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Bimetallic Catalysis

Ag/Au Mixed Sites Promote Oxidative Coupling of Methanol on the Alloy Surface

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Abstract: Nanoporous gold, a dilute alloy of Ag in Au, activates molecular oxygen and promotes the oxygen-assisted catalytic coupling of methanol. Because this trace amount of Ag inherent to nanoporous gold has been proposed as the source of oxygen activation, a thin film Ag/Au alloy surface was studied as a model system for probing the origin of this reactivity. Thin alloy layers of Ag_xAu_{1-x}, with $0.15 \leq x \leq 0.40$, were examined for dioxygen activation and methanol self-coupling. These alloy surfaces recombine atomic oxygen at different temperatures depending on the alloy composition. Total conversion of methanol to selective oxidation products, that is, formaldehyde and methyl formate, was achieved at low initial oxygen coverage and at low temperature. Reaction channels for methyl formate formation occurred on both Au and Au/Ag mixed sites with a ratio, as was predicted from the local 2-dimensional composition.

Introduction

Selective oxidation is one of the key transformations in organic chemistry, the main challenge being suppression of combustion or secondary oxidation of desired products. Gold-based catalysts have great potential for such processes, for example, epoxidation of olefins,[1,2] oxidative coupling of alcohols,[3–6] aldehydes[7] and amines,[8,9] and oxidative carbonylation reactions.[10]

Many of these reactions share a general mechanistic framework. Alcohols, aldehydes, and amines adsorb and desorb reversibly on otherwise clean Au(111).[11,12] However, adsorbed atomic oxygen selectively activates O–H and N–H bonds in alcohols and amines on Au to form the corresponding alkoxy or amido groups.[11] Oxidative coupling then proceeds via a nucleophilic attack of these species at electron-deficient centers, for example, in aldehydes.[11,12] This mechanistic framework, established by studies of reactions with supporting spectroscopic identification of reaction intermediates on well-defined surfaces under ultrahigh vacuum conditions, can be directly transferred to catalysis by nanoporous Au under ambient conditions at modest temperatures.[13,14]

Two striking features of the nanoporous Au catalyst are: 1) a remarkable resistance to deactivation and 2) its activation of O_2 in the absence of a supporting oxide. The first characteristic is likely the result of its ligament structure.[13] However, its facility for activating molecular oxygen cannot be explained by the mechanisms proposed in the literature for supported gold catalyst; namely, a size effect[15,16] or activation at the particle-support interface.[17] However, nanoporous gold is typically prepared by de-alloying Ag/Au alloy, leading to at least 1% of residual Ag. This small amount of Ag present in nanoporous Au has been suggested to dissociate molecular oxygen, producing adsorbed atomic oxygen, which can then spill over to Au and initiate the catalytic cycle for selective oxidation. Indeed, activation of dioxygen on nanoporous Au has been demonstrated in ultrahigh vacuum conditions.[18,19]

The presence of Ag in the nanoporous gold also has the potential to alter bonding and reactivity of intermediates bound to the surface. In alloys, the electronic and geometric structure of the surface can be altered and the nature of bonding and reaction sites changed substantially. These effects—often referred to as electronic and ligand effects—can change selectivity and activity in catalytic processes in a way that is not simply additive.[20,21]

Herein, we report the effect of alloying the surface of Au(111) with Ag on the mechanistic oxidative coupling of methanol. We show that the Ag/Au alloy exhibits different reactivity from either pure Au or Ag surface and attribute the phenomenon to presence of mixed Ag/Au sites on the surface.

Results

Oxygen binding and desorption

The temperature-programmed desorption profile of molecular oxygen from recombination of atomic oxygen on the Ag/Au

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thin film alloy surface is sensitive to the composition of the surface and local bonding environment of the adsorbed oxygen atoms. We focus on $Ag_{0.4}Au_{0.6}$ herein to exemplify the general trend of the binding and desorption of oxygen on the Ag/Au alloy surface. Distinctive O_2 features from recombination of adsorbed O atoms are observed, at approximately 525 and 540 K from the $Ag_{0.4}Au_{0.6}$ alloy; the relative amount of O_2 produced in these peaks depends on the initial oxygen coverage (Figure 1). The peak temperature for the 525 K peak (Figure 1 a–e) is identical to that on Au(111) (Figure 1 f), suggesting that the recombination and desorption occurs from sites similar to those on Au(111), referred to herein as Au-like sites. A desorption peak at 540 K suggests recombination involving adsorbed O atoms bound at sites with a local environment significantly different from either pure Au(111) or Ag(111). We refer to those sites as mixed sites. No O_2 desorption feature near 595 K was observed, suggesting desorption did not occur from surface sites similar to those on Ag(111) (Ag-like sites). Similar results were also observed on alloys with other compositions (Ag_xAu_{1-x}, with $0.15 \leq x \leq 0.40$).

