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Role of Peroxide in the Catalytic Activity of Gold for Oxidation Reactions in Aqueous Media: An Electrochemical Study

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It has been suggested that peroxide could act as an enhancing agent for gold-catalyzed oxidation reactions in the aqueous phase. Here, we probe the potential role of peroxide in the catalytic oxidation of glycerol on gold in the aqueous phase by electrochemical techniques and find that neither the presence of oxygen nor peroxide leads to a significant enhancement of the overall oxidation activity or product selectivity at low temperature. In alkaline media, there appears to be a small suppression of the formation of glyceraldehyde in the presence of hydrogen peroxide but there is no major influence on the overall oxidation pathway. In neutral and acidic media, glycerol oxidation on gold has low activity.

In recent years, there has been an immense interest in the use of gold as a catalyst for oxidation reactions.[1,2] It is well established that in the gas phase, gold is an active oxidation catalyst for certain reactions if it is present as nanoparticles on a suitable oxidic support. It has also been reported that water often has a beneficial effect on the catalytic activity of gold, both as water vapor in the gas phase and under aqueous-phase conditions.[3,4] The enhancing role of water in the catalytic oxidation activity of gold is still vigorously debated. It has been suggested in the literature that oxygen, which is used as an oxidizing agent, is reduced at the gold-water interface to peroxide, and peroxide could act as the enhancing agent for the oxidation reaction under study.[4–6]

In this communication, we probe the potential role of peroxide in the oxidation catalysis of gold in the aqueous phase by electrochemical techniques. The use of electrochemistry is highly suitable because it was recently established that the aqueous-phase oxidation of alcohols by gold follows an electrochemical mechanism, in the sense that oxygen is not an oxygen donor for the oxidation reaction but rather an electron acceptor.[4] Gold acts as a galvanic cell very similar to the way a redox protein functions: the alcohol donates electrons, oxygen accepts electrons, and water, rather than oxygen, acts as the oxygen donor. Alkaline media are attractive for oxidation reactions as the electrocatalysis of alcohol oxidation prefers an alkaline environment, owing to the enhanced deprotonation of the alcoholic group in alkaline solution.[7,8] An oxidic support does not play a role under these alkaline aqueous-phase conditions. However, this mechanism does not exclude the role of peroxide. In fact, hydrogen peroxide is the main product of oxygen reduction on gold,[9–11] and a reactive species such as hydrogen peroxide could, therefore, significantly influence the overall mechanism of gold catalysis.

To study the role of hydrogen peroxide on gold catalysis, we have studied the electrocatalytic oxidation of a model alcohol, that is, glycerol, on a gold electrode in alkaline solution,[12,13] in absence and presence of oxygen and hydrogen peroxide in solution. If there would be any enhancing effect of hydrogen peroxide, there should be a clear effect of the presence of hydrogen peroxide or oxygen on the electrocatalytic activity, as well as on the formation of the various products of glycerol oxidation.

Shown in Figure 1 are the linear sweep voltammetry curves of 0.1 м glycerol and oxygen (saturated solution concentration) on gold in 0.1 м NaOH, in each other's absence and presence, that is, 0.1 м glycerol in an oxygen-saturated 0.1 м NaOH. As can be seen from the comparison of the three voltammograms, the presence of oxygen in solution has no significant effect on the oxidation current of glycerol, other than a small

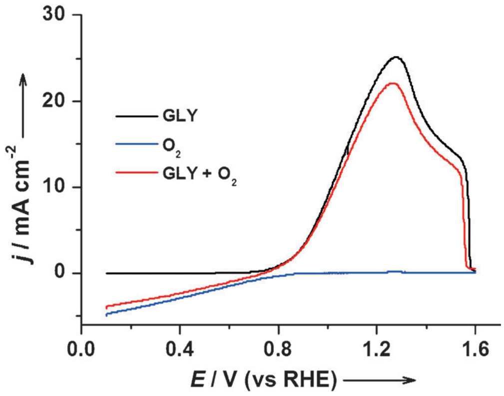

Figure 1. Linear sweep voltammograms of glycerol (GLY, 0.1 м) and oxygen saturated solution on gold in 0.1 м NaOH in each other's absence and presence, with a scan rate of 50 mV s^{-1}.

