Formation of Acetic Acid by Aqueous-Phase Oxidation of Ethanol with Air in the Presence of a Heterogeneous Gold Catalyst**

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Bioethanol is produced by fermentation of biomass in increasing amounts to meet the growing demands for CO_2-neutral transportation fuels and to eventually remove the dependence on fossil fuels. However, bioethanol could also find use as a versatile, sustainable chemical feedstock. Herein,

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it is shown that it is possible to selectively oxidize ethanol into acetic acid in aqueous solution using air as the oxidant with a heterogeneous gold catalyst at temperatures of about 423 K and O_2 pressures of 0.6 MPa. This reaction proceeds readily in aqueous acidic media and yields of up to 90% are achieved, with CO_2 as the only major by-product. Thus, it constitutes a very simple, green route to acetic acid.

The oxidation of ethanol by air into acetic acid over platinum was among the first heterogeneously catalyzed reactions to be reported. The initial discovery was made by Döbereiner about two centuries ago, even before the term catalysis was coined.[1] So far, the reaction has not been used for large-scale production of acetic acid. Instead, three other routes to acetic acid have found industrial application: fermentation (vinegar), catalytic liquid-phase oxidation of butane, naphtha, or acetaldehyde, and the carbonylation of methanol, which has recently become the most important.[2]

In the most widely used industrial processes today, the feedstock is almost exclusively derived from fossil fuels. Thus, the production of acetic acid consumes fossil fuels and therefore contributes slightly to increasing CO_2 levels in the atmosphere, and, more importantly, the cost of acetic acid is strongly dependent on the price of the fossil fuels. Therefore, it is interesting that the cost of renewable feedstocks has decreased dramatically relative to fossil fuel feedstocks over the last four decades. Specifically, the cost of corn relative to oil has decreased fivefold from 1950 to 2005. Today, bio-ethanol is mostly produced by fermentation of starch-containing crops, such as corn or sugar cane, but it seems likely that cellulose-rich agricultural waste will gain importance as a feedstock in the future.[3] Therefore, and also because of the continuing technological improvements of the production process, the cost of bioethanol is expected to decrease.[4] Thus, with increasing fossil fuel prices, the production of acetic acid from bioethanol will become increasingly favorable compared to current fossil fuel-based methods. Clearly, this development requires that an active and selective catalyst for oxidation of ethanol with dioxygen to form acetic acid [Eq. (1)] is available.

$$CH_3CH_2OH + O_2 \rightarrow CH_3COOH + H_2O \qquad (1)$$
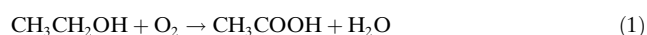
So far, primarily palladium and platinum catalysts have received attention as catalysts for ethanol oxidation.[5] However, with these catalysts it has proven difficult to reach sufficient selectivities at high conversions.

Here, it is reported for the first time that gold catalysts are both very active and selective catalysts for aqueous-phase oxidation of ethanol with air into acetic acid at 373–473 K with O_2 pressures of 0.5–1 MPa. Interestingly, metallic gold was for many years considered too unreactive to be useful as a catalyst.[6] However, this view was challenged in the seminal studies of Haruta and co-workers,[7,8] who showed that gold very efficiently catalyzed the room-temperature oxidation of CO with O_2 to form CO_2, and by Hutchings, who studied acetylene hydrochlorination with gold catalysts.[9] Since then, numerous reports of different gold-catalyzed reactions have appeared and the field has recently been reviewed and highlighted.[10–12]

The catalytic oxidation of alcohols with air has also attracted significant attention as a "green" reaction.[13] Among the heterogeneous catalysts, mainly Pd and Pt have shown promising result.[14,15] Rossi and co-workers were the first to show that alcohols, specifically diols and sugars, can be oxidized to the corresponding acids with gold catalysts but only when a base is present.[16,17] Later, the oxidation of glycerol to glycerate using Au/C was similarly demonstrated.[18] Recently, it was shown that heterogeneous ceria-supported gold catalysts are able to oxidize several higher alcohols into the corresponding carboxylic acids using air as oxidant.[19] In these experiments, the support played an active role in the catalytic cycle. However, it has also been shown that solvent-free oxidations of primary alcohols can selectively yield aldehydes.[20] Thus, it is noteworthy that the gold-catalyzed aqueous-phase oxidation of ethanol with air into acetic acid reported here proceeds readily in acidic aqueous solution.

