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Role of Surface-Bound Intermediates in the Oxygen-Assisted Synthesis of Amides by Metallic Silver and Gold

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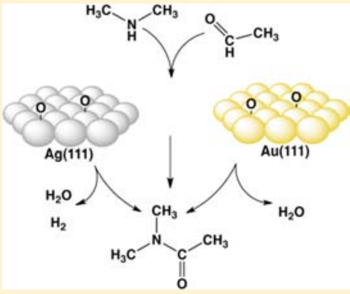
Ⓢ *Supporting Information*

ABSTRACT: A general mechanism for the oxygen-assisted synthesis of amides over metallic gold and silver surfaces has been derived from the study of acetaldehyde and dimethylamine in combination with previous work, allowing detailed comparison of the two surfaces' reactivities. Facile acetylation of dimethylamine by acetaldehyde occurs with high selectivity on oxygen-covered silver and gold (111) crystals via a common overall mechanism with different rate-limiting steps on the two metals. Adsorbed atomic oxygen activates the N−H bond of the amine leading to the formation of an adsorbed amide, which attacks the carbonyl carbon of the aldehyde, forming an adsorbed hemiaminal. Because aldehydes are known to form readily from partial oxidation of alcohols, our mechanism also provides insight into the related catalytic coupling of alcohols and amines. The hemiaminal β-H eliminates to form the coupled amide product. On silver, β-H elimination from the hemiaminal is rate-limiting, whereas on gold desorption of the amide is the slow step. Silver exhibits high selectivity for the coupling reaction for adsorbed oxygen concentrations between 0.01 and 0.1 monolayer, whereas gold exhibits selectivity more strongly dependent on oxygen coverage, approaching 100% at 0.03 monolayer. The selectivity trends and difference in rate-limiting steps are likely due to the influence of the relative stability of the adsorbed hydroxyl groups on the two surfaces. Low surface coverages of oxygen lead to the highest selectivity. This study provides a general framework for the oxygen-assisted coupling of alcohols and aldehydes with amines over gold- and silver-based catalysts in either the vapor or the liquid phase.



1. INTRODUCTION

Oxidative coupling reactions, including production of amides from amines, are among the most important industrial chemical processes. Traditionally, amides are synthesized from carboxylic acids and amines, often by activating the acid to an acyl chloride, which generates HCl waste.[1] Other processes also produce toxic waste; thus there has been a recent surge in research toward simple, green amide production.[2−9] The ease and simplicity of dimethylacetamide production over metallic gold or silver reported here suggest that these noble metals, and alloys therefrom, may be effective catalysts for greener chemical synthesis of amides.

Silver is an established industrial catalyst for the selective oxidation of methanol to formaldehyde[10] and for the epoxidation of ethylene, while gold has recently shown exciting promise for many selective oxidation and coupling processes.[11,12] N-Alkylation of primary amines with alcohols has been reported over both gold[13,14] and silver[15] supported nanoparticles. In addition, there are previous reports of alcohol coupling on metallic silver[16,17] and of alcohol coupling with amines to form amides on single crystal surfaces of gold.[18] Further, direct acylation of dimethylamine with formaldehyde occurs on oxygen-covered Ag(111)[19] and Au(111)[20] surfaces; silver and gold nanoparticles also catalyze amide formation from nitrile oxidation[6] and the coupling of alcohols and amines.[5,7,8]

Establishing reactivity patterns on the surfaces of catalytic metals is a crucial step in the rational design of novel catalytic pathways for chemical production. Usually, the best catalyst for a given reaction is found empirically. Ideally, however, patterns of reactivity would allow a rational choice of catalyst. To evaluate the relative merits of catalytic noble metals, as well as enable rational design of potential alloy systems, a deeper understanding of the mechanism and kinetics of coupling reactions on each surface is vital.

In this work, we identify the elementary steps comprising the mechanism of the reaction, determine the rate-limiting steps on both silver and gold, and take the first step toward generalizing the mechanism for this class of coupling reactions on these noble metals. We observe the highly selective oxygen-assisted coupling of acetaldehyde and dimethylamine to form dimethlyacetamide on the (111) surface of both silver and gold. The differences between metallic gold and silver for these reactions are critically compared, developing more subtle reactivity patterns of the two surfaces.

