

The Effect of Structurally well-defined Pt Modification on the Electrochemical and Electrocatalytic Properties of Ru(0001) Electrodes*

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Abstract

The effects of structurally well defined Pt modifications of Ru(0001) single crystal electrodes on their electrochemical behavior and their CO oxidation properties are identified and quantitatively related to the structural characteristics. Pure Ru(0001) and the bimetallic surfaces, including Ru(0001) surfaces covered by Pt monolayer islands, by a complete Pt monolayer or by monolayer PtRu surface alloys of varying composition, were prepared under ultrahigh vacuum (UHV) conditions and characterized quantitatively by high resolution scanning tunneling microscopy (STM). The electrochemical/-catalytic properties were determined under defined electrolyte flow conditions in an electrochemical flow cell attached to the UHV system. While on pure Ru(0001) the overlapping stability ranges of underpotential deposited hydrogen (H_{upd}) or CO_{ad} on the one hand and $\text{OH}_{\text{ad}}/\text{O}_{\text{ad}}$ on the other hand hinder the adsorption of the respective adsorbates, Pt promotes and catalyzes the potential dependent formation and removal of adlayers. Monolayer Pt islands and pure Pt or mixed $\text{Pt}_x\text{Ru}_{1-x}$ ($x = 1,2$) adsorption ensembles provide additional channels for the adsorption ($H_{\text{upd}} \leftrightarrow \text{OH}_{\text{ad}}$ exchange, $\text{CO}_{\text{ad}} \leftrightarrow \text{OH}_{\text{ad}}$ exchange) and reaction (CO oxidation) of the respective second adsorbate on the adsorbate covered Ru(0001) areas. Quantitative correlation between the surface atom distribution and the electrochemical characteristics shows that the uptake/desorption of H_{upd} is correlated with the abundance of threefold coordinated Ru sites, while on mixed $\text{Ru}_n\text{Pt}_{3-n}$ sites, H_{upd} and OH_{ad} adsorption is much weaker and shifted to lower and higher potentials, respectively. For both types of model surfaces, the availability of Pt sites leads to a substantially higher activity for the electrooxidation of CO as compared to bare Ru(0001), with significant differences between the behavior of surface alloys and Pt island modified Ru(0001). The different effects contributing to the modified adsorption/reaction behavior and the relative contributions are identified and discussed comparing with results obtained on Ru and PtRu electrodes reported previously and on bimetallic PtRu surfaces under UHV conditions.

Keywords: *Scanning Tunneling Microscopy, Local reactivity, Bimetallic electrode, Structure, Electrochemistry, Electrocatalysis*

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