

Understanding the elementary steps in the ethanol oxidation reaction.

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It is well known that the ethanol oxidation is a complex reaction. In the complete oxidation CO_2 , which requires the cleavage of the C-C bond, 12 electrons are transferred and CO is involved as intermediate. However, the cleavage of the C-C bond is the most difficult step in the whole reaction mechanism. In the cases where such process is not occurring, acetaldehyde and acetic acid are the final products. In order to design better electrocatalysts, a detailed knowledge on how the properties of the catalysts affect the oxidation mechanism is required. In this communication, recent results on the effect of the surface structure and composition of the electrocatalyst in the oxidation mechanism are reviewed.

Ethanol oxidation on platinum is a surface structure sensitive reaction. Electrochemical and FTIR results in acidic solution show that the activity and the final oxidation products strongly depend on the surface structure. For the Pt(111) electrode, the only products are acetaldehyde and acetic acid [1]. Formation of CO and CO_2 is only detected when steps with (110) symmetry are introduced on the (111) planes, which indicates that the step sites are effective for breaking the C-C bond. On the other hand, Pt(100) and Pt(110) electrodes yield CO_2 , acetic acid and acetaldehyde, in different ratios depending on the electrode potential. On the other hand, currents on alkaline medium are much higher, but the only detected products are acetate and acetaldehyde.

The enhanced activity of the step sites for breaking the C-C bond can be used to get insight into this process. The spectroscopic studies indicate that the cleavage of the bond is taking place at low potentials and the $\cdot\text{CH}_2\text{OH}$ fragment is immediately transformed into adsorbed CO. The other fragment is only oxidized to CO at higher potentials. Additionally the presence of Ru or Sn on the surface catalyzes the oxidation of CO to CO_2 . Additionally, adsorbed Sn species catalyze the oxidation of ethanol to acetic acid.

Additional surface composition effects can be observed when Pt is deposited on Rh(111) electrodes. The electrochemical and FTIR studies demonstrate that monoatomic Pt islands on the Rh(111) electrode have an activity that is 20 times higher than that recorded for Pt electrodes for ethanol oxidation and that the cleavage of the C-C bond is taking place (figure 1). The electrochemical activity of those islands diminishes significantly when a second Pt layer is grown.

All these surface structure effects have been also examined on nanoparticles. It has been found that the behavior of the nanoparticles can be explained using the observed behavior of the single crystal electrodes.

References.

[1] F. Colmati, G. Tremiliosi-Filho, E.R. Gonzalez, A. Berna, E. Herrero, J.M. Feliu, *Faraday Discuss.*, 140 (2008) 379.

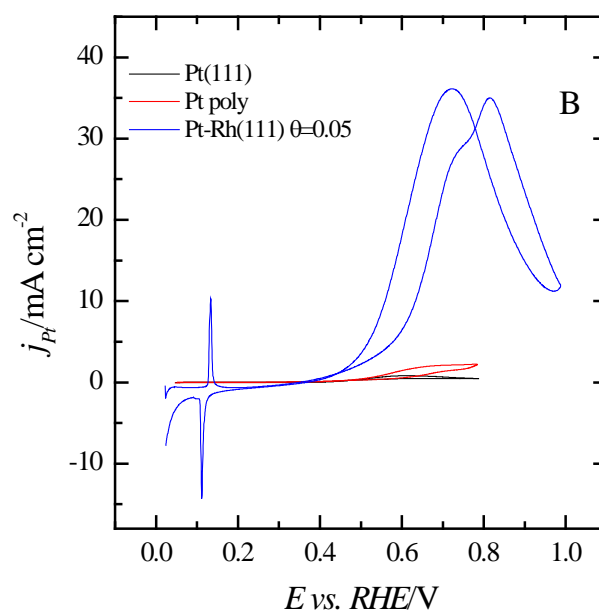


Figure 1. Cyclic voltammograms of ethanol oxidation on Pt(111), polycrystalline Pt and Pt deposited on Rh(111) electrodes in 0.1 M H_2SO_4 + 0.5 M EtOH. The current densities are calculated according to the platinum active area of the electrodes