2. EXPERIMENTAL METHODS

Gold and silver were studied in two separate ultra high vacuum (UHV) chambers, each with a base pressure of 2×10^{-10} Torr. Clean Au(111) and Ag(111) were prepared with Ar^+ sputtering and

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annealing, as well as cleaning with oxidation cycles. On Au the initial surface concentration of adsorbed atomic oxygen was reproducibly varied by dosing a controlled flux of ozone.[21] On Ag adsorbed oxygen was prepared by dosing a controlled flux of NO_2 at 500 K.[22] The exposures reported here in Langmuirs ($1\ L = 1 \times 10^{-6}$ Torr s) take into account an enhancement factor of 100 due to direct dosing, which was estimated by taking into account the geometry of the system and previous measurements of the enhancement factor by the group. Temperature programmed reactions were conducted with well-established protocols.[23] The reaction products were identified by quantitative mass spectrometry (Ag, Prisma QMS 200; Au, Hiden HAL/3F) using fragmentation patterns obtained from authentic samples, unless otherwise stated.

Because prior studies have shown that low oxygen coverage increases the selectivity for coupling product between alcohols,[24,25] alcohols and aldehydes,[26] and formaldehyde and dimethylamine,[19,20] we focus here on low oxygen coverages.

It should be noted that the observed differences in reactivity between silver and gold are not due to the oxygen preparation techniques (NO_2 on silver, O_3 on gold). This was confirmed by using O_3 to prepare the oxygen on silver. The reaction results (not shown) were in agreement with the NO_2 data, so the NO_2 technique was used on silver for its high precision and reproducibility.

Selectivity for the dimethylacetamide product is calculated with respect to amine-derived products, using quantitative mass spectrometry analysis.[24] The selectivity does not include oxidation of the aldehyde. It also does not include reformation of the dimethylamine, which is small and difficult to quantify due to overlap with desorption of the reactant dimethylamine.

3. RESULTS

3.1. Dimethylamine (DMA) and Acetaldehyde on $O_{(a)}$ Covered Au(111) and Ag(111). No reaction of dimethylamine and acetaldehyde occurred on the clean Au(111) surface; however, prior adsorption of atomic oxygen led to dimethylacetamide ($(CH_3)_2N{-}C({=}O)CH_3$) formation. Dimethylamine was dosed onto approximately 0.1 ML of adsorbed O at 150 K to form adsorbed dimethylamide.[20] Subsequent dosing of acetaldehyde and heating at 5 K/s yielded several products, including the coupling product, dimethylacetamide, which evolved at 250 K by a desorption-limited process (Figure 1a). Water evolved between 200 and 300 K, but, except for a gradual rise in pressure near 600 K, no hydrogen evolution was detected. Methylimine ($CH_3N{=}CH_2$), methylformamide ($CH_3NHC({=}O)H$), and methylisocyanate ($CH_3N{=}C{=}O$), originating from the oxidation of dimethylamine ($(CH_3)_2NH$), evolved at 255, 300, and 415 K, respectively, with methylimine being the dominant product. We deduced the identity of methylimine by its mass fragmentation and the previous reports of imine formation by oxidation of amines on gold.[7,27] There is, however, the lesser possibility that the product could be the cyclic amine of the same mass, ethylenimine. Significantly, products characteristic of acetaldehyde oxidation via an acetate intermediate (acetic acid, ketene, CO_2[25]) were not detected. On the basis of the peak temperature of the desorption profile, the upper bound to the activation energy for dimethylacetamide and methylimine evolution is 73 kJ/mol, assuming first-order kinetics and a pre-exponential factor of 10^{15}.[28] The selectivity for dimethylacetamide formation increased to nearly 100% when the initial oxygen coverage was lowered to 0.03 ML, in sharp contrast to the selectivity observed at 0.1 ML O, where the oxidative dehydrogenation of dimethylamine to methylimine dominated.

