

New Mechanistic Insights on Methanol Oxidation Reaction on Pt-based Electrocatalysts as Seen by *in situ* Spectroelectrochemistry

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In this summative presentation, I will discuss several illustrative cases in which the complementary and enabling nature of *in situ* surface-enhanced IR absorption spectroscopy (SEIRAS), surface-enhanced Raman spectroscopy (SERS), and electrochemical NMR (EC-NMR) will be showcased. These cases include, but are not limited to, (1) the chemical state of sulfur adsorbed on Pt surface [1] and the associate enhancement in MOR (methanol oxidation reaction) activity [2], (2) mechanistic investigation of the possible underlying causes for the observed activity enhancement by adsorbed poly(vinylpyrrolidone) [3,4], (3) comparative EC-NMR and SEIRAS studies of Ru@Pt vs Au@Pt [5,6], and (4) a revisit of the widely used but largely unjustified current ratio criterion, which was first proposed by Manoharan and Goodenough [7], for assessing the enhanced activity in MOR on Pt-based electrocatalysts [8]. We discuss briefly two cases below.

Fig.1a shows the cyclic voltammograms (CVs) for MOR on clean and S^{2-} -adsorbed carbon supported Pt NPs. The current density (j) was obtained by normalizing the reaction current by the clean surface areas before S^{2-} adsorption. Surprisingly, despite a decrease in the surface area unoccupied by S^{2-}_{ads} , the Pt NPs having a sulfide coverage of $\theta_{S,H} = 0.24$ and 0.52 still showed higher current density j values than that of the clean Pt NPs above the onset potential. Here $\theta_{S,H}$ was calculated by $1 - Q_{S,H}/Q_{clean,H}$ where $Q_{S,H}$ and $Q_{clean,H}$ were the hydrogen desorption charge with and without adsorbed S^{2-} , respectively. Quantitatively, this enhancement was illustrated by comparing the anodic current density $j_{@0.31V}$ at 0.31 V, a potential that is relevant to MeOH fuel cell application, as shown in Fig.1b (left y-axis). To further illustrate the intrinsic effect of S^{2-}_{ads} , an enhancement factor η defined as $\eta = j_s / [(1 - \theta_{S,H}) j_{Pt}]$, where j_{Pt} and j_s are the anodic current densities for clean and S^{2-}_{ads} -Pt NPs, respectively ($j_s = j_{Pt}$ when $\theta_{S,H} = 0$), was calculated from currents at 0.31 V in Fig.1a. In other words, η is the ratio of current densities normalized by the respective unblocked Pt surface area. As shown in Fig.1b (right y-axis), the η increased linearly as a function of $\theta_{S,H}$ in the η in logarithmic scale versus $\theta_{S,H}$ plot, clearly illustrating the intrinsic enhancement of MOR by S^{2-}_{ads} .

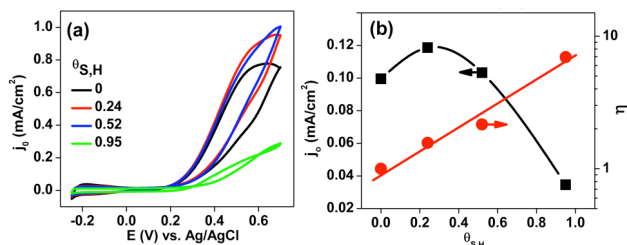


Fig. 1. (a) CV profiles for MOR and (b) the current density ($j_{@0.31V}$) and enhancement factor (η) vs S^{2-} coverage ($\theta_{S,H}$) measured at 0.31 V. Adapted from ref. [2] ©American Chemical Society.

We have carried out detailed electrochemical SEIRAS investigation of two different core-shell, Ru@Pt and Au@Pt/C, metal NPs. We were able to identify the most active sites and surface water species involved in the carbon monoxide oxidation reaction (COR) and MOR on

these NPs. We discovered that exposing the as-synthesized Ru@Pt NPs to air could turn them into largely surface-ruthenated NPs whose structure was rather stable under multiple potential cyclings between -0.2 and 0.7 V (vs Ag/AgCl, 3 M) and reduction at -0.3 V but could be annealed by the COR. The SEIRAS data enabled the identification of the Ru-coordinated-to-Ru, Ru-coordinated-to-Pt, and Pt-islands-on-Ru-core sites on the COR-annealed Ru@Pt NPs among which the most active sites were the Pt-islands-on-Ru-core sites for the COR and MOR, as evidenced by an onset potential as low as -0.1 V for the COR. Among the three different surface water species, namely the water monomer, the weakly hydrogen-bonded water, and the strongly hydrogen-bonded water, the SEIRAS data pointed to the weakly hydrogen-bonded water as the dominant source that provided oxygen for the COR and MOR. All are illustrated in Fig. 2.

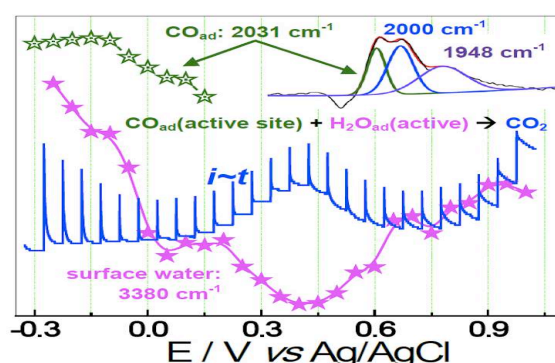


Fig.2. Pt islands on Ru (top) and weakly-hydrogen bound water (bottom) are identified as the most active surface sites and water species on Ru@Pt for methanol electro-oxidation. Adapted from ref. [5] ©American Chemical Society.

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