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Dual-Function of Alcohols in Gold-Mediated Selective Coupling of Amines and Alcohols

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Abstract: Oxidative coupling of alcohols (methanol and ethanol) and dimethylamine on atomic-oxygen-activated Au(111) occurs entirely on the surface to form the corresponding amides when the alkoxy of the alcohol and the amide derived from the amine are coadsorbed. For effective oxygen-assisted coupling the formation of the amide requires excess methanol. Mechanistic

studies reveal that molecularly adsorbed methanol removes excess adsorbed atomic oxygen efficiently, precluding either secondary oxidation or oxidative dehydrogenation of dimethy-

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lamide to the imine. The adsorbed amide then can react with the aldehyde produced by β -hydride elimination from the alkoxy to form the hemiaminal, the reactive intermediate leading to coupling. The selectivity for formamide production can be increased to nearly 100% in excess methanol.

Introduction

The product distribution and selectivity of a catalytic reaction often varies drastically with reaction conditions. Due to the complexity of normal chemical processes, optimizing reaction conditions purely by experimentally mapping out the parameter space is extremely time-consuming and economically costly, if not impossible. Therefore, a set of guiding principles derived from a solid understanding of the elementary steps that comprise the reaction mechanism is very useful to provide a starting point for choosing reaction conditions. In this work, we present a mechanistic study of the gold-mediated coupling between a secondary amine and alcohols that sheds light on the optimal conditions for designing a selective oxidative-coupling process.

Gold-based catalysts show remarkable activity and selectivity in many key chemical transformations, such as lowtemperature CO oxidation,^[1] epoxidation of olefins,^[2] selective oxidation of alcohols,^[3] oxidative-coupling reactions of alcohols,^[4] aldehydes^[5] and amines,^[6] and carbonylation reactions.^[7] A general mechanistic framework for gold-mediated oxidative-coupling reactions has been established using a model surface, that is, the oxygen-activated Au(111) surface (referred to hereafter as O/Au(111)).^[4b,6a,8] The overall ap-

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plicability of such mechanistic frameworks is suggested by results from identical reactions on nanoporous gold and supported gold nanoparticles carried out under working catalytic conditions.^[5b,9]

Gold-mediated oxidative-coupling reactions occur through a surface-bound nucleophile formed from the oxygen-assisted deprotonation of the substrate, for example, deprotonation of dimethylamine by adsorbed atomic oxygen to form adsorbed dimethylamide (Scheme 1), followed by a nucleophilic attack initiated by the newly formed nucleo-



Scheme 1. Mechanism for coupling of dimethylamine and an aldehyde, which could be introduced externally or formed in situ (dashed box).

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phile on a co-adsorbed electrophile. The resultant surface intermediate then undergoes β -H elimination to produce the coupled product, for example, an amide. The electrophile can be either externally introduced or, in principle, formed in situ on O/Au(111), for example, through selective removal of the acidic hydrogen of an alcohol followed by β -H elimination (Scheme 1, dashed box).^[6a] Because alcohols are in general more available and less costly than aldehydes, it is desirable to design processes with alcohols as the raw materials.

Herein, we report a mechanistic study on the selectivity control on the coupling of dimethylamine and methanol (ethanol) on O/Au(111) to form dimethylformamide (dimethylacetamide), which inherently competes with oxidative dehydrogenation and secondary oxidation of the amine. The mechanistic insight sheds light on the guiding principles for achieving optimum selectivity for such coupling reactions.

Results

Selective coupling to form dimethylformamide requires an excess of adsorbed methanol. This effect is reflected in a strong dependence of the product distribution for coupling on the temperatures at which reactants are introduced to O/Au(111) (Figure 1). No coupling is detectable when the reactants are dosed onto O/Au(111) (oxygen coverage θ_0 = 0.1 ML) at 150 K. The dominant product results from the oxygen-assisted dehydrogenation of dimethylamine, forming C₂H₅N and water at approximately 250 K (Figure 1A).^[6a] We were unable to differentiate the two possible isomers of C₂H₅N, CH₃N=CH₂ and ethylenimine, due to the unavailability of authentic samples and reference fragmentation patterns. However, from the work of Angelici on gold particles in solution, we infer that the product is the imine.^[10] The