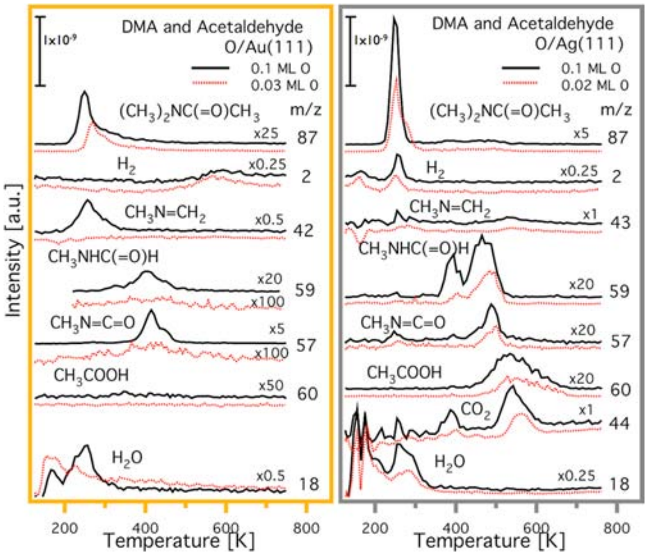


Figure 1. Temperature programmed reaction spectra of (a) dimethylamine and acetaldehyde dosed sequentially (1.5 L) at 150 K on 0.1 and 0.03 ML O/Au(111), and (b) dimethylamine and acetaldehyde dosed sequentially (1.5 L) at 125 K on 0.1 and 0.02 ML O/Ag(111). On each surface, dimethylamine and acetaldehyde couple to form dimethylacetamide, along with secondary oxidation products. Molecular desorption of the reactants dimethylamine and acetaldehyde occurs around 200 K but is not shown here. The contribution of dimethylacetamide, acetaldehyde, and dimethylamine to the $m/z = 44$ trace is subtracted to see the CO_2 product. No CO_2 was observed on gold.

Dimethylamine and acetaldehyde also couple facilely on O/Ag(111), but with significant differences. Following a procedure similar to that with Au(111), we observed dimethylacetamide at 250 K with 80% selectivity (Figure 1b) for an initial oxygen coverage of 0.1 ML. Methylimine formation is not significant, and there is less dependence of the selectivity on the initial oxygen coverage. Water and hydrogen evolve coincident with dimethylacetamide, whereas there was no hydrogen evolution on gold. The water and hydrogen evolve from the rate-limiting step for production of dimethylacetamide, which is β-H elimination from the hemiaminal intermediate precursor, rather than desorption of the amide (see section 3.2).

Although the dominant product on Ag(111) remains dimethylacetamide for all oxygen coverages studied, the route to secondary oxidation is clearly more diverse on Ag(111) than on Au(111). Methylformamide (375−500 K), CO_2 (400 K), and methylisocyanate (500 K) form from the oxidation of dimethylamine;[29] acetic acid (450−650 K), CO_2 (500 K), and ketene (coincident with acetic acid, not shown) form from acetaldehyde oxidation.[30]

Secondary oxidation of the amine is suppressed on silver by using d_6-dimethylamine. Because of the difference in zero point energy, the C−D bond is stronger than a C−H bond, which will result in a kinetic isotope effect if there is significant C−H bond breaking in the transition state. At 0.01 ML oxygen coverage, the adsorbed amide[31] intermediate $(CD_3)_2N_{(a)}$) does not undergo secondary oxidation, demonstrating that C−H(D) bond breaking is clearly important in limiting the secondary oxidation pathway. Coupling of d_6-dimethylamine with acetaldehyde on 0.01 ML O/Ag yields d_6-dimethylacetamide at 285 K without secondary oxidation of the adsorbed amide (Figure 2). While a small amount of CO_2 is present at 550 K due to oxidation of the acetaldehyde, neither of the amine oxidation products, methylformamide (m/z 64) or methyl-

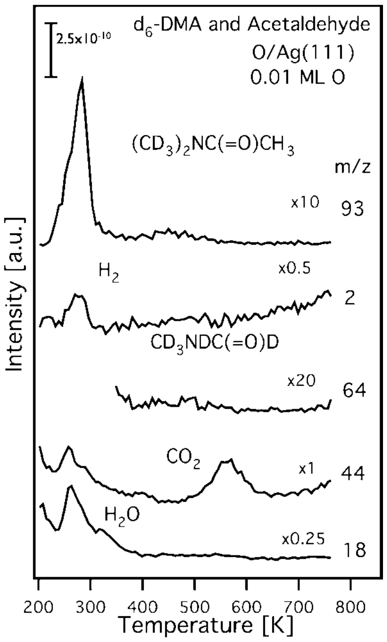


Figure 2. Temperature programmed reaction spectra of d_6-dimethylamine and acetaldehyde dosed sequentially (1.5 L) at 125 K on 0.01 ML O/Ag(111). The reactants couple to form dimethylacetamide, and secondary oxidation of the amine is eliminated. Molecular desorption of the reactant d_6-dimethylamine occurs at 170 K but is not shown here. m/z 64 was present at low temperature due to contamination of the acetaldehyde, so it was removed.

