The electrocatalytic oxidation of ethanol studied on a molecular scale

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Citation

Lai, S. S. S. (2010, June 16). *The electrocatalytic oxidation of ethanol studied on a molecular scale*. Retrieved from https://hdl.handle.net/1887/15725

SUMMARY

This thesis describes the results of the fundamental research on the electro-oxidation of ethanol. In addition, the oxidation of intermediates in the ethanol electro-oxidation reaction, such as acetaldehyde and adsorbed CO, has also been studied. The goal of this research is to provide deeper insight into the molecular level understanding of the mechanism, and how various operational parameters affect this mechanism. With these insights, the development of low temperature direct ethanol fuel cells (DEFC) can be advanced, since, ultimately, the goal of fundamental catalysis research is the rational design of new catalysts, for which the understanding of molecular mechanisms is of essential importance.

The mechanism of the electro-oxidation reaction is investigated using electrochemical techniques, such as cyclic voltammetry and chronoamperometry, as well as *in situ* characterization techniques, such as surface enhanced Raman spectroscopy (SERS), Fourier transform infrared spectroscopy (FTIR) and online electrochemical mass spectrometry (OLEMS).

Various aspects of the electrochemical oxidation of ethanol in an acidic electrolyte are studied in Chapters 3-5, aiming to elucidate the reaction mechanism in acidic media, both in the presence and in the absence of specifically adsorbing anions. The effect of the surface structure on the ethanol oxidation reaction is studied with electrochemical techniques in Chapter 3 by employing platinum single-crystal electrodes of Pt [*n*(111)×(111)] orientation, showing that surface step sites have a pronounced effect on various steps in the mechanism: introducing surface steps increases the ethanol oxidation rate, while it decreases the oxidation rate of acetaldehyde, an intermediate in the ethanol oxidation reaction. In addition, step sites increase the carbon-carbon bond breaking in both ethanol and acetaldehyde. Both these effects of the surface step sites are stronger in a perchloric acid solution (without strongly adsorbing anions) than in a sulfuric acid solution (with strongly adsorbing anions).

The presence or absence of adsorbing anions from the electrolyte does not only influence the catalytic activity, but also the product distribution, as evidenced by OLEMS (Chapter 4). While surface steps increase the total oxidation activity, it does not influence the product distribution in a perchloric acid solution. In a sulfuric acid solution, however, surface step sites strongly favor the formation of

CO_2 over acetaldehyde. This effect can be attributed to the surface structure sensitive sulfate adsorption, which is stronger on surfaces with wide terraces, displacing intermediates for carbon-carbon bond breaking, emphasizing the importance of anion-surface interactions.

When the ethanolic carbon-carbon bond breaks on platinum, it results in adsorbed CH and adsorbed CO at low potentials (Chapter 5). Both adsorbed species can be followed by SERS. Upon slowly increasing the potential, adsorbed CH is slowly converted to adsorbed CO below the potentials at which CO is oxidized to $CO_{2.}$

In an alkaline electrolyte (Chapter 6), adsorbed $CH_{(x)}$, resulting from the dissociation of ethanol, plays a key role in the ethanol oxidation reaction on platinum. On (110) sites, it is quickly converted to CO_{ad} at low potentials. On (111) terrace sites, $CH_{(x)}$ is difficult to oxidize, slowly deactivating the reaction over time. As a result, surfaces with wide terraces display a worse stability than surfaces with short terraces. Due to this self-poisoning effect, the effect of step sites on the activity of the reaction is much more pronounced in alkaline media than in acidic media.

The effect of the electrolyte pH on the ethanol oxidation reaction is further elucidated in Chapter 7, by studying the oxidation of ethanol on platinum and on gold in a wide range of phosphate buffers. It is shown that the oxidation currents increase significantly when the pH of the electrolyte is higher than 10. This large increase can be explained by considering ethoxy rather than ethanol as the main electrochemically active species at high electrolyte pH. Finally, FTIR experiments show that strongly adsorbing anions inhibit carbon-carbon bond breaking, in qualitative agreement with the findings in Chapter 4.