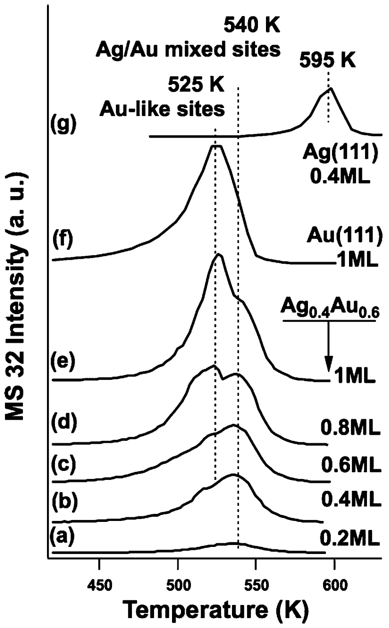

Figure 1. Temperature-programmed desorption of oxygen on $Ag_{0.4}Au_{0.6}$ surface alloy at various initial oxygen coverages (a–e). Temperature-programmed desorption of oxygen on Au(111) (*f*, $\theta_O = 1$ ML) and Ag(111) (*g*, $\theta_O = 0.4$ ML). Atomic oxygen was formed on the Ag/Au alloy by ozone exposure at 200 K; on Ag(111), it was formed by NO_2 exposure at 500 K.

The relative amounts of oxygen desorption from the two channels depends on the initial oxygen coverage. At low oxygen coverage ($\theta_O < 0.8$ ML), desorption from mixed sites dominates (Figure 1). With increasing initial oxygen coverage the Au-like sites become increasingly important, dominating for $\theta_O \geq 0.8$ ML. Similar oxygen desorption profiles were observed for Ag/Au thin film alloys with Ag molar fraction from 0–40%, with the oxygen desorption peak at approximately 540 K growing with the increase of Ag content in the alloy (Figure S1 in the Supporting Information).

Adsorbed atomic oxygen oxidizes both Ag and Au on $Ag_{0.4}Au_{0.6}$. The O (1 s) peak at 529.5 eV is evident, similar to that observed on Au(111).[9,12] Its presence ($\theta_O = 1$ ML) causes the binding energies of both Ag (3d) and Au (4f) peaks to shift (Figure 2 and Figure S3 in the Supporting Information). A new shoulder of the Au ($4f_{7/2}$) peak appears at 85.5 eV, corresponding to oxidized Au.[22] The peak increases in area by approximately 70% after annealing the surface to 440 K and disappears above 500 K with the desorption of the oxygen. A similar shift of the Au(4f) binding energy was observed for O/Au(111) ($\theta_O = 1$ ML). Adsorbed oxygen produces a new Ag ($3d_{5/2}$) peak at 367.2 eV, corresponding to oxidized Ag.[23] The integrated area of the Ag ($3d_{5/2}$) peak is largest at 440 K, and it does not disappear until above 520 K, higher than the temperature at which the feature for oxidized gold vanishes (Figure 2 B).[24] The higher stability of the surface oxide of Ag is evident. The introduction of atomic oxygen on Ag/Au alloy thin film does not change the ratio of the integrated area of Ag ($3d_{5/2}$) and Au ($4f_{7/2}$) peaks, indicating that within the limit of our XPS measurements no preferential segregation of either Ag or Au to the surface occurs.

