Catalytic Production of Methyl Acrylates by Gold-Mediated Cross Coupling of Unsaturated Aldehydes with Methanol.

Stavros Karakalos,^{a,b} Branko Zugic,^{a,b} Kara J. Stowers,^b Monika M. Biener,^d Juergen Biener,^d Cynthia M. Friend,^{b,c} Robert J. Madix,^{c,*}

^a These authors contributed equally to this work.

^b Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02138, United States

^c School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, United States.

^d Nanoscale Synthesis and Characterization Laboratory, Lawrence Livermore National Laboratory, Livermore, California 94550, United States.

*Corresponding author at: Harvard School of Engineering and Applied Sciences

Harvard University, Cambridge, MA 02138, United States.

E-mail address: rmadix@seas.harvard.edu (R. J. Madix)

ABSTRACT

Modern methods of esterification, one of the most important reactions in organic synthesis, are reaching their limits, as far as waste and expense are concerned. Novel chemical approaches to ester formation are therefore of importance. Here we report a simple procedure free of caustic reagents or byproducts for the facile direct oxidative methyl esterification of aldehydes over nanoporous Au catalysts. Complementary model studies on single crystal gold surfaces establish the fundamental reactions involved. We find that methanol more readily reacts with adsorbed active oxygen than do the aldehydes, but that once the aldehydes do react, they form a strongly-bound acrylates that block reactive sites and decreases the yields of acrylic esters under steady flow conditions at 420K. Significant improvements in yield can be achieved by operating at higher temperatures, which render the site-blocking acrylates unstable.

1. Introduction

Environmentally friendly esterification of aldehydes with alcohols is an important goal for sustainable catalysis. The development of a catalytic method for the direct oxidative esterification, which would be more facile and with less waste in comparison to traditional organic synthesis, is highly desirable. During recent years, the direct transformation of aldehydes into esters has developed into a vibrant research area, [1],[2],[3] mainly because aldehydes are available as bulk chemicals.

A range of reactions is promoted by gold catalysts, and their application to catalysis has received significant attention in the past years. Oxidative coupling of a wide range of alcohols and aldehydes is one class of these reactions[4],[5],[6]. The use of gold

as a catalyst, including nanoporous gold, for oxygen-assisted self and cross-coupling of alcohols, [7],[8],[9],[10] cross-coupling of amines with alcohols[11] and cross coupling of amines with aldehydes[12] has been reported. Nanoporous gold (np(Ag)Au, a dilute bimetallic alloy with low silver content (~1-3 at% bulk), can be highly active for the selective oxidative coupling of C₁-C₄ alcohols and aldehydes[13],[14]. These processes provide an insight into optimizing the cross-coupling selectivity/yield on gold surfaces[14],[15] and in reducing the reaction temperatures, leading to environmentally friendly catalysts.

We recently reported studies of the oxygen-assisted direct cross-coupling of two unsaturated alcohols, allyl and methallyl alcohol ($\text{CH}_2=\text{CHCH}_2\text{OH}$ and $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{OH}$) with methanol over np(Ag)Au[16]. Under steady flow conditions at atmospheric pressure and 150 C the selectivity for acrylate formation is optimized at 25% at a methanol mole fraction of 0.97 with conversions of the alcohols of 70-80%. The remaining products are acrolein (methacrolein) and methyl formate, respectively, with nearly equal selectivities. Further oxidative conversion of these aldehydes to the acrylates would enhance the overall efficiency of this process.

In the present work the oxygen-assisted esterification of acrolein ($\text{CH}_2=\text{CHC}(\text{H})=\text{O}$) and methacrolein ($\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{H})=\text{O}$) with methanol on Au to form their respective acrylates ($\text{CH}_2=\text{CHCO}_2\text{CH}_3$ and $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3$) was studied. Ultra high vacuum (UHV) conditions were utilized to understand the oxidative reactions on Au, without the presence of supporting materials. With the use of temperature programmed reaction spectroscopy (TPRS), we establish the mechanism and conditions for the facile esterification of acrolein and methacrolein. Selectivities of ~95%

were achieved on oxygen pre-covered Au (110) with methanol conversions of nearly 100 % under appropriate conditions. Under continuous catalytic production on nanoporous gold (npAu) at 150 °C in a flow reactor methyl acrylate and methyl methacrylate formed with selectivities near 100 % at methanol mole fractions of 0.90, but aldehyde conversions were low. The origin of this low activity is shown to be due to poisoning of active sites by adsorbed acrylates. Increasing the reaction temperature to 200 °C improves catalyst activity by destabilizing this site blocking species.

