

Oxidation and Reduction Reactions on Transition Metals via ab-initio studies - M. Mavrikakis, J. Greeley, and Y. Xu (University of Wisconsin - Madison)

Attempts to correlate kinetics with thermochemistry of elementary reaction steps will be discussed.

Periodic self-consistent Density Functional Theory (DFT-GGA) calculations have emerged as a valuable partner to experiment in explaining reactivity of transition metal surfaces. These *first-principles* calculations provide detailed atomic level mechanistic information on individual elementary reaction steps, in terms of reaction thermochemistry, path, and activation energy barrier. State-of-the-art methods can yield the individual components of the reaction coordinate for a bond breaking/making event, and elucidate the role of the flexible surface in facilitating catalytic reactions. Theory meets experiment at various places including heat of adsorption, vibrational characteristics, and reaction barriers. Insights derived in connection with experimental results pertaining to two specific surface reactions will be discussed:

1. **Methanol decomposition**, a catalytic reaction relevant to low temperature *Direct Methanol Fuel Cells* (DMFC). One-dimensional potential energy surfaces are derived for CH₃OH decomposition on Pt(111) clearly identifying the RLS and revealing the detailed reaction mechanism via alternative competing paths.
2. **Dioxygen activation**, often the first elementary reaction step towards O₂ reduction at the cathode of various types of *fuel cells*. The adsorption of O and O₂, and the O₂ dissociation path on a variety of transition and noble metal surfaces have been studied. Comparing the detailed reaction paths and their energetics on different metals offer useful insights on the electronic and geometric factors controlling surface reactivity. Common trends and distinct differences characterizing different surfaces are highlighted.