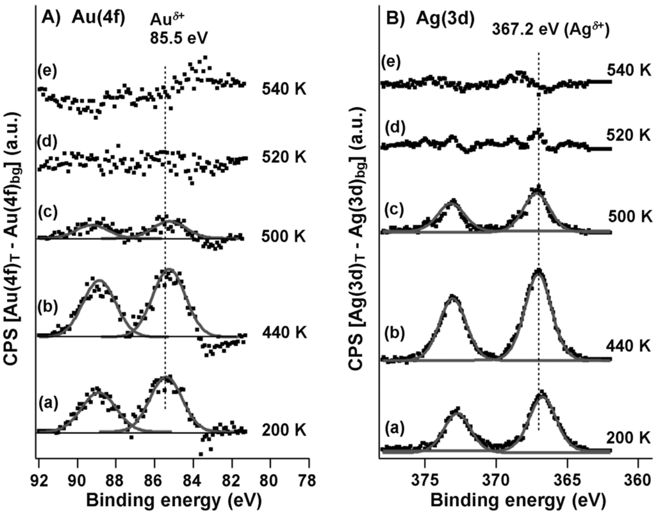

Figure 2. A) Au(4 f) and B) Ag(3 d) X-ray photoelectron difference spectra of atomic oxygen covered $Ag_{0.4}Au_{0.6}$ ($\theta_O = 1$ ML) at a) 200 K, b) 440 K, c) 500 K, d) 520 K, and e) 540 K. The contributions of metallic Au and Ag to the spectra have been subtracted for clarity. The spectra before subtraction are given in Figure S3 in the Supporting Information.

Methanol oxidative coupling

Oxidative coupling of methanol to give methyl formate occurs efficiently on the Ag/Au alloy after activation by atomic oxygen ($\theta_O = 0.1$ ML) at 200 K (Figure 3). Methyl [D_4]formate was observed as the primary product of CD_3OH. [D_2]Formaldehyde and CO_2 were also detected; they are attributed to selective oxidation and combustion of CD_3OH.[25,26] D_2 was also detected at the same temperature range as formalde-

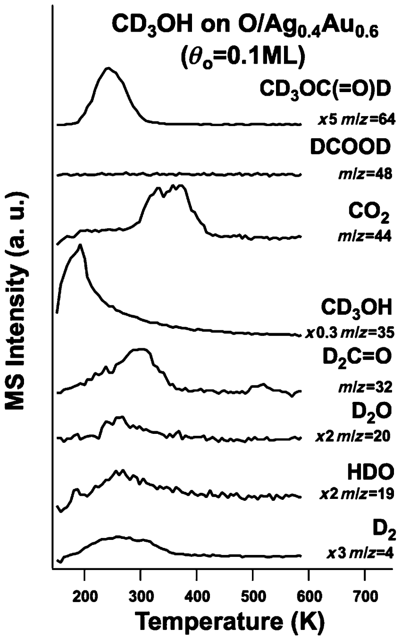

Figure 3. Oxidative coupling of [D$_3$]methanol (CD_3OH) on $O/Ag_{0.4}Au_{0.6}$ ($\theta_O = 0.1$ ML) to produce methyl [D$_4$]formate is demonstrated by using temperature-programmed reaction experiments. Atomic oxygen on $Ag_{0.4}Au_{0.6}$ is created by ozone exposure at 200 K.

hyde and methyl formate; neither formaldehyde nor D_2 were observed for the oxidative coupling of methanol on oxygen-activated Au(111).

The selectivity for the oxidative coupling on the alloy surfaces depends on the initial oxygen coverage in a manner similar to that observed for pure Au(111). As illustrated for $Ag_{0.4}Au_{0.6}$ (Figure 4 A), low oxygen concentrations lead to high selectivity for the coupling to form methyl formate, the selectivity reaching 60 % at an initial oxygen coverage of 0.05 ML.[3] Formaldehyde is also formed appreciably at this low O coverage: there is no detectable amount of CO_2.

At higher oxygen coverage (> 0.1 ML), combustion of methanol dominates (Figure 4 A and Table 1) and excess oxygen remains on the surface, based on the evolution of O_2 above 500 K (Figure 4 B). The yield of methyl formate initially rises, reaching a maximum for an initial oxygen coverage of 0.1 ML.

Table 1. Product distribution of selective oxidation of methanol on $O/Ag_{0.4}Au_{0.6}$.

θ_O [ML]	Selectivity[a] [%] (±10 %) Methyl formate	Formaldehyde	CO_2
0.05	58	42	0
0.1	46	22	32
0.2	7	0	93
0.4	6	0	94
0.6	5	0	95
1.0	4	0	96

[a] Parent ions of methyl [D$_4$]formate (64 amu), [D$_2$]formaldehyde (32 amu), and CO_2 (44 amu) were used as signature masses in the quantification process, following the procedure detailed in Ref. [10].