2. Methods

2.1 Catalyst Sample Preparation.

Ingots of npAu (diameter 5 mm, thickness 200-300 μm) were prepared by the chemical etching of $\text{Ag}_{70}\text{Au}_{30}$ bimetallic alloy disks in concentrated nitric acid as reported previously[17],[18]. The average ligament size of the as-prepared npAu is ~ 30 nm, the BET surface area is $\sim 4.5 \text{ m}^2/\text{g}$ and the bulk Ag content is $\sim 3 \text{ at\%}$ (measured by EDS). The as-prepared npAu surfaces are highly crystalline and, due to the shape of the ligaments, highly stepped. While recent reports indicate that all low index facets can be observed by TEM analysis[19],[20], we have shown by using both Au(111) and Au(110) surfaces that the reaction selectivity for oxidative coupling on Au is structure insensitive.[21],[16] It should also be noted, however, that the residual silver in nanoporous gold plays the critical role of activating molecular oxygen, which drives the selective oxidation reactions on gold-rich surfaces.[18],[22]

2.2 Model Studies in UHV

Ultrahigh vacuum (UHV) experiments were performed on both a Au(110) single-crystal and on npAu ingot samples in separate UHV chambers with a base pressure $< 5 \times 10^{-10}$ Torr. The Au(110) crystal was mounted on a manipulator capable of heating to 1000K and of cooling (via liquid nitrogen) to 100K, as measured by a chromel-alumel thermocouple inserted into a pinhole in the side of the Au(110) crystal. The Au(110) was cleaned by argon ion bombardment followed by cycles of ozone dosing at 200K and flash annealing to 850K to remove surface impurities (as judged by CO and CO₂ production from C contamination).[23]. Surface cleanliness was confirmed by recording the ordered (1x2) reconstruction LEED pattern of Au(110) surface. Adsorbed atomic oxygen was generated by controlled dosing of ozone to the surface, and the coverage was calibrated by comparison of the intensity of the integrated O₂ signal due to O atomic recombination above 500 K to the integrated signal for the saturation coverage of 1 ML.[24],[25] Experiments were performed on the Au(110) surface precovered with 0.1 ML atomic oxygen.

Temperature programmed desorption and quantitative mass spectrometry was used to quantify the relative concentrations of the two aldehydes dosed onto the surface, as reported previously (Fig. S1).[9] The gases were introduced to both the npAu ingot and the Au(110) crystal using a directed dosers with an enhancement factor of ~50.[26]

Reactants methanol, acrolein, and methacrolein were independently introduced to the catalyst surface at the temperatures specified (~120 K) and the dose controlled by monitoring the rise in the ambient pressure in the chamber while leaking the respective vapor into the UHV system. The fragmentation patterns of the background gas, recorded

from condensation experiments of each reactant separately on Au(110), verified the gas purity. All liquids were subjected to several freeze-pump-thaw cycles for purification before use. A typical experiment consisted of ozone exposure [25] to the catalyst surface at 300 K followed by cooling of the sample to ~120 K before dosing the reactants. A trace amount of water condensed on the surface during cooling (less than 1% of the amount observed in a typical oxidation reaction). The catalyst was then heated and the reaction monitored by temperature programmed reaction spectroscopy (TPRS). The heating rate for temperature programmed reactions was constant at $\sim 5 \text{ K s}^{-1}$ for the Au(110) single-crystal and $\sim 3 \text{ K s}^{-1}$ for the npAu. The reaction products were identified by quantitative mass spectrometry (Hiden HAL/3F) using fragmentation patterns obtained from authentic samples (Fig. S2). Overlapping mass fragments have been subtracted for clarity from all TPR spectra. In the cases where ion fragments are not unique to a specific product, the subtraction was performed by using the ion yields referenced in Tables S1 and S2. Following the equations described in Part 2 of the supplemental information, we calculated the selectivity towards the oxidation products (methyl acrylate or methyl methacrylate) by taking into account the number density of molecules (n) in the ionizer of the mass spectrometer. The formula used for the calculation of n for various species is also presented in Part 2 of the supplemental information

The npAu gold sample was activated in UHV for O_2 dissociation by repeated cycles of ozone exposure and annealing to desorb carbonaceous impurities until recombination of atomic oxygen at 550 K[27] was observed, and the evolution of CO_2 and CO ceased. On this cleaned surface O_2 was readily dissociated at 300 K; the relative

O coverages in fractions of a monolayer were determined by comparison to the saturation coverage determined by temperature programmed desorption.[23],[28],[29] It was not possible to determine the absolute coverage of O_{ads} on npAu because the active surface area was not known.

2.3 Flow Reactor Studies.

The npAu ingots (35 mg) were placed on a porous quartz frit that was supported inside a quartz tube reactor (10.5 mm I.D.) by a plug of quartz wool. Prior to reaction the catalyst was activated by ozone treatment followed by exposure to flowing methanol and oxygen at 150 °C under ambient conditions.[30] The catalyst was kept under methanol oxidation conditions at 150 °C for up to 12 hours prior to testing cross-coupling activity. The space velocity for the conditions used based of the catalyst volume was 140 s^{-1} . The activated catalyst exhibited a selectivity and conversion for methanol self-coupling of 32-38% and >94%, respectively. All organics were introduced into the reactor via saturated He flow from temperature-controlled bubbler-condenser assemblies. The gas phase composition was controlled by mass flow controllers (MKS Instruments). The oxygen concentration was kept at 20% during all experiments. The gas phase composition was monitored by GC-MS (Agilent 5975C and Agilent 7890A) equipped with HP-PLOT Q and CARBONPLOT columns. The stability of the coupling reactions was periodically tested for up to 24 h with no decrease in activity.

