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Alcohol Oxidation

Oxygen-Mediated Coupling of Alcohols over Nanoporous Gold Catalysts at Ambient Pressures**

Kathryn M. Kosuda, Arne Wittstock, Cynthia M. Friend, and Marcus Bäumer*

Heterogeneous catalysis is a key technology to address the ever-increasing demand for the cost-effective and environmentally friendly production of commodity and fine chemicals. A major challenge is the development of catalytic processes that operate at low temperatures with high conversion and high selectivity for the desired product.[1] Achieving this goal would be facilitated by the rational design of catalysts based on a molecular-level understanding of the reactive processes that occur on the catalyst surface. However, the transfer of insights from model studies at low pressure to the complex environment of practical catalytic systems—the so-called "material" and "pressure gaps"—often proves challenging.

For catalysis based on metallic gold such a correlation is feasible, opening the possibility of the directed preparation of catalysts. This is because most molecules, including H_2O, bind weakly to metallic gold.[2] Hence, the steady-state concentrations of surface species remain low—conditions that can be mimicked in ultrahigh vacuum (UHV) on metallic gold. This strong correspondence between model studies at very low pressure and the actual working catalyst was previously demonstrated for the selective oxidative coupling of methanol to give methyl formate, which was studied on metallic Au(111) containing atomic O[3] and over nanoporous Au (npAu) catalysts using O_2 as an oxidant.[4] These experiments demonstrated an astonishing correlation between the two regimes, thus making it possible to understand the reactivity and selectivity of npAu on a molecular level. In the present study, we pursued the question of whether the transferability of UHV-based insight is more universal and can be extended to the oxidation of other alcohols as well.

The structure of npAu consists of a three-dimensional network of gold ligaments in the range of a few tens of nanometers (typically 30 to 50 nm, Figure 1) with a high surface area of approximately 10 $m^2 g^{-1}$. The surprising catalytic activity of this gold material for low-temperature oxidation of CO using molecular oxygen was first reported independently by two research groups in 2006 and 2007.[5] As the presence of a reducible metal oxide support and a nanoparticle size of less than 5 nm were believed to determine the activity of gold-based catalysts,[6] the high activity of npAu for this reaction was somewhat surprising. In particular, the activation of molecular oxygen, which is not facilitated on pure gold surfaces, renders the high catalytic activity of this unsupported material intriguing.[2a] Later work focused on the role of low-coordinated gold atoms on the surface and small amounts of Ag resulting from the preparation procedure. Ag can bind O_2 more strongly and thus overcome the low probability for O_2 dissociation on gold without altering the selective surface chemistry.[7] In the meantime several reports have dealt with npAu as a catalyst in the liquid as well as in the gas phase, underlining the potential and versatility of this material for catalytic applications.[4,8]

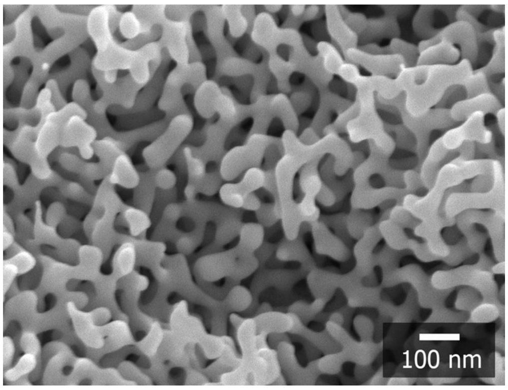

Figure 1. Scanning-electron micrograph of a cross-section of a npAu disk.

Gold-based catalysts have been shown to hold great potential in organic synthesis as they are able to selectively activate heteroatom–carbon bonds.[9] One particularly interesting example is the oxidation and coupling of primary alcohols, yielding a variety of products such as ketones, esters, aldehydes, and carboxylic acids. This type of reaction is one of the cornerstones of synthetic organic chemistry and plays a key role in the production of materials present in our daily life.[10] Recent studies dealing with supported gold catalysts in the liquid phase showed that gold is an active catalyst for this

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[*] Dr. A. Wittstock, Prof. M. Bäumer
Zentrum für Umweltforschung und nachhaltige Technologien und Institut für Angewandte und Physikalische Chemie, Universität Bremen, Leobener Strasse NW2, 28359 Bremen (Deutschland)
E-mail: awittstock@uni-bremen.de
Homepage: http://iapc.chemie.uni-bremen.de
Dr. A. Wittstock
Lawrence Livermore National Laboratory, NSCL
7000 East Avenue, Livermore CA 94550 (USA)
Dr. K. M. Kosuda, Prof. C. M. Friend
Harvard University, Department of Chemistry and Chemical Biology, School of Engineering and Applied Sciences
12 Oxford Street, Cambridge, MA 02138 (USA)