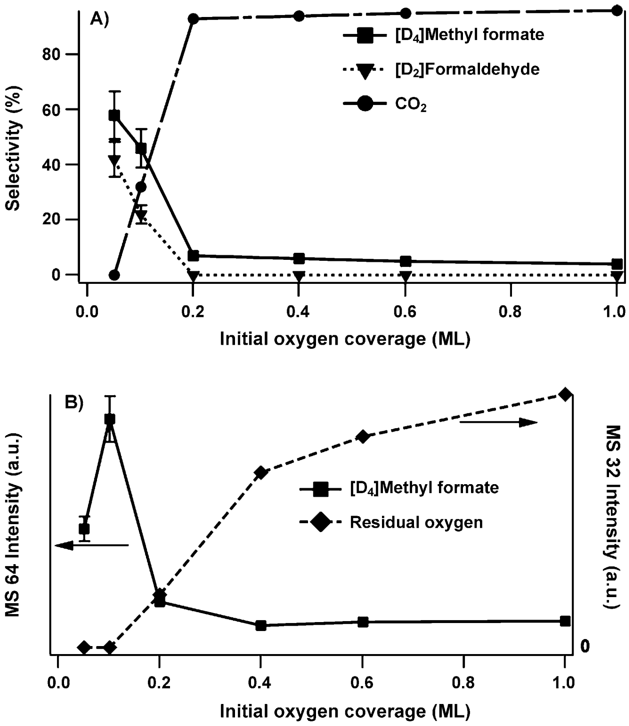

Figure 4. A) Product distribution of oxidative coupling of CD_3OH on $O/Ag_{0.4}Au_{0.6}$ ($\theta_O = 0.1$ ML) as a function of initial oxygen coverage. B) Absolute amount of methyl [D$_4$]formate formed and residual oxygen as a function of initial oxygen coverage.

At higher O coverages the methyl formate and formaldehyde yields diminish, whereas CO_2 increases. Coverages ≤ 0.05 ML clearly favor partial oxidation.

The kinetics for methyl formate evolution reflects the distribution of the sites available on the alloy film. When the reaction is carried out on surfaces ranging from pure Au to pure Ag ($\theta_O = 0.1$ ML), methyl formate is formed at three distinct temperatures (Figure 5 A). The gold- and grey-hatched areas in Figure 5 A are attributed to the contributions form self-coupling on O/Au(111) and O/Ag(111), respectively. On $Ag_{0.15}Au_{0.85}$, approximately 75 % of the methyl formate evolves around 210 K and can be attributed to reaction on Au-like sites.[3,12] The methyl formate formed near 260 K, which accounts for approximately 25 % of the total methyl formate production, is attributed to reaction at mixed Ag/Au, because it is evolved about 90 K lower than on Ag(111). The percentage of coupling due to mixed sites increases with the molar fraction of Ag in the alloy (Figure 5 B), and the contribution from Au sites decreases correspondingly. Only a very small amount of methyl formate evolves from Ag-like sites, even at the highest Ag concentration in the alloy surface ($Ag_{0.6}Au_{0.4}$ (< 1 %)), and no detectable amount was observed for alloys with lower Ag contents. Ester formed from mixed sites is the dominant route on $Ag_{0.6}Au_{0.4}$. The yield for methyl formate increases with the Ag content, the amount of methyl formate produced on $O/Ag_{0.6}Au_{0.4}$ being 50 % higher than that on O/Au(111) (θ_O = 0.1 ML in both cases).

