Advancements in Measuring the Thermal Rates of Gas-Surface Reactions

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The accurate determination of gas-surface reaction kinetics requires the measurement of product formation as a function of reaction time, beginning from when reactant reaches the surface. Velocity-Resolved Kinetics (VRK) techniques[1] employ pulsed supersonic molecular beams to deliver time-resolved packets of reactants from the gas-phase to a catalytic surface. Desorbing product fluxes [e.g. $H_{2(g)} + O_{2(g)} \xrightarrow{Pd(111)/Pd(332)} H_2O_{(g)}$][2] are then ionized via a pulsed laser and detected in the form of velocity-sensitive ion images. Analysis of these isothermal time-resolved measurements allows for the determination of elementary rate constants and energetic barriers for desorption, dissociation, or diffusion; thereby providing benchmarks for theoretical predictions to compare against.[3-6]

Recently, a High-Repetition Rate (HRR-) form of VRK has been achieved using a point focused 100 kHz laser system to produce ions from desorbing fluxes via non-resonant multiphoton ionization; an ionization source that begins to approach a universal detection scheme. Resultant ion images are then generated by a gated microchannel plate + phosphor screen detector and recorded in a quasi-continuous manner by a novel event-based camera (ASI Hyperion TPX3CAM) as a collection of ion events with unique pixel-specific timestamps. The combination of high-repetition rate and event-based sensing yields a temporal evolution of multiple reaction products as a function of each individual molecular beam pulse with microsecond resolution. Conversely, conventional VRK measurements were collected by scanning the delay between molecular beam and laser pulses, necessitating steady-state conditions and rebound by the end of each pump-probe cycle. This renders conventional VRK blind to transient behavior on non-stationary catalysts and insensitive to reactions with timescales exceeding 100 milliseconds (i.e. reactions at low temperature); two limitations overcome by HRR-VRK. Notably, HRR-VRK has been successfully employed to monitor the evolving competition between hydrogen oxidation and recombination rates as a function of changing surface oxygen coverage, as well as the coverage-dependent desorption of nitric oxide on palladium. Further advancements include the direct detection of reaction intermediates using laser-induced desorption, improved mass resolution (relevant to isotope studies), and high-sensitivity universal detection using electron bombardment ionization.

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