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Comparison of Voltammetric Behavior of Adsorbed or Dissolved Unsaturated Alcohols at Vacuum-Annealed and Electrochemically Cycled Pt(111) and Pt(polycrystlline) Electrodes

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Abstract

These studies compare the voltammetric behavior of solutions and adsorbed layers of the following unsaturated alcohols: benzyl alcohol (BZA), 4-pyridylcarbinol (4PC), allyl alcohol (AA), propargyl alcohol (PGA), cis-2-butene-1,4-diol (CBED), and 2-butyne-1,4-diol (BYD). They were undertaken for well-characterized Pt(111) electrode surfaces which were either annealed in an ultrahigh vacuum (UHV) or electrochemically cycled, as well as for annealed (UHV) Pt(poly). Electrochemical oxidation of BZA, AA, PGA, CBED, and BYD in aqueous fluoride electrolyte proceeds in two stages: first the alcohol moiety is oxidized to CO2 (0.4 V), followed by oxidation of the resulting adsorbed hydrocarbon (alkene, alkyne, or phenyl, 1.0 V); 4PC is relatively inert. The alcohol moiety in 4PC, which is located opposite the pyridine ring from the surface, does not undergo oxidation at an appreciable rate. in fact, 4PC effectively passivates the surface and poisons the electrochemical activity. Electrochemical cycling of the annealed Pt(111) single-crystal surface greatly increases the oxidation rates of the aliphatic alcohols and, to a lesser extent, increases the oxidation rate of BZA. The oxidation rate enhancement is somewhat smaller if the electrode is electrochemically cycled in the presence of the alcohol. The majority of the difference effected by cycling can be observed after only one cycle. Voltammetry on polycrystalline Pt surfaces resembles that on cycled Pt(111) surfaces for PGA and AA, but resembles that on cycled Pt(111) surfaces for PGA and AA, but resembles that on annealed Pt(111) more closely for the diols CBED and BYD.