

Achieving Optimum Selectivity in Oxygen Assisted Alcohol Cross-Coupling on Gold

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Abstract: Oxidative coupling of alcohols is of great practical importance due to the wide range of synthetic applications using esters. Controlling the selectivity toward production of specific esters in cross-coupling is a long-sought goal in designing efficient synthetic routes. We report a quantitative study of the factors that determine the esterification selectivity in the oxidative cross-coupling of alcohols mediated by oxygen-covered Au(111). The high reactivity of gold is attributed to the activity of atomic oxygen bound to Au particles in forming surface-bound alkoxy species. The relative surface concentrations of alkoxy species and the ease of the β -H elimination play critical roles in determining the product distribution. For a given reactant composition the surface concentration of alkoxy species is skewed toward the higher molecular weight alcohol in the mixture exposed to the surface. Vibrational spectroscopic studies reveal that the relative stabilities of alkoxy species parallel the gas phase acidities of the corresponding alcohols, in agreement with other coinage metal surfaces. Further, the activation energies for β -H cleavage of alkoxy species are found to follow the descending order: $E_{\text{methoxy}} > E_{\text{ethoxy}} > E_{\text{butoxy}}$. The combination of these factors optimizes cross-coupling in a reactant mixture containing an excess of the lower molecular weight alcohol. The excellent match of product distribution between our low-pressure, single-crystal study and that observed for atmospheric pressure, liquid-phase reactions over supported gold catalysts provides strong evidence that the mechanistic insights gained from fundamental surface science study can serve as guiding principles in controlling selectivity under realistic catalytic conditions.

Introduction

Gold-based catalysts are currently under intense study due to their potential for low-temperature and highly selective oxidative processes. They have been successfully applied to a wide range of important reactions, such as selective oxidation of alcohols,^{1–11} oxidative coupling reactions,^{12,13} selective amidation,¹⁴ and olefin epoxidation.^{15–20} The oxidative coupling of alcohols to form esters is particularly important because of the large-scale production of esters industrially. Currently, there is great interest in the production of methyl esters, in particular, as biofuels. Esters are also important precursors in the production of synthetic fabrics and have wide applications in the flavoring and fragrance industries.

Control of reaction selectivity is a central issue in heterogeneous catalysis in general and for catalytic oxidative coupling of alcohols specifically. By increasing selectivity, energy

efficiency is increased and the need to eliminate unwanted byproducts is reduced. Enhancing selectivity and devising processes that operate at lower temperature can, thus, have a major effect on the environmental impact of commodity chemicals production.

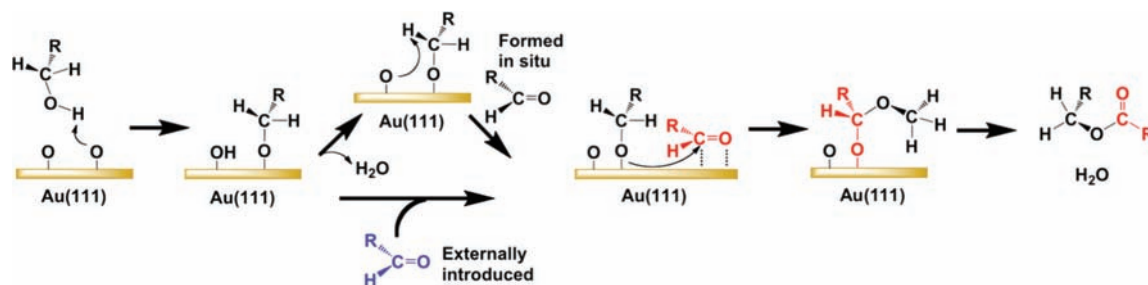
Selectivity can be enhanced by using molecular-level reaction mechanisms to guide the selection of reaction conditions so as

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Scheme 1. Reaction Mechanism for Oxidative Coupling of Alcohols on O/Au(111)^a

^a Aldehyde can be either formed via the β -H elimination (top pathway) of alkoxy or introduced externally (bottom pathway, blue). The subsequent reaction steps are independent of the origin of the aldehyde (red).

to favor the products of interest. A particularly successful example of this approach is the gas phase oxidative coupling of methanol to form methylformate using unsupported nanoporous, metallic Au as a catalyst. By selecting appropriate conditions—reaction temperatures near room temperature and low O_2 partial pressures—methylformate is formed with nearly 100% selectivity using nanoporous Au as a catalyst at atmospheric pressure.²¹ Mechanistic studies on Au(111) and Au(110) containing adsorbed atomic oxygen (O/Au(111)) performed under ultrahigh vacuum (UHV) conditions provided the guiding principles for this catalytic study by establishing the elementary steps and the rate-determining step.^{22–24} Oxygen-assisted coupling of alcohols has also been observed for metallic gold supported on oxides at higher temperatures and pressures in aqueous solution. The dependence of the product distributions on reactant concentrations also corresponds well to this mechanism and the reactive intermediates identified in the studies under ultrahigh vacuum conditions.^{25–27}

We attribute the excellent transferability of the mechanistic framework established on the well-defined single-crystal model at low pressure to the catalyst at atmospheric pressure to several characteristics of gold: (1) the lack of activity for bond activation in alcohols by metallic Au in the absence of adsorbed atomic oxygen, which prevents the buildup of spectator species on the surface; (2) the weak interaction of water with the surface,²⁸ which prevents inhibition of the reaction by the buildup of adsorbed water; and (3) the low steady-state coverage of oxygen due to the low dissociation probability of O_2 . Therefore, the insight gained from the fundamental surface science studies can provide critical information to better understand and improve catalytic processes mediated by gold-based materials at ambient pressure.²⁹

The mechanism for the efficient oxidative self-coupling of alcohols, including methanol and ethanol on O/Au(111),^{22,23} is initiated by activation of the O–H bond in the alcohol by

adsorbed O on the surface to form surface-bound alkoxy and water (Scheme 1). Without adsorbed O, **no** reaction occurs on clean, metallic Au. The rate-determining step is the subsequent β -H bond cleavage in the alkoxy to form the *adsorbed* aldehyde, which, in turn, is attacked by unreacted alkoxy to yield a hemiacetal species, which then rapidly eliminates another hydrogen to yield the ester (Scheme 1). This mechanism has been established for both the self-coupling of ethanol and methanol on O/Au(111).^{22,23} We have also demonstrated that cross-coupling between methoxy and various aldehydes to selectively form methyl esters is promoted on O/Au(111)¹³ and that methylacetate is formed from the reaction of acetaldehyde with methanol over nanoporous Au under catalytic conditions.²¹

There is considerable interest in *cross-coupling* of alcohols for ester synthesis, and the increased complexity of the reactant mixture leads to a multiplicity of possible product esters. We have, for example, previously reported the cross-coupling between methanol and either ethanol or *n*-butanol on O/Au(111).¹² Selective synthesis of the methyl esters of several primary alcohols, including 1-hexanol and aromatic alcohols, has also been reported for Au nanoparticles supported on TiO_2 or within a polymer in a dilute methanol solution using O_2 as the oxidant.^{26,30} These studies indicate that Au-based catalysts have the potential for selective and complex ester synthesis, rendering fundamental understanding of the factors that control selectivity important.

