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ARTICLE

Methyl Ester Synthesis Catalyzed by Nanoporous Gold: From 10^{-9} torr to 1 atm

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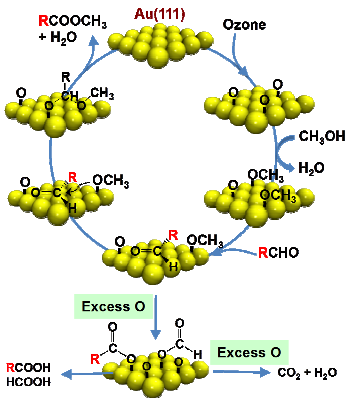
The oxidative coupling reaction of aldehydes with methanol occurs in the vapor phase over a support-free nanoporous gold (npAu) catalyst over a wide pressure range—from 10^{-9} torr to 1 atm. The dependence of the aldehyde-to-ester reaction rate on the oxygen, methanol and aldehyde partial pressures suggests that the rate-limiting step for coupling is the reaction of the aldehyde with surface sites saturated with adsorbed methoxy. Stable catalyst activity is achieved for aldehyde-methanol coupling in flowing reactant mixtures at 70 °C. While the conditioned npAu catalyst exhibits high selectivity for methanol-aldehyde coupling, its activity for the self-coupling reaction of methanol to methyl formate is reduced by the exposure to the alcohol-aldehyde mixture in a manner that is consistent with the buildup of spectator species. The activity for methanol self-coupling can be regenerated by extended exposure to flowing methanol, CO and O_2 at 70 °C. Overall, the observed catalytic esterification is consistent with model studies of both the npAu catalyst and single crystal gold in ultrahigh vacuum.

Introduction

Sustainable chemical processing is a potential step toward addressing the environmental imbalances brought about by human activities through the development of energy-efficient catalytic processes. Recently, selective oxidation of alcohols promoted by gold-based catalysts has received special attention partly due to the potential of biomass conversion to fuels and to commodity and fine chemicals.[1] A long-sought goal is to develop highly efficient and selective catalytic processes that operate under mild conditions. To this end, model studies on well-defined single crystal surfaces under ultrahigh vacuum (UHV) conditions have significantly contributed to the mechanistic understanding of catalytic processes on a molecular basis.[2-4]

Transference of understanding of reactions from model studies under ultrahigh vacuum conditions to catalytic reactor environments is uniquely possible for reactions catalyzed by metallic gold[2-4] because metallic Au has low reactivity. Although the correspondence in the qualitative activity of O-covered Au(111) to studies over nanoporous Au (npAu) catalysts using O_2 for the oxidative coupling of methanol to methyl formate[5] and the oxidation of ethanol and 1-butanol illustrate the parallel between these vastly different conditions, it is still important to establish this correspondence for complex reaction environments.

Herein, we report on the coupling of alcohols with aldehydes with special emphasis on the deactivation mechanisms for selective oxidation processes under catalytic conditions. These results directly interrogate the reaction mechanism under working catalytic conditions and underline the value of investigating complex materials under well-defined ultrahigh vacuum conditions. These results provide insight into deactivation mechanisms for selective oxidation processes under catalytic conditions and also establish the value of investigating complex materials under ultrahigh vacuum conditions as a means of probing reaction mechanism on the actual catalyst.



Scheme 1 Schematic of reaction mechanism for aldehyde coupling with methanol on the oxygen-covered Au(111) surface.[7]

The coupling of several different aldehydes, including formaldehyde, acetaldehyde, benzaldehyde, and benzeneacetaldehyde, with methoxy on oxygen-covered Au(111) was previously demonstrated to proceed via the mechanism[7] depicted in Scheme 1. Methyl esters are selectively formed well below room temperature when the aldehyde reacts with surface bound methoxy groups, indicating rapid kinetics for coupling.

Preliminary studies of npAu showed that coupling of acetaldehyde with methanol in the presence of O_2 under ambient conditions can occur;[5] however, neither the selectivity for coupling nor the stability of the catalyst under reaction conditions were investigated. In principle, the formation of other products, such as methyl formate or carboxylic acids, is possible, depending critically on the specific reaction conditions. Herein, we report detailed kinetic studies of the oxidative coupling of methanol with acetaldehyde and butyraldehyde over npAu catalysts at ambient pressure and under UHV conditions. We find that npAu catalysts exhibit stable catalytic activity and high selectivity (>90%) in the coupling of methanol and aldehydes over a wide range of methanol fraction (up to 95 mol.%) in the reaction mixture. These results show that the aldehyde is an intermediate in the direct coupling reaction of longer-chain alcohol with methanol. In addition, the aldehyde could be oxidized by reaction with surface oxygen to yield acid and/or combustion process. The observed reaction behavior under ambient conditions is consistent with model studies of both the npAu catalyst and single crystal gold in ultrahigh vacuum; thus, providing insight into the overall mechanism.

