Probing minority sites and their activity using chemical perturbations and Fast Fourier Transformed Ambient Pressure X-ray Photoelectron Spectroscopy

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The large majority of all surface sensitive in situ experiments of catalyst surfaces correlate the observed majority phase on the surface with observed activity without considering highly active minority phases, since such phases currently are difficult/impossible to detect. In this presentation we will present a new methodology that selectively probe phases that oscillate on the surface and link this to oscillations observed in the gas phase, while spectator species on the surface and in the gas phase are filtered away. In short, the new methodology is based on ambient pressure x-ray photoelectron spectroscopy combined with rapid gas composition – or temperature oscillations and fast Fourier transformation of the data, all of which we will discuss in detail.

As case studies we will focus on CO oxidation on two different catalyst surfaces: Pd(100) and Pt₂₅Rh₇₅(100). For the Pd(100) system we used the new methodology to study CO pulses injected every 5 second into a CO:O₂ carrier gas mixture combined with 70 Hz spectra acquisition. With this experimental setup we will demonstrate that we can establish parameters such that CO with varying coverage is present on the surface and correlate this to catalytic function. For illustration figure 1(a) shows an image plot of C 1s raw spectra recorded with 70 Hz, figure 1(b) shows the Fourier transformed spectra, while figure 1(c) finally shows the treated spectra with the new methodology. For the Pt₂₅Rh₇₅(100) system we used temperature oscillations instead of gas pulses to study the CO oxidation reaction. For this system we will demonstrate how the new methodology can be used to identify short-lived components in the Rh 3d and Pt 4f spectra assigned to the metallic clean surface and discuss how this relate to catalyst function.



Figure 1: (a) image plots of C 1s raw spectra recorded with 70 Hz for a Pd(100) surface exposed to CO pulses every 5 seconds injected into a CO:O₂ carrier gas at 533 K at mbar pressures. A single spectrum along the red dotted line is shown with dark blue color (b) Fourier transformed spectra from panel a. The arrow marks the oscillating signal (c) Final treated time-resolved spectra with the new methodology. A single spectrum along the red dotted line is shown with dark blue color.