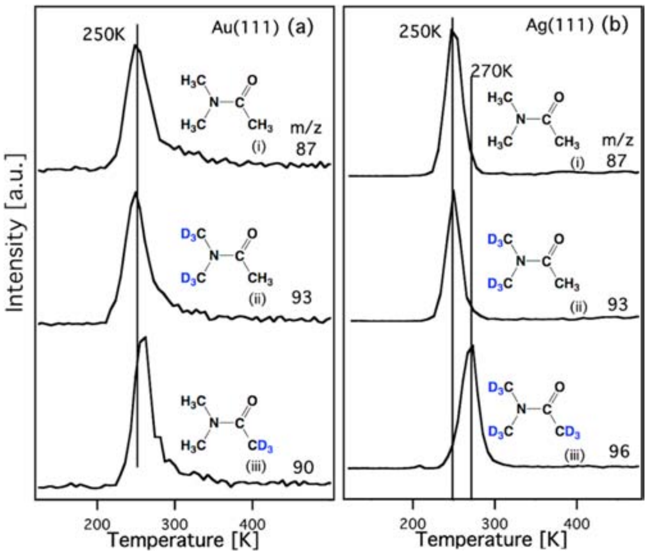


Figure 3. (a) Dimethylamine and acetaldehyde (1.5 L) were dosed sequentially at 150 K on 0.05 ML O/Au(111) with the following isotopic labels: (i) d_0-dimethylamine and d_0-acetaldehyde, (ii) d_6-dimethylamine and d_0-acetaldehyde, and (iii) d_0-dimethylamine and d_4-acetaldehyde. (b) Dimethylamine and acetaldehyde (1.5 L) were dosed sequentially at 125 K on 0.1 ML O/Ag(111) with the following isotopic labels: (i) d_0-dimethylamine and d_0-acetaldehyde, (ii) d_6-dimethylamine and d_0-acetaldehyde, and (iii) d_6-dimethylamine and d_4-acetaldehyde. Peaks are scaled to the same size to see differences in peak shape and temperature.

isocyanate (m/z 60), is observed. (Traces of m/z 60 were detected but were too small to be quantified.)

As the initial oxygen coverage was decreased from 0.1 to 0.01 ML on the silver surface, the overall yield decreased. Also, although the rate-limiting step appears to remain the same, the dimethylacetamide peak shifted to higher temperature, forming an additional peak approximately 30 K above the peak seen initially for an oxygen coverage of 0.1 ML (Figure S1a,b). The same effect occurs for desorption of the neat product at low coverages (Figure S2).

3.2. Isotopic Labeling: Product Identity and the Kinetic Isotope Effect.

Isotopic labeling of the reactants was used to confirm the identity of the coupling product on both O/Au(111) and O/Ag(111). Reacting d_0- and d_6-dimethylamine with d_0-acetaldehyde yielded d_0-dimethylacetamide (m/z = 87) and d_6-dimethylacetamide (m/z = 93), respectively. This increase in mass confirms that all six C−D bonds in dimethylamine are retained in the dimethylacetamide product. Reacting d_0- and d_6-dimethylamine with d_4-acetaldehyde produced d_3-dimethylacetamide (m/z = 90) and d_9-dimethylacetamide, (m/z = 96), respectively (Figure 3), clearly showing that one of the hydrogens in acetaldehyde is lost in forming the coupled product.

A kinetic isotope effect for the rate-liming step was clearly observed on Ag(111) but not Au(111). On the gold surface, the slight shift in the peak temperature observed with d_4-actetaldehyde in place of d_0-acteldehyde was within the experimental reproducibility of the measured peak temperature (±5 K) and temperature shift due to slightly lower coverage on the surface, which is determined by the oxygen coverage (±10%, Figure 3a). Further, no shift in peak temperature for dimethylacetamide was observed when reacting d_6-dimethylamine (as compared to d_0-dimethylamine) with d_0-acetaldehyde on either surface. However, the reproducible shift of 20 K observed on silver when using d_4-acetaldehyde in place of d_0-acteldehyde is indicative of a kinetic isotope effect for the formation of dimethylacetamide.[19,32] This difference indicates clearly that the rate-limiting step on silver is loss of a hydrogen from the carbonyl carbon originally associated with the aldehyde.

The absence of a clear kinetic isotope effect on Au(111) suggests that the production of dimethylamide is desorption limited (Figure 3a). As an independent test, d_0-dimethylamine, d_4-acetaldehyde, and d_0-dimethylacetamide were coadsorbed on 0.05 ML O/Au(111) prior to the temperature programmed reaction. The temperatures of evolution of the d_3-dimethylacetamide formed in the coupling reaction and d_0-dimethylacetamide initially adsorbed on the surface were identical to within experimental uncertainties (Figure S3), confirming that this product is desorption-limited on Au(111).

