Atomic scale insights on the electronic and geometric effects in the electro-oxidation of CO on Pt\textsubscript{x}Ru\textsubscript{1-x}/Ru(0001) surface alloys

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Abstract

The enhanced activity of various bimetallic catalysts / electrodes in electrocatalytic reactions is usually ascribed to a bifunctional mechanism. This seems to neglect other effects arising from electronic modifications and further geometric effects, which are known to strongly affect the interaction of these surfaces with adsorbed species. In this work we want to elucidate the role of electronic and geometric effects on the activity of structurally well-defined PtRu electrodes in the bulk CO oxidation reaction, using model electrodes prepared and structurally characterized on an atomic scale by scanning tunneling microscopy under ultrahigh vacuum (UHV) conditions. Samples include Pt\textsubscript{x}Ru\textsubscript{1-x}/Ru(0001) surface alloys with varying Pt content consisting of a Ru(0001) substrate and a Pt\textsubscript{x}Ru\textsubscript{1-x} alloy surface layer and a Ru(0001) electrode covered by a pseudomorphic Pt monolayer (x=1), as well as Pt(111) for comparison. Comparing the structural/chemical properties and the relative abundance of specific Pt\textsubscript{n}Ru\textsubscript{m} ensembles on the electrode surfaces with the respective bulk CO electro-oxidation activity enabled us to identify Pt\textsubscript{1}Ru\textsubscript{3} ensembles as the most active ensembles under the present conditions. The importance of electronic and geometric ensemble effects are discussed. The results demonstrate that the reactivity of bimetallic surfaces is much more complex than described by the classical bifunctional mechanism, which is proposed as a general feature.

Keywords: CO oxidation, Bimetallic electrodes, Bifunctional mechanism, Electronic effects, Geometric effects,

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