Results

The as-prepared npAu sample used in this study consists of a three-dimensional network of gold ligaments of ca. 50 nm (Fig. 1), with a surface area of 3.9 m^2 g^{-1}. The content of residual Ag in the bulk phase and on the surface is ~2.4 at% and ~10 at%, respectively.

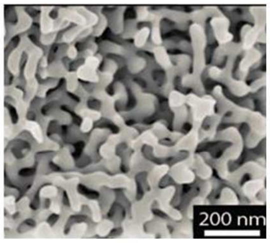


Fig. 1 Scanning-electron micrograph of the npAu disk before reaction.

Oxidative coupling of methanol and aldehydes on npAu in UHV

Coupling of methanol and acetaldehyde occurs during temperature programmed reaction (TPR) on oxygen-covered npAu. It should be noted that the characteristic diffusion time of the reactants through the npAu ingot sample is estimated to be less than 0.1 s, much faster than the time scale of the TPR experiments. Therefore, the reaction is considered to occur both in the inner and outer surface of the catalyst.

Atomic oxygen was deposited on npAu via dissociation of O_2 at 300 K.[8,9] In these studies, methanol reacts with the surface reactive oxygen (O_{ads}) and forms adsorbed methoxy, analogous to studies of methanol reaction with O/Au(111).[10] Sequential exposure of the O-precovered npAu to methanol and acetaldehyde at 180 K yields methyl acetate upon heating in a peak at ~300 K (Fig. 2, left panel). Methyl acetate is the dominant coupling product, accounting for 46% of the product, compared to 10% methyl formate; H_2O (270 K) and CO_2 (512 K) are also produced.[7] Notably, neither methanol nor acetaldehyde reacts on clean npAu (i.e. without adsorbed O). Both methanol and acetaldehyde also desorb from the oxygen-covered npAu surface in two peaks at ~200 K and ~300 K. The low temperature peak is attributed to multilayer molecular physisorption. The high temperature peak at ~300 K can be attributed to either oxygen-stabilized species or reactive desorption of methanol and acetaldehyde molecules since methanol and acetaldehyde desorb at 235 K and 227 K from the clean surface, respectively.

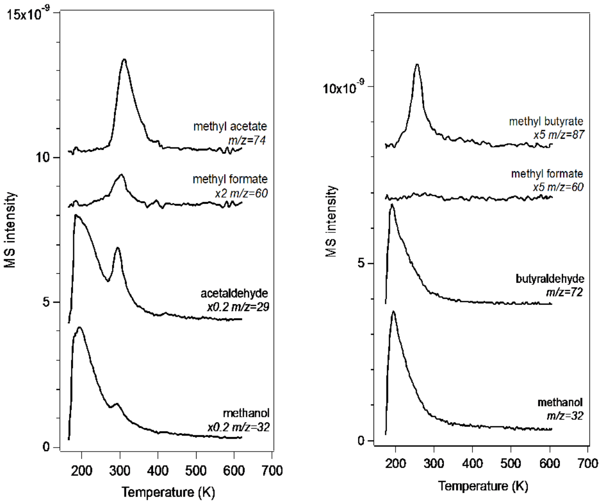


Fig. 2 Temperature programmed reaction of methanol on O/npAu after subsequent exposure aldehdyes: acetaldehyde (left) and butyraldehyde (right). Methanol was dosed at 180 K for 0.02 L followed by an equal dose of the aldehyde (either acetaldehyde or butyraldehyde) at the same temperature. Before organic reagents were dosed, atomic O was formed on the npAu by exposure to 0.3 Langmuir of O_2 at 300 K to achieve 7% saturation coverage. Overlapping mass fragments have been subtracted for clarity. The heating rate was approximately 6 K s^{-1}.

