

Quantitative DEMS study of ethanol and methanol oxidation: effect of Pt single crystalline surface structure and bimetallic surface modification

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Step decoration is often observed for single crystalline Pt surfaces having terraces with a (111) orientation. We have shown in the past that the ordered bimetallic arrangement of the two components due to step decoration by a co-catalyst such as Ru, Sn and Mo helps elucidating their way of action on the CO oxidation. Because of the usually higher catalytic activity of (100) sites, these are preferable substrates for catalytic studies. Although step decoration is not observed on such surfaces, at least in the case of Cu upd^[1], the preferential adsorption at terraces also leads to an ordered bimetallic surface. On such a Ru modified Pt(19,1,1) surface, CO Oxidation occurs in well separated peaks, both shifted to lower potentials, similar to the Ru modified Pt surfaces with large (111) terraces (Pt(S)[n(111)x(111)] or Pt(S)[n(111)x(100)]^[2,3]. Measurements with our newly developed potential modulation technique^[4] revealed that the Tafel slope is around 120 mV ($\alpha=0.5$) at both type of surfaces, whereas on unmodified Pt at low potential it amounts to 40 mV ($\alpha=1.5$).

We now extended this technique to the oxidation of methanol and the methanol adsorption product. In both cases the Tafel slope is around 120 mV ($\alpha=0.5$).

For the examination of the activity and the mechanism with respect to other 'fuels', the determination of the products and the effect of convection are crucial. This will be demonstrated for the oxidation of methanol and ethanol on the title surfaces with and without modification. We will also present a new design of a cell allowing the reaction product analysis by DEMS for small crystals with short time constants.^[5]

Using the dual thin layer flow through cell, a semi-quantitative analysis of the volatile products during the electrooxidation of adsorbed and bulk solution of 0.01 M ethanol at polycrystalline platinum, smooth, roughened and modified Pt(S)[n(100)x(111)] electrodes has been done by on-line differential electrochemical mass spectroscopy (DEMS). In addition to the current efficiency of CO₂, that of acetaldehyde was determined as a function of the flow rate. At polycrystalline platinum, ethanol oxidation produces only acetaldehyde; the amount of acetaldehyde further oxidized to acetic acid is negligible due to convection conditions. For comparison and for calibration purposes, i-propanol oxidation was examined for which acetone is the only oxidation product. At Pt(11,1,1), the main oxidation product is acetaldehyde. At Pt(311), in addition to acetaldehyde, acetic acid was also formed. Surface modification with Sn did not increase the reactivity of Pt(11,1,1) instead it led to inhibition of the ethanol oxidation. In the case of Pt(311), the onset potential of oxidation was shifted negatively by 0.2 V in the presence of Sn. The results of the potentiostatic measurements showed that this shift is not associated with the production of CO₂; rather acetic acid and acetaldehyde are the main oxidation products.^[6,7]

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