3. Results and discussion

3.1 Model studies of the reactions of acrolein, methacrolein and methanol on oxygen precovered Au(110) and npAu in ultrahigh vacuum.

Model studies were conducted under UHV conditions on both the O/Au(110) and on O/npAu surfaces. Adsorbed atomic oxygen was formed on the Au(110) surface via ozone exposure ($p=5\times 10^{-8}$ torr) at 300 K and via O₂ exposure on the activated npAu surface ($p=4\times 10^{-10}$ torr) at 300 K. Reactants were dosed at 120K so that no residual oxygen was detectable by temperature programmed desorption ($m/z=32$ above 500 K).

Methanol, acrolein and methacrolein each show characteristic reaction patterns with preadsorbed atomic oxygen. As previously reported, methanol self-couples to form methyl formate at 250 K via adsorbed methoxy intermediate.[8],[23],[30] The reaction of acrolein with oxygen-precovered Au(110) yields, characteristically, carbon suboxide ($m/z=68$) at 443 K with minor amounts of acrylic acid ($m/z=72$) (Fig. 1a). Acrolein ($m/z = 56$) desorbing below 300 K corresponds to unreacted aldehyde. There is some combustion to carbon dioxide ($m/z = 44$), due to over-oxidation under the conditions employed and production of water ($m/z = 18$) below 400K. Methacrolein is oxidized to methacrylic acid at 300 – 450 K as well as CO₂ at 350 K (Fig. 1c). When coadsorbed at 120 K on Au(110) precovered with 0.1 ML of adsorbed O, methanol and acrolein (methacrolein) cross-couple to form methacrylate and methyl methacrylate at 280 and 320 K, respectively (Fig. 1b, d). Similar results were observed on np(Ag)Au for acrolein in ultrahigh vacuum (Fig. S3).

Figure 1. TPR spectra of acrolein and methacrolein oxidation and cross-coupling with methanol on O/Au(110) interface. 0.1ML of atomic oxygen was dosed at 300 K via ozone exposure, subsequently the organics were dosed at 130 K. (a) Excess acrolein (~1ML) was dosed independently (b) 0.3 ML acrolein and 0.7ML methanol (c) Excess methacrolein (~1ML) was dosed independently (d) 0.3 ML methacrolein and 0.7 ML methanol; (Methanol was dosed prior to acrolein and methacrolein in b and d). Overlapping mass fragments have been subtracted for clarity. The heating rate was 5 K s^{-1} .

Since it is well understood that methoxy is formed from reaction of methanol with adsorbed atomic oxygen, but the reactivity of the aldehydes is not understood, the reactivity of the aldehydes with the surface oxygen was first examined in detail. Acrolein or methacrolein was first adsorbed on the 0.1ML O/Au(110) interface at 120K. The sample was then heated to a prescribed temperature, (below the desorption temperature of the aldehyde), cooled to 120K and methanol dosed before ramping the temperature to perform TPRS to detect any coupling product that formed (methyl acrylate or methyl methacrylate) (Fig. 2).

Figure 2. Methyl acrylate and methacrylate detected by TPRS resulting from a) adsorption of 2 ML of acrolein on 0.1ML O/Au(110) at 120K, then flashing of the sample to various temperatures and finally cooling down to 120K to adsorb 2ML of methanol, b) exact same procedure for methacrolein and methanol sequential dosing. Inset figures show the amount of the acrylate produced on the surface for each annealing. The intermediate coverage was calculated by the differences in the integrated peak areas between 120K and the target temperature. For all experiments the sample temperature was ramped to a preset temperature at 5Ks^{-1} . When the target temperature was reached the heater was turned off immediately.

For both aldehydes the amount of ester formed decreased progressively as the annealing temperature was increased up to 240K, above which no production of the cross coupling products was detected subsequent to methanol exposure. The reduction in the

amount of acrylate produced was accompanied in the same fashion by increase in the oxidation product of the aldehyde (Fig S4a, b). These observations indicate that the aldehydes are simply molecularly adsorbed the O/Au(110) interface at 120K and start reacting with the surface oxygen at ~160K, completing reaction with the surface oxygen at 240K. Water production is observed for oxidation of both acrolein and methacrolein on the O/Au(110) surface at 240K (Fig. 1a, c), indicating the formation of acrylates as surface intermediates as suggested by previous studies[21]. The fact that the aldehydes do not react with the surface oxygen when dosed at 120K, results in free adsorbed oxygen atoms on Au(110) which are available for methoxy formation upon subsequent methanol adsorption at 120K. Furthermore, as expected from previous work[15], methanol cannot displace the acrylate intermediate formed from the reaction of the aldehyde with adsorbed O.

