

Elucidation of CO Adsorption Sites on Pt-Ru Alloy Electrodes using *in situ* X-ray Absorption Spectroscopy

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It has been known for many years that Pt-M binary alloys (M = Ru, Sn or Mo) are better catalysts for CO oxidation than pure Pt. Nevertheless, the optimum alloy composition and the role of the alloy catalysts are still the subject of much debate. It is generally accepted that Ru leads to an increase in the oxidation rate through the bi-functional mechanism, which suggests that the OH adsorbs more easily at Ru sites. This OH then oxidizes the CO poison to CO₂ releasing CO from the surface.¹

In this work, the methanol oxidation and CO adsorption on well-characterized Pt-Ru supported nanoclusters on amorphous carbon is studied *in situ* using Pt L_{2,3} and Ru K level X-ray Absorption Spectroscopy (XAS utilizing both the XANES and EXAFS techniques). It has been recently shown that the XANES data may be exploited to determine not only the adsorbate coverages on platinum, but also the site specificity of these adsorbates.² A novel analysis technique is used to extract this information from XANES, combined with full multiple scattering theoretical results obtained from the FEFF 8.0 code.³ Comparison of experimental results with theory has been previously used to determine specific spectral signatures for H and O(H) in atop, bridged, and 3-fold sites, and even of anions such as bisulfate on a Pt surface.⁴

Here, spectral signatures for CO are determined from FEFF8 calculations and compared with experimental data. EXAFS data taken simultaneously provide information on the average cluster size, the homogeneity of the Pt nanoparticle (i.e. whether M distribution is homogenous, or concentrated in the interior of the cluster), and other morphology changes. XANES analysis of several commercially available Pt-Ru alloys in 1 M HClO₄ with and without 0.3 M CH₃OH are examined. Spectral $\Delta\mu$ signatures for CO, both the Pt L_{2,3} and Ru K edge XANES, were collected at room temperature in transmission mode on beamlines X11A and X23B at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory.

Figure 1 shows the difference in Pt L₃ XANES data, $\Delta\mu(x) = \mu(V) - \mu(\text{clean})$, for a Pt-Ru electrode obtained from ETEK at the Pt L_{2,3} edge, where V is the indicated electrochemical potential (RHE). This difference has been shown to isolate the effect of the adsorbates on the surface, and includes the direct Pt-adsorbate scattering and changes in the Pt-Pt scattering due to this adsorption.⁴ Prior to the subtraction, the respective μ 's must be carefully aligned using Pt foil reference spectra taken simultaneously. The relatively adsorbate free ("clean") spectra are taken at 0.58V for the scans without methanol, and at 0.40 V on the return scan for those in methanol (indicated by 40r in Fig. 1). These potentials were chosen as the cleanest available (relatively free of adsorbates), based on cyclic voltammetry scans on these same samples.

The $\Delta\mu(0.0 \text{ V})$ spectrum in methanol shows a broad

positive feature between -3 and 0 eV and between 5 and 15 eV. These features correlate well with theoretical predictions for CO in n-fold Pt sites (bridged and 3-fold). As the potential moves to 0.24 V, the -3 - 0 peak disappears and the 5-15 eV feature narrows dramatically, indicating the relaxation of CO from n-fold to atop sites, consistent with previous SNIFTER data on Pt after slight oxidation of CO.⁵ The real onset of CO stripping occurs at 0.40 V, as indicated by the significant decrease in this feature. By 0.56 V (i.e. nearly past the primary CO stripping peak seen in the CV curves) the CO peak is reduced further, but surprisingly the $\Delta\mu$ signature shows a more n-fold binding site again. Finally at 0.70 V, the appearance of significant amounts of O(H) appears in atop, bridged, and 3-fold sites as indicated by the label in Fig. 1.

Similar results are obtained for other Pt-Ru samples with different Pt and Ru morphologies and structure at the surface as indicated by the EXAFS analysis. These results show that the coverages of CO and O(H), and the potentials where these sharp coverage changes fall depend dramatically on the cluster structure and morphology. Although many studies of CO oxidation on Pt-Ru have been reported previously, these *in situ* spectroscopic results represent one of the first to reveal both CO and OH coverage and binding sites, along with cluster structure, and therefore provide unique insight into CO oxidation on Pt-Ru. Based on these results a mechanism for the CO oxidation will be suggested.

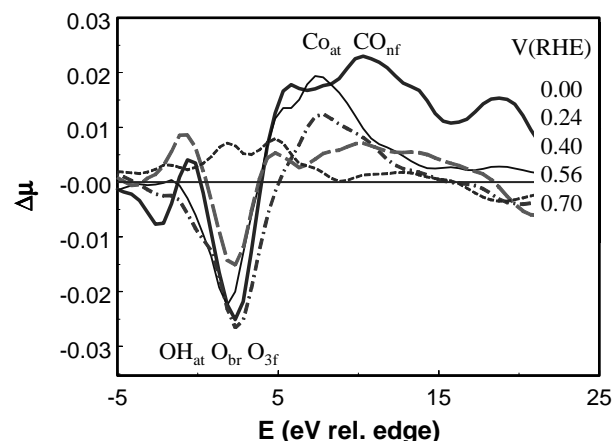


Figure 1: Comparison of the Pt L₃ XANES difference, $\Delta\mu = \mu(V) - \mu(40r)$, at the indicated potentials. Also indicated are features due to CO in atop(at) and nf (2 or 3 fold) sites, and O(H) in atop, bridged, and 3 fold sites at 0.70 V

References

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