Herein, we report a quantitative study of the selectivity for alcohol cross-coupling which reveals a surprising dependence on the composition of the reactant mixture among dissimilar alcohols reported earlier.¹² In this study, we find that a pre-equilibrium between the alcohol mixture and the adsorbed alkoxy is an important factor in determining selectivity for specific esters, even in vapor phase reactions. The result is that the relative concentration of the alkoxy on the surface is not the same as the ratio of the parent alcohols in the reactant mixture. The other significant factor in determining selectivity is the relative ease of β -H elimination among the respective alkoxy, in agreement with our previous work.^{13,22,23} For example, only ethylacetate and methylacetate were observed when a mixture of methanol and ethanol (1:2 volumetric ratio in liquid phase) was reacted with O/Au(111).¹² Similarly, only *n*-butanal and butyrates (methylbutyrate and butylbutyrate) were detected for a methanol/*n*-butanol mixture (1:3 volumetric ratio).¹² These model studies provide guiding principles for

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selecting conditions for selective cross-coupling of alcohols using Au-based catalysts.

Experimental Section

All experiments were performed in a chamber with a base pressure below 2×10^{-10} Torr. The preparation of the clean Au(111) surface has been described elsewhere.³¹ The surface was first populated with 0.1 ML O (O/Au(111)) by introducing an appropriate amount of ozone at 200 K according to established procedure.³² On the basis of previous studies on self-coupling of alcohols,^{22,23} this specific initial oxygen coverage was chosen to optimize the yield of coupling products relative to combustion. It is thus expected to be representative of the surface reactivity at low surface oxygen concentrations. The oxygen atom coverage was calibrated by comparing the amount of O₂ evolution at ~ 550 K in temperature programmed desorption to that evolved from a surface saturated with oxygen atoms, which is 1.1 ML.³² The error in oxygen coverage on the Au(111) surface is $\pm 15\%$ due to day-to-day variation in O₃ concentration. Oxidation of the surface in this manner leads to release of Au atoms to form nanostructures containing Au and O, most of which are smaller than 2 nm in diameter.³¹ We refer below to the oxygen-covered Au nanoparticles on Au(111) as O/Au(111).

Mixtures of two alcohols (methanol/ethanol and methanol/*n*-butanol) with various molar ratios were prepared in solution and introduced to the O/Au(111) at 150 K. The gas-phase compositions above the liquid mixtures in the dosing vessel were estimated from the relative vapor pressures of the alcohols at room temperature, using relative liquid volumes expected to yield specific gaseous mixtures. The actual compositions of the mixtures dosed to the surface were measured using quantitative mass spectrometric analysis of sublimation peaks from the mixtures condensed on clean Au(111). (No reaction occurs on clean Au(111), whether flat or rough—alcohol adsorption is completely reversible.) For example, the methanol molar fraction (χ_{MeOH}) is calculated from

$$\chi_{\text{MeOH}} = \frac{n_{\text{MeOH}}}{n_{\text{MeOH}} + n_{\text{RCH}_2\text{OH}}} \times 100\% \quad (1)$$

R = CH₃— or CH₃CH₂CH₂—

where n_{MeOH} and $n_{\text{RCH}_2\text{OH}}$ are the number densities of the alcohols in the condensed layers (see Supporting Information).

The relative selectivity for the formation of a specific ester among all esters formed was calculated on a molar basis using the formula:

$$S_{\text{ester}_i} = \frac{n_{\text{ester}_i}}{\sum_i n_{\text{ester}_i}} \times 100\% \quad (2)$$

The equation for calculating the selectivity for combustion on a per carbon atom basis is:

$$S_{\text{CO}_2} = \frac{n_{\text{CO}_2}}{\sum_{i,j} (c_{\text{ester}_i} n_{\text{ester}_i} + c_{\text{aldehyde}_j} n_{\text{aldehyde}_j}) + n_{\text{CO}_2}} \times 100\% \quad (3)$$

where c_{ester_i} and c_{aldehyde_j} are the number of carbon atoms in ester *i* and aldehyde *j*, respectively.

The overall selectivities for production of esters and aldehydes were calculated according to:

$$S_{\text{esters}} = \frac{\sum_i n_{\text{ester}_i}}{\sum_{i,j} (n_{\text{ester}_i} + n_{\text{aldehyde}_j})} \times (100\% - S_{\text{CO}_2}) \quad (4)$$

$$S_{\text{aldehydes}} = \frac{\sum_i n_{\text{aldehyde}_i}}{\sum_{i,j} (n_{\text{ester}_i} + n_{\text{aldehyde}_j})} \times (100\% - S_{\text{CO}_2}) \quad (5)$$

Sequential dosing of organic molecules was employed in the coupling reactions between alcohols and formaldehyde. In these experiments, the alcohol was introduced to the O/Au(111) first at 150 K, followed by formaldehyde. Exposures, corrected for dosing enhancement, are given here in terms of langmuir (L, 1 langmuir = 1×10^{-6} Torr·s). The total pressure rise in the vacuum chamber during the dosing of the reactants was used as a measure of the total exposure. Unless otherwise noted, 6 L was the typical dose for organic molecules. Paraformaldehyde was used as the formaldehyde source and was introduced to the system following the procedure described in the literature.³³

Temperature programmed reaction experiments were conducted according to well-established protocols, described in detail elsewhere.³¹ The heating rate for all temperature programmed experiments was nearly constant at 5 K/s. Reaction products were identified by quantitative mass spectrometry (Hiden HAL/3F) using fragmentation patterns obtained from authentic samples; they were generally in good agreement with NIST reference data (see Supporting Information).³⁴

Results

Efficient and selective cross-coupling between methanol and either ethanol or *n*-butanol to their respective methyl esters is promoted by O/Au(111) when methanol is in excess (Figure 1). The reaction of a methanol/ethanol mixture (85:15) yielded methylformate, methylacetate, and ethylacetate, but no detectable ethylformate (Figure 1a).¹² The cross-coupling product, methylacetate, is the predominant product under these conditions, accounting for $\sim 75\%$ of the ester yield, whereas the self-coupling products, that is, methylformate and ethylacetate, account for $\sim 10\%$ and $\sim 15\%$, respectively. The overall selectivity for methylacetate production from the 85:15 methanol/ethanol mixture is $\sim 55\%$. The relatively small amount of CO₂ formed in two broad peaks between 300 and 550 K is attributed to the combustion of methanol and ethanol, based on comparison with CO₂ production from the pure alcohols.^{22,23}

Similarly, the cross-coupled product, methylbutyrate, accounts for $\sim 75\%$ of the ester production for reaction of the (90:10) methanol/*n*-butanol mixture on O/Au(111) (Figure 1b). Methylformate and butylbutyrate are also formed, accounting for $\sim 5\%$ and $\sim 20\%$ of the esters produced, respectively (Figure 1b). There is no detectable butylformate, and only a small amount of butanal ($<1\%$) and CO₂ ($<5\%$) are formed. There is one qualitative difference between *n*-butanol and ethanol reactions with the mixtures of methanol. For low methanol molar fractions, the aldehyde, *n*-butanal, evolves from the surface in significant quantities at ~ 240 K (Figure 3b), whereas acetaldehyde production was never detected. The yield of *n*-butanal decreases nearly linearly with decreasing *n*-butanol content,

