideal for investigations spanning vast pressure and temperature ranges. Besides the potential influence of spectators, the distribution of the reactive minority metal on the surface is also a key factor, as discussed below.

Understanding the function of dilute alloy catalysts. The specific focus on dilute alloy catalysts for improving reaction selectivity was motivated by the potential to use the bifunctionality of two dissimilar materials. The underlying principle is that the more reactive minority metal, e.g., Pd, Ni, Pt, or Ag would initiate the catalytic cycle, and the less reactive host, e.g Au, Ag or Cu, would impart selectivity. Based on the progress so far, it is clear that this concept, while valuable, is too simplistic. First of all, the distribution of the reactive minority metal on the surface is important but often difficult to control. Bonding and reactivity are generally different for single atoms, small ensembles of a few atoms, and larger islands, rendering specific knowledge of the state of the surface crucial. Furthermore, migration of intermediates across boundaries between dissimilar metals may also be challenging and may only occur under specific conditions that are not readily accessible either during catalysis or in model studies. The migration of adsorbed hydrogen atoms from Pd to Ag, discussed in section 4.3, is such an example.[255]

Control of the distribution and concentration of the minority metal atoms at the surface of the catalyst under reaction conditions is critical, as mentioned above. The reactive metal atoms must be at or near the surface to participate in reactive steps. On the other hand, the active metals are often more stable in the bulk. For example, Pd is most stable as dispersed atoms in the bulk of either Au or Ag on a pristine surface.[25,104]

Fortunately, pretreatment of the dilute alloys can be used to provide a thermodynamic driving force for segregation of the reactive metal to the surface. For example, Pd is segregated to the surface of dilute PdAu NPs via oxidation at higher temperature (573K)[104]—an effect also previously demonstrated on single-crystal Pd/Au(111) models.[369] Similarly, segregation of Ag in the npAgAu catalysts was effected by oxidative pretreatment.[62,74] In both of these cases, the reactive state of the material was maintained under catalytic conditions by operating in a temperature regime where diffusion of the minority metal is not too rapid. A second factor is that reactants present in the ambient gas phase can stabilize the more reactive metal at the surface. Clearly, it is important to determine the distribution and structure of the active metal on the catalyst surface under reaction conditions.

The ability to synthesize well-defined and stable catalyst materials is essential to testing the underlying principles developed in fundamental work. The intrinsic behavior of dilute alloy catalysts would ideally be tested in the absence of a support material. The success of understanding the catalytic function of npAgAu is illustrative of this approach. On the other hand, not all dilute alloy catalysts of interest can be synthesized as support-free materials. Furthermore, practical catalysts generally contain an inert support material, such as a metal oxide. Advances in materials synthesis have resulted in the ability to prepare NP alloys with controlled composition and structure with homogeneity achieved at the atomic scale.[141,370–373] These materials can be incorporated into oxide or other supports and studied as catalysts. The specific creation of the RCT oxides[101,138] has been particularly successful because the synthetic method yields a very stable material that is resistant to sintering. This stability is attributed to the fact that the alloy NPs are embedded in the oxide support.

While metallic species play the most prominent role in the catalytic processes discussed above, recent work provides evidence that confinement effects at the interface between the metal and support can influence both activity and selectivity.[374–376] Confinement effects in catalysis are somewhat understood for microporous materials such as zeolites, but the interface between metals and oxides is less explored. Understanding such effects could allow tailoring these interfaces to favor specific reaction pathways, thus inducing changes in selectivity. Moreover, nanoarchitectures in which the oxide support is permeable to small molecules, such as in the case of some silicates, can benefit not only from confinement effects but also from size-selective access of reactant molecules to the active site.[374–376] This provides exciting new opportunities to carry out systematic studies comparing these interfaces for 2D-silicates on metal supports and encapsulated NPs in RCT-SiO_2 catalysts.

Advancing characterization and modeling for catalysts in action. Development of cutting-edge theoretical and experimental tools is essential to understanding how to optimize the distribution of the active metal on the surface under reaction conditions. Operando tools, such as EXAFS and ambient pressure TEM, are examples of powerful experimental tools; however, very dilute alloys present challenges in sensitivity. Accordingly, new approaches to determining metal atoms distribution, such as application of ML techniques, are being developed.