Figure 1. A) No dimethylformamide (m/z=73) is observed when dimethylamine and methanol are introduced to O/Au(111) ($\theta_0=0.1$ ML) at 150 K; whereas, B) coupling of dimethylamine and methanol occurs when the reactants are introduced to O/Au(111) ($\theta_0=0.1$ ML) at 120 K. The exposure for all reactants is 6 L. The heating rate is 5 K s⁻¹. Surface oxygen was prepared by ozone exposure at 200 K.

secondary oxidation product of dimethylamine (methyl isocyanate), was also observed in small amounts, which is consistent with our previous studies.^[6b] Further oxidation of dimethylformamide was not observed, likely due to the absence of excess surface oxygen. In contrast, when dimethylamine and methanol are sequentially dosed at 120 K, a significant amount of the coupling occurs near 235 K (Figure 1 B). C_2H_3N is still the dominant product, along with a small amount of methyl isocyanate. Little of the possible oxidation products of methanol, such as formaldehyde, formic acid and methyl formate, or the combustion product, CO_2 , is detected following dosing at either temperature, indicating that excess adsorbed atomic oxygen preferentially attacks the adsorbed dimethylamide under these conditions.

Significantly more methanol is co-adsorbed at 120 K than 150 K, as evidenced by the observation that the amount of the unreacted methanol that desorbs is about 25 times higher following adsorption at 120 K vs. 150 K (Figure 1). This difference is expected, as the temperature of desorption of methanol from the multilayer on Au(111) has been reported to be 134 K.^[11] In contrast, the amount of unreacted dimethylamine increases only by about a factor of 1.5. Therefore, the different dosing temperatures result in significantly different relative concentrations of the preadsorbed reactants, which apparently affects the product distribution.

Indeed, for a fixed initial oxygen adatom coverage of 0.1 ML, the amount of dimethylformamide formed correlates well with the absolute amount of adsorbed methanol rather than the relative ratio of adsorbed methanol and dimethylamine. Similar ratios of methanol-to-dimethylamine condensed on O/Au(111) were created at surface temperatures of both 120 and 150 K with varying absolute amounts. For example, both 6 L of dimethylamine and 0.06 L of methanol dosed at 120 K and 0.24 L of dimethylamine and 6 L of methanol dosed at 150 K result in a methanol-to-dimethylamine ratio of approximately 1 desorbing from the surface; however, the absolute amount of methanol or dimethylamine initially adsorbed when dosed at 120 K is higher by a factor of approximately 15. The yield of the coupling product, dimethylformamide, increases almost linearly as the methanol-to-dimethylamine ratio rises when reactants are introduced at 120 K (Figure 2 A, black solid trace). In contrast, little coupling occurs when reactants are introduced at 150 K, independent of the methanol to dimethylamine ratio (Figure 2A, gray dotted trace). The amount of dimethylformamide formed correlates well with the amount of adsorbed methanol when both reactants were introduced at 120 K (Figure 2B). Similar results were observed for dimethylamine and ethanol; a small amount of coupling product, dimethylacetamide, was detected when dimethylamine and ethanol were dosed onto O/Au(111) ($\theta_0 = 0.1 \text{ ML}$) at 150 K, whereas a significant amount of dimethylacetamide was formed with reactants co-adsorbed at 120 K (Figure 3).

X-ray photoelectron spectroscopy suggests that less atomic oxygen remains after reaction of 6 L of methanol and dimethylamine with 0.1 ML adsorbed oxygen at 120 K compared with 150 K (Figure 4). A single O (1 s) peak at

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Figure 2. A) The amount of dimethylformamide produced as a function of the ratio of methanol to dimethylamine. Gray dotted trace: dimethylamine (different doses) and methanol (6 L) introduced at 150 K. Black solid trace: dimethylamine (6 L) and methanol (different doses) were introduced at 120 K. B) The amount of dimethylformamide produced as a function of the amount of residual methanol when both dimethylamine and methanol were introduced at 120 K. Surface oxygen coverage is 0.1 ML in all experiments shown in this figure.



Figure 3. Dimethylacetamide is formed from the coupling between dimethylamine and ethanol on O/Au(111) (θ_0 =0.1 ML) when they are introduced at 120 K (top trace). No dimethylacetamide formation is detected when the reactants are introduced at 150 K (bottom trace). The exposure for these reactants is 6 L. The heating rate is 5 K s⁻¹. Surface oxygen was prepared by ozone exposure at 200 K.