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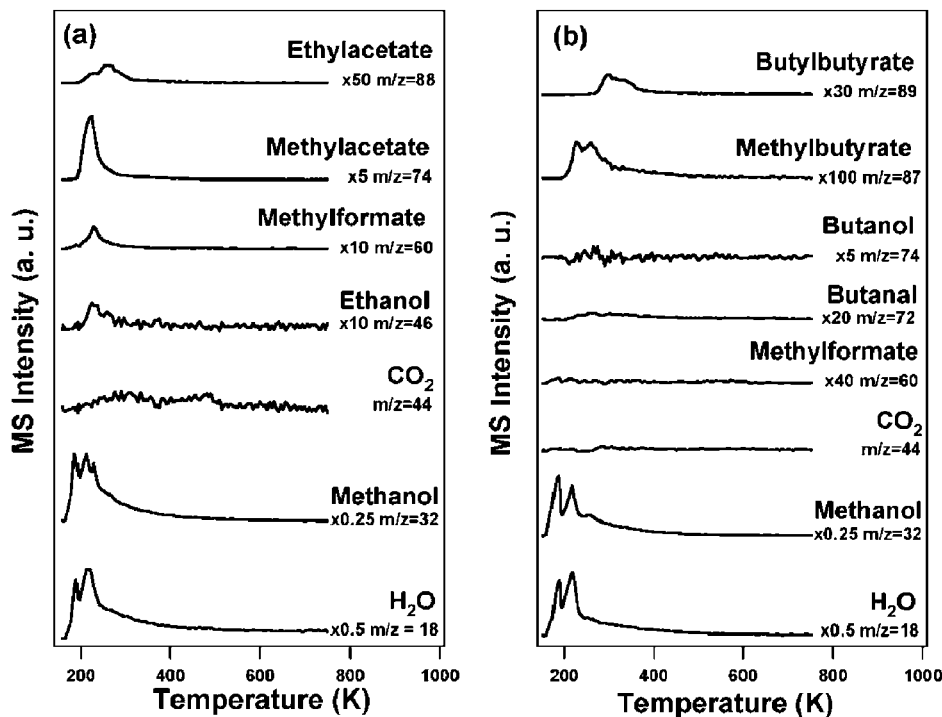


Figure 1. Temperature programmed reaction spectra following exposure of two different alcohol mixtures on O/Au(111) ($\theta_{\text{O}} = 0.1$ ML): (a) methanol (85%) and ethanol (15%) and (b) methanol (90%) and *n*-butanol (10%). Adsorbed atomic oxygen was introduced by ozone exposure at 200 K, producing O-covered Au nanoparticles, primarily ~ 2 nm in diameter. Alcohol mixtures were introduced (6 L) at 150 K. The composition of the alcohol mixtures reported was calculated on a molar basis.

becoming nearly undetectable for a mixture with a 90:10 ratio of methanol/*n*-butanol (Figures 1b and 3).

The product distributions for these reactions depend strongly on the composition of the alcohol mixture; however, they do not have a one-to-one correspondence to the gas-phase concentration of the alcohols (Figures 2 and 3). As expected, at low methanol content in the reactant mixture self-coupling of the longer-chain alcohols predominates. Ethylacetate is the dominant product for an ethanol-rich mixture, and butylbutyrate is formed from mixtures rich in *n*-butanol (Figures 2 and 3). However, the methyl esters, methylacetate and methylbutyrate, are only observed in significant quantities for methanol mole fractions above 20%. Furthermore, there is an excess of the self-coupled products—ethylacetate and butylbutyrate—that persists to high methanol content. Equal amounts of methylacetate and ethylacetate are reached for a 65:35 mixture of methanol and ethanol; equal amounts of butylbutyrate and methylbutyrate are produced for the 80:20 CH₃OH:*n*-C₄H₉OH mixture. Further, the highest selectivity for cross-coupling to the methyl esters is observed for methanol-to-ethanol and methanol-to-*n*-butanol molar ratios in the gaseous mixtures of 85:15 and 90:10, respectively (Figures 2 and 3), **not** for 50:50 mixtures. These results indicate that the surface concentration of the alkoxy species favor the higher molecular weight alcohol disproportionately to the reactant composition.

The dependence of the product distributions on the methanol content also indicates that the rate of β -H elimination from the adsorbed alkoxy is an important factor. Under no circumstance was ethylformate or butylformate detected. Furthermore, methylformate—the product of methanol self-coupling—is only formed at very high methanol content in the dosed mixture, above 70% methanol for the methanol/ethanol mixtures (Figure 2) and above 90% methanol for the methanol/*n*-butanol case

(Figure 3). The total selectivity for ester formation, however, is nearly 100% for the 90:10 methanol/*n*-butanol mixture, and the selectivity for cross-coupling to produce methylbutyrate is also a maximum. If there were equal rates of β -H elimination from the adsorbed alkoxy, such discrimination against formate esters would not be observed.

The rate of β -H elimination from methoxy is expected to be slower than that of ethoxy or butoxy, based on prior studies on Ag and Cu,^{35,36} consistent with our observations that the products of the reactions of methoxy with either acetaldehyde (methylacetate) or butanal (methylbutyrate) are favored. Altogether, these results are consistent with a relatively slower rate of formaldehyde formation from β -H elimination from methoxy, than for production of the aldehydes from ethoxy or *n*-butoxy via an analogous process.

Combustion shows a strong variation with the molar fraction of methanol. Production of CO₂ accounts for $\sim 5\%$ of all the products for pure ethanol and increases monotonically in the CH₃OH–C₂H₅OH mixtures to 35% for pure methanol (Figure 2b), in agreement with our previous work.^{22,23} No CO₂ was detected up to a 90:10 methanol/*n*-butanol mixture (Figure 3b). At these high methanol molar fractions, the yield of CO₂ and methylformate parallel each other.

Since the coverages of the different alkoxy moieties on the surface during reaction are clearly a critical factor in determining the product distribution, we quantified the relative surface coverages of the alkoxy for each reactant mixture. The alkoxy has been previously identified using vibrational spectroscopy for methanol and ethanol reactions on O/Au(111)^{22,23} and reproduced herein (see below). The relative coverage of each

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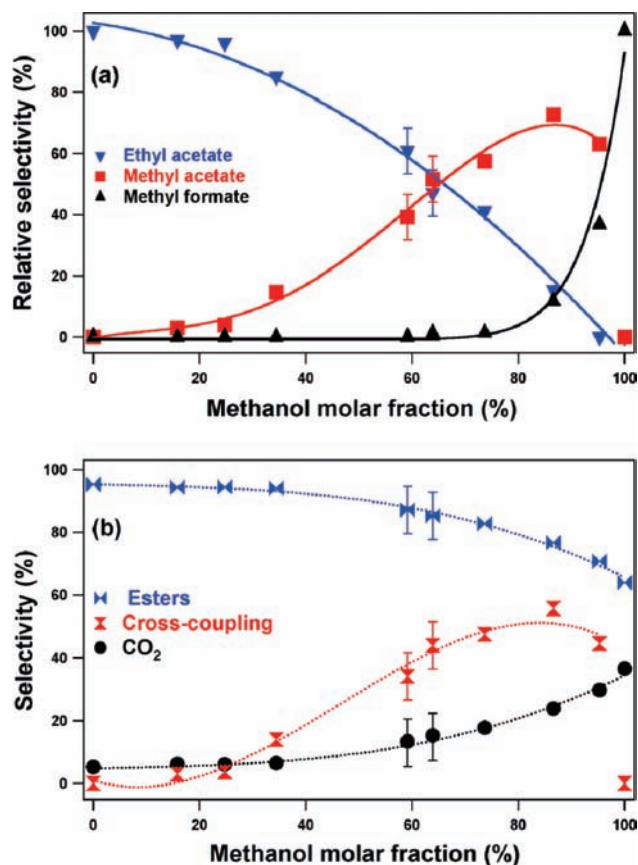