Bioethanol is typically produced in a series of steps, namely fermentation in a batch process (yielding 3–15 vol% aqueous ethanol), distillation to obtain the azeotrope (containing 96 vol% ethanol), and further distillation to achieve the anhydrous ethanol that is required as a fuel additive.[21] Therefore, we decided to study the oxidation of ethanol in a batch process with ethanol concentrations corresponding to those obtained during fermentation, as this is expected to represent the easiest scheme for acetic acid production from bioethanol. All catalysts were prepared on a porous support of $MgAl_2O_4$ (65 $m^2 g^{-1}$) using $HAuCl_4 \cdot 3 H_2O$, $PtCl_4$, and $PdCl_2$ as metal precursors. The catalytic experiments were conducted in stirred reactors (50 mL, Parr Autoclaves, stainless steel). Liquid samples were drawn from the reactor periodically using the sampling system and analyzed by gas chromatography (GC). Similarly, gas samples were also analyzed by GC. No reaction was observed in the absence of catalyst or when using the pure supports without gold. The metal content of all catalysts was analyzed by atomic absorption spectroscopy (AAS). The gold catalysts were also characterized by transmission electron microscopy (TEM) before and after testing. Typically, 20 images were recorded for each catalyst sample.

Initially, we studied whether gold could catalyze the selective oxidation of ethanol into acetic acid with air in aqueous solution, and how such a catalyst would compare with previously reported systems based on platinum and palladium. Table 1 compares the performance of Au, Pt, and Pd catalysts on a $MgAl_2O_4$ support. Previously, the nature of the support has been shown to be critically important for gold

catalysts.[19,22] $MgAl_2O_4$ was chosen as the support material here since it is stable at high water pressures and because it can be considered completely inactive in redox processes. Thus, the observed activity can be attributed solely to the metal nanoparticles, and no synergistic effect with the support is expected. Other supports might be found to affect the catalytic performance.

Remarkably, the gold catalyst not only exhibits similar or higher catalytic activity than palladium or platinum but, in particular, a significantly higher selectivity towards acetic acid than both of these well-known catalysts. The major by-product for the gold catalyst is CO_2, whereas the Pd and Pt catalysts also produce significant amounts of acetaldehyde. Thus, we decided to further investigate the performance of gold catalysts for ethanol oxidation to gain a more detailed insight into this reaction and to identify suitable reaction conditions.

Figure 1 shows representative TEM images of the 1 wt% Au/$MgAl_2O_4$ catalyst used in this study. Generally, gold particle sizes of 3–6 nm are observed both before and after testing, with no sign of sintering. Figure 1 also illustrates how the ethanol conversion and the acetic acid yield depend on the reaction time. The reaction is conducted with only a slight excess of oxygen and therefore the reaction rate does not obey pseudo-first-order kinetics.
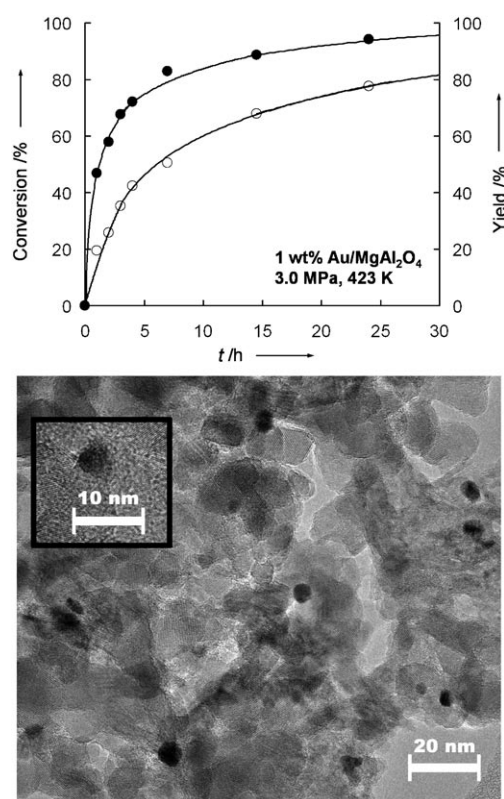

