

Electrochemical studies of irreversibly adsorbed ethyl pyruvate on Pt{*hkl*} and epitaxial Pd/Pt{*hkl*} adlayers

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Abstract

Cyclic voltammetry (CV) has been used to investigate the irreversible adsorption of ethyl 2-oxopropanoate (ethyl pyruvate (EtPy)) on well-defined Pt and Pd electrodes. Following dosing of EtPy at open circuit on Pt and Pd surfaces, adsorption was found to be structure sensitive with extensive chemisorption being exhibited at {110} and {100} terraces together with {111} × {100} and {111} × {111} steps. However, only very limited adsorption of EtPy was observed at {111} terraces under identical dosing conditions. In particular, Pt{100} terraces were found to give rise to significant decarbonylation of molecularly adsorbed EtPy in the hydrogen underpotential deposition (H up) potential region to generate chemisorbed CO. This finding concerning EtPy adsorption and decomposition agrees with previous investigations on polycrystalline Pt. In contrast, no electrochemical evidence for EtPy decomposition to form adsorbed CO on Pd was ever detected, irrespective of the surface crystallography of the electrode. EtPy decarbonylation was found to be suppressed on Pt{100} by pre-modification with (R)-[(4S,5R,7S)-5-ethenyl-1-azabicyclo[2.2.2]octan-7-yl]-quinolin-4-yl methanol (cinchonidine (CD)), often applied as a chiral modifier in the Pt-catalyzed enantioselective hydrogenation of α -ketoesters. The degree of inhibition was found to be proportional to the amount of CD adsorbed. This surface sensitivity suggested that EtPy requires a very specific adsorption geometry or number of free Pt sites to undergo decarbonylation. For all surfaces studied, EtPy adsorption products could readily be removed either by electrochemical hydrogenation (leaving behind a clean metal surface) or, in the case of adsorbed CO, by performing potential excursions to 0.85V (Pd/H) to facilitate electrooxidation of CO to CO₂. The results highlight the relative importance of ‘active’ {110} and {100} defect sites (relative to {111} terraces) for the chemisorption of EtPy on polycrystalline Pt catalysts used in the enantioselective hydrogenation of α -ketoesters and this finding may have wider implications for catalyst design methodologies.

Keywords: ethyl pyruvate; platinum; palladium; single crystal electrodes; cyclic voltammetry