The oxygen-assisted coupling proceeds through the reaction of the adsorbed methoxy intermediate with formaldehyde

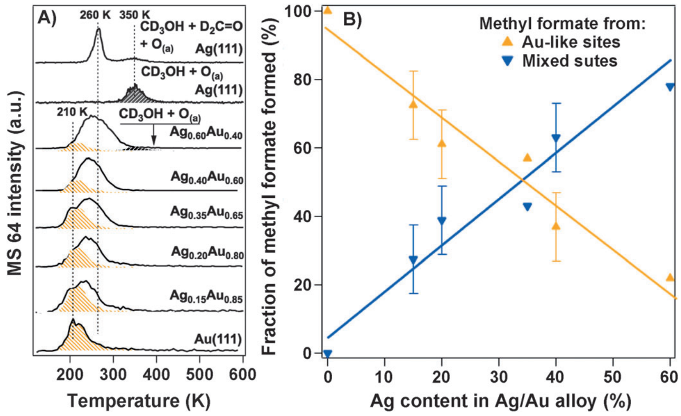

Figure 5. A) Self-coupling of methanol on atomic-oxygen-covered ($\theta_O = 0.1$ ML) Au(111), Ag(111), and Ag/Au surface alloys with various Ag contents. Cross-coupling between co-adsorbed methanol and formaldehyde on atomic-oxygen-covered Ag(111) ($\theta_O = 0.1$ ML). B) Percentage of methyl [D$_4$]formate attributed to self- and cross-coupling, as well as the total yield of methyl [D$_4$]formate as a function of Ag content in the Ag/Au alloy. Atomic oxygen on Ag(111) is introduced by NO$_2$ exposure at 500 K. Atomic oxygen on Au(111) and Ag/Au surface alloys was introduced by ozone exposure at 200 K. All chemicals were introduced to the surface at 150 K.

when it is formed by β-H elimination from methoxy itself.[12] It is thus possible that β-H elimination on Au-like sites, which proceeds at lower temperature than on Ag(111), could releasing formaldehyde to react with methoxy adsorbed on Ag-like or mixed sites. To test this possibility, adsorbed methoxy and formaldehyde were reacted on Ag(111) by co-adsorbing methanol and formaldehyde on at 0.1 ML oxygen coverage (Figure 5 A). The oxidative coupling reaction between co-adsorbed methanol and formaldehyde occurred at approximately 260 K on O/Ag(111), which corresponds to the temperature attributed to methyl formate formation at mixed sites on the alloy, supporting this suggestion.

CO$_2$ also appears to be produced from different types of surface sites. When the initial oxygen coverage on Ag$_{0.4}$Au$_{0.6}$ is increased, its formation progresses from a pathway characteristic of clean Ag(111) to that of clean Au(111), exhibiting formation via mixed states at intermediate coverage (Figure 6). The low temperature peak for CO$_2$ at approximately 330 K, appearing at initial oxygen coverages below 0.4 ML (gold shade, Figure 6 d–f), lines up with that on Au(111), and is therefore attributed to combustion occurring on Au-like sites. The high-temperature-desorption feature at approximately 405 K at initial oxygen coverage >0.2 ML is similar to that on Ag(111) (grey shade, Figure 6 b–e) and is attributed to Ag-like site-mediated combustion. Mixed sites are proposed to be responsible for the CO$_2$ at approximately 375 K, because the desorption temperature is in between that on the pure Au and Ag surfaces (unshaded area, Figure 6 a–g).

Discussion

Based on the XPS measurements, no detectable enrichment of Ag occurs in the in Ag/Au thin film alloy upon the adsorption of atomic oxygen. However, XPS measurements have limited sensitivity for the distribution of Ag and Au within the top layers of the alloy surface. According to a simple estimate assuming only the top two layers of metal atoms are involved in alloying (procedure is shown in the Supporting Information), only changes of Ag percentage that are greater than 25 % can be detected by XPS measurements. For example, a change of Ag percentage from 100 and 0 % (in the first and second layer, respectively) to 75 and 25 % due to oxygen adsorption will be indistinguishable. Therefore, slight surface enrichment of Ag into the top layer cannot be ruled out based on the current results.