Analogously, O/npAu drives the reaction of butyraldehyde and methanol to yield methyl butyrate near 250 K (Fig. 2, right panel); in this case essentially no methyl formate is produced. Furthermore, there is eight times more CO_2 formed by reacting butyraldehyde instead of acetaldehyde with methoxy-covered npAu (not shown). The products observed are consistent with methanol reacting with the O_{ads} to form methoxy to which the aldehydes then couple, as established in studies of methanol coupling reactions on O/Au(111)[10,7] (Scheme 1). An estimate of the activation energies for product evolution are 63 kJ/mol for methyl butyrate and 76 kJ/mol for methyl acetate using a Redhead analysis of a first-order process and assuming that reaction instead of desorption is rate determining.[11]

Flow Reactor studies

Co-reaction of methanol and acetaldehyde in the presence of O_2 in the flow reactor yielded the coupling products, methyl acetate and/or methyl formate, with the product distribution dependent on the specific reaction conditions (see GC-MS data in Fig. S1 and S2). In summary, methyl acetate was observed as the main product, and methyl formate was only observed under extreme conditions, such as high temperature or high methanol mole fraction in the reaction mixtures. In contrast to the studies in UHV, no CO_2 formation was detected in any of the experiments. These results are qualitatively consistent with preliminary studies of the oxidative coupling of acetaldehyde and methanol[5] (1 vol.% acetaldehyde + 2 vol.% methanol + 10 vol.% O_2) in which methyl acetate formation, not methyl formate, was reported. Indeed, in experiments that replicated the conditions of the previous work only trace amounts of methyl formate were detected. To study the influence of different reaction conditions on the product distribution, in most of the experiments we used reaction mixtures dilute in aldehyde, (i.e., 10 vol.% methanol, 0.5 vol.% acetaldehyde and 20 vol.% O_2), so that appreciable amounts of methyl formate product could be detected.

Effect of reaction temperature. The reaction rate of acetaldehyde increased steadily with temperature from 0.96×10^{-6} mol s^{-1} g_{cat}^{-1} at 30 °C to 2.9×10^{-6} mol s^{-1} g_{cat}^{-1} at 90 °C (Fig. 3a).

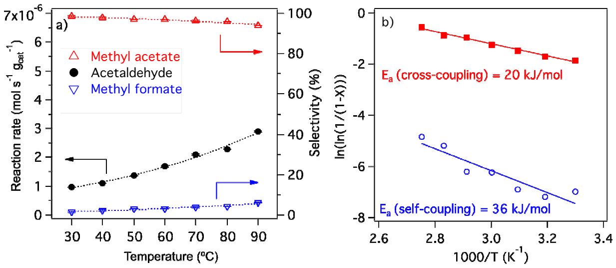


Fig. 3 a) The steady state reaction rate and selectivity (see ESI for the definitions, similarly hereinafter) for methanol-acetaldehyde coupling using a npAu catalyst as a function of reaction temperature. Reaction conditions: 20 vol.% O_2, 10 vol.% methanol, 0.5 vol.% acetaldehyde, 50 mL/min. b) Arrhenius plot of methanol self-coupling (○) and cross-coupling with acetaldehyde (■) reactions on the npAu catalyst. The error bars are smaller than the points in the legend (see Experimental section.)

The reaction rate of methanol was not quantified because it was in 20-fold excess in the reactant mixture, making its conversion significantly lower and difficult to measure small changes. At all temperatures investigated methyl acetate was the predominant product (selectivity higher than 90%); CO_2 was close to the detection limit (ca. 10^{-3} vol%). Trace amounts of methyl formate were also produced via self-coupling of methanol even below 60 °C, most likely because of the excess methanol. Both the formation of methyl formate and methyl acetate increased with temperature, but since methyl formate production is enhanced by a factor of 5.5 from 30 °C to 90 °C, while the latter only increased by a factor of 3.5, there is a slight decrease in the selectivity for methyl acetate over the range of temperatures studied. The apparent activation energies (E_a) of methanol-acetaldehyde coupling and of methanol self-coupling were estimated to be ~20 kJ mol^{-1} and ~36 kJ mol^{-1}, respectively (Fig. 3b) (see ESI).

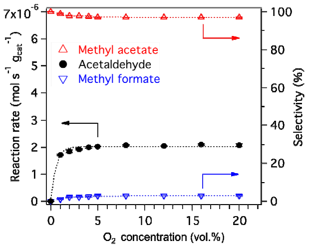


Fig. 4 The reaction rate and selectivity for co-reaction of methanol and acetaldehyde as a function of O_2 concentration using a np Au catalyst. Reaction conditions: 10 vol.% methanol, 0.5 vol.% acetaldehyde, 70°C, 50 mL/min.

Effect of O_2 concentration. The reaction rate of acetaldehyde over the npAu catalyst is nearly constant with the O_2 concentration from 1 - 20 vol.% for a 10 vol.% methanol, 0.5 vol.% acetaldehyde mixture at a reaction temperature of 70 °C (Fig. 4). As the rate increases with decreasing O_2 concentrations (below 5 vol.%) there is a slight decrease in the selectivity for methyl acetate formation as a result of an enhancement in methyl formate production.

