

A First Principles Analysis of the Mechanisms and Site Requirements for the Electrocatalytic Oxidation of Methanol and Formic Acid

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Introduction

The electrocatalytic oxidation of small oxygenate molecules such as methanol, formic acid and ethanol which have high energy densities and low toxicities is of great interest in the development of direct liquid fuel cells for portable and potentially automotive power. Despite their importance, the mechanisms that control the electrocatalytic oxidation of these fuels is still not very well understood and often debated. Theory and simulation have made important advances in modeling electrocatalytic systems over the past few years. Herein we discuss the advances in theory and compare in detail the mechanisms and the sites that control the electrooxidation of methanol and formic acid over different transition metals and their alloys. The results are used to elucidate mechanisms and suggest potentially more active catalytic alloys.

Methods

Nonlocal gradient corrected plane wave density functional theoretical methods were used to calculate potential-dependent reaction energies and activation barriers involved in the electrooxidation of methanol and formic acid over different transition metals and transition metal alloys. The simulations explicitly account for the role of solution, the electrochemical potential and the double layer that forms at the metal/solution interface.

Results and Discussion

The results help to confirm that methanol oxidation proceeds through both direct and indirect pathways that are governed by C-H and O-H bond activation respectively. The indirect path which proceeds via the formation of CO is the dominant path. The rate, however, is significantly lower at potentials less than 0.6 V NHE over Pt(111) where CO is strongly chemisorbed and inhibits oxidation. The ensemble size required for the indirect and direct paths are characteristically different. The indirect path requires 3-4 Pt atoms in order to accommodate the carbon bound CH_xO fragments that form which is consistent with experimental results[1]. The direct path which leads to the production of formaldehyde and/or formic acid, on the other hand, requires only 1-2 Pt atoms, and as such, is much less influenced by the anion adsorption which also agrees with experimental results [2-3].

Formic acid oxidation oxidized to CO_2 via direct and indirect pathways. In addition, there is a third path which involves the formation of formate intermediates on the surface. Similar to that for methanol, the direct path occurs via the initial activation of the C-H bond. The barrier to activate the O-H bond of the hydroxyl carbonyl that forms is very low over a range of potentials and is thus readily activated to form CO_2 directly. Based on the calculated activation

barriers, this path appears to be the dominant route to form CO_2 . At lower potentials, however, the direct path is blocked by CO which covers the surface. The indirect path which is responsible for CO formation is controlled by the non-Faradaic hydrolytic activation of the C-O bond of formic acid or formate. At potentials lower than 0.67 V NHE, the CO that forms is thermodynamically quite stable and can not be oxidized from the surface. At potentials greater than 0.6 V, CO is oxidized and the direct path is much less inhibited. The formate path, which involves the activation of the O-H bond of formic acid, initiates quite readily over Pt thus resulting in the formation of formate intermediates. At lower potentials, this path is blocked due to the presence of CO on the surface. Higher potentials increases the formation formate intermediates. The activation barrier for the subsequent activation of the formate C-H bond, however, is prohibitive. The computational results indicate that formate forms on the surface at these higher potentials but acts as a spectator which is consistent with experimental results [4].

The site specificity for the direct and indirect paths involved in the oxidation of formic acid were found to be quite similar to those found for methanol. The direct path appears to occur over just 1 or 2 Pt atoms. The indirect path, however, requires splitting the C-O bond which requires a significantly greater ensemble size. There is one significant difference, however, between the ensemble size effects for methanol and formic acid. In methanol, the indirect path through CO is the major path to CO_2 over a wide range of potentials. In formic acid, however, the direct path is actually the dominate path to CO_2 over nearly all potentials. This helps to explain the significant differences concerning the influence of Ru on methanol and formic acid oxidation. Ru significantly enhances the methanol oxidation but has only a small influence on formic acid oxidation.

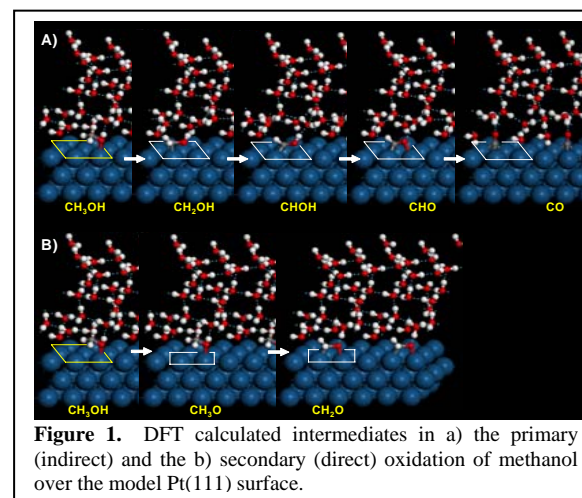


Figure 1. DFT calculated intermediates in a) the primary (indirect) and the b) secondary (direct) oxidation of methanol over the model Pt(111) surface.

References

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