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BEYOND STRUCTURE-PROPERTIES RELATIONSHIPS: TEMPORAL ANALYSIS OF PRODUCTS (TAP) AND CHEMICAL CALCULUS

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Catalytic properties of complex solids derive from nanoscale assemblies (active sites) of atoms and molecules working in-concert with the underlying bulk structure. Catalytic properties emerge during synthesis, activation, and reaction and are the result of a complex sequence of physical and chemical processes that are kinetically controlled. During a catalytic process, molecules interact with active sites to form products. Under reaction conditions diffusion and exchange of atoms, along with the exchange of energy, create a dynamic environment in which the composition and structure of the surface can change.

Catalyst development methodologies typically involve data-driven high-throughput testing of vast libraries of composition and surface science studies of model surfaces. This talk presents the concept of chemical calculus in which a researcher incrementally builds a new nanoscale chemical architecture and at every change in composition revises the direction of the experiment based on analysis of the evolution of kinetic properties. This approach addresses complexity by focusing on the evolution of kinetic properties to reveal connections between the physical features of the material and the multi-step reaction mechanism. A distinguishing feature of chemical calculus is a process called IKS (Incremental Kinetic Synthesis) that involves infinitesimal changes in surface composition, to understand the role of different components and processes in forming the nanostructures that control a complex reaction mechanism. Modified surfaces are fabricated on micron-sized particles using atoms, clusters and nanoparticles as component parts.

The modified particles are reactively characterized using TAP (Temporal Analysis of Products) pulse response experiments. Feedback from these experiments provides unique information, which describes the kinetic state of the sample. During TAP experiments the deposited components may react with probe molecules, may self-assemble into unique nanostructures or undergo phase transitions that induce changes in the kinetic dependencies that are uniquely observable with TAP. With the addition of more metal atoms the surface composition further evolves and this change will propagate through the reaction mechanism and be reflected in the kinetics. Each iterative cycle provides new insight into the nature of

the active material and the underlying kinetic processes as they diminish/accelerate with the changing surface.

A new advanced Temporal Analysis of Products (TAP) – Atomic Level Synthesis (ALS) System is described that allows one to perform incremental surface modification and precise kinetic characterization. This new system builds on the TAP-2 and TAP-3 reactor systems developed by Gleaves and co-workers [1-4]. The purpose of the proposed instrumentation is to provide a well-defined procedure for altering the nanoscale composition and structure of complex particles and model surfaces, and a well-defined procedure for determining the intrinsic kinetic or catalytic properties that result from those alterations. Using this system mixed metal and metal-metal oxide films can be deposited on a variety of different substrates, and a continuous range of metal dispersions from discreet atoms to nanoparticles, to multilayer metal films and deposits composed of several different metals can be produced. Exposing a substrate to a beam of metal atoms and low background pressure of oxygen mixed metal-metal oxide deposits can be created. Altering the metal atom deposition rate, the oxygen feed (using continuous or intermittent input), or other reaction factors can control the metal-oxygen ratio and the nature and amount of the deposit. Deposits ranging from nonstoichiometric metal oxide islands to full metal oxide films can be produced in this fashion.

Intrinsic catalytic properties including kinetic parameters, the nature of reaction intermediates, and the reaction mechanism can be monitored immediately after depositing submonolayer quantities of material. As a result it is possible to follow the kinetic evolution of a catalytic surface starting with the conditions of a surface prior to deposition of catalytic material to the onset of catalytic properties to the final form of a catalytic surface after multiple deposits and exposure to reactant mixtures. By monitoring kinetic properties as a catalytic surface evolves one gains insight into how different substrate materials, catalyst pretreatments, and reaction conditions influence the development of a catalytic surface.

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