Figure 1. Top: Performance of 150 mg of 1 wt% Au/$MgAl_2O_4$ catalyst in the oxidation of 10 mL of aqueous 5 wt% ethanol with air at 423 K and 3.0 MPa (● ethanol conversion, ○ acetic acid yield). Bottom: TEM images of the 1 wt% Au/$MgAl_2O_4$ catalyst used for ethanol oxidation. The inset shows a high-resolution image of a gold particle with a diameter of about 5 nm.

Table 1: Comparison of $MgAl_2O_4$-supported Au, Pt, and Pd catalysts for oxidation of aqueous ethanol to acetic acid with air.[a]

Cat.	T [K]	p [MPa]	t [h]	Conv. [%]	Yield [%]	STY[b] [mol h⁻¹ L⁻¹]
Au[c]	453	3	4	97	83	0.21
Pt	453	3	4	82	16	0.047
Pd	453	3	4	93	60	0.15

[a] Conditions: 150 mg catalyst, 1 wt% of metal, 10 mL of 5 wt% aqueous ethanol, [b] Space-time yield. [c] Corresponding to 0.07 mol% Au.

Figure 2 shows how the performance of the catalyst depends on temperature and pressure. It is noteworthy that yields above 80% are obtained without any special effort to optimize the reaction conditions or catalyst composition. It can also be seen that the reaction rate and selectivity are only slightly influenced by the total pressure when oxygen is present in excess.
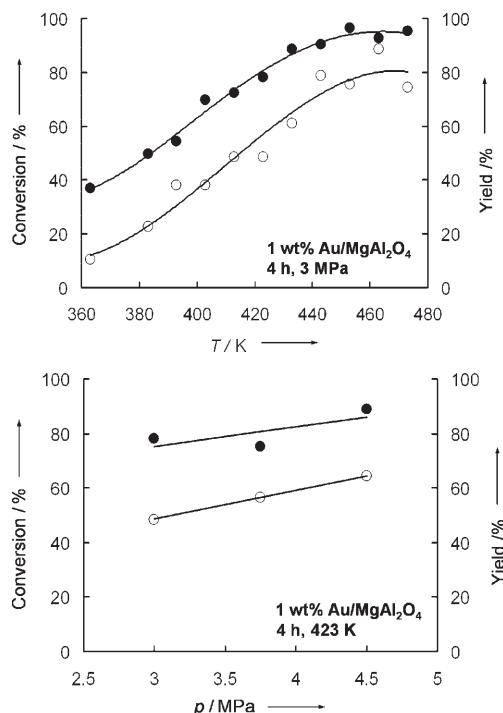

Figure 2. Ethanol conversion (●) and acetic acid yield (○) with 10 mL of 5 wt% aqueous ethanol after 4 h in the presence of 150 mg of 1 wt% Au/MgAl$_2$O$_4$ catalyst. Top: temperatures of 363–473 K and an air pressure of 3 MPa. Bottom: pressures of 3–4.5 MPa and a temperature of 423 K.

As the reaction progresses, the solution becomes more and more acidic, but this does not influence the catalyst's performance. By more careful selection of reaction conditions, for example by increasing the reaction time at 423 K or at 453 K and 3.5 MPa, it is possible to achieve acetic acid yields of over 90% (e.g., 92% yield after 8 h at 453 K and 3.5 MPa). The spinel is found to be quite stable under the present reaction conditions. After a typical reaction run, less than 1% is lost according to ICP-MS. Additionally, only phase-pure spinel is found by powder X-ray diffraction. This is in agreement with the previous finding that magnesium aluminum hydroxide (Al/Mg = 2) transforms into spinel under hydrothermal conditions.[23]