The apparent activation energy of acrolein and methacrolein reaction with the surface oxygen on Au(110), towards acrylate formation, can be calculated from the data in Fig. 2 (Figs. S5, S6). Both aldehydes exhibit low activation energies for the formation of their respective surface intermediates of ~3 kcal/mol.

Sequential dosing of methanol – acrolein **multilayers** on two different O/Au(110) interfaces (0.05ML and 0.1ML O coverage) at 120K, resulted in methyl acrylate production (Figs. 3a, b). Independent of the order of the dosing of the reactants on the surface, the amount of the methyl acrylate production was the same and equal to the case of 0.5ML of methanol and 0.5ML of acrolein (50 – 50%) dosed sequentially at 120 K (see below). Reduction of the initial oxygen coverage from 0.1ML to 0.05ML cut the amount of methyl acrylate production in half (Fig. 3c).

Figure 3. TPR spectra for the sequential dosing of multilayers of methanol and acrolein on the O/Au(110) interfaces for three cases: a) 2 ML methanol first and then 5ML of acrolein at 120K, b) 2ML of acrolein first and then 5ML of methanol at 120K, c) 0.5ML of methanol first and then 0.5ML of acrolein at 120K. The relative amounts of methyl acrylate production for the three cases is also shown, indicating that the final coupling product is proportional to methoxy formation on the surface.

The fact that the order of dosing of multilayers of the reactants at 120K does not change the amount of acrylate formed, indicates that at this low temperature, methanol preferentially reacts with the surface oxygen. Methyl acrylate results subsequently from

the coupling of a methoxy with coadsorbed molecular acrolein. Finally, the fact that the amount of methyl acrylate reduces in proportion to the amount of preadsorbed oxygen is further indication that the oxygen is removed preferentially by methanol to form methoxy which reacts stoichiometrically with the molecularly adsorbed acrolein.

Further, in order to confirm that cross-coupling reactions between acrolein and methacrolein with methanol does not occur *via* the surface intermediate produced by reaction of the aldehyde with adsorbed O, we first annealed the coadsorbed aldehyde/O/Au(110) interface to 240K before cooling to 120 K and subsequently adsorbing methanol. The amount of the aldehyde dosed initially was low enough so it did not consume all surface oxygen after heating the sample at 240K. After this procedure only the separate oxidation products of the individual reactants were detected, not the cross-coupling product (Fig. S7a, b), indicating that once the aldehyde reacts with oxygen no esterification reaction can take place. This is clear evidence that methanol does not react with the intermediate formed by reaction of acrolein with adsorbed O to reform adsorbed acrolein and methoxy methanol; nor does methanol displace the adsorbed acrylate intermediate by proton transfer, as the acrylic acid would be readily observed in the TPRS.

To examine this issue further methanol and acrolein were dosed sequentially on Au(110) at 120 K under UHV conditions and heated to determine the optimum initial reactant ratios for cross-coupling. Such experiments have revealed reversible competition of the alkoxy reactive intermediates that lead to an unexpected optimization of cross-coupling of methanol with ethanol, butanal and allyl alcohol at high methanol

mole fraction. Indeed, cross coupling to form methyl acrylate ($m/z = 55$) occurred over a wide range of the relative amounts of the reactants dosed (Figs. 4a, b; S8).

Figure 4. Cross-coupling selectivity over (a) 0.1ML O/Au(110) interface, subsequently methanol and acrolein were dosed at 120 K, over (b) 0.1ML O/Au(110) interface, subsequently methanol and methacrolein were dosed at 120 K. In the same figure the adsorbed methoxy coverage (as a surface intermediate) as the methanol dose was increased is shown. Atomic oxygen was dosed at 300 K via ozone exposure on Au(110).

The overall product selectivity was highly dependent on the methanol mole fraction, with methyl formate ($m/z = 60$, 220K) being the dominant product at high methanol mole

fractions (>0.8). Initially at low methanol mole fractions, carbon suboxide ($m/z = 68$), the product of acrolein partial oxidation, was the dominant product. Increasing the relative amount of methanol dosed gave rise to an increase in acrylate formation up to 50% methanol, as the carbon suboxide decreased to zero. Above 50% methanol the amount of acrylate decreased, giving way to methyl formate. Very similar results were observed with TPRS on npAu under UHV conditions for the conditions examined, particularly with respect to the methyl acrylate production (Fig. S3). Table 1 shows the integrated areas of the TPRS spectra obtained from Au(110) for a methanol mole fraction of 0.7.

Table 1. Total product selectivity of acrolein, methacrolein oxidation reactions and cross coupling reactions with methanol on O/Au(110). The carbon containing product selectivity is included in parenthesis.