Figure 2. Selectivity variation as a function of methanol molar fraction for reaction of mixtures CH_3OH and $\text{CH}_3\text{CH}_2\text{OH}$ on $\text{O}/\text{Au}(111)$, $\theta_{\text{O}} = 0.1$ monolayers (ML). (a) Relative selectivity among esters formed in the self-coupling—methylformate and ethylacetate—and cross-coupling (methylacetate) reactions; no ethylformate is detected in any of the experiments. (b) Selectivities for total ester production (blue; the sum of methylformate, methylacetate and ethylacetate); for the cross-coupled product, methylacetate (red); and CO_2 from combustion (black). Selectivities were obtained from temperature programmed reactions of various mixtures of methanol and as described in the Experimental Section above. Surface atomic oxygen was introduced by ozone exposure at 200 K, yielding O-covered Au nanoparticles. All alcohol mixtures were introduced (6 L) at 150 K.

alkoxy moiety was determined from our temperature programmed data for each reactant mixture. The coverage of each alkoxy can be determined directly from the stoichiometry of the esters formed, corrected for combustion to form CO_2 . This calculation applies for all surface concentrations of these intermediates, even though the product distribution may be affected by different rates of β -hydride elimination. For example, the relative coverage of methoxy at a given reactant mixture of methanol and ethanol is given by:

$$F(\text{methoxy}) = \frac{\theta_{\text{CH}_3\text{O}_{(\text{a})}}}{\theta_{\text{CH}_3\text{O}_{(\text{a})}} + \theta_{\text{CH}_3\text{CH}_2\text{O}_{(\text{a})}}} \quad (6)$$

where $F(\text{methoxy})$ is the fraction of methoxy in surface alkoxy. The derivation of the equation is detailed in the Supporting Information. The corresponding equation for reactions of methanol and *n*-butanol is:

$$F(\text{methoxy}) = \frac{\theta_{\text{CH}_3\text{O}_{(\text{a})}}}{\theta_{\text{CH}_3\text{O}_{(\text{a})}} + \theta_{\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O}_{(\text{a})}}} \quad (7)$$

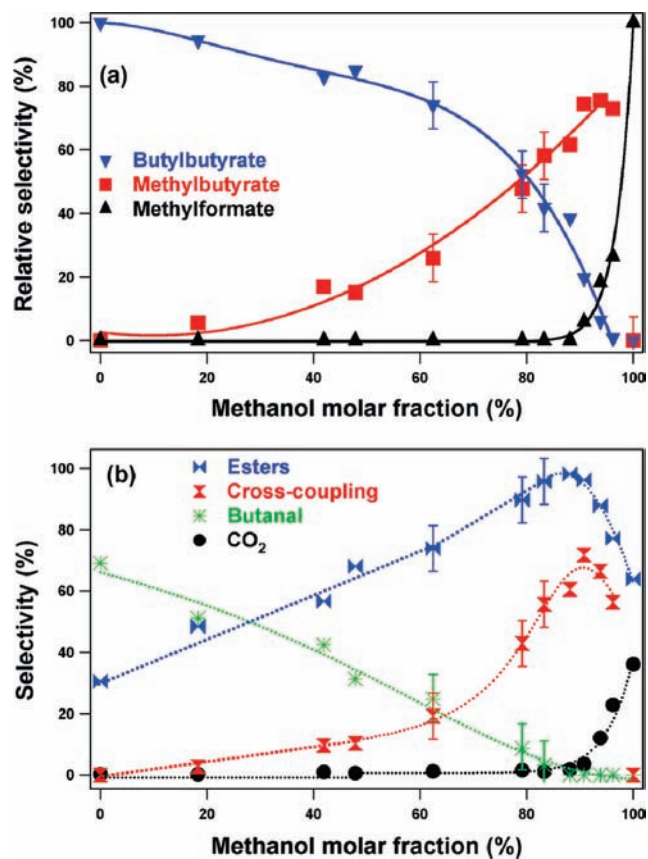


Figure 3. Selectivity variation as a function of methanol molar fraction for reaction of mixtures CH_3OH and *n*- $\text{C}_4\text{H}_9\text{OH}$ on $\text{O}/\text{Au}(111)$, $\theta_{\text{O}} = 0.1$ monolayers (ML). (a) Relative selectivity among the esters formed—methylformate (black), butylbutyrate (blue), and methylbutyrate (red)—as a function of methanol molar fraction in the mixtures. (b) Selectivity for total ester production (blue), compared to that of for methylbutyrate (cross-coupling, red), butanal (green), and CO_2 (black) as a function of methanol molar fraction. Selectivities were determined from analysis of our temperature programmed data, as described in the Experimental Section and Supporting Information. Surface atomic oxygen was introduced by ozone exposure at 200 K and alcohol mixtures were introduced (6 L) at 150 K.

In these calculations, we assume that the CO_2 formed originated from each of the alkoxy groups in proportion to the relative combustion yields measured for the pure alcohols. The relative yields of each of the products are determined by quantitative mass spectrometry in each temperature programmed reaction experiment.

These results indeed show that one major factor in determining the product distribution is the inequivalent amount of methoxy formed in competition with formation of the longer-chain alkoxy (Figure 4). The details of these calculations are given in Supporting Information.

To verify that differences in the rate of β -H elimination from the respective alkoxy affected the product distributions, the reactions of formaldehyde with all three alcohols (CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, and *n*- $\text{C}_4\text{H}_9\text{OH}$) at the adsorption temperature of 150 K were studied. The reactions of methanol, ethanol, and *n*-butanol with formaldehyde were investigated on $\text{O}/\text{Au}(111)$ (Figure 5). When formaldehyde-*d*₂ was introduced following methanol exposure of $\text{O}/\text{Au}(111)$ at 150 K, only methylformate-*d*₁ ($\text{DC}(\text{=O})\text{OCH}_3$) (no methylformate-*d*₂) was detected during temperature programmed reaction (Figure 5a), in agreement with our previous work.¹³ This result confirms that coupling exclusively occurs between the $\text{CH}_3\text{O}_{\text{ads}}$ and the $\text{D}_2\text{C}=\text{O}$, that is, that

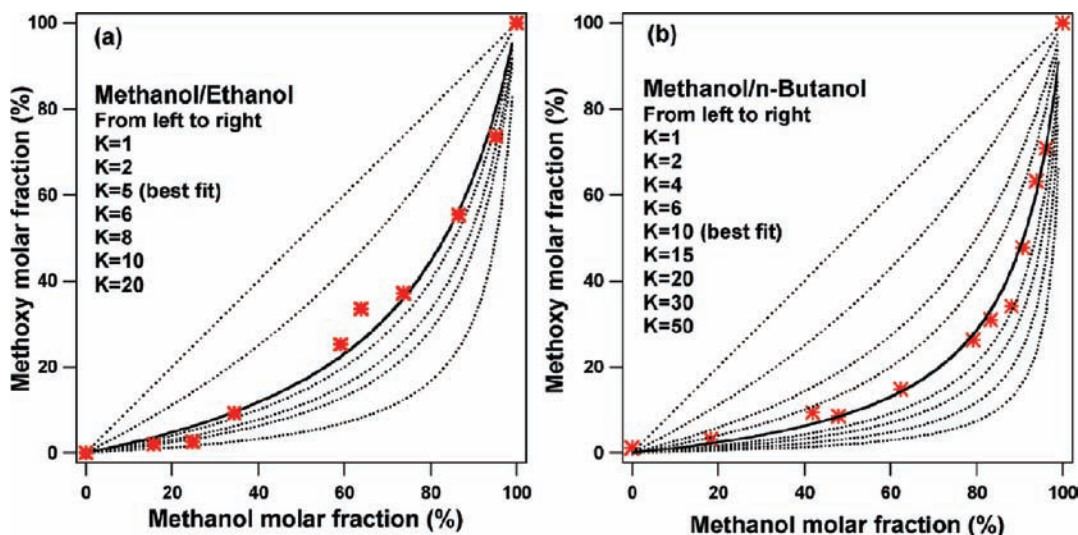


Figure 4. The fraction of surface methoxy as a function of methanol molar fraction in the alcohol mixtures for: (a) methanol/ethanol and (b) methanol/*n*-butanol systems. Red stars are the data analyzed according to eqs 6 and 7, respectively. The various dashed lines represent the methoxy surface concentrations as a function of methanol molar fraction for different equilibrium constants between the reactant mixtures and the surface alkoxy from eq 10 (see below).