Effect of methanol and acetaldehyde concentration. The catalytic activity for co-reaction of acetaldehyde and methanol in the presence of 10 vol.% O_2 over npAu depends on their relative concentrations at 70 °C (Fig. 5a). The conversion rate of acetaldehyde stays nearly constant at 2.0×10^{-6} mol s^{-1} g_{cat}^{-1} above a methanol concentration of ~2 vol.% (Fig. 5a). On the other hand, the reaction rate increases steadily with increasing concentration of acetaldehyde, consistent with a fractional order dependence of the rate on the aldehyde concentration (see ESI).

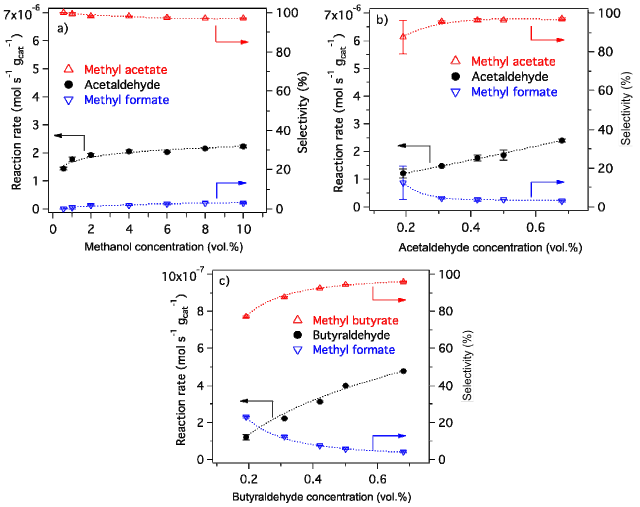


Fig. 5. The dependence of the activity and selectivity for methanol-aldehyde coupling on npAu as a function of a) methanol, b) acetaldehyde, and c) butyraldehyde concentration. Reaction conditions: 20 vol.% O_2, 70°C, 50 mL/min, a) 0.5 vol.% acetaldehyde, methanol: 0.5 ~ 10 vol.%, b) 10 vol.% methanol, acetaldehyde: 0.2 ~ 0.7 vol.%, c) 10 vol.% methanol, butyraldehyde: 0.01 ~ 0.06 vol.%.

The product distribution strongly depends on the relative concentrations of methanol and acetaldehyde. Generally, methyl acetate, the product of acetaldehyde and methanol coupling, is predominant. Under methanol-rich conditions (> 1% methanol or ~ twice the acetaldehyde concentration) the reaction rate and selectivity for methyl acetate becomes independent of methanol concentration (Fig. 5a). Methyl formate, resulting from self-coupling of methanol, is only produced when there is a substantial excess of methanol (Fig. 5b). Even then, with a 30-fold excess amount of methanol, increasing the acetaldehyde concentration from 0.2 to 0.3 vol.% reduced the selectivity of methyl formate rapidly - from 12.5% to 4.7%. Indeed, methyl formate is produced in significant amounts only at methanol molar fractions above 90% (Fig. 6a). These results demonstrate that the reaction of the adsorbed methoxy intermediate with the aldehyde reactant dominates over self-coupling with formaldehyde produced by β-H elimination from adsorbed methoxy. Only under methanol-rich conditions formaldehyde is formed at a rate sufficient to compete with the methoxy-acetaldehyde reaction.

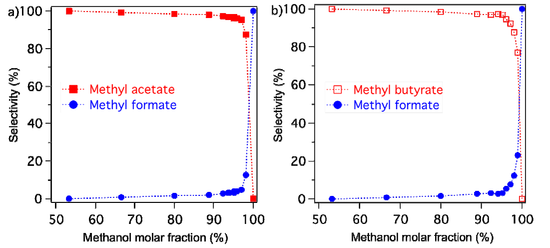


Fig. 6. The product distribution in methanol-aldehyde coupling reaction as a function of methanol molar fraction. Reaction conditions: 70°C, 50 mL/min, a) 20 vol.% O_2, 0.57 ~ 10 vol.% methanol, 0.2 ~ 0.7 vol.% acetaldehyde. b) 20 vol.% O_2, 0.5 ~ 10 vol.% methanol, 0.01 ~ 0.06 vol.% butyraldehyde.