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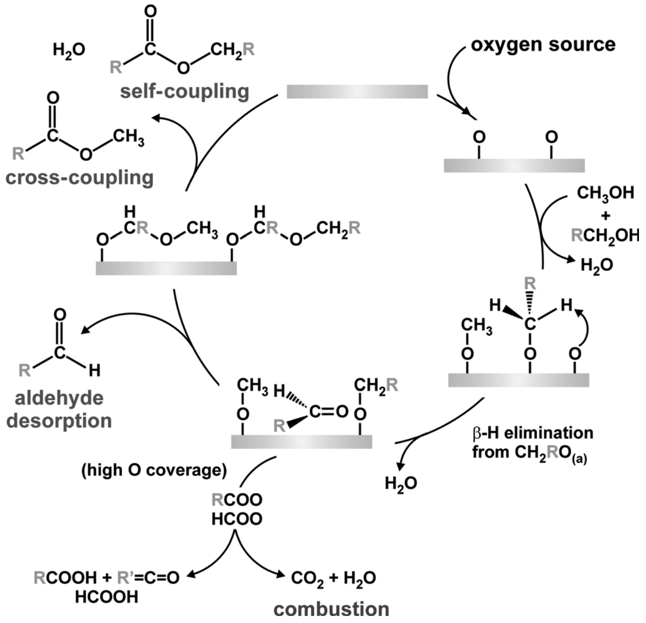
type of reaction.[11] In particular, the work of Jorgensen et al.[11c] and Nielsen et al.[12] revealed the versatile oxidation chemistry accessible on gold.

Herein, we report on gas-phase studies of the aerobic oxidation and coupling of primary alcohols—methanol, ethanol, and *n*-butanol—using npAu as an unsupported catalyst at ambient pressures and low temperatures. In this way, possible side reactions, such as hydrolysis of the products, can be suppressed, enabling a clear comparison to ultrahigh-vacuum model studies and thus identification of the mechanistic key factors that control the selectivity of the reaction.

The corresponding model studies on metallic Au(111) demonstrated that atomic O is necessary for the initial scission of the O–H bond to form the alkoxides of the three alcohols.[2c,d,3,13] The general reaction scheme for the oxidation and coupling of primary alcohols as well as the resulting mixtures is shown in Scheme 1. There are three major pathways for alcohol oxidation on Au: 1) coupling to form esters, 2) formation of aldehydes, and 3) complete oxidation (combustion).



Scheme 1. Pattern of reactivity for oxidation and coupling of alcohols on Au according to refs.[2c,d,3,13] Surface oxygen initiates scission of the alcoholic O–H bond, forming an alkoxy unit. Subsequent β-H elimination from the alkoxy by reaction with surface oxygen or an adjacent alkoxy leads to adsorbed aldehyde which is then attacked by unreacted alkoxy, forming a hemiacetal species which eliminates a hydrogen to yield the ester.

The two predominant products we observed for ethanol oxidation over npAu are acetaldehyde and ethyl acetate (Figures 2 and 4) which form at reaction temperatures as low as 40 °C. The conversion steeply increases with temperature. The two products are formed in a molar ratio of about 2:1, corresponding to an equal conversion of ethanol into the two products. The total oxidation of ethanol to CO_2 was found to be close to the detection limit (ca. 10^{-3} vol %). In contrast, there was no detectable evolution of formaldehyde from methanol oxidation over nanoporous Au under similar conditions; the coupling product, methyl formate, was produced exclusively (Figure 4).[4] The conversion of ethanol is weakly dependent on the oxygen partial pressure (Figure 2): the conversion to acetaldehyde and ethyl acetate increases from 1.5 % (1 vol % O_2) to about 2.0 % (10 vol % O_2). The selectivity was not substantially altered at the different oxygen partial pressures (Figure S3 in the Supporting Information). This weak dependence of the reaction on the oxygen concentration in the gas phase implies that the supply of active oxygen is limited by a surface reaction or the saturation of adsorption sites. In the course of days the selectivity with respect to the formation of either the coupling product or the aldehyde was found to vary from about 50 % up to about 70 % selectivity in favor of the coupling product. It is likely that in case of npAu the state of the surface with respect to activation of molecular oxygen may slightly vary over time.