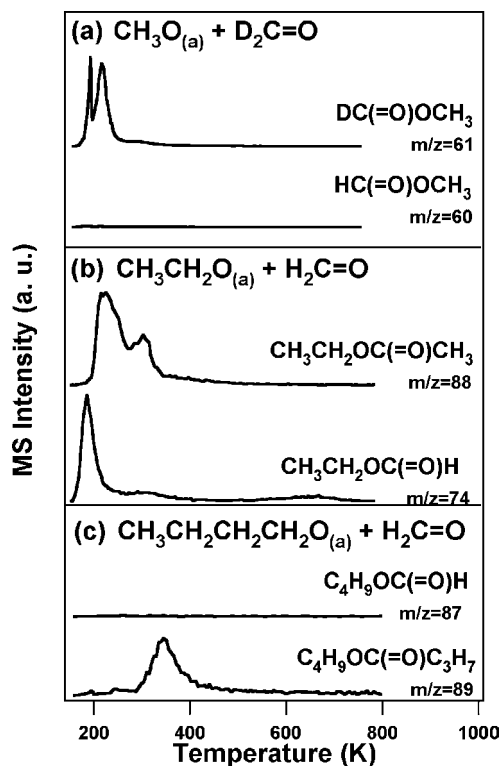


Figure 5. Temperature programmed reaction spectra showing the esters formed from reactions formaldehyde with the three different alkoxy to probe for β -H elimination of the alkoxy at 150 K. (a) Selective formation of $\text{CH}_3\text{O}(\text{D})=\text{O}$ from reaction of $\text{CH}_3\text{O}_{\text{ads}}$ from methanol followed by exposure to $\text{D}_2\text{C}=\text{O}$. (b) Sequential adsorption of ethanol and $\text{H}_2\text{C}=\text{O}$, yielding ethylformate ($\text{CH}_3\text{CH}_2\text{OC}(\text{=O})\text{H}$) and ethylacetate ($\text{CH}_3\text{CH}_2\text{OC}(\text{=O})\text{CH}_3$). (c) Exposure of *n*-butanol followed by $\text{H}_2\text{C}=\text{O}$ to exclusively yield the *n*-butanol self-coupling product, $\text{C}_4\text{H}_9\text{OC}(\text{=O})\text{C}_3\text{H}_7$. In all cases, reaction was performed on O/Au(111) ($\theta_{\text{O}} = 0.1$ ML). Surface atomic oxygen was introduced by ozone exposure at 200 K and all organic molecules were introduced (6 L) at 150 K. Other products formed include *n*-butanal, CO_2 , and water (data not shown).

there is no detectable β -H scission from methoxy during coupling at 150 K. In contrast, only butylbutyrate was detected

following the sequential dosing of *n*-butanol and formaldehyde at 150 K (Figure 5c), indicating that butylbutyrate forms rapidly upon *n*-butanol exposure to the surface at 150 K and before formaldehyde is added. Both ethylacetate and ethylformate form when ethanol and formaldehyde were dosed sequentially (Figure 5b), indicating that some but not all ethoxy has β -H eliminated at 150 K prior to the introduction of formaldehyde. These results show that the relative rates of β -H elimination in the three alkoxy vary significantly at 150 K and that the dependence of the ester distribution on the methanol content of the reactants also reflects the relative rates for β -H elimination between the alkoxy groups. The order of rates for β -H elimination is $\text{CH}_3\text{O}_{\text{ads}} < \text{C}_2\text{H}_5\text{O}_{\text{ads}} < n\text{-C}_4\text{H}_9\text{O}_{\text{ads}}$, as anticipated from prior studies on Ag and Cu.^{35,36}

Vibrational Spectroscopy. Vibrational spectroscopy also provides evidence that the longer-chain alcohols (ethanol and *n*-butanol) displace methoxy from the surface (Figures 6–8). Methoxy, which is known to form at 150 K on O/Au(111),²³ was prepared by dosing 6 L of methanol on O/Au(111) ($\theta_{\text{O}} = 0.1$ ML) at 150 K, a temperature sufficiently high to prevent accumulation of molecular methanol but below that for further reaction of methoxy. As expected, the $\nu_{\text{C-O}}$, $\delta_{\text{C-H}}$, and $\nu_{\text{C-H}}$ modes characteristic of methoxy on O/Au(111) are clearly visible at 995, 1425, and 2910 cm^{-1} , respectively (Figure 6a).²³ Notably absent is the OH bend at ~ 650 cm^{-1} which is prominent for adsorbed molecular methanol, clear evidence for methoxy.

Ethanol clearly displaces methoxy from the surface at 150 K, probably desorbing as methanol. The modes characteristic of methoxy disappear after 6 L of ethanol- d_6 ($\text{CD}_3\text{CD}_2\text{OD}$) was introduced to the methoxy-covered surface at 150 K (Figure 6b). The presence of the $\nu_{\text{C-O}}$ (995 cm^{-1}), $\delta_{\text{C-D}}$ (1140 cm^{-1}), and $\nu_{\text{C-D}}$ (2170 cm^{-1}) modes characteristic of ethoxy- d_5 and the absence of the OH bending mode (~ 650 cm^{-1}) provide clear evidence that adsorbed ethoxy is formed. Reintroduction of methanol (6 L) at 150 K led to only minor changes in the spectrum, indicating little or no displacement of the ethoxy- d_5 . There is a small change in the ratio of intensities for modes characteristic of ethoxy- d_5 at ~ 995 and ~ 1140 cm^{-1} , a hint of intensity for the $\delta_{\text{C-H}}$ and $\nu_{\text{C-H}}$ modes of $\text{CH}_3\text{O}_{\text{ads}}$ at 1425 and 2910 cm^{-1} (Figure 6c). Subsequent temperature programmed