The overall trends in activity and selectivity for methanol-butyraldehyde with variations in the concentration of reactants and temperature are qualitatively similar to the pattern observed for methanol-acetaldehyde coupling (see Fig. 5c). Only methyl butyrate was detected below 40 ºC; methyl formate production becomes only significant at higher temperatures (see Fig. S3) or methanol molar fractions above 95% (see Fig. 6b). Selectivity to methyl butyrate reaches 95% above 0.06 vol.% of butyraldehyde with a reaction rate of.0.48 × 10^{-6} mol s^{-1} g_{cat}^{-1}. The apparent E_a of methanol-butyraldehyde coupling is □15 kJ mol^{-1}, slightly lower than that of methanol-acetaldehyde coupling. The reaction rate depends only weakly on O_2 (below 5 vol.%) and methanol (0.5 ~ 10 vol.%) concentrations, and increases with increasing butyraldehyde concentration, similar to the behavior observed for acetaldehyde (0.01 ~ 0.06 vol.%).

The reason that the activation energies determined in the flow reactor are lower than those observed for formation of the same product on npAu in UHV is not understood at this time. Possible explanations include (1) more complex kinetic expressions or a change in the rate limiting step in the kinetic steady state vs. the temperature programmed experiments, (2) pore diffusion effects in the npAu ingot under steady state operation and (3) different surface coverage of oxygen and reaction intermediates in the different reaction conditions. These effects are currently under further study. Nevertheless, the observed reaction behaviors, including the major product distribution and reaction pathways, are qualitatively consistent with each other.

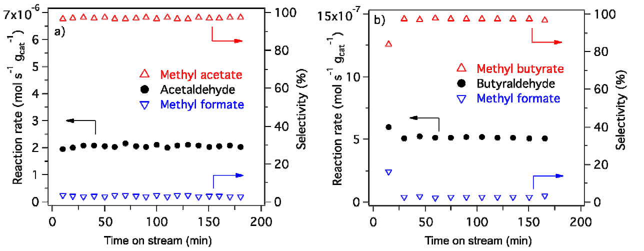


Fig. 7. The activity and selectivity of npAu catalyst in oxidative coupling of methanol with a) acetaldehyde and b) butyraldehyde as a function of time on stream. Reaction conditions: 70°C, 50 mL/min, 20 vol.% O_2, 10 vol.% methanol, a) 0.5 vol.% acetaldehyde, b) 0.057 vol.% butyraldehyde.

The npAu catalyst exhibited excellent stability of both activity and selectivity for the oxidative coupling of methanol with either acetaldehyde (Fig. 7a) or butyraldehyde (Fig. 7b), with no appreciable change in two hours of reaction under the conditions studied.

In the course of these experiments, it was observed that the catalyst became nearly inactive for the self-coupling of methanol after exposure to the aldehyde-containing reaction mixture. This deactivation may have contributed to the high selectivity for cross-coupling with the aldehyde. The catalyst could be completely reactivated for the methanol oxidation reaction after treatment in a mixture of 10 vol.% methanol, 2 vol.% CO, and 20 vol.% O_2 at 70 °C for over 20 h.

Discussion

Our studies clearly show that the selective cross-coupling of methanol and aldehydes to produce the corresponding methyl esters is efficiently promoted by the support-free npAu catalysts in the gas phase. Previous studies of supported gold catalysts in the liquid phase proposed that the coupling step occurs via an acid-catalyzed reaction of alcohol and the aldehyde rather than being mediated by the Au catalyst.[12-16] Although the reaction mechanism on supported Au catalysts may be different from that on npAu catalysts, especially for O_2 activation, the present work clearly demonstrates that the npAu surface plays an essential role in all steps of the esterification process and that the support materials are not required for the coupling reaction.

Since npAu contains a small amount of Ag (~3%), it is important to establish the roles of Ag vs. Au in the catalysis. The Ag clearly plays a critical role in delivering oxygen atoms to the surface so as to initiate the reactions.[17] The coupling reactions are, however, characteristic of Au. Under the same conditions used herein, catalytic coupling of dissimilar alcohols occurs over npAu.[6] Since coupling of dissimilar alcohols does not occur on pure silver surfaces, but readily occur on pure gold, this behavior is interpreted as due to migration of reactive intermediates onto gold or the perimeter of Ag patches to the gold,[18] where subsequent reaction can take place (see Scheme 1).

Prior studies on methanol coupling with various aldehydes, including benzaldehyde, hexanal, 2-methyl pentanal, and acrolein, in liquid phase using supported Au catalysts showed that high yields (> 90%) of the corresponding methyl esters could also be achieved under mild reaction conditions,[14,15] in accord with our observations in this study. Specifically, no ^{18}O was incorporated into the esters formed when $^{18}O_2$ was used,[15] which is consistent with the adsorbed oxygen being removed as water as shown in the mechanism (Scheme 1). On the other hand, essentially all methyl esters contained ^{18}O when ^{18}O-labeled methanol was introduced into the reactor scheme.[15] Indeed, in the studies reported here, O_2 is *necessary* to achieve a high activity in the methanol-aldehyde coupling reactions.

