Mechanistic insights into the oxidation of organic fuels at Pt and Pd through support effect screening

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Support effects on the oxidation of organic fuels at Pt and Pd have been demonstrated, and pure support effects on the oxidation of methanol, ethanol, and formic acid (FA) isolated, through drop coating of preformed catalyst nanoparticles (NP) onto thin layers of a modifier (e.g. metal oxides and conducting polymers).[1-3]

In the development of the methodology, it was shown that a thin layer of Ru oxide spontaneously deposited on a glassy carbon electrode (GC) enhanced methanol oxidation at Pt through a bifunctional mechanism (i.e. Ru oxide acting as the agent for CO oxidation). Then we extended the approach to FA oxidation at Pd, coated on polyaniline (PANI)-modified and unmodified GC supports, where we reported clear promotional effects of PANI. Furthermore, we studied ethanol oxidation at Pt supported on Ru and Sn oxide-containing GC electrodes, where we observed that Ru oxide promoted the reaction through a bifunctional mechanism, in contrast to the prevailing electronic (ligand) effects for Sn oxide and mixed oxides containing Sn.

The present talk will be mainly focussed on investigating synergy between polycarbazole (PCZ) and Pt in FA oxidation. We have applied the above methodology to investigate the effect reported by Zhou et al. [4] in order to determine whether it originates from a synergy between PCZ and Pt, or is due to accelerated electron/ion transport. On this basis, we have found that while FA oxidation at Pt occurs mostly through the indirect pathway (i.e. dehydration; peak A2 in Fig. 1), a thin layer of PCZ on GC (designated as GC/PCZ) dramatically activates the direct oxidation (i.e. dehydrogenation; peak A1 in Fig. 1) while simultaneously enhancing the indirect oxidation. As well, a strong dependence of the prevailing mechanism on PCZ loading provides important mechanistic insights for FA oxidation at PCZ-Pt composites, also pointing to the complexity of the synergy.

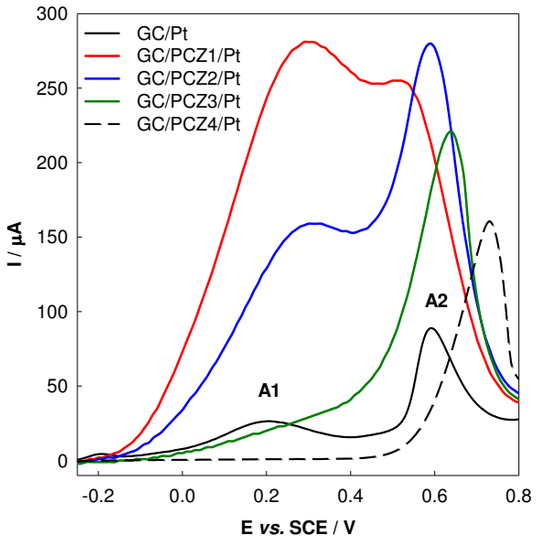

Fig.1. Linear sweep voltammograms in 0.1 M H_2SO_4 containing 0.5 M formic acid for GC and GC/PCZ electrodes drop coated with Pt NP. GC/PCZ1, GC/PCZ2, GC/PCZ3, and GC/PCZ4 were prepared using polymerization charges of 10.6, 14.1, 21.1, and 28.2 mC cm^{-2}, respectively.

References

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