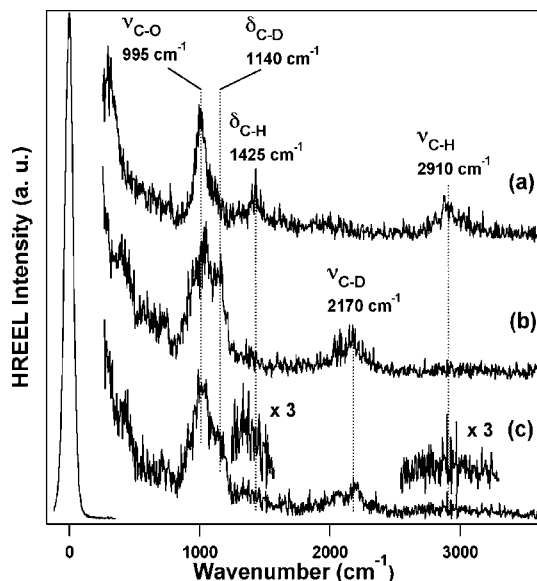


Figure 6. Vibrational (high resolution electron energy loss) spectra illustrating the displacement of $\text{CH}_3\text{O}_{\text{ads}}$ by $\text{CD}_3\text{CD}_2\text{OD}$ in the process depicted in Scheme 2. (a) $\text{CH}_3\text{O}_{\text{ads}}$, prepared by introducing methanol (6 L) to $\text{O}/\text{Au}(111)$ ($\theta_{\text{O}} = 0.1$ ML) at 150 K; (b) after introducing $\text{CD}_3\text{CD}_2\text{OD}$ (6 L) to $\text{CH}_3\text{O}_{\text{ads}}$ covered surface (prepared in (a) at 150 K; and (c) after introducing CH_3OH (6 L) to surface prepared by (b) at 150 K. Surface oxygen was introduced by ozone exposure at 200 K prior to the introduction of alcohols. The low signal-to-noise ratio results from the roughness of the surface.

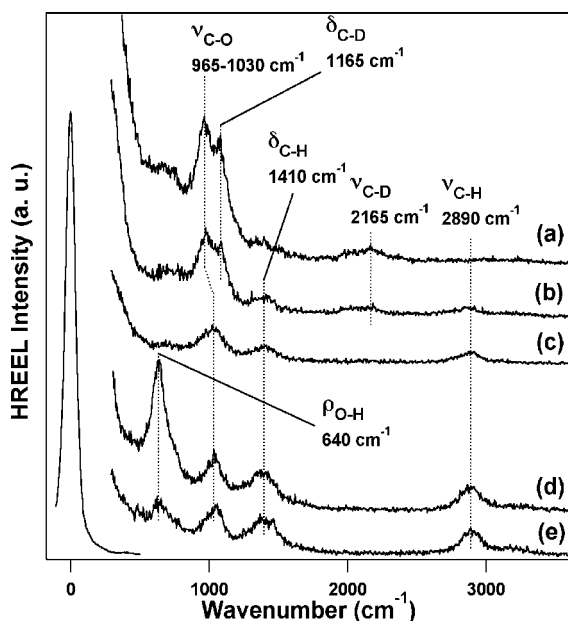


Figure 7. Vibrational (high resolution electron energy loss) spectra demonstrating the displacement of $\text{CD}_3\text{O}_{\text{ads}}$ by $n\text{-C}_4\text{H}_9\text{OH}$. (a) Spectrum for $\text{CD}_3\text{O}_{\text{ads}}$, prepared by introducing methanol- d_3 (CD_3OH) (6 L) to $\text{O}/\text{Au}(111)$ ($\theta_{\text{O}} = 0.1$ ML) at 150 K; those obtained following introduction of (b) 0.1 L, (c) 0.3 L, and (d) 3 L of $n\text{-C}_4\text{H}_9\text{OH}$ at 150 K; and, (e) after introducing 6 L of CD_3OH to the surface prepared in (d). Surface oxygen was introduced by ozone exposure at 200 K prior to the introduction of alcohols. The low signal-to-noise ratio results from the roughness of the surface.

reaction confirmed that ethoxy is the primary species present after collection of the spectrum in Figure 6c; ethylacetate accounts for $\sim 90\%$ of the ester formed, with methylacetate accounting for the remaining 10% (data not shown). No methylformate was detected. These results show that there is a

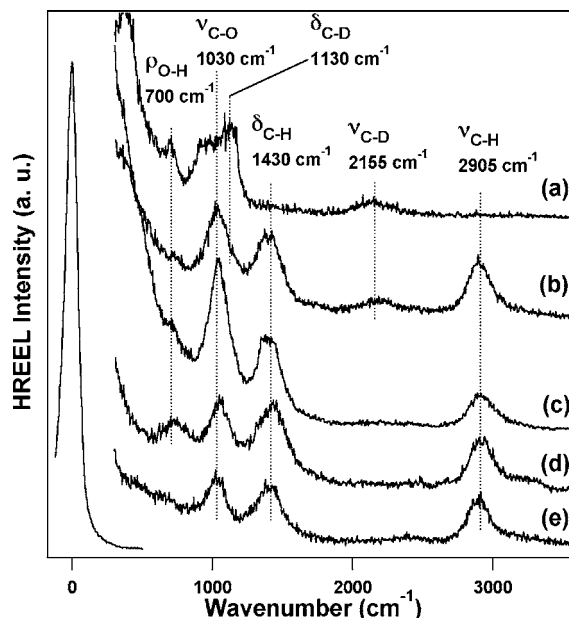


Figure 8. Vibrational (high resolution electron energy loss) spectra of (a) $\text{CD}_3\text{CD}_2\text{O}_{\text{ads}}$, prepared by introducing ethanol- d_6 (6 L) to $\text{O}/\text{Au}(111)$ ($\theta_{\text{O}} = 0.1$ ML) at 150 K; and after introducing (b) 0.2 L, (c) 0.4 L, and (d) 3 L of $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ to CD_3O -covered surface (prepared in (a)) at 150 K; (e) after introducing 6 L of $\text{C}_2\text{D}_5\text{OH}$ to the surface prepared in (d). Surface oxygen was introduced by ozone exposure at 200 K prior to the introduction of alcohols. The low signal-to-noise ratio results from the roughness of the surface.

Scheme 2. Schematic of the Equilibrium between Adsorbed Methanol and the Higher Molecular Weight Alcohols ($\text{R} = \text{CH}_3\text{-}$ or $\text{CH}_3\text{CH}_2\text{CH}_2\text{-}$) and Their Corresponding Alkoxy on the Surface^a



^a Higher molecular alcohols displace methoxy, indicating the equilibrium constant $K_{\text{RCH}_2\text{OH}/\text{MeOH}}$ in eq 8 is greater than unity for the reactions as written.

preference for ethoxy formation on the surface over methoxy, shown in Scheme 2, with the equilibrium lying far to the right.

$$K_{\text{RCH}_2\text{OH}/\text{MeOH}} = \frac{\theta_{\text{MeOH}_{\text{(a)}}} \theta_{\text{RCH}_2\text{O}_{\text{(a)}}}}{\theta_{\text{CH}_3\text{O}_{\text{(a)}}} \theta_{\text{RCH}_2\text{OH}_{\text{(a)}}}} \quad \text{R} = \text{CH}_3\text{- or CH}_3\text{CH}_2\text{CH}_2\text{-} \quad (8)$$

where θ refers to surface coverage of the various species.

The consequence of the equilibria for between the different alcohols and their alkoxy is that the surface coverage of methoxy and ethoxy in our reactivity measurements will substantially deviate from the molar fraction of the alcohol mixture in the gas phase. The surface will be enriched in ethoxy relative to ethanol in the gaseous mixture with methanol, in agreement with the quantitative analysis of our temperature programmed measurements (Figure 4).