The expansive configurational space of dilute metal sites in bimetallic catalysts results in a vast ensemble of candidate structures that cannot be handled by theoretical methods, even with the advent of exascale and petascale computational capabilities. One promising method is to narrow the range of candidate structures by using experimental XANES and/or EXAFS spectra for obtaining their descriptors from the spectra. New directions in this area will also aim at exploring in greater detail the information content in experimental data to understand the number, and the physical meaning, of descriptors stored in the spectra. More work is needed to identify those which are directly responsible for reactivity, i.e., activity descriptors.

New computational tools are also required to understand how the components of the alloy materials distribute under various conditions. To this end, automated workflows[245] and ML techniques are under development. Accurate ML interatomic potentials[341,342,344] can replace DFT force calculations and accelerate MD by several orders of magnitude. Furthermore, dimensionality reduction and multi-task learning[377] can be employed to extract data-driven collective variables that are then used to guide enhanced sampling techniques for efficient calculations of free energy barriers and transition rates of reactions.

Advances in automated training of fast accurate uncertainty-aware ML interatomic potentials (MLIPs) and data-driven discovery of low-dimensional reaction manifolds will enable new types of multi-scale computational methods to study the reactive dynamics of heterogeneous catalysis systems. In this emerging direction there remain several key challenges: (1) developing fast and accurate MLIPs that break the cost-accuracy trade-off for highly diverse chemical configurations, (2) devising autonomous training and benchmarking protocols that ensure the transferability of MLIPs over different intermediate structures in the reaction network, (3) advancing autonomous algorithms for detecting and analyzing rare events in large-scale MD, (4) designing robust unsupervised and efficient algorithms for free energy landscape exploration and estimation of reaction rates.

Further advancement of these and other methods that probe surface structure, composition and rearrangement will provide insights into how to control the state of the catalyst surface to optimize selectivity using reaction conditions and materials properties. These same methods will be broadly applicable to understanding complex materials relevant to other applications, such as electrocatalysis and energy storage.

Challenges. Significant advances in understanding of catalytic processes at a molecular scale have clearly been made; however, several challenges remain. One of the most significant challenges is the need to accelerate the development of new and efficient catalytic processes through a more rapid cycle of prediction-synthesis-characterization-testing.

Rapid screening of specific alloy configurations and compositions can be performed for simple elementary steps, e.g., H_2, O_2 or C-H dissociation. These initial steps can be modeled for specific ensembles and for simple steps using DFT. On the other hand, modeling a complex reaction network without input from experiment is currently very challenging. Furthermore, accurate modeling of the state of the surface under reaction conditions is not possible from first principles only.

Rapid controlled synthesis of specific alloy catalyst materials is also challenging, often requiring specialized synthetic methods and detailed experimental characterization. Once a material is made, catalytic testing is required under different conditions and using specific pretreatment protocols. Detailed understanding of these phenomena is time-intensive; hence, efficient approaches are needed.

One potential approach is to test the efficacy of initial elementary steps, e.g., H_2, O_2 or C-H dissociation, on low surface area, unsupported thin film alloys. Indeed, it is even possible to investigate alloys with gradients of composition as a means of screening composition effects.[378] This approach could be coupled with investigation of pretreatment and reaction conditions and with spectroscopic methods to provide more rapid evaluation and comparison to theoretical predictions. The use of thin films is compatible with fundamental studies of elementary steps using temperature programmed methods and with the use of surface-sensitive spectroscopic probes. While the challenge of making well-controlled catalysts will remain, this more rapid screening would provide guidance on the most promising compositions.

Computational challenges lie in the need for improved kinetic modeling that spans the multitude of length and time scales relevant to heterogeneous catalytic processes. As described above, enhanced sampling techniques for efficient calculation of free energy barriers and transition rates of reactions is crucial.

Significant progress in understanding how dilute alloy catalysts can be used to enhance the selectivity of key synthetic reactions has been made. Insights at the molecular scale provide predictive power over a wide range of conditions. Even so, advancement in methods to probe structure-reactivity relationships and rapidly screen specific systems is required. The bifunctionality of dilute alloy catalysts, where the reactive minor metal initiates the catalytic cycle while the host metal imparts selectivity, can improve the activity, selectivity and stability in oxidation and hydrogenation reactions. However, the complexity of the structure under pretreatment and/or reaction conditions along with the migration of reactive species still needs careful consideration. The challenges brought by the dilute nature of materials of interest has stimulated the advancement of new experimental and theoretical methodologies to understand the evolution of structure and composition of catalysts and their relationship to catalytic function. The integrated theoretical-computational-experimental approach has been shown able to "bridge the divide" between fundamental knowledge and design of catalytic processes in complex dilute alloy systems spanning vast pressure and temperature ranges. This comprehensive approach provides a framework for generalization to other related catalytic processes and a new paradigm for catalyst discovery.