The results of catalytic conversion of methanol and the two different aldehydes over the nanoporous gold are also consistent with the mechanism established for O/Au(111) under ultrahigh vacuum conditions. Specifically, adsorbed O is required to activate methanol to yield methoxy. Our current understanding of the methanol-aldehyde coupling reactions on npAu is that the required adsorbed O atoms result from activation of O_2 on silver present in the npAu.[17] This is confirmed by model studies on O-precovered Au(111) surfaces,[8,10,4,7] which showed that adsorbed atomic O is the active species[19,20] and plays a direct and *essential* role in the esterification by generating methoxy (Scheme 1). The adsorbed O also can facilitate the hydrogen elimination (Scheme 1) which yields the ester product.[7]

Generally, the results of the methanol-aldehyde coupling reaction on npAu catalysts under both ambient and UHV reaction conditions are in good agreement with those of studies on the O/Au(111) surface under highly controlled UHV conditions.[7] The corresponding cross-coupled methyl ester (methyl acetate, not methyl formate) was observed as the predominant product, even in the presence of excess methanol. The high selectivity for the cross-coupling reaction pathway and the relatively low temperature at which it occurs indicates that attack of the aldehydes by methoxy is quite facile. In line with previous studies of alcohol oxidation reactions,[5,6,10] the strong parallels between the methanol-aldehyde coupling reactions on the O/Au(111) surface and npAu catalysts provide further evidence that for these gold-based catalysts, the mechanistic insights gained from model studies can be used to predict reactions at ambient pressures.

There are slight but notable differences between the coupling reactions of acetaldehyde and butyraldehyde with methanol. In ultrahigh vacuum the evolution reaction temperature for the formation of methyl acetate is ~50 K higher than that for the evolution of methyl butyrate. This is consistent with the results obtained on the same catalyst in flow reactor, where slightly lower E_a was derived for methanol-butyraldehyde coupling than that for methanol-acetaldehyde reaction. In addition, a similar trend was also found in our prior studies on O/Au(111) surface, where kinetics are faster for acetaldehyde versus formaldehyde with methoxy.[7] The origin for the faster formation of methyl butyrate is not clear yet, but may be due to differences in surface binding of aldehydes with different molecular structures[7] or differences in the ease of H-elimination from the different intermediates yielding the esters.

The competing formation of methyl formate vs. methyl ester is another apparent difference in kinetics for the two different aldehydes. While in both cases the methyl formate production is much lower than the methyl ester formation, it appears that more methyl formate could be produced in the reaction of methanol with acetaldehyde than with butyraldehyde even if the acetaldehyde concentration is almost ten times higher. This observation is in line with the fact that a higher methanol fraction in the reaction mixture is required for the methanol-butyraldehyde reaction to achieve comparable methyl formate selectivities, as obtained in the flow reactor studies (see Fig. 6). As discussed above, the relatively higher selectivity of methyl formate in the reaction of methanol with acetaldehyde could be explained by the slower cross-coupling reaction kinetics compared to butyraldehyde.

Despite the excellent qualitative agreement between the flow reactor and UHV studies, there are some differences in the product distributions. On npAu catalysts in UHV carboxylic acids and/or CO_2 were produced from secondary oxidation of aldehydes and combustion, respectively, even with a limited supply of surface atomic oxygen;[7] similar products were observed under UHV conditions on O-covered Au(111). Furthermore, in UHV studies methyl formate was not observed after adding excess aldehyde to adsorbed methoxy. Neither CO_2 nor carboxylic acids were produced in the flow reactor, and methyl formate was observed, but only at very high mole fractions of methanol in the reactant mixture (>90% for methanol-acetaldehyde reaction).

These differences can be explained by differences in the oxygen distribution under the two conditions due to the different experimental procedures. In the UHV studies oxygen is first adsorbed on the surface and then exposed to methanol and subsequently to the aldehyde. Though the initial oxygen coverage is low, it nonetheless can form both locally dense and dilute phases of chemisorbed atomic oxygen known to exist on Au(111), which affect combustion and selective oxidation, respectively.[21,22] In the flow reactor methanol and aldehyde compete for adsorbed oxygen, which, due to its low probability of oxygen dissociation on these surfaces, reaches a low steady-state coverage. Given the large excess of methanol employed in these experiments, the reaction of adsorbed oxygen with methanol to form methoxy (see Scheme 1) is expected to dominate, leading to a low steady-state coverage of methoxy on an otherwise bare surface. The strong preference for formation of the methyl ester product on nanoporous gold indicates that, even though the methanol is in great excess, reaction of the aldehyde (see Scheme 1) is much faster than hydrogen elimination from methoxy to yield formaldehyde, which would couple with adsorbed methoxy to form methyl formate.

