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Surface kinetics and energetics from single crystal adsorption calorimetry lineshape analysis: Methyl from methyl iodide on Pt(1 1 1)

Trent L. Silbaugh [a], Eric M. Karp [a], Charles T. Campbell [a,b,*]

[a] Department of Chemical Engineering, University of Washington, Box 351750, Seattle, WA 98195-1750, United States
[b] Department of Chemistry, University of Washington, Box 351700, Seattle, WA 98195-1700, United States

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ABSTRACT

The first use of single crystal adsorption calorimetry (SCAC) to probe the kinetics of surface chemical reactions is presented. It is applied to study a common situation encountered in catalytic mechanisms, wherein a gas quickly populates a molecularly adsorbed state that then converts to more stable products on a slower timescale (10–1000 ms). We show that for such a two-step process, detailed analysis of the heat-detector signal's time-response lineshape to a single pulse of gas provides the rate constant for the second step and the heats of reaction for both of the elementary reactions. We apply this analysis to the dissociative adsorption of methyl iodide (CH_3I) on Pt(1 1 1) at 270 K, to measure the heats of reaction for the elementary steps involved and the rate constant for the slow step, all as a detailed function of coverage. At low coverage, the reaction is $CH_3I_g \rightarrow CH_3I_{ad} \rightarrow CH_{3,ad} + I_{ad}$, followed at high coverage by $CH_{3,ad} \rightarrow CH_{ad} + 2H_{ad}$ and $CH_{3,ad} + H_{ad} \rightarrow CH_{4,g}$ (above 0.08 ML total $CH_{3,ad}$ plus I_{ad}). These results provide the rate constant for the dissociation of CH_3I_{ad} and the heats of formation of both $CH_{3,ad}$ and CH_{ad}. These two heats agree with values determined at 320 K where the rates are so fast that lineshape analysis is not needed, proving the validity of the lineshape analysis method introduced here for analyzing SCAC data.

1. Introduction

Measuring the kinetics of elementary steps occurring on solid surfaces is crucial for fundamental understanding in heterogeneous catalysis and many other technologies. Yet, few techniques allow one to measure the rate constants for processes where the product is adsorbed and the reaction's time constant is faster than 1 s. When the reactant begins as a gas, this can be done with sticking probability measurements by monitoring the depletion of the gas (for example, using the King and Wells method [1]). However, this fails when most of the gas reacts. In that case, one must monitor the appearance of some surface species using a surface analysis technique that measures surface concentrations faster than 1 s. There are few such techniques and the ones that exist tend to be very expensive, require very special situations to apply and/or use probe techniques that do surface damage during the measurements. Here, we show that analysis of the heat signal lineshape in single crystal adsorption calorimetry (SCAC) can provide the rate constant for the conversion of one surface species to another when that process has a characteristic time constant between 10 and 1000 ms. Specifically, we address here the very common situation that occurs in catalysis studies where a molecule adsorbs molecularly with almost unit sticking probability and then has a slower second step that leads to adsorbed product(s). For example, the initial molecular adsorbate dissociates to adsorbed fragments or reacts with another pre-adsorbed species to make an adsorbed adduct. We show that the rate constant for this slower second step can be determined from detailed fitting of the SCAC heat signal lineshape with a convolution of the instrument response function with a kinetic model for the deposition of heat by the two elementary reaction steps (one fast and one slow). This simultaneously provides the enthalpies for each of these two elementary steps, so that the information content is very rich, providing a powerful approach for analyzing fundamental aspects of surface reactions. Importantly, this can all be done on single crystal surfaces, so that the nature of the adsorbed species involved can be fully characterized using the array of surface analysis techniques that work so much better on single crystals, and which can be fully modeled using computational techniques that require periodic boundary conditions (as is used for most DFT studies of surface reactions).

Knowledge of the relative stabilities of chemical species adsorbed on surfaces is important to the advancement of the field of heterogeneous catalysis. Thus, a large body of work exists that use techniques such as temperature programmed desorption (TPD) or adsorption isotherms to extract heats of adsorption of well-defined adsorbates on single crystal surfaces. The limitation of these techniques is that they require the species of interest to

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* Corresponding author at: Department of Chemistry, University of Washington, Box 351700, Seattle, WA 98195-1700, United States.

E-mail address: campbell@chem.washington.edu (C.T. Campbell).

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be reversibly adsorbed. Because many catalytically interesting intermediates may exist in metastable states or undergo decomposition or reaction with coadsorbed species rather than desorbing, a direct measurement technique is required.