Oxidation products	Acrolein <u>Oxidation</u> Total Sel. (Carbon Sel.) (%)	Methacrolein <u>Oxidation</u> Total Sel. (Carbon Sel.) (%)	Acrolein – MeOH <u>Cross coupling</u> Total Sel. (Carbon Sel.) (%)	Methacrolein – MeOH <u>Cross coupling</u> Total Sel. (Carbon Sel.) (%)
Hydrogen	-	-	1	1
Water	49	69	22	19
Carbon dioxide	24 (47)	27 (87)	4 (6)	6 (9)
Methyl formate	–	-	8 (13)	6 (9)
Carbon suboxide	24 (47)	-	-	-
Acrylic acid	3 (6)	-	-	-
Methacrylic acid	-	4 (13)	-	-
Methyl acrylate	–	-	66 (81)	-
Methyl methacrylate	-	-	-	68 (82)

The reaction of methacrolein alone with oxygen-precovered Au(110) yields mainly methacrylic acid ($m/z=86$) as its signature product (Fig. 1c). The methacrolein peak ($m/z = 70$) observed at temperatures less than 300 K corresponds to the unreacted aldehyde. There is some combustion to carbon dioxide ($m/z = 44$) observed from over-oxidation under the conditions tested and production of water ($m/z = 18$) below 400K.

As with acrolein, the optimal oxidative coupling of methacrolein with methanol to methyl methacrylate subsequent to sequential dosing of methanol and methacrolein at 120 K on oxygen-precovered Au(110) surfaces was also reached at ~ 0.5 methanol mole fraction (Fig. 4b, S9). Methyl formate was produced predominantly at methanol mole fractions >0.8 . Methacrylic acid, the product of methacrolein partial oxidation is also produced in significant quantities for methanol mole fractions below 0.3 and is the main product when the methanol mole fraction reaches <0.15 . Notably, these reactions occur without oxidation of the unsaturated C=C bond. None of these reactions occurs on clean Au, on which only the condensation of the reactants could be detected.

The dependence of the product selectivity on the relative amounts of methanol and aldehyde dosed can be understood from the preferential reactivity of methanol for the preadsorbed oxygen. When the methanol dose at 120 K is increased (keeping the sum of the methanol and aldehyde dosed constant), methanol removes progressively more adsorbed O to form methoxy. Upon heating this methoxy reacts to completion with coadsorbed molecular aldehyde, until, after consumption of the methoxy, the aldehyde is oxidized by the remaining adsorbed O. At a dose of 0.5 ML methanol (mole fraction 0.5) all of the O is titrated by methanol and it reacts with the coadsorbed aldehyde to form the acrylate. The fact that the oxidation product of the aldehydes fall to zero at this dose of

methanol clearly indicates that there is no excess adsorbed O after reaction with 0.5 ML of methanol. Above a dose of 0.5 ML of methanol, the amount of aldehyde dosed is decreasing so that excess methoxy remains after acrylate formation. This methoxy self-couples to form methyl formate. The relative methoxy coverage can be determined at each methanol mole fraction dosed by summing the amounts of methyl formate and acrylate formed. The methoxy surface concentration reached its limit at 0.5 mole fraction and remains constant up to 1.0 as expected from this analysis (see inserts in Figs. 4a, b).

Scheme 1(a) illustrates these reactions. When the adsorption of both acrolein and methanol takes place at 120K on the O/Au(110) interface, the aldehyde is molecularly adsorbed and all oxygen is available for methoxy formation; the aldehyde then oxidatively cross couples, resulting in the production of methyl acrylate and water. In contrast Scheme 1(b) shows that if the aldehyde / O / Au interface is annealed to 240K or above and then methanol adsorbed at 120K, the predecessor to carbon suboxide is created at 240K, blocking the cross-couple reactions with methoxy. Under these circumstances only methyl formate and carbon suboxide are detected as the final oxidation products.

Scheme 1: Proposed reaction mechanisms for the cross-coupling reaction of acrolein with methanol: a) Adsorption of the reactants takes place at 120K, b) Flashing the acrolein / O/ Au(110) interface at 240K and cooling back down to 120K before dosing methanol.

3.2 Catalytic cross-coupling of acrolein and methacrolein with methanol on npAu under catalytic conditions on npAu

The stable coupling of methanol with acrolein to form methyl acrylate occurs at 150 °C at **ambient pressure** at high methanol mole fractions in the continuous flow reactor. Two major coupling products form – methyl acrylate and methyl formate; the relative distribution of these products changed sharply between 90 – 100 % methanol (Fig. 5a). The cross-coupling to methyl acrylate takes place most efficiently at a methanol mole fraction of 90 %; above this mole fraction methyl formate is produced in significant quantity and becomes dominant near 100 % methanol. The maximum yield of methyl acrylate of 9.1% (calculated as the conversion of acrolein to methyl acrylate; 12% conversion, $2.6 \times 10^{-7} \text{ mols}^{-1} \text{ gcat}^{-1}$) occurs at $X_{\text{MeOH}} = 0.97$. Although the selectivity for methyl acrylate formation approaches 100% at a methanol mole fraction of 0.90, the conversion of acrolein drops to ~3%. This compares to a total conversion of allyl alcohol on the same catalyst of 56% (conversion to methyl acrylate of 9.6%) and a rate of $1.3 \times 10^{-6} \text{ mols}^{-1} \text{ gcat}^{-1}$.