Though the reactor was not optimally designed for kinetic studiesand the reaction kinetics are influenced (but not controlled) by pore diffusion (see ESI), which is why we did not attempt to derive rate equations based on the kinetic experiments, overall the dependence of the conversion rate to the esters on the partial pressures of the reactants reflects general agreement with the mechanism gleaned from UHV. The reaction rate is only weakly dependent on the partial pressure of oxygen and methanol, indicating that the sites available for methoxy formation are saturated at the oxygen partial pressures studied. The rate-limiting step appears to be the reaction of the aldehyde with the adsorbed methoxy (Scheme 1).

The loss of activity for oxygen-assisted methanol self-coupling after extended reaction with the aldehyde indicates a modification of the surface in the presence of the aldehyde and a reduction in the capability of the npAu catalyst to activate O_2. This effect may be due to the blocking of a fraction of the silver sites by the formation of a “spectator” species, which prevents self-coupling of methanol. As mentioned in the experimental section, the deactivated catalyst could be regenerated by exposure to a mixture of 10 vol.% methanol, 2 vol.% CO, and 20 vol.% O_2 at 70 °C for over 20 h. During the regeneration process, a slow but continuous increase in a trace amount of methyl acetate was detected, suggesting that there was accumulation of residual species, most likely adsorbed carboxylate species, on the catalyst surface during the methanol-aldehyde reactions. These carboxylate species are known to be stable to about 450 K.[23] The excellent stability of the catalyst for cross-coupling reactions (Fig. 7) suggests that the surface coverage of these species reaches a steady state value and that the methanol-aldehyde cross-coupling reaction requires a different distribution of reactants on the npAu surface than does the self-coupling of methanol. It is conceivable that the surface coverage of methoxy would go down once the active catalyst is exposed to methanol-aldehyde reaction mixtures. In particular, isolated methoxy can readily react with aldehyde from the gas phase, whereas nearby pairs of methoxy species may be required for methanol self-coupling.

Conclusions

The mechanistic insights gained from studies of oxygen-assisted alcohol-aldehyde coupling on both single crystal Au model surfaces and on npAu catalysts in UHV can be applied to the same reactions on unsupported npAu catalysts under ambient conditions. In agreement with our prior work on the self-coupling reactions of alcohols, this study demonstrates that complex surface reactions involving several chemical entities, specifically the cross-coupling of aldehydes and alcohols, can be anticipated from the molecular level understanding obtained from the model single-crystal studies. Due to the different surface oxygen coverages, care still must be taken in order to relate the results of temperature programmed reaction in UHV to conditions of steady state in the flow reactor to predict the product distribution under steady state conditions. The use of the npAu catalyst for highly selective alcohol/aldehyde cross-coupling leads to pronounced deactivation in the self-coupling reaction of the alcohol. The deactivated catalyst can be regenerated by an extensive treatment with a high concentration of methanol and O_2.

Experimental

Preparation of npAu samples

Round disks of npAu with a diameter of ca. 5 mm and a thickness of 200-300 μm were prepared by free corrosion of Ag-Au alloys in nitric acid (HNO_3, 68-70 wt%, Alpha Aesar Chemical Corp.). The master alloy for all samples was prepared by melting Au and Ag pellets with a composition of 70 at% Ag and 30 at% Au. After verification of the alloy composition by energy dispersive X-ray spectroscopy (EDX), the ingots were annealed under an argon atmosphere for 140 hours at 875 °C. After this homogenization the ingots were rolled, cut into the desired shape and again annealed for 6 hours at 800 °C. The Ag-Au alloy disks were etched in 100 mL of HNO_3 for 48 hours at room temperature to remove Ag. After dealloying, the samples were rinsed 10 times with 60 mL of deionized and filtered H_2O (obtained from a Milli-Q purification system) and then dried overnight at room temperature. The residual content of Ag in the bulk phase as well as that on the surface was determined by EDX and X-ray photoelectron spectroscopy (XPS), respectively.