4. DISCUSSION

4.1. General Reaction Mechanism.

Oxygen adsorbed on coinage metals exhibits patterns of reactivity that provide guidelines for predicting new reaction sequences.[33] In particular, adsorbed oxygen acts as a Brønsted base toward gas-phase acids and also exhibits strong nucleophilicity. Prior studies show that adsorbed atomic oxygen activates O−H, C−H, and N−H bonds in a variety of molecules, a guiding factor being their gas-phase acidities. In this activation process, water is released, and the conjugate base of the acid is bound to the surface and itself can act as a nucleophile. For example, the O−H bond in alcohols is readily activated to water and surface-bound alkoxy. This adsorbed alkoxy group nucleophilically attacks the electron-deficient carbon in aldehydes to form the corresponding esters via an adsorbed hemiacetal.[16,26] The reactive coupling between the dimethylamine and acetaldehyde reported here was anticipated from these principles, illustrating their predictive utility.

On both silver and gold surfaces adsorbed atomic oxygen is essential for initiating the sequence leading to coupling. The adsorbed oxygen activates N−H bonds in amines[34,35] and ammonia[36,37] on the group 1B metals to form adsorbed amides. We predicted, by analogy with reactivity of the adsorbed alkoxy, that the adsorbed amide would react as a nucleophile toward an aldehyde to form a hemiaminal, which would subsequently undergo β-H elimination to form an amide product. This reaction pathway was initially verified by coupling dimethylamine and formaldehyde to form dimethylformamide with high selectivity on the oxygen-activated (111) surface of silver and gold under controlled conditions in ultra high vacuum.[19,20]

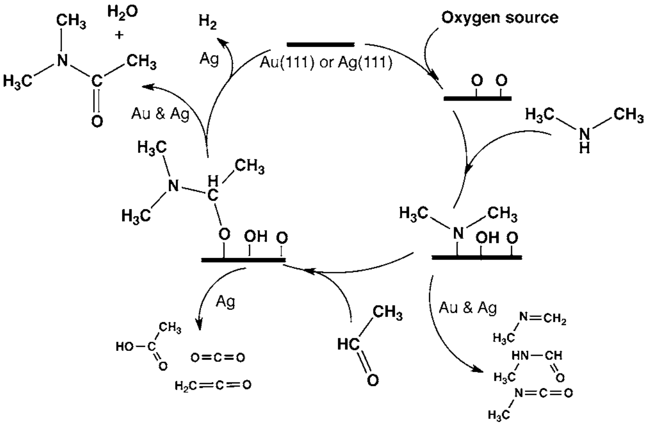
The results reported here indicate that the mechanism for the reaction between secondary amines and aliphatic aldehydes is general on oxygen-activated metallic gold and silver. The complexity introduced by the alkyl functionality in the acetaldehyde appears to be primarily the competing oxidation pathways not found with formaldehyde.

The mechanism for dimethylacetamide formation on Ag(111) can be deduced from isotope experiments (Figures 3a and S1). The temperature shift observed when using d_4-acetaldehyde in place of d_0-acetaldehyde is as expected for C−H versus C−D bond cleavage on metal surfaces.[32] A similar kinetic isotope effect was also observed for dimethylamine and formaldehyde coupling on this surface.[19] The kinetic isotope effect shows that the C−D bond breaking from the carbonyl carbon is rate-limiting. Furthermore, deuterium and dimethylacetamide evolve at the same temperature, which indicates they are produced from the same intermediate (Figure S1b). Therefore, β-H elimination from a hemiaminal intermediate appears to be the rate-limiting step. We conclude that the reaction mechanism is identical on both gold and silver, but is reaction-limited on silver and desorption-limited on gold. The fact that the β-H elimination must happen at a lower temperature on gold than silver (because the product evolves at 250 K on both surfaces, but is desorption limited on gold) indicates that the β-H elimination from the hemiaminal is more facile on gold. We postulate that greater ease of β-H elimination from the hemiaminal on gold suggests that the adsorbed O aids in the β-H elimination on gold, but on silver, the β-H elimination is surface-mediated (see section 4.2).

This mechanism, along with differences between the reaction on silver and gold, is depicted in Scheme 1. The coupling between dimethylamine and aliphatic aldehydes on gold occurs by (a) amine activation by $O_{(a)}$ to form the surface-bound amide, (b) nucleophilic attack of the adsorbed amide on the electron-deficient aldehydic carbon accompanied by rearrangement to form a surface-oxygen bond, (c) β-H elimination from a hemiaminal intermediate to yield the dimethyl amide, and (d) product desorption.

