



Electrocatalytic oxidation of CO on Pt-modified Ru(0001) electrodes

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Abstract

Various amounts of Pt were electrodeposited onto a Ru(0001) electrode, and the kinetics of electrooxidation of CO was studied by cyclic voltammetry. Ru(0001) covered with small amounts of Pt forming patches of 2D-monolayers exhibits only low activity if compared with the bare Ru(0001) or Pt(111) electrodes. However, with high Pt coverages associated with 3D cluster deposits the reactivity is markedly enhanced and reaches a maximum at about 50% surface coverage and then decreases again. The results bear close resemblance to the properties of the reverse system, viz. Ru deposited onto Pt or even of Pt–Ru alloys and are rationalized in terms of a bifunctional mechanism: CO adsorbed at Pt sites react preferentially with OH[−]-species formed at adjacent Ru sites, while reaction on either Pt or Ru sites alone is less facile.

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1. Introduction

In the platinum based methanol fuel cell CO is a reaction intermediate at the anode and blocks

there the active sites [1]. If, however, the Pt electrode is modified by Ru the CO tolerance and thereby the activity becomes improved [2,3]. The origin of this effect is still under debate [4,5].

So far a variety of binary Pt–Ru electrodes has been investigated: PtRu alloys [4,6–9], Ru deposited onto polycrystalline Pt [10,11], Ru–Pt codeposits [12,13], as well as Pt–Ru catalysts supported on carbon [14,15]. Apart from an electronic effect of Ru on the bond strengths of adsorbates on Pt surfaces [16–19], a bifunctional mechanism

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was proposed whereafter the high affinity of Ru to oxygenated species at low potentials facilitates oxidation of CO while this species is adsorbed on neighboring Pt sites [1,4,20]. This mechanism also served to rationalize the observed optimum 50:50 alloy composition [4,16,21].

Although the Pt-modified Ru(0001) electrodes [22,23] and a reverse system, namely Pt deposited onto a Ru single crystal surface, have been studied before with respect to the voltammetric feature and structure by STM [17,22] and with regards of CO adsorption and oxidation in UHV by thermal desorption spectroscopy [17], there exists to our knowledge so far no report about the electrocatalytic properties of a series of measurements varying Pt coverage on Ru(0001). We therefore prepared various Pt overlayers on Ru(0001) by electrodeposition and characterized their structures by reflection high-energy electron diffraction (RHEED) and scanning electron microscopy (SEM). At low Pt surface coverage the deposit grows as a 2D pseudomorphic adlayer, while with higher Pt coverages 3D clusters develop with their (111) basal plane preferentially parallel to the hexagonal Ru(0001) substrate whereby the bulk Pt lattice constant remains unaltered (no Pt–Ru alloy formation occurs) [23]. In this paper we have studied the influence of Pt surface coverage and surface structures on the oxidation of saturated CO on the Pt-modified Ru(0001) electrodes in comparison with the bare Pt(111) and Ru(0001) electrode surfaces. The onset of CO oxidation and the peak potential at the Pt-modified Ru(0001) electrodes are at much lower potentials compared to the bare Pt(111) and Ru(0001) surfaces, showing that the catalytic enhancement is dependent on the coverage of Pt deposit as well as the structure of Pt deposit. To get insight into the nature of the CO diffusion and the binding states, the CO_{ad} was sequentially removed by potential steps.

2. Experimental

The experiments were performed with an apparatus consisting of an UHV chamber (base pressure $<1.5 \times 10^{-10}$ mbar), containing facilities for

low energy electron diffraction (LEED), RHEED, and Auger electron spectroscopy (AES) techniques, and an electrochemical chamber (base pressure $<1 \times 10^{-9}$ mbar) housing the electrochemical cell. Both parts were connected through a closed UHV sample transfer system. RHEED was performed with an incident electron beam (40 keV) at a grazing angle of $1\text{--}2^\circ$ to the surface. This electron beam also acts as the excitation source for AES so that the information from both techniques originates from the same surface region, correlating structure and chemical composition.

The working electrodes, Ru(0001) and Pt(111) single crystal discs of ≈ 7 mm diameter with 2 mm thickness, were mounted between tungsten wires which also served for resistive heating of the sample. Smooth electrode surfaces were prepared by cycles of argon ion bombardment (5×10^{-5} mbar) at room temperature and annealing at 700°C until the sample surface was free from disorder and impurities as controlled by LEED/RHEED and AES, while rough electrode surfaces were sputtered by argon ion at room temperature without subsequent annealing. The clean electrode was then transferred to the electrochemical chamber under UHV conditions. After backfilling of the electrochemical chamber with 5 N Ar gas up to 1 atm pressure, the electrochemical cell was placed into the electrochemical chamber and contacted with the sample for the cyclic voltammetry measurements and Pt electrodeposition. To facilitate experiments on Pt electrodeposition, CO electroadsorption and electrooxidation, we have used two cells with flow-cell procedure, which allowed changing electrolyte solutions under potential control and in air-free atmosphere. The electrode surface after the electrochemical treatments and emersion was again characterized by LEED/RHEED and AES. The experimental details have been reported elsewhere [24,25]. All solutions were prepared with ultrapure water (Millipore Milli-Q water, $18 \text{ M}\Omega \cdot \text{cm}$). A platinum wire with 0.4 mm diameter was used as the counter electrode in the electrolyte vessel on top of a glass capillary [24]. All potentials are given versus the Ag/AgCl electrode in saturated KCl solution. Three electrodes system and a home-made potentiostat (ELAB,

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