Thus, it is seen that gold catalysts are indeed able to selectively oxidize ethanol to acetic acid in air at moderate temperatures and dioxygen pressures with very high yields. This suggests that it might prove viable to produce aqueous acetic acid in a gold-catalyzed process using aqueous bioethanol as the feedstock. Acetic acid can also be obtained directly by fermentation, however this also represents a challenge since the bacteria do not thrive under the highly

acidic reaction conditions.[2] Here, the very high stability of the gold-on-MgAl$_2$O$_4$ catalyst allows the use of high temperatures and pressures, which results in high rates. Recently, bioethanol has also received attention as a feedstock for renewable dihydrogen by steam-reforming[24] or autothermal reforming.[25] Figure 3 illustrates some proven possibilities for using bioethanol, including both fuel and feedstock applications.
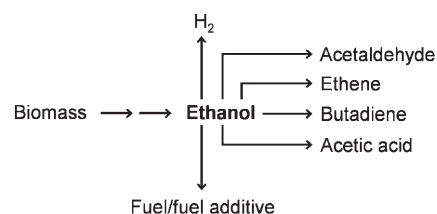
Figure 3. Possible uses of bioethanol as a fuel or as a feedstock for important bulk chemicals.[26]

A future challenge for chemists could be to find efficient routes from bioethanol to fuels and chemicals. Such processes will also compete with other new processes that allow direct conversion of carbohydrates into, for example, dihydrogen[27,28] or synfuels,[28,29] which are currently being explored. Here, we have focused on synthesizing acetic acid from ethanol in a simple, green process since acetic acid has a significantly higher value than fuels (including dihydrogen) and also than ethene, acetaldehyde, and butadiene, for example. Therefore, this might represent the currently most efficient use of part of the available bioethanol.

Experimental Section

The gold catalysts were prepared by deposition-precipitation[30] of HAuCl$_4$·3H$_2$O (supplied by Aldrich) on MgAl$_2$O$_4$. Stoichiometric MgAl$_2$O$_4$, calcined at 1000°C,[31] was tabletized, crushed, and sieved to a particle size of 100–250 μm prior to use. For comparative purposes, Pd and Pt catalysts supported on MgAl$_2$O$_4$ were prepared by incipient-wetness impregnation of hydrochloric acid solutions of PdCl$_2$ and PtCl$_4$, respectively. The resulting catalyst precursors were dried at 120°C for 6 h and calcined at 773 K for 2 h. The pure, stoichiometric, and calcined spinel used here is neutral and causes essentially no change of pH (less than ±0.05) when suspended in water or treated hydrothermally in water.

The reactor (total free volume of 55 mL) was charged with 5 wt% aqueous ethanol (10 mL), and the catalyst (150 mg) was added. After closing the autoclave, it was charged with technical air (80 vol% N$_2$, 20 vol% O$_2$) at the required pressure (2.5–5.0 MPa) and sealed. No dioxygen was added to replace that consumed by the reaction and consequently only a limited excess of oxygen is present after reaction. The reactor was then heated to a reaction temperature between 373 and 473 K where it was kept for the desired time period (4 to 45 h). The time required to reach the reaction temperature varied slightly. The pressure was monitored during the reaction and the pH was determined in the product. After the reaction, the autoclave was cooled to about 278 K. After each run, the reactor and internal components were cleaned by polishing and washing with water. The catalyst was separated by ultrafiltration and used up to three times. At this point it had lost most of its activity, which corresponds to TONs of more than 10000. The content of Al, Mg, and Au in solution after each run was measured by ICP-MS. In a separate experiment, pure spinel was treated under hydrothermal conditions (150°C, 3.0 MPa)

with 5 wt% acetic acid. No acetic acid was found to be lost onto the support.

The GC apparatus was equipped with both FID and TCD detectors to allow identification of all liquid and gaseous products present in amounts above about 1 vol%. Product compositions and concentrations were determined using standard solutions. In some cases, the entire reaction mixture was also titrated with aqueous sodium hydroxide after the reaction run to validate the GC results. In all cases, the analyses gave identical results within the experimental uncertainties.

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