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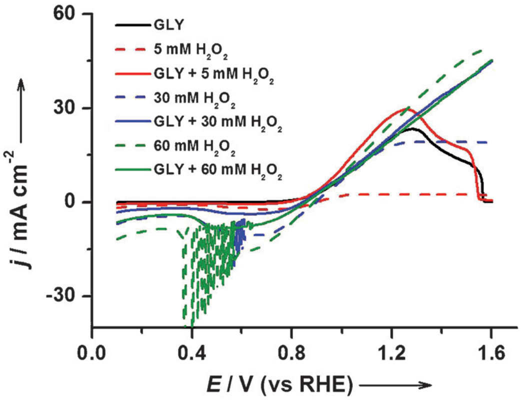

Figure 2. Linear sweep voltammograms of glycerol (GLY, 0.1 M) and various concentrations (5, 30 and 60 mM) of hydrogen peroxide in solution on gold in 0.1 M NaOH, both in each other's absence and presence, with a scan rate of 50 mV s^{-1}.

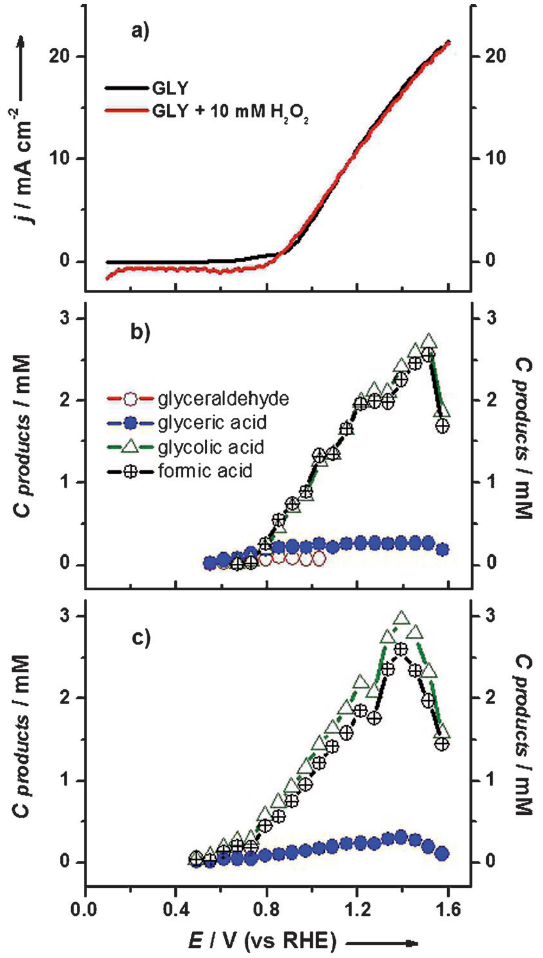

Figure 3. Glycerol (GLY, 0.1 M) oxidation in the absence and presence of H_2O_2 (10 mM) on gold electrode in 0.1 M NaOH: a) current density profile during linear sweep voltammetry with a scan rate of 1 mV s^{-1}, concentration changes of reaction products from glycerol oxidation b) in the absence of H_2O_2 and c) in the presence of H_2O_2.

decrease in oxidation current at high potentials. This suggests that the presence of oxygen itself, or one of its reduction products, has no strong effect on the electrocatalytic oxidation of glycerol, and certainly does not enhance it.

To test whether high concentrations of peroxide in solution affect the glycerol oxidation, we show in Figure 2 the linear sweep voltammetry of 0.1 M glycerol and various concentrations (5, 30 and 60 mM) of hydrogen peroxide in solution, both in each other's absence and presence. Again there is no strong evidence for any (positive) interaction between hydrogen peroxide and glycerol. During the reduction of hydrogen peroxide, current oscillations are observed between 0.3 and 0.5 V_{RHE}[14,15] and, interestingly, these current oscillations are suppressed by the presence of glycerol (more details are shown in Figure S1 in the Supporting Information), though the average current for hydrogen peroxide reduction remains quite similar.

Shown in Figure 3 are the products formed during glycerol oxidation in 0.1 M NaOH, as detected by online HPLC,[12,13] both in the absence and presence of 10 mM H_2O_2. We chose a relatively low concentration of H_2O_2 as this would mimic more closely the conditions of aqueous-phase oxidation of glycerol by oxygen, even though 10 mM is still very much higher than the concentration expected under those conditions. Figure 3 shows that there are no strong effects of H_2O_2 on the product distribution of glycerol oxidation. The only really significant difference is that in the presence of H_2O_2 we were not able to detect glyceraldehyde as oxidation product at low potential, whereas glyceraldehyde is observed in low concentrations in the absence of H_2O_2. This could suggest that a reaction between H_2O_2 and glyceraldehyde. However, the other products of glycerol oxidation on gold (glyceric acid, glycolic acid, formic acid) are not significantly influenced by the presence of H_2O_2.

