

Electrocatalysis on Bare and Pt Modified Ru(0001) and Ru(10-10)

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The interest for the electrochemical behavior of well-ordered Ru surfaces has been increasing in connection with the effort to improve Pt-Ru fuel cell electrocatalysts. In this work, surface oxidation, CO oxidation and spontaneous deposition of Pt and Pd on Ru(0001) and Ru(10-10) single crystal surfaces were investigated. The surfaces were prepared by sputtering, annealing and oxidation/reduction cycles in UHV, or by annealing in H₂. The crystals were transferred to electrochemical or spectroelectrochemical cells protected by CO. The measurements involved electrochemical, SXS, STM and SNIFTIRS techniques.

Voltammetry and x-ray specular reflectivity studies of the oxidation of Ru(0001) indicate that the RuOH species is formed at potentials above 0.4V in a one-electron exchange process. The spacing between the top two Ru layers is 2.13Å at 0.1V, which increases to 2.20Å when oxidized at 1.0V. No place exchange or multilayer oxide growth is observed during the Ru(0001) oxidation, as indicated by both electrochemical and x-ray specular reflectivity studies.

Voltammetry and infrared spectroscopy data for Ru(0001) show an unusual stability of CO on this surface. Linear and triply bonded CO molecules were identified from infrared spectra, which desorb at positive potentials without oxidizing to CO₂. This is consistent with a lack of pronounced oxidation of Ru(0001). Contrary to this behavior, the oxidation of CO on polycrystalline Ru and Ru(10-10) surfaces is facile. Fig. 1 displays the curves for Ru(0001) and Ru(10-10). A very pronounced structural effect for CO oxidation is observed. Linear and multibonded CO were detected on Ru(0001) at the frequencies 2030cm⁻¹ and 1790cm⁻¹, respectively. In the case of Ru(10-10), the frequency of a linear CO is 2055cm⁻¹, while the other observed band is at 1990cm⁻¹, which is very close to that of a linear CO. This band appears to be determined by Ru atoms in trough sites on the Ru(10-10) surface.

We have demonstrated that Pt can spontaneously form monolayer-to-multilayer deposits on Ru(0001). The morphology and coverage of Pt deposits depend on experimental conditions. Fig. 1 displays a representative STM image of a Pt deposit obtained by immersing a freshly prepared Ru single crystal in the 10mM H₂PtCl₆ in 0.1 M H₂SO₄ solution for one minute. Uniform, 1-2 monolayer thick Pt deposits can be obtained on Ru(0001) surface. The entire Ru surface is covered with 2-6 nm-sized clusters. The average height of the Pt clusters deposited on the Ru terraces is 2 ML, while the clusters that are deposited along the step edges are in general one monolayer higher (3 ML). There is an indication of a slight preferential deposition of Pt on step edges. The STM images show that about 92 % of the Ru surface is covered and the total amount of deposited Pt is approximately ~2 ML. The mechanism of this deposition is not clear. It is likely that the Ru surface oxide formation supplies the electrons for the reduction of Pt or Pd ions.

Spontaneous deposition of Pt established with Ru(0001) can be used to tailor an active, low Pt loading electrocatalyst with metallic Ru nanoparticles.

Ru nanoparticles with submonolayer Pt islands of monolayer-height may provide efficient catalysts since the remaining Ru surface acts as an oxygen supplier for the oxidative removal of CO. In contrast to the Pt-Ru alloy nanoparticle catalysts, where the Pt atoms inside nanoparticles do not take part in the reaction, this structure allows all the Pt atoms to be at the surface available for the catalytic reaction. At the same time, all the Pt atoms are in direct contact with Ru atoms, which facilitates a strong electronic interaction between Pt and Ru atoms and, hence, a strong reduction of the CO adsorption energy on Pt. Fast H₂ oxidation kinetics has to be preserved in order to achieve an active catalyst. The oxidation of CO and H₂ containing 1000ppm of CO has been investigated. Spontaneous deposition of Pt on Ru nanoparticles yields an electrocatalyst that, even for a very low Pt loading, has a higher activity for CO oxidation and a better CO tolerance than the commercial state-of-the-art electrocatalysts. with 20% of Pt:Ru 1:1 alloy.

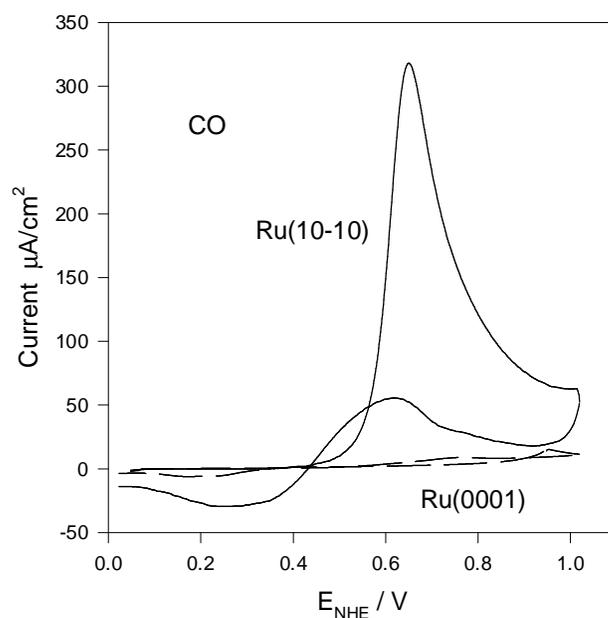


Fig. 1 CO oxidation on Ru(0001) and Ru(10-10) in 0.05M H₂SO₄; sweep rate 20mV/s.

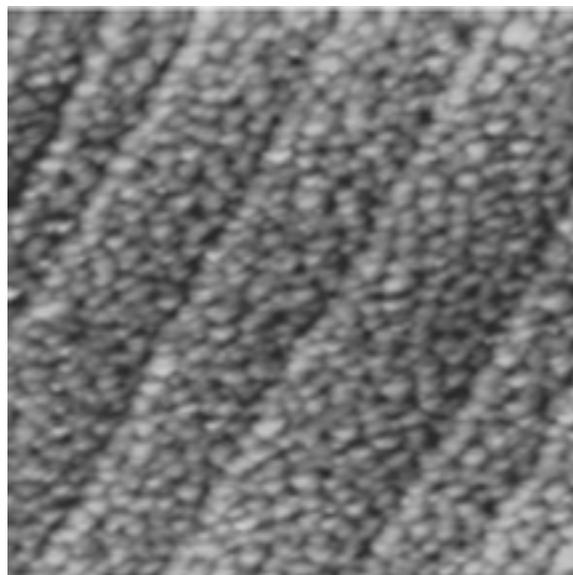


Fig.2 STM image (100 x 100 nm) of a Pt adlayer spontaneously deposited on Ru (0001) in 10 mM H₂PtCl₆ + 0.1 M H₂SO₄ solution. Image recorded at open circuit potential in 0.1 M H₂SO₄, Z range 2 nm.