Similarly, evidence indicates the displacement of methoxy by n -butanol from $\text{O}/\text{Au}(111)$, which leads to an enrichment of the surface n -butoxy relative to the mole fraction of n -butanol in the gaseous methanol/ n -butanol mixture (Figure 7). As described above for the ethanol- d_6 , changes in the intensities of vibrational modes characteristic of methoxy- d_3 upon exposure to n -butanol provide evidence for displacement of methoxy from

the surface. After 0.1 L of *n*-butanol was introduced to methoxy-*d*₃ (CD₃O_(a)) on the surface (prepared by exposing O/Au(111) to 6 L of CD₃OH at 150 K), a significant decrease in the intensities of modes characteristic of CD₃O_(a), δ_{C–D} at 1165 and ν_{C–D} at 2165 cm^{−1}, was accompanied by the growth of modes for species derived from *n*-butanol, δ_{C–H} at 1410 cm^{−1} and ν_{C–H} at 2890 cm^{−1} (Figure 7a,b). Complete displacement of CD₃O_(a) was achieved after additional 0.2 L of *n*-butanol was introduced, as evidenced by the disappearance of modes associated with CD₃O_(a), δ_{C–D} and ν_{C–D} (Figure 7c). Further introduction of *n*-butanol (2.7 L) led to the buildup of molecular *n*-butanol on the surface, indicated by the appearance of the ρ_{O–H} mode at 640 cm^{−1} (Figure 7d). No peaks characteristic of C–D bonds were detected upon reintroduction of CD₃OH, indicating that methoxy formation is not favorable on the surface covered with species derived from *n*-butanol. Butylbutyrate was the only ester detected in temperature programmed reaction performed after acquisition of the spectrum in Figure 7e, confirming that little or no methoxy-*d*₃ was present (data not shown). Therefore, the equilibrium (Scheme 2, eq 8) for the methanol–*n*-butanol mixture favors *n*-butoxy production over methoxy.

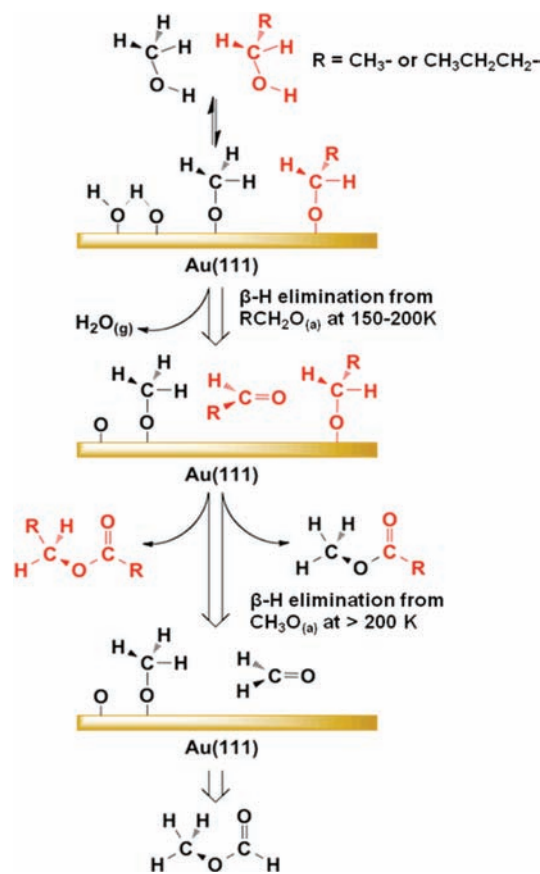
Displacement of ethoxy by *n*-butanol was also observed using vibrational spectroscopy, indicating a trend with increasing preference for alkoxy formation with increasing alkyl chain length. The ν(C–O) at 1030 cm^{−1}, δ_{C–D} at 1130 cm^{−1}, and the ν_{C–D} at 2155 cm^{−1} modes of CD₃CD₂O_(a) were all observed after the introduction of 6 L of ethanol-*d*₆ to O/Au(111) (Figure 8a). The small peak at near 700 cm^{−1} suggests the presence of some molecular ethanol, but its intensity indicates it is a small fraction of the ethoxy coverage. Most of the CD₃CD₂O_(a) was displaced after 0.2 L of *n*-butanol was introduced, as evidenced by the reduction in the intensity of modes characteristic of the ethoxy-*d*₅ and the appearance of δ_{C–H} and ν_{C–H} modes at 1430 and 2905 cm^{−1} derived from *n*-C₄H₉OH reaction on the surface (Figure 8b). No peaks associated with CD₃CD₂O_(a) were detected after the introduction of an additional 0.2 L of *n*-butanol, indicating complete displacement (Figure 8c). The absence of the ρ_{O–H} mode indicates little molecular *n*-butanol was adsorbed on the surface. Introduction of more *n*-butanol (2.6 L) led to condensation of *n*-butanol, based on the appearance of the ρ_{O–H} mode at 700 cm^{−1} (Figure 8d). No modes characteristic of CD₃CD₂O_(a) were observed after reintroduction of 6 L of ethanol-*d*₆. Like methanol, the introduction of ethanol did not displace the butoxy intermediate. Only butylbutyrate was observed in temperature programmed reaction after acquisition of the spectrum in Figure 8e (data not shown), confirming the irreversibility of the displacement of ethoxy by *n*-butoxy.

Discussion

As suggested above, two factors play critical roles in determining the product distribution of the coupling reactions between different alcohols: (1) the relative concentration of surface alkoxy intermediates, which is determined by the equilibrium between the alcohol reactants and the adsorbed alkoxy species, and (2) the relative rates of β-H elimination in the alkoxy species to form the corresponding aldehydes (Scheme 3).

By rearranging eq 8, we can express the methoxy molar fraction as a function of methanol molar fraction in the alcohol mixture, as in eq 9:

Scheme 3. Schematic of the Competing Coupling Reactions between Dissimilar Alcohols on O/Au(111)^a



^a β-H elimination of higher molecular weight alkoxy (ethoxy or *n*-butoxy) takes place at lower temperature (150–200 K) than that of methoxy; therefore, no higher molecular weight alkoxy is left on the surface by the temperature formaldehyde is formed.

$$\frac{\theta_{\text{CH}_3\text{O}_{(a)}}}{\theta_{\text{CH}_3\text{O}_{(a)}} + \theta_{\text{RCH}_2\text{O}_{(a)}} = \frac{1}{K_{\text{RCH}_2\text{OH/MeOH}} \left(\frac{\theta_{\text{MeOH}_{(a)}} + \theta_{\text{RCH}_2\text{OH}_{(a)}}}{\theta_{\text{MeOH}_{(a)}}} - 1 \right) + 1}$$

R = CH₃– or CH₃CH₂CH₂– (9)

which can be simplified as:

$$F(\text{methoxy}) = \frac{1}{K_{\text{RCH}_2\text{OH/MeOH}} \left(\frac{1}{F(\text{MeOH})} - 1 \right) + 1}$$

R = CH₃– or CH₃CH₂CH₂– (10)

The constants for the equilibria between the alcohols and the alkoxy species (Scheme 2) are determined from the methanol molar fraction obtained from desorption of the reactant mixtures from the clean surface and substituted into eq 10. Using this analysis, *K*_{EIOH/MeOH} is estimated to be ~5 and *K*_{BuOH/MeOH}, ~10 (Figure 4) based on the data of Figure 3. These fits indicate that *n*-butanol preferentially displaces methoxy to a greater extent than ethanol, in agreement with the vibrational data.