We have also studied the oxidation of glycerol in neutral and acidic media in the absence and presence of H_2O_2. At these pH values, glycerol oxidation on gold is very slow.[13] The presence of H_2O_2 has no significant effect on this oxidation activity. We did observe that at higher concentrations of H_2O_2, however, glyceraldehyde can be observed as an oxidation product of glycerol in the potential region in which H_2O_2 is oxidized, as shown in Figure S2 in the Supporting Information. The most likely explanation for this effect is the formation of $OH^{\bullet}$ radicals during the H_2O_2 oxidation. As we have recently shown,[16] the presence of $OH^{\bullet}$ radicals leads to the oxidation of organic molecules, such as polyols. However, the effect under the conditions considered here appears to be small, there is no clear evidence for the effect of $OH^{\bullet}$ radicals under alkaline conditions, and it is unlikely that $OH^{\bullet}$ radicals would play a role during the aqueous phase oxidation of glycerol on gold by oxygen.

In conclusion, the presence of H_2O_2 during the gold-catalyzed electrochemical oxidation of a model alcohol, such as glycerol, has no significant effect on the overall glycerol oxidation activity or selectivity, at least at the low (room) temperature of the experiments conducted here. This would also suggest that the low-temperature aqueous-phase reforming of glycerol (and other alcohols) by gold, which follows an electro-

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chemical mechanism,[4] is not likely influenced significantly by the presence of the reduction product of oxygen, that is, hydrogen peroxide. In alkaline media, there appears to be a small suppression of the formation of glyceraldehyde in the presence of hydrogen peroxide, but there is no major influence on the overall oxidation pathway. In neutral and acidic media, in which glycerol oxidation on gold has low activity, the formation of $OH^{\bullet}$ radicals during hydrogen peroxide oxidation at high potential may enhance glycerol oxidation, but this is not expected to play a role during heterogeneously catalyzed gold-oxidized aqueous-phase reforming of glycerol, as under such conditions such high surface potentials seem unlikely to be reached.

Experimental Section

Electrochemical characterization was carried out in a standard three-electrode cell, which was cleaned by employing a standard procedure[17] to remove all traces of organic contaminations, controlled by a potentiostat/galvanostat (μ-Autolab Type III). Glycerol (0.1 M) and various concentrations of H_2O_2 were dissolved into solutions of different pH values (0.1 M NaOH, 0.1 M Na_2SO_4, 0.1 M phosphate buffer (pH 7), and 0.5 M H_2SO_4) under deaerated condition by purging Ar or aerated condition by purging air. Working electrode in the experiment was polycrystalline gold (diameter 2 mm) disk, which was mechanically polished with diamond paste and alumina (up to 0.05 mm) and cleaned ultrasonically in ultrapure water before use. In all experiments, a gold coil was used as a counter electrode while a reversible hydrogen electrode (RHE) was employed as a reference electrode. Electrochemically active surface area of a gold electrode is calculated based on the charge transferred during mono-layer gold oxide reduction.

The reaction products during voltammetry were collected and analyzed with an online HPLC system as described in our previous work.[7,8,12,13,16,18–23] Residual H_2O_2 was quenched by stoichiometric excess amount of Na_2SO_3 and pH of the collected samples was adjusted below 7 during sample collection with modified sampling tip.[13] Sample volumes of 30 μL were injected into the columns in series of Aminex HPX 87-H (Bio-Rad) and Sugar SH1011 (Shodex) with diluted sulfuric acid (0.5 mM) as eluent. The selected temperature of column oven was 85 °C.

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Keywords: electrocatalysis · glycerol · gold · hydrogen peroxide · online HPLC

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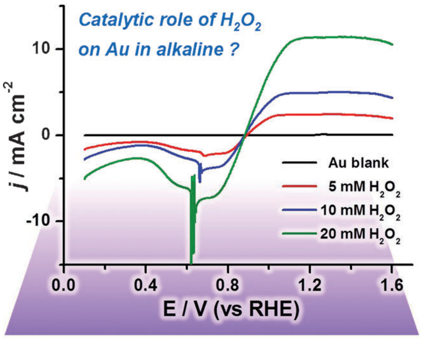

Going blonde? Think twice! The presence of peroxide has no significant effect on the overall oxidation activity or product selectivity during the gold-catalyzed (electro-)catalytic oxidation of glycerol at low temperature.

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