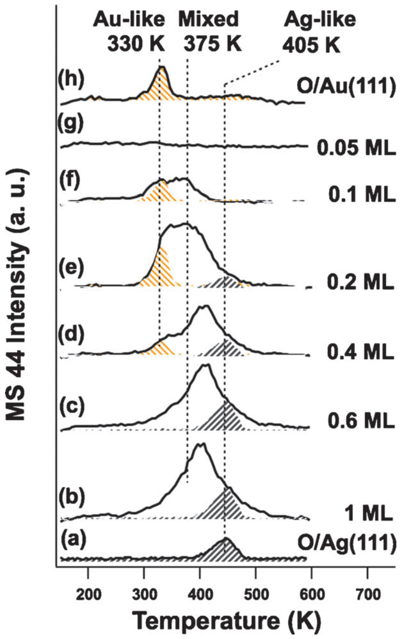

Figure 6. CO$_2$ production in the self-coupling of methanol on a) O/Ag (111) ($\theta_O = 0.1$ ML), O/Ag$_{0.4}$Au$_{0.6}$ with initial oxygen coverages of b) 1, c) 0.6, d) 0.4, e) 0.2, f) 0.1, and g) 0.05 ML, and h) O/Au(111) ($\theta_O = 0.1$ ML). The gold- and grey-shaded areas represent contributions of CO$_2$ formation from Au-like and Ag-like sites, respectively.

The Au (4f$_{7/2}$) peak at 85.5 eV and the Ag (3d$_{5/2}$) peak at 367.2 eV observed upon adsorption of atomic oxygen ($\theta_O =$ 1 ML) on Ag$_{0.4}$Au$_{0.6}$ at 200 K indicate the presence of oxidized Au and Ag species.[22, 23] The amount of oxidized Ag is approximately four times as much as that of Au at 200 K, suggesting that the surface oxide of Ag is more stable than Au (Table S1 in the Supporting Information). Also, because the oxygen coverage is near saturation, the higher amount of oxidized Ag suggests some preferential accumulation of Ag into the topmost layer, assuming that the oxygen cannot diffuse into the surface at 200 K. The fractions of oxidized Ag and Au grow from 29 and 7 % at 200 K to 45 and 13 %, respectively, after annealing the surface to 440 K, indicating further restructuring of the surface with annealing in the presence of oxygen, though annealing may allow atomic oxygen to diffuse into the surface or to form agglomerates of surface oxide.

Previous experimental and computational studies showed that atomic oxygen and surface intermediates, such as methoxy, prefer to adsorb on threefold hollow sites,[27] suggesting the local environment of the threefold sites could play a critical role in mediating surface reactions. The distribution of the three types of surface sites can be semi-quantitatively predicted by a three-atom model, in which Au-like, mixed and Ag-like sites are defined as having 3, 1–2, and 0 neighboring Au atoms, respectively. The fraction of surface sites attributed to Au-like, mixed and Ag-like can be computed statistically assuming a random distribution of surface Ag and Au atoms (Figure 7 A, open symbols). The percentage of mixed sites estimated by deconvoluting the oxygen desorption profiles from the alloy surfaces at constant initial oxygen coverage is also shown in Figure 7 A ($\theta_O = 1$ ML; see also Figure S1 in the Supporting Information), and the agreement is excellent.

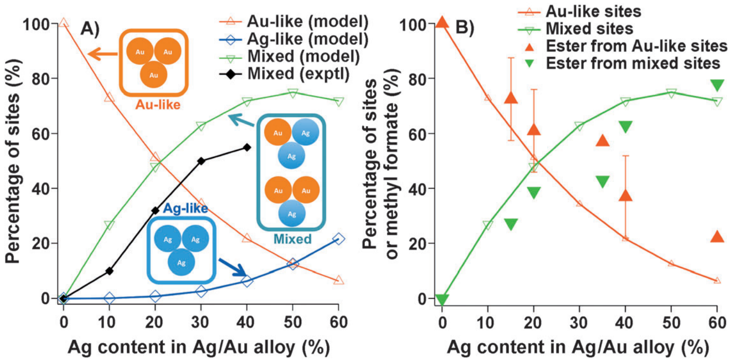

Figure 7. A) Percentages of Au-like, mixed and Ag-like sites (open orange, green, and blue symbols) as a function of Ag content in the Ag/Au alloy predicted from the three-atom model. The percentage of mixed sites was obtained by deconvoluting the oxygen-desorption profiles in Figure S1 (in the Supporting Information; black solid symbols). B) Comparison of the percentage of methyl formate formed at 210 and 260 K (solid red and green symbols) with the distribution of surface sites.

The distribution of the three types of surface sites calculated from the three-atom model also correlates well with the amount of methyl formate evolved in the three reaction routes (Figure 7 B). This match indicates the assumption that local composition of the threefold sites largely determines their reactivity is a good approximation. Furthermore, only one Ag atom in three atoms surrounding a threefold site appears to be sufficient to convert it from Au-like to a mixed site.