Methanol does not displace either ethoxy or butoxy, based on our vibrational data. The irreversibility of the displacement reaction between ethanol and methoxy is identical to that

previously observed on Ag(110), reflecting the greater gas phase acidity of ethanol.³⁷ On the same basis, it would be expected that butoxy would not be displaced by methanol on Au(111), but the absence of reaction in our experiments can also be attributed in part to the low activation energy for β -H elimination of butoxy, rendering butoxy unstable with respect to formation of adsorbed butylbutyrate at 150 K. The relative stabilities of alkoxys on other coinage metal surfaces such as Cu(110) and Ag(110) strongly parallel the trend observed on Au(111) in this work; the order of these displacement reactions has been shown to follow the gas-phase acidities of the alcohols.^{37,38} This trend appears to be characteristic of the coinage metal surfaces.

The other significant factor in determining the product distributions is the relative rates for β -H elimination. As previously established for methanol²³ and ethanol²² self-coupling and for the cross-coupling of methanol with various aldehydes,¹³ the rate-determining step in ester formation is β -H elimination from the alkoxys on the surface. Thus, the temperature at which the various alkoxys convert to their corresponding aldehydes is a determining factor in the esterification process, since this aldehyde reacts efficiently with alkoxy groups remaining on the surface.^{13,22,23} Here, we established the relative rates of β -H elimination from the alkoxys as n -butoxy > ethoxy > methoxy by using reaction with formaldehyde as a sensitive probe for the presence of the alkoxys (Figure 5). Since formaldehyde is readily attacked by methoxy at 150 K on O/Au(111), and ethoxy and butoxy react rapidly with their corresponding aldehydes, we anticipate facile reactions of formaldehyde (if formed) with ethoxy and n -butoxy under the same conditions (Figure 5).^{22,23}

The sequential doses of formaldehyde and methanol, ethanol, or butanol at 150 K (Figure 5) indicate that (1) methoxy is present on the surface at 150 K, reacting with formaldehyde to produce methylformate; (2) β -H elimination of ethoxy to produce ethylacetate competes with reaction of ethoxy with formaldehyde, to yield ethylformate; and (3) β -H elimination from n -butoxy occurs at or below 150 K and self-couples to form butylbutyrate prior to formaldehyde adsorption. These results indicate that relative activation energies of the β -H elimination reaction of alkoxys are $E_{\text{methoxy}} > E_{\text{ethoxy}} > E_{\text{butoxy}}$, in agreement with previous studies on Ag(110) and Cu(110) surface,^{37,38} assuming that the preexponential factors are the same for each case. The homolytic C–H bond dissociation energies from the carbon atom adjacent to OH group of methanol (401.2–402.5 kJ/mol), ethanol (389.1–410.0 kJ/mol), and propan-1-ol (389.9–392.0 kJ/mol) show the same trend.³⁹

The relative activation energy of the β -H elimination reaction of different alkoxys explains the absence of formate esters among the products at low to moderate methanol concentration in the reactant mixture. Since the longer chain alkoxys, ethoxy or n -butoxy, form their respective aldehydes, acetaldehyde or n -butanal, at temperatures lower than methoxy can form formaldehyde, no methylformate is formed. Instead, a mixture of the self-coupling products, ethylacetate from ethanol and butylbutyrate from n -butanol, and the methyl esters, methylacetate and methylbutyrate, are formed (Figures 2 and 3). Methylformate is only formed under conditions where there is a significant excess of methoxy on the surface, which then can undergo β -H elimination and subsequent coupling with coadsorbed methoxy at higher temperature.

Our fundamental studies suggest a mechanistic framework for controlling selectivity of complex cross-coupling reactions promoted by Au-based catalysts even in the solution phase. Strong parallels between our studies on O-covered metallic gold provide strong and compelling evidence that the activity of Au for complex oxidative coupling of alcohols is due to the high reactivity of atomic oxygen on Au, not the activity of Au itself. We assert that atomic O must play a key role in the reactivity even for supported Au nanoparticles.

Our previous work established strong parallels between the reactions of alcohols on the O/Au(111) surface and gold-based catalysts, in particular, nanoporous gold,²¹ and even supported gold catalysts.²⁷ For example, oxidative coupling of methanol to methylformate was catalyzed in the vapor phase by nanoporous Au at atmospheric pressure using O₂ as an oxidant.²¹ Nanoporous gold is an unsupported metallic material. Cross-coupling of methanol and acetaldehyde to form methylacetate was similarly catalyzed by the nanoporous Au.²¹ There is even a parallel between the product distributions as a function of ethanol concentration in the solution phase oxygen-assisted esterification of ethanol over Au supported on titania and of the mechanism we have determined for ethanol self-coupling over single crystal gold with preadsorbed atomic oxygen. In the case of Au supported on titania, the oxide may facilitate the transfer of atomic oxygen to the surface of the gold. The strong parallels between oxygen-assisted Au catalysis and our model studies, which suggest a bridging of the so-called pressure gap in this case, are attributed to the low intrinsic reactivity of gold.

The parallels between our model studies and catalytic reactions also extend to the oxidative cross-coupling of several higher molecular weight alcohols and methanol. Nielson et al. reported that methyl esters were the dominant products in oxidative coupling reactions in solution between higher molecular weight alcohols (hexanol, benzyl alcohol, and cinnamyl alcohol) and methanol on gold-based catalysts.²⁶ The methanol molar fraction in Nielson's work is 80–95%, which is in the range of methanol content where the cross-coupling reaction dominates on O/Au(111) in the vapor phase (Figures 2 and 3). The major byproduct of these reactions is the self-coupled product formed from reaction of the longer chain alcohol and its corresponding ester. Similar results have also been obtained on gold nanoclusters encased in a polymer matrix.³⁰ The results in solution are in qualitative agreement with our studies on O/Au(111) in that formation of the methyl esters of these more complex alcohols is favored when there is an excess of methanol.

The strong parallels between the product distributions observed in our studies and those obtained in solution suggest that β -H elimination from the various alkoxys determines the relative rates of coupling. Nielsen and co-workers proposed a slightly different mechanism than that determined for our vapor phase reactions.²⁶ Similar to our studies, they propose that oxidation of the substrate alcohol, that is, 1-hexanol, benzyl alcohol, and cinnamyl alcohol, to the corresponding aldehydes is mediated by the Au catalyst under aerobic conditions; however, the ensuing coupling reaction is proposed to occur in solution via reaction of intact methanol in solution and the aldehydes. While we cannot exclude the possibility of liquid-phase reactions, our studies clearly demonstrate that coupling between an aldehyde and alkoxys occurs efficiently on the surface, based on the low temperature for esterification. We plan to further investigate these reactions to more effectively probe reactivity of more

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complex alcohols in order to further understand the mechanisms for these cross-coupling reactions.

Conclusions

The product distribution of oxidative cross-coupling of alcohols mediated by atomic oxygen covered Au(111) surface is determined by the equilibrium between reactants and surface alkoxy groups and the relative facility of the β -H elimination of different alkoxy. The relative ease of the β -H elimination of alkoxy is: $E_{\text{methoxy}} > E_{\text{ethoxy}} > E_{\text{butoxy}}$. The relative stabilities of alkoxy on Au(111) follow the gas-phase acidities of the corresponding alcohols (butoxy > ethoxy > methoxy), consistent with the trend on other coinage metal surfaces. The mechanism for these reactions determined here has direct applicability to the reaction patterns of oxidative cross-coupling reactions of alcohols on gold-based catalysts under realistic conditions.

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Supporting Information Available: Procedures for determining the composition of alcohol mixtures and selectivity from temperature programmed reaction data and for estimating the relative concentration of methoxy on the surface. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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