Figure 5. Cross-coupling selectivity over (a) an activated npAu ingot of methanol with acrolein in a continuous flow reactor, over (b) an activated npAu ingot of methanol with methacrolein in a continuous flow reactor. Reaction conditions: 5% Total Organics (acrolein or methacrolein + methanol) – 20% O₂ – He, flow rate 50 mL/min; catalyst weight ~35 mg; reaction temperature 150 °C.

Similarly, the catalytic coupling of methanol with methacrolein occurs efficiently at high methanol mole fractions over npAu in the flow reactor at ambient pressure and 150 °C (Fig. 5b). The maximum yield of methyl methacrylate is achieved at very high methanol mole fractions (yield of ~9% at $X_{\text{MeOH}} = 0.98$). At these compositions, methanol self-coupling to methyl formate is also observed, indicating a significant concentration of methoxy species on the npAu surface. As the methanol mole fraction is decreased, the selectivity for methyl methacrylate formation increases to 100% at $X_{\text{MeOH}} = 0.92$, although the methacrolein conversion decreases to 1.2% (Fig. 4b). As with acrolein, the product selectivity on npAu under ambient pressure flow conditions differs significantly from that on Au(110) at methanol mole fractions near 90% methanol.

Clearly the dependence of product selectivity on reactant composition is quite different on npAu under ambient pressure catalytic flow conditions than that observed following sequential dosing on Au(110) at 120 K. These differences are quite unlike that reported previously for methanol-alcohol mixtures, including methanol-allyl alcohol.[9], [14]. However, on Au(110) a selectivity for methyl acrylate formation of ~95% from methanol and acrolein was achieved on Au(110) for an appropriate dosage (methanol first) at 120K. As discussed above the dependence of selectivity on methanol fraction probed on Au(110) reflects the temperature at which the sequential dosing was done, leading to preferential reaction of the adsorbed O with methanol with replacement of all the O with methoxy. The acrolein then reacts with the methoxy to produce the coupled product.

The steady state behavior the catalyst can be understood from the model studies on Au(110). At 150 C the aldehyde and methanol compete for adsorbed O, activated by

the npAu. The fact that the adsorbed acrylate is more stable than the adsorbed methoxy leads to its buildup on the surface, and it poisons a large fraction of the active sites. However, since its rate of decomposition is finite at 150 °C, sites turn over at which adsorbed O, and, in turn, methoxy establish a low steady state concentration. Thus, the acrylates form *via* coupling with a low conversion.

The reaction was therefore examined in the reactor over an extended range of temperatures between 150 and 225 °C. (Figs. 6 and 7). Increasing the reactor temperature increases the rate of decomposition of the adsorbed acrylate and thereby increases the site availability and turnover toward cross coupling due to the preferential reactivity of methanol with adsorbed O. At the higher temperatures studied in the reactor methyl formate begins to dominate the product; no attempt was made to optimize the reactant composition for enhancing selectivity at these temperatures. In the temperature range where the adsorbed acrylate is expected to decompose at a higher rate the conversion increases from 3% to 10 %, a significant effect. That this loss in selectivity is not due to catalyst degradation (coarsening of the npAu, for example) was demonstrated from the preservation of activity for methanol self-coupling before and after temperature cycling. The yield of methyl acrylate maximizes near 225 °C.

Figure 6. The effect of temperature on the methanol-acrolein cross-coupling activity (conversion) in flow reactor. Flow conditions during cross coupling: $X_{\text{MeOH}} = 0.91$, 20% O₂, 50 mL/min.

Figure 7. The effect of temperature on the methanol-acrolein cross-coupling activity (selectivity) in flow reactor. Flow conditions during cross coupling: $X_{\text{MeOH}} = 0.91$, 20% O₂, 50 mL/min.

In the flow reactor, while the product distribution of the reactions for methyl acrylate compared to methyl methacrylate vary in a similar fashion with methanol mole fraction, the cross-coupling yields for each methanol mole fraction are generally higher for methanol coupling with acrolein than for methacrolein (Fig. 8). The lower conversion of the methacrolein after the deactivation period suggests that the methyl group further stabilizes the acrylate species, resulting in fewer sites for methoxy formation to drive the cross-coupling reaction.

Figure 8. Cross-coupling ester yield (based on unsaturated aldehyde conversion to methyl ester product) over (a) an activated npAu ingot in the catalytic reaction of methanol with, acrolein, and methacrolein (same flow conditions as Fig. 5) in a continuous flow reactor, (b) 0.1ML of atomic oxygen was dosed at 300 K via ozone exposure on Au(110) with subsequent dosing of the reactants at 120 K (methanol first).

