

**Development of Hybrid Mixed Zirconium-Tungsten Oxide Supports for Activation of Dispersed Pt and PtRu Nanoparticles towards Oxidation of Alcohols**

Iwona A. Rutkowska, Anna Wadas, Diana Marks, Karolina Klak, Sylwia Zoladek, Pawel J. Kulesza

*Department of Chemistry, University of Warsaw, Pasteura 1, PL-02-093 Warsaw, Poland*

Recently, there has been growing interest in development of the direct alcohol fuel cells as alternative technology to hydrogen based electrochemical energy systems. For example, ethanol can be ideally oxidized to carbon dioxide thus delivering twelve electrons. But realistically the reaction is rather slow at ambient conditions. Obviously, there is a need to develop novel electrocatalytic materials. Our interests also concern further improvement of activity of electrocatalytic materials for oxidation of formic acid.

Platinum has been recognized as the most active catalytic metal towards oxidation of ethanol at low and moderate temperatures. But Pt anodes are readily poisoned by the strongly adsorbed intermediates, namely by CO-type species, requiring fairly high overpotentials for their removal. To enhance activity of Pt catalysts towards methanol and ethanol oxidation, additional metals including ruthenium, tin, molybdenum, tungsten or rhodium are usually introduced as the alloying component. More recently it has been demonstrated that catalytic activity of platinum-based nanoparticles towards electrooxidation of ethanol has been significantly enhanced through interfacial modification with ultra-thin monolayer-type films of metal oxo species of molybdenum or tungsten. Also gold in combination with platinum has been demonstrated to produce novel high performance bimetallic catalysts.

We pursue a concept of utilization of hybrid mixed metal (zirconium/tungsten) oxide matrices (by admixing them with polyoxometallate-modified gold nanoparticles) for supporting and activating noble metal nanoparticles (e.g. Pt, Pt-Ru, Rh, Pd) during electrooxidation of methanol, ethanol and formic acid. Remarkable increases of electrocatalytic currents measured under voltammetric and chronoamperometric conditions have been observed. The most likely explanation takes into account improvement of overall conductivity (due to the presence of nanostructured gold) at the electrocatalytic interface (formed by metal oxide support), as well as and possibility of specific Pt-metal oxide or Pt-Au electronic interactions and existence of active hydroxyl groups

on transition metal oxo species in the vicinity of catalytic Pt sites. Further, the capping layers of Keggin-type phosphomolybdates, which are known to undergo fast stepwise multi-electron redox processes as well as to activate Pt-based electrocatalysts during methanol, ethanol or formic acid oxidation, may also contribute to the overall enhancement effect.