The higher evolution temperature of methyl formate from mixed sites compared to Au-like sites could be due to the enhanced stability of methoxy thereon. The rate-determining step for the oxidative coupling of methanol on O/Au(111) is β-H elimination of methoxy to form formaldehyde, consistent with the fact that reacting formaldehyde with pre-adsorbed methoxy leads to the formation of methyl formate at significantly lower temperatures than methanol self-coupling on both O/Au(111)[7] and Ag(111) (Figure 5 A). Therefore, in the absence of an external source of formaldehyde, the stability of methoxy with respect to β-H elimination determines the formation temperature of formaldehyde, and in turn, methyl formate. It is likely that the stability of methoxy on mixed sites lies between that on the pure Au and Ag surfaces, leading to an intermediate temperature at which formaldehyde, and hence methyl formate, is formed. This temperature gradually increases when the Ag molar fraction rises in the alloy, demonstrating that the stability of methoxy on the mixed sites can be tuned over a wide range.

In addition, the higher temperature of methyl formate formation from the mixed sites indicates that the mobility of methoxy adsorbed on the mixed is limited at the temperatures over which this reaction occurs, consistent with it being more strongly bound at the mixed sites. Otherwise, methoxy bound to the mixed sites would migrate to Au-like sites and form methyl formate at the same temperature as Au-like sites. In contrast, the weak interaction between formaldehyde and both Au[28] and Ag[26] suggests formaldehyde formed on Au-like sites migrates to nearby mixed sites to react with methoxy. It is not until the formaldehyde from Au-like sites is depleted that the slower β-H elimination on mixed sites commences.

Additionally, mixed sites are able to directly activate the β-C–H bonds in $CH_3O_{(a)}$, leading to higher yield of methyl formate. The fact that D_2 is formed along with [D_2]formaldehyde and methyl [D_4]formate (Figure 3) when CD_3OH reacts on O/$Ag_{0.4}Au_{0.6}$, is clear evidence for the surface-assisted β-C–D bond activation. Because hydrogen evolution is never observed in these reactions on Au(111)[12] but is on Ag(110),[25,26] surface-assisted C–H bond activation apparently occurs on mixed sites. The increase in yield for methyl formate with the Ag content in the alloy could be attributed in part to the extra formaldehyde formed via surface-assisted β-H elimination of methoxy. The ability of the Ag-modified surface to facilitate direct β-H elimination of methoxy hemiacetal to methyl formate and H2 is also likely to be another pathway leading to the increased yield of methyl formate.

Conclusion

Atomic-oxygen-covered Ag/Au thin film alloys selectively mediate oxidative coupling of methanol to methyl formate at low temperature. Surface sites on an Ag/Au alloy can be classified into Au-like, Ag-like, and mixed sites, with Au- and Ag-like sites exhibiting reactivity characteristic of Au(111) and Ag(111), respectively. The kinetics of recombination of adsorbed atomic oxygen and of the oxidative coupling of methanol from mixed active sites of Ag/Au reflect the modification of the reactivity of metallic gold due to stabilization of the atomic oxygen and methoxy, respectively, by local coordination to Ag. The relative surface concentrations of the Au-like and mixed sites calculated from a simple statistical model correlate semi-quantitatively with the conversion to methyl formate.

Experimental Section

All experiments were performed in an ultrahigh-vacuum (UHV) chamber with a base pressure below 2×10^{-10} Torr. The preparation of the clean Au(111) surface has been described elsewhere.[29] Thin films of Ag/Au alloys were prepared by physical vapor deposition (Omicron EFM 3 metal evaporator) of Ag atoms onto Au(111) at

200 K, followed by annealing to 650 K for 10 min to allow the mixing of Ag and Au atoms.

The composition of the surface alloy was monitored by calculating the relative ratio of the integrated area of Ag ($3d_{5/2}$) and Au ($4f_{7/2}$) peaks (corrected for the atomic sensitivity factors of Ag and Au) in the X-ray photoelectron spectrum taken immediately after preparation. The surface compositions obtained by this method are average values for the first 4–6 atomic layers, estimated from the electron-escape depths for Ag and Au (10–20 Å) estimated based on the kinetic energies of the Au(4f) and Ag(3d) photoelectrons created with the $Mg_{K\alpha}$ radiation used in our experiments. We refer to the Ag/Au surface alloy as Ag_xAu_{1-x}, with x being the molar fraction of Ag in the alloy thin film.