The formation of the strongly bound acrylates also progressively deactivates the catalyst for the cross-coupling reactions (Fig. 9a, b). The extent of npAu poisoning by surface acrylates on npAu in the flow reactor was evident following the introduction of

acrolein or methacrolein to a methanol-oxygen reaction mixture at 150 °C. At the conditions used (methanol mole fractions of 0.97 to 0.98), the aldehyde conversion dropped immediately from ~46% to 20% for acrolein and to 9% for methacrolein over the following 80-90 min.

Figure 9. Deactivation of npAu during the initial introduction of aldehydes during cross-coupling experiments. Reaction conditions: (a) $X_{\text{MeOH}} = 0.97$, 5% MeOH/R=O (Total) – 20% O₂, 50 mL/min, 150 °C (b) $X_{\text{MeOH}} = 0.98$, 5% MeOH/R=O (Total) – 20% O₂, 50 mL/min, 150 °C.

4. Conclusions

The esterification of unsaturated aldehydes with methanol can be achieved selectively at relatively low temperature by oxygen-assisted coupling on np(Ag)Au in a continuous flow gas phase reactor. A decline in activity observed at 150 °C over a period of hours is shown to be due to the buildup of adsorbed acrylates; conversion can be restored to higher values by operation near the temperature of decomposition of the acrylate (>200 °C). Model studies of the mechanism on single crystal gold surfaces indicate that facile esterification of acrolein and methacrolein with methanol can be achieved with ~95% selectivity provided the oxidation of the aldehyde can be suppressed.

Acknowledgement

This work was supported as part of the Integrated Mesoscale Architectures for Sustainable Catalysis, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under award #DE-SC0012573. Work at LLNL was performed under the auspices of the U.S. Department of Energy by LLNL under Contract DE-AC52-07NA27344.

References

- [1] J. Han, S. Zhang, J. Zhang, R. Yan, Modified extra-large mesoporous silica supported Au–Ni as a highly efficient catalyst for oxidative coupling of aldehydes with methanol, *RSC Adv.*, 4 (2014) 58769-58772.
- [2] B. Wang, W. Sun, J. Zhu, W. Ran, S. Chen, Pd–Pb/SDB Bimetallic Catalysts for The Direct Oxidative Esterification of Methacrolein to Methyl Methacrylate, *Ind. Eng. Chem. Res.*, 51 (2012) 15004–15010.
- [3] K. Suzuki, T. Yamaguchi, K. Matsushita, C. Iitsuka, J. Miura, T. Akaogi, H. Ishida, Aerobic Oxidative Esterification of Aldehydes with Alcohols by Gold–Nickel Oxide Nanoparticle Catalysts with a Core–Shell Structure, *ACS Catal.*, 3 (2013) 1845-1849.
- [4] B. Xu, J. Haubrich, T.A. Baker, E. Kaxiras, C.M. Friend, Theoretical study of O-assisted selective coupling of methanol on Au(111), *J. Phys. Chem. C*, 115 (2011) 3703-3708.
- [5] D.I. Enache, D.W. Knight, G.J. Hutchings, Solvent-free Oxidation of Primary Alcohols to Aldehydes using Supported Gold Catalysts, *Catalysis Letters*, 103 (2005) 43-52.
- [6] A. Corma, A. Leyva-Pérez, M.J. Sabater, Gold-Catalyzed Carbon–Heteroatom Bond-Forming Reactions, *Chem. Rev.*, 111 (2011) 1657-1712.
- [7] X. Liu, B. Xu, J. Haubrich, R.J. Madix, C.M. Friend, Surface-Mediated Self-Coupling of Ethanol on Gold, *J. Am. Chem. Soc.*, 131 (2009) 5757-5759.
- [8] B. Xu, X. Liu, J. Haubrich, R.J. Madix, C.M. Friend, Selectivity Control in Gold-Mediated Esterification of Methanol, *Angew. Chem. Int. Ed.*, 48 (2009) 4206-4209.

- [9] B. Xu, R.J. Madix, C.M. Friend, Achieving Optimum Selectivity in Oxygen Assisted Alcohol Cross-Coupling on Gold, *J. Am. Chem. Soc.*, 132 (2010) 16571–16580.
- [10] B. Xu, C.M. Friend, Oxidative coupling of alcohols on gold: Insights from experiments and theory, *Faraday Discuss.*, 152 (2011) 307-320.
- [11] B. Xu, R.J. Madix, C.M. Friend, Dual-Function of Alcohols in Gold-Mediated Selective Coupling of Amines and Alcohols, *Chem. Eur. J.*, 18 (2012) 2313-2318.
- [12] B. Xu, C.M. Friend, R.J. Madix, A paradigm for predicting selective oxidation on noble metals: oxidative catalytic coupling of amines and aldehydes on metallic gold, *Faraday Discuss.*, 152 (2011) 241-252.
- [13] L.-C. Wang, K.J. Stowers, B. Zugic, M.M. Biener, J. Biener, C.M. Friend, R.J. Madix, Methyl ester synthesis catalyzed by nanoporous gold: from 10–9 Torr to 1 atm, *Catal. Sci. Technol.*, 5 (2015) 1299-1306
- [14] L.-C. Wang, K.J. Stowers, B. Zugic, M.L. Personick, M.M. Biener, J. Biener, C.M. Friend, R.J. Madix, Exploiting basic principles to control the selectivity of the vapor phase catalytic oxidative cross-coupling of primary alcohols over nanoporous gold catalysts, *Journal of Catalysis*, 329 (2015) 78-86.
- [15] J.C.F. Rodriguez-Reyes, C.G.F. Siler, W. Liu, A. Tkatchenko, C.M. Friend, R.J. Madix, van der Waals interactions determine selectivity in catalysis by metallic gold, *J. Am. Chem. Soc.*, 136 (2014) 13333-13340.
- [16] B. Zugic, S. Karakalos, K.J. Stowers, M.M. Biener, J. Biener, R.J. Madix, C.M. Friend, Continuous Catalytic Production of Methyl Acrylates from Unsaturated Alcohols by Nanoporous Gold: The Strong Effect of C=C Unsaturation on Reaction Selectivity, *ACS Catalysis*, 216 (2016) 1833-1839.