529.4 eV (characteristic of adsorbed atomic oxygen) is clearly observed upon formation of O/Au(111) ($\theta_0 = 0.1$ ML), which is consistent with previous studies.^[4a,6b] After dosing the reactants at 150 K and subsequently heated up to 190 K, the atomic oxygen persists with an integrated peak area about half of that of its initial value. No other peaks, for example, the O (1 s) peak at 531.5 eV (corresponding to the oxygen in methoxy)^[4a] are observed. Notably, after the same dose of reactants at 120 K, best fits to the data indicate that the amount of atomic oxygen left on when the surface is heated to 190 K is about one third of that remaining following the dose at 150 K, that is, approximately 0.02 ML. Moreover, an O (1 s) peak corresponding to methoxy (531.5 eV) appears (Figure 4(d)), which has an integrated peak area of approximately three times that of the peak for the residual



Figure 4. X-ray photoemission spectra showing the O (1 s) region after: (a) deposition of O on Au(111) (θ_0 =0.1 ML) using ozone exposure at 200 K; (b) exposure of the surface in (a) to 6 L each of dimethylamine and methanol at 150 K followed by heating to 190 K; (c) exposure of the surface in (a) to 6 L of dimethylamine and methanol at 120 K and subsequently heated to 190 K to desorb water and excess methanol; and (d) O_(a) and CH₃O_(a) by introducing 6 L of methanol to O/Au(111) (θ_0 = 0.1 ML) at 150 K (see ref. [6]). All spectra were taken at 150 K.

atomic oxygen. Though the signal-to-noise ratio in Figure 4(d) is poor, there is a clear broadening of the composite peak toward higher binding energies, which is attributable to the formation of methoxy. The low coverage of each species leads to a low signal-to-noise ratio. These results suggest that excess methanol adsorbed may control the amount of excess oxygen adsorbed and suppress the secondary oxidation processes.

To test this hypothesis, temperature-programmed reaction experiments were conducted in which the adsorbed amide (CH₃)₂N was treated with a steady background pressure of methanol, the amide having been formed by reaction of dimethylamine with O/Au at 150 K. The yield for dimethylformamide rises dramatically with the steady-state background pressure of methanol (Figure 5). The coupling reaction between dimethylamine and methanol is observed at a methanol background pressure as low as 5×10^{-9} Torr (Figure 5 A(g) corresponding to a methanol dose of 0.45 L during the course of the heating from 150 to 600 K. This exposure is only approximately 10% of the methanol dosed at 150 K in the conventional temperature-programmed reduction (TPR; Figure 5A(h)). The amount of dimethylformamide formed with a methanol background pressure of approximately 10^{-7} Torr is equivalent to that observed when 6 L of methanol was introduced at 120 K.

Remarkably, almost total conversion to the coupling product is achieved at a methanol background pressure of 10^{-6} Torr. Apparently all other reaction channels, such as dehydrogenation of dimethylamine, are suppressed (Figure 6), even though dehydrogenation of dimethylamine dominates at background pressures of methanol below 10^{-6} Torr, accounting for more than 80% of all products.



Figure 5. A) Dimethylamide produced from coupling of dimethylamine and methanol on O/Au(111) ($\theta_0 = 0.1$ ML) during temperature-programmed reaction. Dimethylamine (6 L) was initially reacted with 0.1 ML O/Au(111) at 150 K for all experiments. Subsequently, methanol (6 L) was introduced at 120 K and 150 K for traces (a) and (h). For traces (b–g) different background ambient pressures of methanol were maintained during the temperature-programmed reaction. B) The dependence of the yield of dimethylformamide as a function of background pressure of methanol is illustrated. The black open circles refer to the effective methanol pressure when 6 L of methanol was introduced at 120 K, respectively.

aldehyde from methoxy occurs near 200 K. Thus, in the presence of excess adsorbed oxygen, the secondary oxidation of the adsorbed amide is preferred, which precludes the coexistence of dimethylamide and formaldehyde, and coupling is not possible. When methanol and dimethylamine are introduced at 150 K, there is insufficient methanol present to react away the adsorbed oxygen, and secondary oxidation occurs (Scheme 2).^[6] However, when the reactants are dosed at 120 K, more methanol is initially co-adsorbed, the majority of the excess oxygen is reacted away, and the adsorbed amide intermediate is stable to sufficiently high temperatures to couple with the formaldehyde



Figure 6. Product distribution for the reaction of dimethylamine and methanol on O/Au(111) (θ_0 =0.1 ML) as a function of methanol background pressure. In all experiments dimethylamine (6 Langmuir) was introduced to O/Au(111) at 150 K. The yield of each product was determined by integration of the temperature-programmed reaction traces. Surface oxygen was deposited by exposure of the Au to ozone at 200 K.

