ADSORPTION CALORIMETRY TECHNIQUES ON WELL-DEFINED SURFACES AND THEIR APPLICATION IN UNDERSTANDING CATALYSIS, PHOTOVOLTAICS AND ATOMIC-LAYER DEPOSITION

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David King and his group developed the first calorimeter that could measure heats of adsorption on the welldefined surfaces of single crystals with sufficient precision to reveal new understanding of surface chemistry, especially by determining the energies of adsorbed molecular fragments that are catalytic reaction intermediates and otherwise inaccessible experimentally. Since then, other groups including our own have adopted this technique and made substantial extensions, including: (1) heat detector replacement with a pyroelectric polymer ribbon that is pressed against the back of the sample, allowing routine measurements from 100 to 350 K with high precision (a standard deviation of 1.3 kJ/mol with gas pulses that contain only 1% of a monolayer), (2) adsorption energies on well-defined metal nanoparticles grown on single crystal oxides as a function of particle size, (3) metal adsorption and adhesion energies during thin film growth, (4) energetics of oxide-supported metal nanoparticles versus size which correlate with catalytic performance, (5) measurements of electrochemical adsorption and reactions at liquid/solid interfaces, and (6) transient measurements of heat-signal line-shapes during two-step reaction mechanisms (e.g., molecular adsorption followed by dissociation) that give the heats for both steps and the rate constant for the second step during every gas pulse. These extensions and their applications will be reviewed to assess the current state of adsorption calorimetry on single-crystal surfaces, and its future prospects. These energies of well-defined adsorbates provide crucial benchmarks for assessing the energy accuracy of quantum mechanical approximation like those in density functional theory (DFT). The same type of pyroelectric heat detector has also been extended to measurements of adsorption energies on thin films that have been deposited directly onto the detector's surface, affording a further 10-fold improvement in sensitivity but now limited to polycrystalline surfaces. Applications of this approach will be described which clarify: (1) metal/organic interfaces of importance in photovoltaics and LEDs, and (2) mechanistic and energetic details of thin-film growth by atomic layer deposition (ALD).

Work supported by NSF grant #CHE-1361939 and DOE-OBES grant #DE-FG02-96ER14630.