- [17] Y. Ding, Y.-J. Kim, J. Erlebacher, Nanoporous Gold Leaf: “Ancient Technology”/Advanced Material, *Advanced Materials*, 16 (2004) 1897–1900.
- [18] A. Wittstock, V. Zielasek, J. Biener, C.M. Friend, M. Bäumer, Nanoporous Gold Catalysts for Selective Gas-Phase Oxidative Coupling of Methanol at Low Temperature, *Science*, 327 (2010) 319-322.
- [19] T. Fujita, P. Guan, K. McKenna, X. Lang, A. Hirata, L. Zhang, T. Tokunaga, S. Arai, Y. Yamamoto, N. Tanaka, Y. Ishikawa, N. Asao, Y. Yamamoto, J. Erlebacher, M. Chen, Atomic origins of the high catalytic activity of nanoporous gold, *Nature Materials*, 11 (2012) 775-780.
- [20] T. Fujita, T. Tokunaga, D.L. Ling Zhang†, L. Chen, S. Arai, Y. Yamamoto, A. Hirata, N. Tanaka, M.C. Yi Ding, Atomic Observation of Catalysis-Induced Nanopore Coarsening of Nanoporous Gold, *Nano Lett.*, 14 (2014) 1172-1177.
- [21] X. Deng, B.K. Min, X. Liu, C.M. Friend, Partial Oxidation of Propene on Oxygen-Covered Au(111), *J. Phys. Chem. B*, 110 (2006) 15982–15987.
- [22] L.V. Moskaleva, S. Röhe, A. Wittstock, V. Zielasek, T. Klüner, K.M. Neyman, M. Bäumer, Silver residues as a possible key to a remarkable oxidative catalytic activity of nanoporous gold, *Phys. Chem. Chem. Phys.*, 13 (2011) 4529-4539.
- [23] K.J. Stowers, R.J. Madix, C.M. Friend, From model studies on Au(1 1 1) to working conditions with unsupported nanoporous gold catalysts: Oxygen-assisted coupling reactions, *Journal of Catalysis*, 308 (2013) 131-141.
- [24] R.J. Madix, Through the labyrinth of surface reaction mechanism: a personal account, 1964–1992, *Surface Science*, 299-300 (1994) 785-797.

- [25] N. Saliba, D.H. Parker, B.E. Koel, Adsorption of oxygen on Au(111) by exposure to ozone, *Surface Science*, 410 (1998) 270.
- [26] X. Deng, B.K. Min, A. Guloy, C.M. Friend, Enhancement of O₂ Dissociation on Au(111) by Adsorbed Oxygen: Implications for Oxidation Catalysis, *J. Am. Chem. Soc.*, 127 (2005) 9267–9270.
- [27] K.J. Stowers, R.J. Madix, M.M. Biener, J. Biener, C.M. Friend, Facile Ester Synthesis on Ag-Modified Nanoporous Au: Oxidative Coupling of Ethanol and 1-Butanol Under UHV Conditions, *Catalysis Letters*, 145 (2015) 1217-1223.
- [28] A. Schaefer, D. Ragazzon, A. Wittstock, L.E. Walle, A. Borg, M. Bäumer, A. Sandell, Toward Controlled Modification of Nanoporous Gold. A Detailed Surface Science Study on Cleaning and Oxidation, *J. Phys. Chem. C*, 116 (2012) 4564–4571.
- [29] J.M. Gottfried, K.J. Schmidt, S.L.M. Schroeder, K. Christmann, Oxygen chemisorption on Au(1 1 0)-(1 × 2) I. Thermal desorption measurements, *Surface Science*, 525 (2003) 184–196.
- [30] M.L. Personick, B. Zugic, M.M. Biener, J. Biener, R.J. Madix, C.M. Friend, Ozone-Activated Nanoporous Gold: A Stable and Storable Material for Catalytic Oxidation, *ACS Catal.*, 5 (2015) 4237–4241.