Influence of oxygen and pH on the selective oxidation of ethanol on Pd catalysts

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ABSTRACT

The selective oxidation of ethanol on supported Pd is catalytically promoted by the presence of hydroxide species on the Pd surface as well as in solution. These hydroxide intermediates act as Brønsted bases which readily abstract protons from the hydroxyl groups of adsorbed or solution-phase alcohols. The C_1—H bond of the resulting alkoxide is subsequently activated on the metal surface via hydride elimination to form acetaldehyde. Surface and solution-phase hydroxide intermediates can also readily react with the acetaldehyde via nucleophilic addition to form a germinal diol intermediate, which subsequently undergoes a second C_1—H bond activation on Pd to form acetic acid. The role of O_2 is to remove the electrons produced in the oxidation reaction via the oxygen reduction reaction over Pd. The reduction reaction also regenerates the hydroxide intermediates and removes adsorbed hydrogen that is produced during the oxidation.
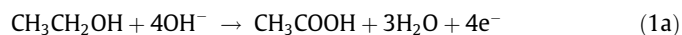
1. Introduction

The selective oxidation of alcohols in aqueous media provides an attractive route to organic acids from biorenewable feedstocks. For example, glycerol, produced from the transesterification of fatty acids [1,2], can be oxidized to form glyceric and tartronic acids used in pharmaceutical and cosmetics industries [3]. Similarly, hydroxymethylfurfural (HMF) produced from the dehydration of fructose [4] can be oxidized to produce 2,5-furandicarboxylic acid (FDCA), which can be used to create PET plastics, offsetting the demand for oil-based terephthalic acid [5].

Aerobic oxidation of alcohols is often carried out over supported noble metal catalysts, including Pt, Pd, and Au [6,7]. Liquid-phase in situ XANES experiments have confirmed that these catalysts are active in their reduced, metallic state during oxidation [8,9]. Kinetic studies reported in the literature suggest that the mechanism proceeds via the formation of an aldehyde intermediate and that activity and selectivity to the acid product increases significantly when the reactions are carried out at high pH [6]. While Pt and Pd demonstrate some activity at neutral and slightly acidic pH, the reaction is inactive over Au at neutral pH for the activation of various alcohols [10–14].

Rigorous isotopic labeling studies along with density functional theory (DFT) calculations were recently carried out by Zope et al. [12] to determine the roles of both molecular oxygen and hydroxide in the mechanisms of glycerol and ethanol oxidation over supported Au catalysts. The results from this work suggest that the metal-solvent interface provides a unique environment that promotes the oxidation of the alcohol via the hydroxide present on the surface as well as in solution. Molecular oxygen, which is necessary to carry out this reaction, is an indirect reagent that removes electrons from the catalytic metal surface produced during oxidation. This occurs via the reduction with water as summarized in Eq. (1b). The oxidation mechanism on supported Au is very similar to the mechanism of electrooxidation on supported Au electrodes (with the exception of the applied potential). In the direct alcohol fuel cells, the rate of oxidation that occurs at the anode is balanced by the rate of oxygen reduction at the cathode [15–18].

$$CH_3CH_2OH + 4OH^- \rightarrow CH_3COOH + 3H_2O + 4e^- \tag{1a}$$

$$O_2 + 2H_2O + 4e^- \rightarrow H_2O_2 \rightarrow 4OH^- \tag{1b}$$

However, other investigators have suggested that molecular oxygen first dissociates to form atomic oxygen on the surface, which subsequently behaves as a Brønsted base on the surface to carry out the oxidation chemistry, similar to the role of hydroxide above [19]. Oxygen is known to dissociate over Pt and Pd surfaces [20,21], and although oxygen dissociation is not observed over Au(1 1 1) [22], there is the possibility that low-coordinated sites or defect sites on Au nanoparticles may dissociate oxygen, and the presence of oxygen atoms can increase the rate of oxygen dissociation due to the formation of partially oxidized Au clusters [22]. Furthermore, over Pt and Pd catalysts, there is some activity reported at neutral or slightly acidic pH [23,24], suggesting that there are pathways

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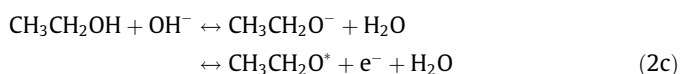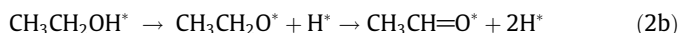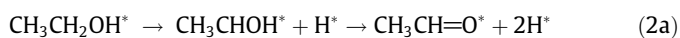E-mail address: mn4n@virginia.edu (M. Neurock).

available which do not require large amounts of hydroxide to be present. The mechanisms, as discussed in the next section, vary significantly across the literature, and a thorough examination of the reaction network has not yet been presented.