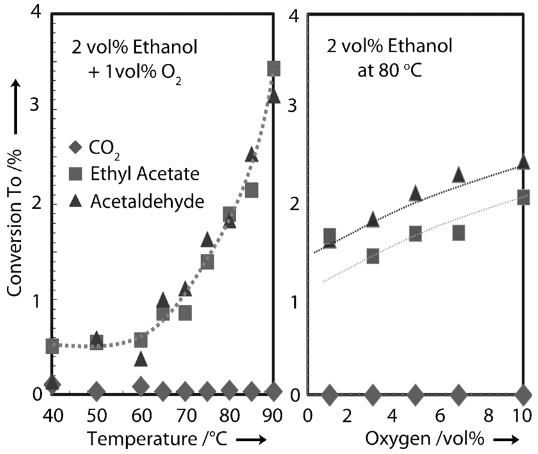


Figure 2. Oxidation of ethanol to ethyl acetate and acetaldehyde for temperatures between 40 °C and 80 °C (left) and for various oxygen partial pressures at a reaction temperature of 80 °C (right).

The oxidation of *n*-butanol leads exclusively to the production of the aldehyde, *n*-butanal (Figures 3 and 4). The reaction already proceeds at 40 °C and the conversion steeply increases with temperature in the same fashion as described for ethanol oxidation. Here, too, the formation of CO_2 was close to the detection limit of about 10^{-3} vol %. Similar to the oxidation of ethanol the conversion of *n*-butanol increased approximately in a square root-like fashion with increasing oxygen concentration and reached saturation at concentrations above 10 vol % (Figure 3). This behavior may indicate a mass-transport-limited reaction of 0 order appearing as a reaction of the order of 0.5 for low oxygen concentrations.[7] The formation of the coupling product, butyl butyrate, was not observed at oxygen concentration up to 20 vol % and at temperatures up to 80 °C.

As one can derive from UHV experiments, one of the main intermediates is a surface-bonded carboxylate (i.e. formate, acetate; see Scheme 1) stemming from the oxidation of surface-bonded aldehyde. This carboxylate surface species can either desorb after reaction with water, forming the

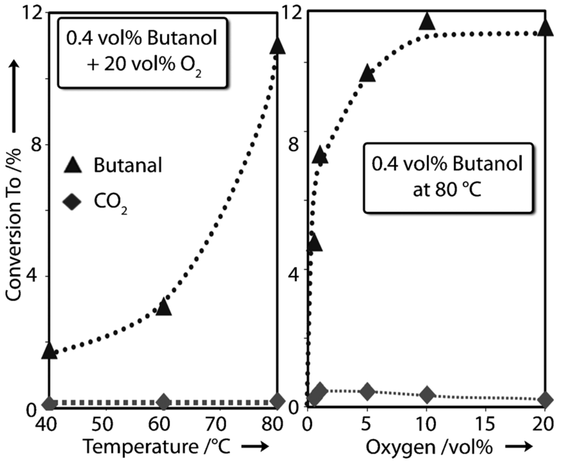
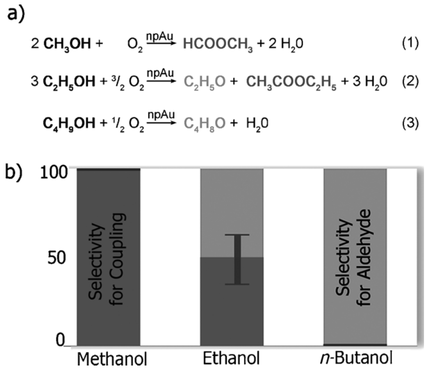


Figure 3. Oxidation of *n*-butanol to *n*-butanal for temperatures between 40 °C and 80 °C (left) and for various oxygen partial pressures at a reaction temperature of 80 °C (right).



$$2\,CH_3OH + O_2 \xrightarrow{npAu} HCOOCH_3 + 2\,H_2O \quad (1)$$

$$3\,C_2H_5OH + {}^3/_2\,O_2 \xrightarrow{npAu} C_2H_5O + CH_3COOC_2H_5 + 3\,H_2O \quad (2)$$

$$C_4H_9OH + {}^1/_2\,O_2 \xrightarrow{npAu} C_4H_8O + H_2O \quad (3)$$

Figure 4. a) Oxidation and self-coupling of alcohols over nanoporous Au. b) Selectivity towards the aldehyde or self-coupling product (ester) depends on the chain length of the alcohol. The greater facility for β-hydride elimination from longer-chain alkoxy groups favors aldehyde production.