These studies provide mechanistic insight into recently reported catalytic reactions on gold nanoparticles.[5,7,8,27] Angelici et al.[27] observed formation of imines over both alumina-supported gold and bulk gold powder. For cyclic and primary amines, they also observed the coupling product. They proposed that under the conditions of their experiments an imine first forms, which then couples with another amine. Our results suggest that this imine comes from an adsorbed amide intermediate. Christensen et al.[5] reported coupling in alcohol solution between alcohol and amines over a supported gold catalyst, which is consistent with the mechanism elucidated here: the alcohol first forms the alkoxy, which is known to eliminate H to yield the aldehyde; then the aldehyde can couple with an adsorbed amide. We have specifically demonstrated the coupling of methanol and dimethylamine on gold via this mechanism,[18] and, in general, aldehydes are known to form from partial oxidation of alcohols on both metallic gold and silver.[16,24,38,39]

Scheme 1. Direct Acetylation of Amines on Both Silver and Gold



Ishida and Haruta[7] reported N-formylation of amines in methanol solution over gold nanoparticles. They deduce a mechanism via aminolysis, where methlyformate is formed from the methanol over gold and then interacts with the amine to form the amide. To investigate whether this aminolysis pathway occurs in our studies, we condensed ethylacetate with dimethylamine on O/Ag(111), but did not detect any dimethylamide product (not shown). Thus, although this reaction may proceed in methanol solution, we conclude that this mechanism does not occur on the surface in our vapor-phase conditions.

In a comprehensive study, Kobayashi et al.[8] recently expanded the range of catalysts for the amine−alcohol coupling system using gold and gold/nickel,−iron,−cobalt nanoparticles. To explain the coupling process, they invoke a tandem oxidative process via a carbinolamine formed by reaction of the amine and an aldehyde (the aldehyde being produced by catalytic oxidation of the alcohol), which they suggest is then further catalytically oxidized to the amide. Their mechanism involves a series of steps with no specific recognition of the role of the surface, each step producing a molecular intermediate, the carbinolamine being the immediate precursor to the amide. However, the mechanism we describe in this Article is more direct, involves reactions on the surface dictated by clear principles of surface reactivity, and is entirely compatible with the reactions they observe. The adsorbed hemianimal we identify is the immediate precursor to the amide, not the carbinolamine. In fact, both the N−H and the O−H bond in the carbinolamine would be expected to be activated by oxygen on the gold surface, severely limiting the selectivity for amide production. The results presented here appropriately focus attention on the surface-bound reaction intermediates affected by the heterogeneous catalyst.

Overall, the partial oxidation and coupling reactions observed in solution-phase catalysis using molecular oxygen as the oxidant appear to follow the same acid−base reaction and coupling patterns as seen in our model studies using O-activated gold. To the best of our knowledge, no similar studies have been undertaken on metallic silver catalysts. In solution, the added dimension is the possibility of homogeneous reactions between an intermediate product and one of the reactants, as exemplified by others.[7]

4.2. β-H Elimination on Ag(111) and Au(111). On Ag(111), the rate-limiting β-H elimination from the hemiaminal intermediate appears to occur via reductive elimination to the silver surface, whereas on the gold surface it appears to be assisted by adsorbed oxygen, because H_2 is evolved from Ag(111) during amide evolution, whereas only water forms on Au(111) (Figure 1a,b). The water and hydrogen peaks from Ag(111) usually lag the dimethylacetamide by 5−15 K, indicating that the surface reactions involving the hydrogen are not instantaneous.[16] This fact suggests that on Ag(111) hydrogen is transferred to the surface, and then combines with $O_{(a)}$, $OH_{(a)}$, or $H_{(a)}$ to yield both hydrogen and water (if excess adsorbed oxygen is present). The absence of H_2 evolution observed on Au(111) for this reaction as well as in other oxidation and oxidative couping reactions on Au(111) involving β-H elimination[20,24,39] suggests that if there is excess oxygen, an oxygen-assisted β-H elimination pathway is favored on Au(111). To date, there are no conclusive experiments to prove this hypothesis, but experiments to examine these reactions in the absence of excess adsorbed oxygen are planned.

This role of adsorbed oxygen or OH in facilitating β-H elimination on gold is suggested by recent theoretical work, which demonstrates the thermodynamic favorability of direct H-transfer to adsorbed O or OH, forming OH or water, as opposed to H-transfer to the Au surface.[40,41] An alternative explanation is that in the presence of excess oxygen on gold, all released hydrogen immediately reacts to form water due to the high activation barrier for recombinative desorption of H_2 on Au.[42] Other factors such as the different structures of the adsorbed O on Ag(111) and Au(111) could also strongly influence the selectivity toward H_2 and H_2O. These factors remain to be studied.