Atomic oxygen was introduced to Au(111) and Ag/Au surface alloy by ozone exposure at 200 K, because O_2 does not dissociate on the alloy surfaces within the range of composition studied in this work under the conditions of our experiments (up to 1200 L of O_2 dose within the temperature range of 200–400 K). There is no measurable dissociation of O_2 on either pure Ag(111) or Au(111) under the conditions of our experiments, consistent with the absence of O_2 activation on the alloy films.

The oxygen-atom coverage was calibrated by comparing the amount of O_2 evolution in temperature-programmed reaction to that formed for a saturation coverage of oxygen atoms on clean Au(111), which is 1.1 ML.[30] Variations in oxygen coverage of $\pm 15\%$ are expected due to the day-to-day variation in O_3 concentration of the ozone source. Atomic oxygen was deposited on Ag(111) by exposing the surface to NO_2 at 480 K.[31] We refer to the atomic-oxygen-covered Au(111), Ag(111), and Ag/Au alloy surfaces as O/Au(111), O/Ag(111), and O/Ag_xAu_{1-x}, respectively.

Temperature-programmed reaction experiments were conducted according to well-established protocols, which are described in detail elsewhere.[29] Regardless of the temperature at which reactants were dosed, the surface was cooled to 120 K before collecting reaction data. The heating rate for all temperature-programmed experiments was nearly constant at $5\ K s^{-1}$ up to the maximum surface temperature of 600 K, chosen to minimize changes in the alloy composition at the surface with heating. No change in the Ag/Au ratio was detected after temperature-programmed reactions.

The reaction products were identified by quantitative mass spectrometry (Hiden HAL/3F) by using fragmentation patterns obtained from authentic samples, which were found to be in good agreement to NIST reference data (see the Supporting Information).[32] The detailed protocol for quantitative analysis is described in detail elsewhere.[33]

Methanol and formaldehyde were introduced to surfaces at 150 K in all experiments. A directed doser with an enhancement factor of approximately 50 was used. Exposures, calculated from background pressure and corrected for the enhancement factor, are given in units of Langmuir [L]; one Langmuir corresponds to the equivalent of a dose of 1×10^{-6} torr sec. These exposures were not corrected for relative ionization efficiencies in the ion gauge. Unless otherwise noted, 6 L was the typical dose for organic molecules.

X-ray photoelectron spectra were acquired with an analyzer passing energy of 17.9 eV and a multiplier voltage of 3 kV by using $Mg_{K\alpha}$ X-rays (1253.6 eV, 300 W) as the excitation source. The binding-energy (BE) calibration was referenced to the Au ($4f_{7/2}$) peak at 83.9 eV. The XPS peaks were fitted after the Shirley background was subtracted. The relative ratios of the integrated area of Ag ($3d_{3/2}$) versus Ag($3d_{5/2}$), and Au($4f_{5/2}$) versus Au($4f_{7/2}$) was fixed to 2:3 and 3:4, respectively, due to the spin–orbit coupling effect. The Ag (3d), Au (4f), and O (1 s) spectra were accumulated with 10, 10, and 100 scans, respectively, to enhance the signal-to-noise ratio. The composition of the alloy film was calculated from the measured XPS intensities.

Acknowledgements

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Keywords: alloys · gold · mixed sites · oxidative coupling · silver

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FULL PAPER

Bimetallic Catalysis

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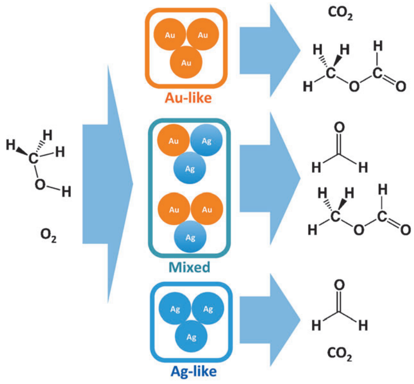
Ag/Au Mixed Sites Promote Oxidative Coupling of Methanol on the Alloy Surface



Activation and promotion: Au/Au mixed sites promotes selective oxidation of methanol to formaldehyde and methyl formate without producing any CO_2 (see scheme).