To evaluate these possible mechanisms, density functional theory (DFT) calculations were performed to establish the activation barriers and reaction energies for a large set of elementary reactions. The work examined herein will focus on the selective oxidation of ethanol, which follows similar kinetics and mechanisms as glycerol and other polyols but is more computationally tractable. We examine Pd, as it is known to readily dissociate oxygen and reduce O^* and OH^* intermediates that result to form water [20,25]. Pd, however, has a much lower tendency to completely oxidize the alcohol to CO_2 and H_2O as a result of the difficulty in activating C—C bonds on Pd compared to on Pt [6].
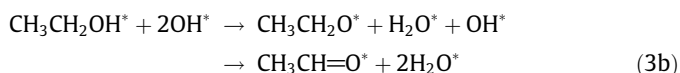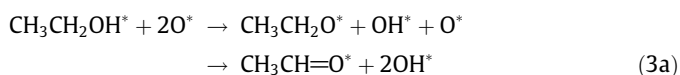
## 2. Proposed mechanisms

2.1. Ethanol dehydrogenation

The dehydrogenation of ethanol (CH_3CH_2OH) to acetaldehyde (CH_3CHO) can proceed by the initial activation of either the C—H or O—H bond of ethanol as shown in Eqs. (2a)–(2c). Studies of ethanol oxidation over Pt and Pd electrocatalysts suggest that C—H activation occurs via the oxidative insertion of the metal into the C—H bond to form hydroxyethylidene (CH_3CH^*OH) and hydride (H^*) surface intermediates [16,17,26] as shown in Eq. (2a). Alternatively, studies in the heterogeneous catalysis literature report that alcohol oxidation proceeds via the initial activation of the O—H bond to form ethoxide ($CH_3CH_2O^*$) and H^* surface intermediates [6,7,23] as shown in Eq. (2b). In solution, an equilibrium exists between the ethanol and the ethoxide ion through base-catalyzed deprotonation as shown in Eq. (2c).

$$CH_3CH_2OH^* \rightarrow CH_3CHOH^* + H^* \rightarrow CH_3CH{=}O^* + 2H^* \qquad (2a)$$

$$CH_3CH_2OH^* \rightarrow CH_3CH_2O^* + H^* \rightarrow CH_3CH{=}O^* + 2H^* \qquad (2b)$$

$$CH_3CH_2OH + OH^- \leftrightarrow CH_3CH_2O^- + H_2O$$
$$\leftrightarrow CH_3CH_2O^* + e^- + H_2O \qquad (2c)$$

Adsorbed oxygen or hydroxide can also act as a Brønsted base to partially reduce the hydrocarbon as shown below in Eq. (3). This mechanism is supported by kinetic studies which suggest a Langmuir–Hinshelwood mechanism [27,28] where the rate-limiting step involves the reaction between surface oxygen and an ethanol intermediate [19]. We recently demonstrated that hydroxide behaves as a Brønsted base on Au and Pt(1 1 1) surfaces where it abstracts the more acidic proton of the alcohol [12].

$$CH_3CH_2OH^* + 2O^* \rightarrow CH_3CH_2O^* + OH^* + O^*$$
$$\rightarrow CH_3CH{=}O^* + 2OH^* \qquad (3a)$$

$$CH_3CH_2OH^* + 2OH^* \rightarrow CH_3CH_2O^* + H_2O^* + OH^*$$
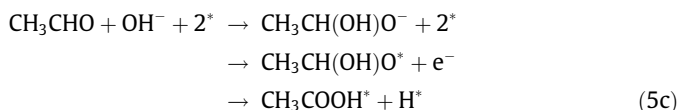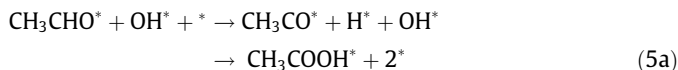$$\rightarrow CH_3CH{=}O^* + 2H_2O^* \qquad (3b)$$