The temperature at which β-H elimination from the hemiaminal occurs on silver is consistent with other, similar reactions (Table 1). Metallic silver is known to cleave β-C−H bonds from methoxy at 310 K[16] and from ethoxy at 285 K[38] in the low coverage limit, in general agreement with a decrease in activation energy with increasing carbon chain length. Similarly, for the hemiaminal precursor to dimethylformamide, β-H elimination takes place at 270 K,[19] whereas β-H elimination of the dimethylacetamide precursor occurs at 250 K (this work), indicative of a difference of approximately 5 kJ/mol in the activation energy. We attribute this difference to the presence of the methyl group in the latter case. The energy for β-H elimination decreases from a primary to secondary (alkoxys) or secondary to tertiary (hemiaminals) carbon. These β-H elimination reactions occur around or below room temperature, indicating that silver could be a facile low-temperature catalyst for these synthetic reactions, provided the buildup of more stable intermediates due to the secondary oxidation does not occur and block reactive sites.

Table 1. Temperatures and Activation Energies (by Redhead Analysis, Assuming a Pre-exponential Factor of $\upsilon = 10^{15}$)[28] for β-H Elimination from Similar Intermediates on Silver Surfaces

Intermediate on Ag	β-H bond cleavage T (E_a)	Reference
methoxy	310 K (90 kJ/mol)	16
ethoxy	285 K (83 kJ/mol)	38
dimethylformamide precursor	270 K (78 kJ/mol)	19
dimethylacetamide precursor	250 K (73 kJ/mol)	this work

The stoichiometry of the coupling reaction could be different for silver and gold catalysts depending on whether or not surface oxygen participates in β-H elimination, particularly at low oxygen coverages. For example, on Ag:

$$2(CH_3)_2NH + O_{(a)} + 2CH_3CHO \rightarrow 2(CH_3)_2NC(=O)CH_3 + H_2O + H_2 \quad (1)$$

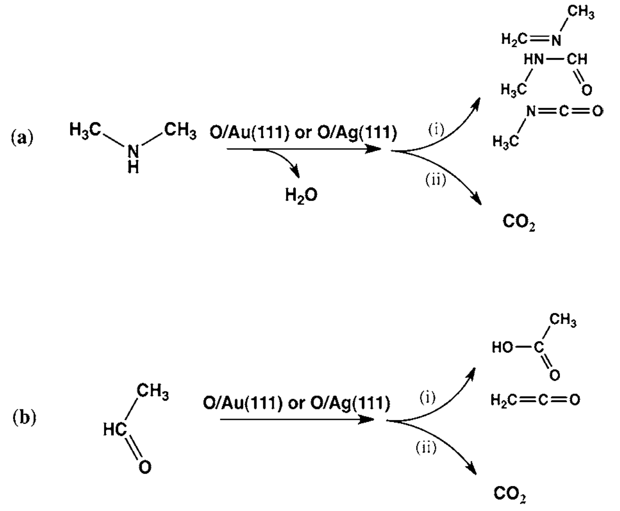
and on Au:

$$(CH_3)_2NH + O_{(a)} + CH_3CHO \rightarrow (CH_3)_2NC(=O)CH_3 + H_2O \quad (2)$$

This difference does not affect the yield of dimethylacetamide, although the percent conversion of dimethylamine would be affected under oxygen-limiting conditions.

4.3. Secondary Oxidation and Selectivity. Gold and silver exhibit distinct differences with regard to both the extent and the type of secondary oxidation. To appreciate the differences, we must first understand the secondary oxidation process for each reactant on both surfaces (Scheme 2).

Scheme 2. Oxidation Pathways for (a) Dimethylamine and (b) Acetaldehyde on Oxygen Activated Au(111) and Ag(111)[a]



[a](i) and (ii) designate more selective and less selective oxidation, respectively.

Both O/Ag(111) and O/Au(111) activate dimethylamine to form an adsorbed amide, which can dehydrogenate to methylimine or further oxidize to methylformamide, methylisocyanate, and, with excess oxygen, to CO_2.[18,29] (NO and N_2 would be expected products with higher oxygen coverage, but were not observed here.) Acetaldehyde reacts with O/Ag(111) or O/Au(111) to form adsorbed acetate, which leads directly to acetic acid and CO_2, as well as ketene.[25,30] Methane has also been previously reported[30] as a product of acetaldehyde oxidation on silver, but was not detected in this study.

The main differences in secondary oxidation during the coupling reaction are two-fold: (1) on gold, methylimine was the dominant amine oxidation product at both 0.1 and 0.05 ML O, but only occurred in trace amounts on silver; and (2) on silver, products of acetaldehyde oxidation were observed, but they were never detected on gold. The conspicuous absence of acetaldehyde oxidation on gold suggests that the acetate intermediate does not form or is formed reversibly under these conditions.