corresponding carboxylic acid, or be further oxidized to the ketene and eventually CO_2. It is thus likely that with increasing chain length and increasing tendency to form a surface-bonded aldehyde (methanol < ethanol < *n*-butanol) the amount of this carboxylate species increases. Under the chosen water-free conditions, such species supposedly lead to partial blocking of active sites on the catalyst surface.[14] In accordance, we indeed observe reduced activity with increasing chain length. When comparing the activity (conversion) in terms of turnover frequencies (TOF; see also the Supporting Information), the activity at 80 °C decreases from $0.11\,s^{-1}$ in the case of methanol to $0.01\,s^{-1}$ for ethanol and further to $0.007\,s^{-1}$ in the case of *n*-butanol. Considering that no co-catalyst such as a base was used and the chosen conditions do not necessarily reflect the maximal achievable activity, for example, higher concentrations of reactants, these numbers are nevertheless competitive with activities achieved at this temperature using supported Au catalysts.[15]

As a matter of fact, this pattern of reactivity is not limited to the self-coupling of alcohols but can be extended to more complex surface reactions involving multiple chemical entities, for example the oxygen-activated coupling of two different alcohols. Model studies performed in UHV have shown that methanol can react with other alkyl alcohols on O-covered Au(111) to form cross-coupling products.[2c,3,13] In general, the number of possible oxidation products is considerably greater as not only the self- but also the cross-coupling products evolve. But again, gold exhibits a very selective surface chemistry. The selectivity of the reaction is guided by the activation energy for β-hydrogen elimination and the tendency to form the particular aldehyde, thus decreasing the number of products. Indeed, in the case of alcohol oxidation over npAu catalysts the observed reactivity is in accordance with the predicted selectivity (Scheme 1 and Figure S2 in the Supporting Information).

When methanol and ethanol are co-dosed, only one cross-coupling product is observed, methyl acetate, stemming from the reaction of the surface-bonded methoxy group with surface-bonded acetaldehyde (Figure S2 in the Supporting Information). The other potential cross-coupling product, ethyl formate, arising from the reaction of the ethoxy group and formaldehyde, was not observed. This reactivity follows the anticipated greater tendency for ethoxy groups to undergo β-hydrogen elimination. The formation of acetaldehyde on the surface accordingly will be dominant, and the reaction of acetaldehyde with the methoxy group is the dominant cross-coupling reaction. Besides cross-coupling, the formation of acetaldehyde and the self-coupling product ethyl acetate was observed. The absence of methyl formate production (self-coupling of methanol) suggests that methoxy is depleted prior to formaldehyde formation and further emphasizes that acetaldehyde is the dominant reactive species on the catalyst surface.

We conclude that for the oxidative coupling of alcohols on unsupported npAu the mechanistic insights gained from UHV experiments can be transferred to reactions at ambient pressure. The nanoporous material provides a self-contained extended gold surface without the need of an additional support. The lack of a support material simplifies our understanding of npAu catalysis and enables the prediction of surface reactivity based on fundamental insights gained from UHV experiments. Importantly, complex surface reactions involving several chemical entities, such as the cross-coupling of alcohols, can still be fully anticipated on the molecular level. This material constitutes an interesting example of how novel nanotechnology provides valuable input towards the development of concepts for rational catalyst design.

Experimental Section

Catalysis experiments were performed in a laboratory-type continuous-flow reactor at ambient pressure (for further details and a schematic of the experimental setup see Figure S1 and the Supporting Information). Disks of npAu with a diameter of 5 mm and a thickness of 200–300 μm were prepared by etching Ag/Au alloys (70:30 atom %) in conc. nitric acid (65 wt %, Fluka Chemicals) for 48 h. This treatment is known to result in npAu material with a continuous porosity of 70 vol % consisting of more than 99 atom % gold. The concentration of alcohol was controlled by its vapor pressure. A stream of carrier gas (helium) was guided through a saturator and subsequently the amount of alcohol within the stream was adjusted by condensation. The composition of the gas stream after catalytic conversion at the exit of the reactor was determined by IR gas analyzers and a gas chromatograph coupled with a mass spectrometer.

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