Photoemission During Plasma Exposure (Plasma XPS) on the Example of Ru Model Catalyst Surfaces

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Identifying the underlying mechanisms of surface reactions, surface degradation, and stability in challenging environments are prime examples of research questions for X-ray photoelectron spectroscopy (XPS). Despite remarkable developments of *in situ* XPS towards high pressures and liquid environments, electron spectroscopies in other challenging environments such as plasmas remain elusive. The electromagnetic fields and high densities of charged particles are considered a particular challenge for reliable electron spectroscopy in plasmas.

Here, we demonstrate a pathway to probe the evolution of surfaces in plasmas using "Plasma XPS", photoemission from samples placed downstream of a low-density microwave plasma discharge. Measurements on thin metal films yield reproducible XPS spectra without artifacts in the tested pressure range up to 5×10^{-3} mbar and provide new insights into the interaction of model catalyst surfaces with simple plasmas, such as hydrogen and nitrogen. On the example of Ru, an excellent Haber-Bosch catalyst, we demonstrate chemical resolution during *in situ* exposures to hydrogen and nitrogen plasmas, as well as oxygen ions. While oxygen ions (400 eV) result in several nanometers of oxide growth at room temperature, we observe the removal of oxidic components and hydroxide formation in hydrogen plasma. In N-dominated plasma, N-containing species build up at the Ru surface but remain below monolayer coverage even at 5×10^{-3} mbar, indicating that significant amounts of Ru should remain available for catalytic reactions. Further experiments in hydrogen-rich environment will shed light on the active surface of Ru during plasma-catalytic interaction with hydrogen and nitrogen.

Our findings show that Plasma XPS can resolve the formation of new species at surfaces live during plasma exposure, demonstrating its promise for studies on plasma catalysis, materials in space applications, and surface degradation in plasma environment.