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Robert J. Madix's pioneering fundamental research established the molecular foundation for elementary surface reactions on catalytic metals. Madix was the first surface scientist to undertake cutting-edge research on the surface chemistry of complex molecules on well-defined metallic surfaces. The first application of surface science studies to heterogeneous catalysis was achieved by Madix in the seminal studies of methanol oxidation to formaldehyde over Ag(110) surfaces. These seminal studies also significantly influenced the surface science community in subsequent years. These studies provided additional fundamental insight into the kinetics and mechanisms of surface reactions. Madix is the Charles Lee Powell Emeritus Professor of Chemical Engineering at Stanford University and Senior Research Fellow in the School of Applied Science & Engineering at Harvard University. He received a B.S. degree in chemical engineering from the University of Illinois and a Ph.D. degree in chemical engineering from the University of California, Berkeley. He is the recipient of an Alexander von Humboldt Senior Scientist Award, the Paul Emmett Award for Fundamental Studies in Heterogenous Catalysis, the Alpha Chi Sigma Award for Fundamental Research from the AIChE, the Arthur Adamson Award of ACS, the Henry J. Albert Award of the International Institute of Precious Metals, and the Gabor Somorjai Award in Catalysis of the ACS. Madix is co-Deputy Director of the IMASC Energy Frontier Research Center.

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List of Abbreviations

ab initio molecular dynamics (AIMD)
ambient pressure infrared reflection adsorption spectroscopy (AP-IRRAS)
ambient pressure X-ray photoelectron spectroscopy (AP-XPS)
bilayer (BL)
Brunauer-Emmett-Teller (BET)
cluster expansions (CE)
collective variables (CVs)
CO-Fourier-transform infrared spectroscopy (CO-FTIR)
density functional theory (DFT)
diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)
electron energy-loss spectroscopy (EELS)
energy-dispersive X-ray spectroscopy (EDS)
environmental transmission electron microscope (ETEM)
extended X-ray absorption fine structure (EXAFS)
fast learning of atomistic rare events (FLARE)
Gaussian approximation potential (GAP)

Gaussian process (GP)
high dimensional neural network (HDNN)
high resolution electron energy loss spectroscopy (HREELS)
high resolution transmission electron microscopy (HRTEM)
hydrotalcite (HT)
infrared reflection-absorption spectra (IRRAS)
infrared (IR)
interatomic potentials (IPs)
latent space analysis of spectra (LSAS)
low energy electron diffraction (LEED)
low energy electron microscopy (LEEM)
mapped force field (MFF)
machine learning (ML)
machine-learned interatomic potentials (MLIPs)
molecular dynamics (MD)
metal oxide (MOx)
moment tensor potential (MTP)
nanoparticles (NPs)
neural networks (NNs)
neural network assisted extended X-ray absorption fine structure (NN-EXAFS)
neural network X-ray near edge structure (NN-XANES)
neuro equivariant interatomic potentials (NequIP)
nudged elastic band (NEB)
partial radial distribution function (PRDF)
polarization-modulation infrared reflection absorption spectroscopy (PM-IRAS)
raspberry colloid templated (RCT)
reverse Monte Carlo (RMC)
self-organizing map (SOM)
single-atom alloys (SAA)
scanning electron microscopy (SEM)
spectral neighbor analysis potential (SNAP)
scanning transmission electron microscopy (STEM)
scanning transmission electron microscopy-energy-dispersive X-ray spectroscopy (STEM-EDS)
scanning tunneling microscope (STM)
strong metal-support interactions (SMSI)
temporal analysis of products (TAP)
temperature programmed desorption (TPD)
temperature programmed reaction spectroscopy (TPRS)
transition state (TS)
transition state theory (TST)
transmission electron microscope (TEM)
turn over frequency (TOF)
ultra-high vacuum (UHV)

X-ray absorption fine structure (XAFS)
X-ray absorption near edge structure (XANES)
X-ray photoelectron spectroscopy (XPS)
X-ray photoemission electron microscopy (XPEEM)

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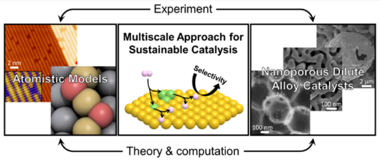

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