

A FIRST PRINCIPLES ANALYSIS OF THE INFLUENCE OF OXYGEN AND ALKALINITY ON THE SELECTIVE OXIDATION OF ETHANOL OVER Pd(111)

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Summary

The mechanism and kinetics for the selective oxidation of ethanol to acetic acid over Pd(111) was examined using first principles density functional theoretical calculations. Surface oxygen and hydroxyl intermediates were found to significantly influence the activation barriers as well as the available reaction pathways. The results show that O-H bond dissociation paths are enhanced via $-O$ and $-OH$ abstractions, whereas the C-H bond activation is hindered by the presence of any adsorbates on the surface.

Keywords

Computational Catalysis, Reaction Path Analysis, Chemical feedstocks from biomass, Green CRE

Introduction

The increasing demands for oil along with its limited supply will likely force much of the current petroleum-based chemical industry to transition to renewable feedstocks and their conversion into value added chemicals. The selective oxidation of complex biomass derivatives, such as hydroxymethylfurfural (HMF), glycerol and other polyols offers one such attractive route to selective production of organic acids used in polymerization processes. In order to understand the governing elementary steps involved in the catalytic oxidation of polyols, we examined in detail the selective oxidation of ethanol over Pd.

The aerobic oxidation of ethanol has shown activity over many noble metals, including Pt^{1,2,4} and Pd¹⁻⁷ as well as bimetallic alloys⁶. Unlike platinum, palladium does not readily break the C-C bond of ethanol², reducing the production of the CO₂ byproduct and it has been shown that the active phase during oxidation is the metal rather than an *in-situ* formed metal-oxide.³

Many of the mechanisms proposed for alcohol oxidation suggest that the alcohol dehydrogenates to form the carbonyl via the metal. This is supported by studies carried out with ¹⁸O-labeled oxygen which confirm that the oxygen present in the carbonyl group of the product is from the original alcohol⁴. The presence of adsorbed hydrogen is evident by the propensity for these reactions to occur along with hydrogenation and hydrogenolysis reactions which require large amounts of adsorbed hydrogen.¹

However, the mechanism by which dehydrogenation occurs is still up for debate. An examination of alcohol oxidation across many catalysts, conditions and alcohols seems to suggest a route which proceeds through the formation of an alkoxide¹:

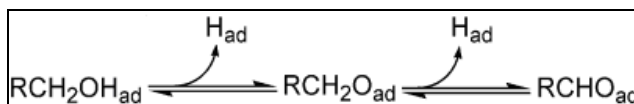


Figure 1. Ethanol dehydrogenation via ethoxy.

While specific studies of ethanol over Pt and Pd catalysts^{2,6} suggest that dehydrogenation proceeds through the formation of a $CH\cdot$ radical as shown in in Fig. 2, there is no supporting mechanistic data to defend such a path.^{2,6,8}

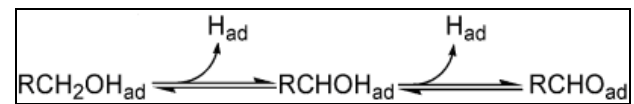


Figure 2. Ethanol dehydrogenation via $CH\cdot$ radical.

The role of oxygen and hydroxyl in the above dehydrogenation is also unknown. For oxygen, the simplest interpretation is that the oxygen exists only to shift the equilibrium by removing the adsorbed hydrogen to form water as shown in Figure 3 below. This role of oxygen as merely a hydrogen acceptor is also demonstrated by the ability of an olefin to act as the oxidizing agent¹.

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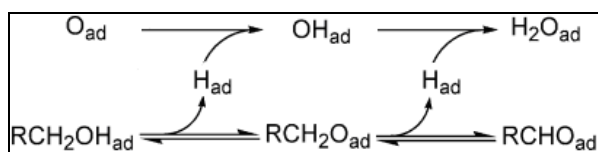


Figure 3. Oxygen's role to remove the product hydrogen from the surface.

Adsorbed oxygen can also act to partially reduced hydrocarbon as shown below in Figure 4. This mechanism has been supported through kinetic modeling which reveal distinct Langmuir-Hinshelwood behavior¹. There is little doubt due to numerous electrochemical and spectroscopic studies that there is partial oxygen coverage on the surface.

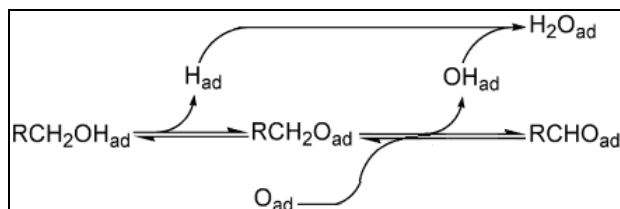


Figure 4. Oxygen directly interacts to remove the hydrogen on the β -carbon to form the carbonyl.

It has been shown that Pd is primarily active in high pH aqueous solutions,^{1,2,6} whereas Pt activity shows no dependence upon pH.² However, the role of the alkalinity is unknown. Through DFT, Cui, et al. have stated that the alkalinity creates an increase of hydroxyl on the metal surface which facilitates the dehydrogenation of ethanol through acetoxy on the palladium surface as shown in Figure 5.

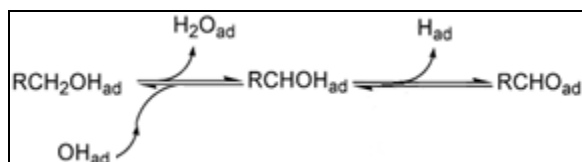


Figure 5. Hydroxyl directly interacts to remove the hydrogen on the β -carbon first.

Methodology

To investigate the mechanisms outlined above, DFT calculations were carried out using VASP with the PW-91 GGA. All structures were converged to a max atom force of 0.05 eV/ang. All energies were computed using a 6x6x1 sampling of the brillouin zone. The transition states were obtained through a combination of the NEB and dimer methods.

Results and Discussion

Based on our results, the alkaline environment is necessary for the initial dehydrogenation of ethanol via ethoxy to acetaldehyde on Pd(111). As summarized in the example below, the activation barrier for the $-OH$ assisted conversion of ethanol to

ethoxy is very small compared to the activation upon a bare metal.

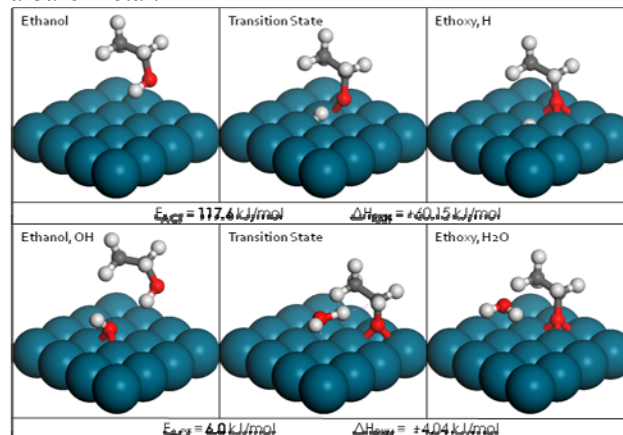


Figure 6. OH assisted conversion of ethanol to ethoxy.

Overall, our results across the reaction network show that O-H bond dissociations are enhanced through $-O$ and $-OH$ species on the surface whereas C-H bond dissociations are hindered by the competing adsorbates.

References

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