The selectivity towards another secondary oxidation product of dimethylamine, methyl isocyanate, is around 5% at methanol background pressures below 1×10^{-6} Torr. No detectable amount of CO₂ is formed across the methanol pressure range tested.

Discussion

The unusual dependence of the selectivity for dimethylamide formation on the dosing temperature and the absolute amount of methanol preadsorbed can be explained by the effect of excess adsorbed oxygen. Secondary oxidation of dimethylamide to methyl isocyanate due to excess adsorbed oxygen occurs below 170 K, whereas the formation of form-



Scheme 2. Reaction mechanism for dehydrogenation and secondary oxidation of dimethylamine. Steps (2) and (3) (boxed) indicate that excess atomic oxygen creates an oxidizing surface environment.

formed by β -H elimination from the adsorbed methoxy, yielding dimethylformamide near 235 K. The variation of the residual oxygen concentration with dosing conditions are shown directly by the XPS results.

The mechanistic details of these reactions are shown in Scheme 3. Upon introduction to O/Au(111), dimethylamine and methanol are deprotonated below 150 K by adsorbed

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Scheme 3. Reaction mechanism for adsorbed molecular methanol-promoted coupling between dimethylamine and methanol. Steps (1) and (2) depict the participation of the molecularly adsorbed methanol in the reaction. Steps (2) and (3) (boxed) indicate that molecularly adsorbed methanol creates a reducing surface environment.

atomic oxygen, forming dimethylamide and methoxy (see Scheme (1)). In the presence of additional methanol excess oxygen (hydroxyl can be viewed as a half oxygen since two units of hydroxyl combine to form one unit of oxygen and one unit of water that leaves surface readily) is reacted to form methoxy (Scheme 3(2)) and prevent total secondary oxidation of the adsorbed amide, allowing coupling to occur.^[6b] Even if all the excess oxygen is removed, methoxy can attack the β -H of another methoxy, leading to disproportionation to form methanol and formaldehyde.^[4b] Dimethylamide then nucleophilically couples with the newly formed formaldehyde, leading to the formation of the hemiaminal intermediate. Dimethylformamide is formed via the β-H elimination of the hemiaminal intermediate, assisted either by the gold surface or adsorbed surface species such as O, OH or methoxy.

Furthermore, the yield of dimethylformamide can be increased with a steady-state background pressure of methanol, demonstrating the importance of a low surface concentration of adsorbed atomic oxygen for high selectivity for coupling. In the normal temperature-programmed reaction experiment, desorption of methanol limits the methanol coverage at the temperatures in which coupling occurs (>170 K). However, the presence of methanol in the gas phase ensures a steady-state coverage of methanol during the temperature ramp and the removal of excess atomic oxygen. At the highest methanol background pressure studied, both oxidative dehydrogenation and secondary oxidation of dimethylamine are suppressed, with almost total conversion to the coupling product. Apparently, at or above the ambient pressure of 10⁻⁶ Torr, methanol completely removes excess atomic oxygen, leaving only methoxy and dimethylamide on the surface. The fact that only dimethylformamide is then formed is strongly suggestive that atomic oxygen is

necessary for dehydrogenation to form the imine, as well as for secondary oxidation of the adsorbed amide. Furthermore, it implies that disproportionation of adsorbed methoxy is an efficient source of formaldehyde.

The plot of the yield of dimethylformamide as a function of the methanol background pressure (Figure 5B) can be used to identify the "equivalent background pressure of methanol" at reaction temperatures for conventional temperature-programmed reactions, in which methanol is introduced prior to heating. For example, 6 L of methanol dosed at 120 and 150 K correspond to equivalent background pressures of methanol of 10^{-7} and 10^{-10} Torr, respectively.