Previous theoretical results suggest that the high alkalinity in this reaction would result in a high coverage of hydroxide groups on the metal surface which would facilitate the C—H activation of ethanol to form the adsorbed hydroxyethylidene intermediate as is shown in Eq. (4) [17]. This work however was carried out using small Pd clusters (14–20 atoms) and does not consider the ethoxide route or the possibility of aqueous-phase deprotonation. It also does not consider the possible effects of hydroxide groups upon the subsequent oxidation of acetaldehyde to acetic acid (CH_3COOH).

$$CH_3CH_2OH^* + OH^* + {}^* \rightarrow CH_3CHOH^* + H_2O^* + {}^*$$
$$\rightarrow CH_3CH{=}O^* + H^* + H_2O^* \qquad (4)$$
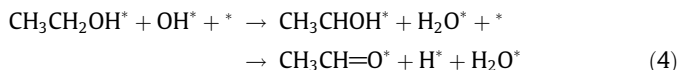
2.2. Acetaldehyde oxidation

The oxidation of the aldehyde to the acid can proceed via two competing intermediates (Eqs. (5a)–(5c)): acetyl (CH_3CO), which is the more commonly proposed route in the literature [6,16,18,23] and ethoxy-diol ($CH_3CH(OH)O$), which can be formed on the surface as well as in solution [7,12,23]. These steps are presented in Eq. (5). Other routes involving the oxidation of the aldehyde, however, may also exist.

$$CH_3CHO^* + OH^* + {}^* \rightarrow CH_3CO^* + H^* + OH^*$$
$$\rightarrow CH_3COOH^* + 2^* \qquad (5a)$$

$$CH_3CHO^* + OH^* \rightarrow CH_3CH(OH)O^* + {}^* \rightarrow CH_3COOH^* + H^* \qquad (5b)$$

$$CH_3CHO + OH^- + 2^* \rightarrow CH_3CH(OH)O^- + 2^*$$
$$\rightarrow CH_3CH(OH)O^* + e^-$$
$$\rightarrow CH_3COOH^* + H^* \qquad (5c)$$

These pathways alone, for example, do not explain isotopic labeling studies performed by multiple investigators, which show that the oxidation of ethanol [12,29], glycerol [12], and other alcohols [5] with $H_2{}^{18}O$ labeled water in alkaline media result in the formation of the acetate product which contains multiple ^{18}O groups. This suggests that at some point within the mechanism, an intermediate with an equivalence between the ^{16}O on the alcohol intermediate and the ^{18}O in solution is formed. One possibility for this equivalence is the aqueous-phase hydration of the aldehyde to form a geminal diol as shown in Eq. (6). If this process is equilibrated, the aldehyde can exchange its oxygen with that of the labeled oxygen in water, which can lead to two ^{18}O being observed in the acid product.

$$RCHO + OH^- + H_2O \leftrightarrow RCH(OH)O^- + H_2O$$
$$\leftrightarrow RCH(OH)_2 + OH^- \qquad (6)$$
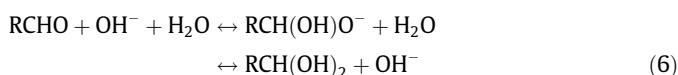
The gem-diol intermediate, once formed, can subsequently dehydrogenate to form the corresponding acid product, which subsequently deprotonates in basic media to form the corresponding carbonate.

2.3. Role of oxygen

During aerobic alcohol oxidation, oxygen is reduced to form water, thus removing electrons from the catalyst surface. This reduction can occur in various ways: Oxygen can dissociate to form atomic oxygen on the surface, which can react with adsorbed atomic hydrogen formed from oxidation reactions as shown in Eq. (7a) [30–32]. In this case, oxygen is merely a hydrogen acceptor, removing electrons from the metal and adsorbed hydrogen from the surface, if that is oxygen's only purpose, then another hydrogen acceptor, such as an olefin, can be substituted for O_2 in order to remove the electrons and adsorbed hydrogen as presented in Eq. (7b). Hayashi et al. [33] have shown that for the selective oxidation of alcohols to aldehydes, the reaction is active in the absence of oxygen under an ethylene atmosphere, demonstrating that the oxidative dehydrogenation of alcohols does not require O_2 present, and it merely requires an electron and H^* acceptor (such as ethylene). They did not report any further oxidation to acid products. Alternatively, atomic oxygen can act as a Brønsted base as previously discussed, directly abstracting hydrogen from the alcohol as shown in Eq. (3a). A third possibility is that O_2