Probing Catalysis in Real Time; New Opportunities with Non-Linear X-ray Spectroscopy

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In heterogeneous catalysis, reactants adsorbed on surfaces are converted to products, which eventually desorb via various intermediates. The transition state separates reactants and intermediates from products and the free energy required to reach it determines the kinetics of an elementary chemical reaction. Many surface reaction intermediates are, however, transient species with a short residence time and the population of species in the transition state region is near-zero making their observation a challenge during steady state conditions. Ultrafast pump-probe techniques have, however, opened up opportunities by promoting a sufficient population of molecules in transient states to allow detection on short time scales.

Here recent results on probing chemical reactions on surfaces using X-ray free-electron lasers (Linac Coherent Light Source, or LCLS, at SLAC National Accelerator Laboratory) will be presented. We induced the hot electron and phonon mediated excitation of adsorbates on Ru(0001) with synchronized excitation by a femtosecond optical laser pulse. We have followed the ultrafast evolution of the bond weakening and breaking and bond formation using x-ray absorption spectroscopy (XAS) and x ray emission spectroscopy (XES) resonantly tuned to the oxygen core level with ultrashort x-ray pulses delivered from LCLS (1,2). This allows us to follow the time evolution of the molecular orbitals in an atom-specific way on a 100th femtosecond timescale. Four examples will be shown CO desorption, Oxygen activation, CO oxidation and CO hydrogenation on Ru(0001). We demonstrate that both transient intermediates and the transition state region can be detected in surface chemical reactions (1,2).

Future development of non-linear spectroscopies will be discussed in the context of this research program with an emphasis on improving detection efficiencies and accessing short time scales.

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