Overall, the results presented here indicate that after activation of the reactants by adsorbed atomic oxygen, maximum selectivity for coupling is achieved when the surface is in a reduced state; that is, there is no excess adsorbed oxygen. This mechanistic insight shows a dual function of alcohols in the coupling reaction as both reactant and scavenger of excess adsorbed atomic oxygen and provides guiding operating principles for steady state processes for similar chemical transformations. Specifically, low oxygen-to-alcohol ratios should be employed to prevent dehydrogenation and secondary oxidation of amines.

Conclusion

Selective oxygen-assisted coupling of alcohols and amine can be expected on metallic gold provided that a low concentration of adsorbed atomic oxygen is maintained by the presence of sufficient alcohol. The alcohol serves as both reactant and scavenger of excess atomic oxygen in the coupling reaction. Excess atomic oxygen on gold rapidly dehydrogenates dimethylamide and promotes secondary oxidation, short-circuiting the coupling reaction. Almost total conversion of dimethylamine to dimethylformamide, the coupling product, can be achieved at a sufficiently high ambient pressure of alcohol.

Experimental Section

General: All experiments were performed in an ultrahigh vacuum (UHV) chamber with a base pressure below 2×10^{-10} Torr. The clean Au-(111) surface was prepared by successive Ar ion sputtering at room temperature for 30 min and annealing at 900 K for 10 min until no C, O or S impurities can be detected by XPS. The surface was then further annealed at 700 K for 1 h. This procedure yields well-ordered Au(111) with herringbone reconstruction and with large terraces as determined by LEED and STM.^[12] The surface was first populated with 0.1 ML O (O/ Au(111)) by introducing an appropriate amount of ozone at 200 K. The oxygen atom coverage was calibrated by comparing the amount of O₂ evolution in temperature programmed reaction to that formed for a saturation coverage of oxygen atoms, which is 1.1 ML.^[13] Variations in oxygen coverage of $\pm 15\,\%$ are expected due to the day-to-day variation in O3 concentration of the ozone source. The oxidation of the surface in this manner leads to the release of Au atoms to form nanostructures containing Au and O, most of which are smaller than 2 nm in diameter. We refer to these oxygen-covered Au nanoparticles on Au(111) as O/Au-(111).[12]

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Temperature-programmed reactions (TPR): TPR reactions were conducted according to well-established protocols, which are described in detail elsewhere.^[12] In short, reactants were introduced to O/Au(111) at 120 or 150 K, depending on the experiment. The surface was then cooled to 120 K before it was heated linearly at 5 K s^{-1} in front of a mass spectrometer (Hiden HAL/3F). Products were identified by quantitative mass spectrometry, that is, by quantitatively comparing the fragmentation patterns of the detected products with those obtained from authentic samples, which were found to be in good agreement to NIST reference data (see the Supporting Information). The selectivity for different products was calculated on a per dimethylamine molecule basis, as described in the Supporting Information.

In the coupling reactions dimethylamine and alcohol were sequentially introduced to the O/Au(111) surface at 120 or 150 K, before the temperature-programmed reaction was conducted. Exposures, corrected for the enhancements caused by differences in the sample positions with respect to the doser, are given here in terms of Langmuir (L); 1 Langmuir corresponds to the equivalent of a dose of 1×10^{-6} Torr-seconds. Note that these exposures were not corrected for relative ionization efficiencies in the ion gauge or possible errors due to adsorption, reaction, or displacement at chamber walls. Unless otherwise noted, 6 L was the typical dose for organic molecules.

X-ray photoelectron spectra: XPS were acquired with an analyzer passing energy of 17.9 eV and a multiplier voltage of 3 kV using $M_{g_{k\alpha}}$ X-rays (300 W) as the excitation source. The binding energy (BE) calibration was referenced to the Au $4_{7/2}$ peak at 83.9 eV. The O (1 s) spectra were accumulated with 300 scans to enhance the signal-to-noise ratio, with an acquisition time of approximately 40 min. The position and width of the peak corresponding to adsorbed oxygen was obtained by fitting the curve of Figure 4(a). The position and width of the O (1 s) peak corresponding to methoxy was obtained by fitting curve (d) with the parameters for adsorbed oxygen obtained by fitting curve (b) and (c) were fitted using the parameters of peak position and width obtained in the previous two steps and adjusting the relative areas of the two components.

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