Structure and Reactivity of Pt and Ru Catalysts for Fuel Cell Applications: from Single Crystals to Nanoparticles

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The structure, reactivity and surface catalytic processes of the well-defined Pt(111), Ru(0001) and various PtRu (e.g., Ru_ads/Pt(111), Pt_ads/Ru(0001), Ru_ads/pc-Pt, PtRu alloys and PtRu nanoparticles supported on TiO_2 and Ti meshes) electrodes towards the adsorption and electro-oxidation of small organic fuel molecules in various electrolyte solutions have been studied by combined ex-situ (emersion) electron diffraction (LEED/RHEED), STM, XPS and Auger spectroscopy and in-situ electrochemical FTIR spectroscopy, and the new insight into the surface electrocatalysis has been obtained at atomic and molecular level.

It has been shown that the electro-deposition of Ru on Pt(111) forms a monatomic commensurate layer at low coverage, while at higher coverage the epitaxial growth is changed to the Volmer-Weber growth mode, i.e., higher layers are populated before the first layer is completed. Because of electronic effects and structural properties (presence of Ru islands), the electrocatalytic activity of Ru modified Pt(111) surfaces toward CO oxidation is substantially higher than that of the pure metals and even slightly better than that of PtRu alloys. Both linear (CO_L) and bridged (CO_B) binding CO adsorbates were observed on Pt(111) domains, whilst only CO_L was observed on Ru domains. On the other hand, both linear (CO_L) and threefold-hollow (CO_H) binding CO adsorbates were observed on the Ru(0001) electrode at lower potentials where an (2x2)-O(H) layer was also present. The (2x2)-O(H) phase was found to be inactive towards CO ads (electro-)oxidation. The electro-oxidation of CO_ads took place via reaction with the active (1 x 1)-O(H) surface oxide/hydroxide phase formed at higher potentials.

On Ru_ads,pc-Pt, two CO_L were observed on Pt and Ru domains, respectively. On PtRu alloy and PtRu nanoparticles supported on TiO_2/Ti substrates, only single CO_L was observed. PtRu significantly promotes CO oxidation due to both the electronic effect and the bifunctional mechanism (Ru adsorbs the active oxygen species at lower potentials than Pt). The electrooxidation of CO takes place preferentially at the Ru islands, while CO adsorbed on Pt migrates to them.

Build upon these fundamental studies, optimum PtRu nanocatalysts (include size and shape control) have been prepared and tested in the direct methanol/ethanol fuel cells as well as in the half cells and the data will be present.

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