Ultrahigh vacuum experiments

All ultrahigh vacuum (UHV) experiments were performed in a chamber with a base pressure below 4×10^{-10} Torr. The preparation of the clean npAu sample has been described elsewhere.[8] The surface was populated with 7% of saturation coverage of atomic oxygen by introducing the appropriate amount of oxygen at 300 K according to an established procedure.[24] This coverage was selected to optimize for coupling products while minimizing combustion. The methanol and acetaldehyde were introduced sequentially to the O/npAu surface through independent gas lines. Exposures corrected for dosing enhancement are given here in terms of Langmuir (1L = 10^{-6} torr sec). The total pressure rise in the vacuum chamber during the dosing of the reactants was used to measure the total exposure for the organic reagents. Typical doses were 2 L unless otherwise noted. Temperature programmed reaction (TPR) experiments were conducted according to well-established protocols described previously.[25] The heating rate for all experiments was nearly constant at 6 K s^{-1}. Reaction products were identified by quantitative mass spectrometry (Hiden HAL/3F) using fragmentation patterns obtained from authentic samples (See ESI for more information).

Catalytic experiments in flow reactor

Catalytic measurements were conducted using a glass continuous flow-reactor described in detail elsewhere.[6,5] The inlet tubing and the reactor were embedded in a water bath for precise temperature control (in the range of 30 to 90 °C). The samples were mounted at the lower end of the reactor in direct contact with a gold plate with a circular opening (ca. 2 mm) in the center. The gas mixtures flowed upward through this opening directly across the bottom of the catalyst ingot into a larger reactor housing, which had an inner diameter of ca. 2.0 cm and a total volume of 26 ml. With respect to the dimensions of the reactor, the Péclet number (defined as the ratio of the advective transport rate to the diffusive transport rate) was approximately 4.0, ensuring limited back diffusion of the reactants and products in the vicinity of the catalyst. Though the reactor configuration is not ideal for quantification of kinetic parameters, the measured dependencies on reactant pressures and temperature are sufficiently well defined to allow qualitative comparison of the reactor and the model UHV studies.

The reaction gas mixtures were composed of He (Airgas, 5.0), O_2 (Airgas, 4.5), and a specific amount of methanol and/or aldehyde, with a total flow rate of 50 mL/min. The composition was precisely controlled via mass flow controllers (MKS Instruments, USA). The concentration of alcohols and aldehydes in the reaction mixture was adjusted via their vapor pressure, by guiding the saturated He gas stream (at around 22 °C) through a coiled condenser. The vapor pressure at different temperatures was calculated using the KDB database (Korea Thermophysical Database). Due to the temperature fluctuations (±1 °C) of the condenser, the concentration of the acetaldehyde may deviate by ±5% of the nominal values during the experiments; however, the influence of this deviation on the kinetic results as well as the conclusions of this study, is negligible thus can be regarded as the experiment error. Prior to the methanol-aldehyde coupling reactions, the fresh npAu sample was activated in a stream (total flow rate 50 mL/min) of methanol (10 vol.%), carbon monoxide (4 vol.%), and O_2 (20 vol.%) at 70 °C for over 24 h. The same treatment conditions were also applied to regenerate the deactivated catalyst after the methanol-aldehyde reactions.

The stream of gases at the exit of the reactor was monitored online by a gas chromatograph (Agilent 7890A series, Column HP-Plot/Q and GS-CARBONPLOT) coupled with a mass spectrometer (Agilent 5975C series, inert MSD with triple-axis detector). The measurement of each data point reported in the present paper was repeated for at least three times and the error bars are given, although in most cases too small to be discernable (see Figs. 3-5 and S5). In the studies of coupling between the aldehydes and alcohols the experiments were conducted in alcohol rich environments. No reactions were detected in the absence of the npAu catalyst under the conditions studied in the present work. Nor were products observed in the absence of dioxygen in the reactant mixture. More details about the data analysis including the derivation of reaction rates and selectivity can be found in the ESI.

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Notes

The authors declare no competing financial interests.

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† Electronic Supplementary Information (ESI) available: Evaluation of the activity and selectivity of npAu catalyst in flow reactor; TPRS experiments on npAu catalyst in UHV and data evaluation; Procedure for selectivity calculations based on TPRS data; typical chromatograms for cross-coupling of methanol with acetaldehyde or butyraldehyde over the npAu catalyst and the mass spectrum of the cross-coupling product methyl esters; the activity and selectivity of npAu catalyst in methanol-butyraldehyde coupling reaction as a function of reaction temperature; evaluation of the influence of mass transport limitation on the reaction kinetics in the flow reactor. See DOI: 10.1039/b000000x/

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Highly selective synthesis of methyl esters can be achieved by oxidative coupling of methanol and aldehydes (acetaldehyde, butyraldehyde) under mild conditions using unsupported nanoporous gold catalysts over a wide pressure range (from 10^{-9} torr to 1 atm).