On gold, there is a dramatic change in selectivity with respect to conversion of the amine with oxygen coverage, favoring the coupling product at the lowest oxygen coverages (0.02 ML), but favoring methylimine at higher oxygen coverage (Figure 4).

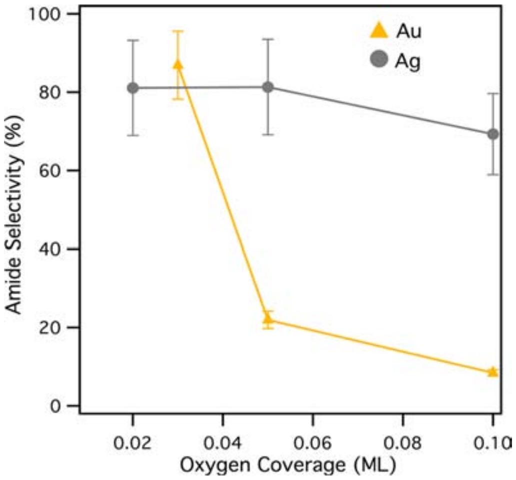


Figure 4. Selectivity toward dimethylacetamide with respect to the total amount of amine-derived products on O/Au and O/Ag. Not included in this calculation is reformation of dimethylamine. The error bars are estimated; the large error bars on the silver data account for possible trace amounts of methylimine.

In stark contrast, the selectivity for the amide on silver was 70% even at the higher oxygen coverages studied and increased to only 80% at the lowest oxygen coverage. The reactions with d_6-dimethylamine on silver noted above (Figures 2 and S4) were not included in the selectivity comparison. The selectivity for coupling depends much more strongly on oxygen coverage on metallic gold, and under very specific conditions nearly 100% selectivity may be obtainable.

4.4. Reactivity of Adsorbed Oxygen Species. The contrast in methylimine production on silver and gold at low oxygen coverages may be due to the difference in reactivity of the surface oxidant available under reaction conditions. The following reactions are envisioned for formation of methylimine, where O/OH is used to indicate reaction with either adsorbed O or OH:

$$(CH_3)_2NH + O_{(a)}/OH_{(a)} \rightarrow (CH_3)_2N_{(a)} + OH_{(a)}/H_2O \quad (3)$$

$$(CH_3)_2N_{(a)} + O_{(a)}/OH_{(a)} \rightarrow CH_3NCH_2 + OH_{(a)}/H_2O \quad (4)$$

The relative reactivity of the $O_{(a)}$ or $OH_{(a)}$ present on the surface may dictate whether or not the imine forms before the amide reacts with the acetaldehyde. It is known that on Au(111) adsorbed O and OH equilibrate to favor adsorbed O,[43] leaving it free to facilitate C−H bond activation in the amide and form the imine. However, on Ag(111), $OH_{(a)}$ is quite stable, disproportionating to adsorbed O and H_2O near 300 K, which is well above the temperature of formation of the dimethylacetamide coupling product. Thus, if adsorbed OH is ineffective in activating the C−H bond in the adsorbed amide on silver, the amide can couple with the aldehyde. There are many other factors that could also have an effect on the selectivity difference and remain to be studied, such as proximity and mobility of adsorbates and morphology of the surface.

5. CONCLUSIONS

Both metallic silver and gold facilitate the direct coupling of amines and primary aldehydes for amide synthesis. The oxygen-assisted reaction proceeds on the surface via activation of N−H to form adsorbed amides. Coupling then occurs via a nucleophilic attack by the amide on the carbonyl carbon of the aldehyde. At low coverages of adsorbed atomic oxygen on silver, the selectivity for coupling is consistently near 80%, whereas on gold it exhibits a strong dependence on the oxygen coverage, increasing from 8% toward 100% between 0.1 and 0.03 ML oxygen. While the overall mechanisms on silver and gold are essentially identical, the rate-limiting step differs, indicative of greater facility of C−H bond activation on the gold surface. Differences are also manifested in the secondary oxidation products, the selectivity for coupling, and hydrogen production. Reactivity of the adsorbed oxygen species with the amine and the relative stability of adsorbed O and OH appear to determine the differences in secondary oxidation. Finally, dominance of oxygen-assisted hydrogen abstraction on gold may contribute to the absence of hydrogen formation on gold.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Temperature programmed reaction details, mass spectrometry fragmentation for identification of product, isotope reactions on silver with low oxygen coverage, and determination of the rate-limiting step on gold by dimethylacetamide coadsorption during reaction. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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