These limitations in existing surface science techniques have led to the development over the past several decades of a calorimetric technique [2–4] that now has sufficient sensitivity to measure the temperature change in single crystal samples that arise from the adsorption of molecular pulses containing only 1% monolayer with a detection limit of only 3 kJ/mol [5,6]. This technique, known as single crystal adsorption calorimetry (SCAC), was first developed in the group of David A. King at Cambridge University [7–9] and then further improved in our group [10–12] and others [13,14]. SCAC utilizes well-defined single crystal surfaces on which the chemical structures and bonding configurations of adsorbates can be determined using other surface science characterization techniques, thus allowing for measurements to be easily converted to heats of formation or bond energies of adsorbed species. These direct calorimetric measurements have led to the determination of the heat of formation of a wide range of catalytically relevant oxygenates (e.g., water [15] and hydroxyl [16,17], methanol and methoxy [18]), hydrocarbon fragments (e.g., CH [6], CH_3 [5], C_2H_2, C_2H_3, $CHCH_3$ and C_2H_4 [19,20], di-σ cyclohexene [21], benzene [22] and naphthalene [23]), and other small molecules (e.g., NO, CO, and atomic oxygen [2]) on metal single crystal surfaces.

In parallel with the development of experimental methods, theoretical methods such as DFT calculations have been implemented to determine bond strengths of catalytic intermediates and the activation barriers of elementary chemical reactions. This allows for the theoretical identification of complex reaction mechanisms using microkinetic modeling as well as the development of trends that link catalytic performance to bond strengths of key adsorbed intermediates. However, without experimental data, the accuracy of theoretically determined bond strengths is not known. A recent perspective by Klimes and Michaelides [24] highlights the efforts over the past decade to greatly improve the accuracy of calculations for molecular adsorption processes that involve a large dispersion component. The experimental determination of these values can therefore provide benchmarks for the continued improvement in the accuracy of theoretical calculations.

To date, SCAC studies have investigated systems in which heat deposition from molecular adsorption/reaction is extremely fast in comparison with the timescale of the heat measurement. Under these conditions, the heat detector's response signal from the molecular beam pulse exhibits a nearly identical intensity-normalized lineshape to that seen from the laser pulses used to calibrate the heat signal. In this case, any kinetic information for the process of interest is completely lost. However, the important potential for the determination of dynamical information from SCAC data was emphasized by King when he first started talking about his results from SCAC and can be inferred from the early discussion by Stuck et al. [25] of the change in detector signal lineshape that results from a change in the molecular or laser pulse duration. There are a few examples in the literature where SCAC lineshapes have already been used to obtain some qualitative kinetic information, including work by Lytken et al. where mass spectrometer measurements of the short-term and long-term sticking probabilities were introduced to allow a proper accounting for a contribution to the heat signal lineshape that arises from slower molecular desorption after the initial fast heat deposition from adsorption. This endothermic desorption process removes heat signal at long times and thus leads to an apparent narrowing of the peak width of the heat signal [21]. Similarly, Lew et al. observed a slight broadening of the peak width which they attributed to the time constant associated with adsorption kinetics into the final surface structure, for which the signal intensity was corrected to obtain accurate heats [15]. However, no attempt was made to use the detector response as a probe of the reaction kinetics.

Here, we show for the first time that it is possible to extend quantitative measurements of adsorption heats to cases where all or some portion of the heat is deposited on a timescale similar to the heat measurements (i.e., 10–1000 ms, compared to the molecular beam pulse width of 50–100 ms). Previous SCAC studies required that the intermediates of interest be produced on a timescale much faster than the measurement time (∼100 ms) *and* be stable on a timescale much longer than the measurement, thus greatly limiting the systems that could be studied. The analysis method presented here greatly expands the number of systems whose energetics can be studied using SCAC, including the *simultaneous* energy measurement of adsorbed intermediates that are only stable for 10–1000 ms, and products that do not appear until 10–1000 ms after the gas strikes the surface.

We also show how this analysis provides important kinetic rate constants for the studied systems, thus demonstrating for the first time the extraction of quantitative dynamical information from the heat pulse lineshape in SCAC. Specifically, we study the dissociative adsorption of methyl iodide on Pt(111) at 270 K by SCAC and determine from pulseshape analysis three kinetic/thermodynamic properties of the adsorbates involved: the rate constant for the dissociation of adsorbed methyl iodide into adsorbed methyl plus iodine on Pt(111) plus the heats of reaction for both the slow and the fast reactions. At low coverage, the mechanism is simple: $CH_3I_{ad} \rightarrow CH_{3,ad} + I_{ad}$, but this is followed by $CH_{3,ad} \rightarrow CH_{ad} + 2H_{ad}$ and $CH_{3,ad} + H_{ad} \rightarrow CH_{4,g}$ when the total coverage of $CH_{3,ad}$ plus I_{ad} exceeds 0.08 ML. The heat signal analysis provides the rate constant for the dissociation of CH_3I_{ad} and the heat of formation of both $CH_{3,ad}$ and CH_{ad}. These two heats agree with values determined by SCAC at 320 K where the rates are so fast that lineshape analysis is not needed [5,6]. This agreement proves the validity of the lineshape deconvolution method introduced here for analyzing SCAC pulseshapes when the pulseshape changes from that seen in heat calibration (i.e., where the heat is provided by laser pulses that deposit heat instantaneously).

2. Pulseshape and heat measurement for fast heat deposition

If the heat deposition from a molecular pulse is fast in comparison with the calorimetric measurement, the heat-detector signal's lineshape will match that seen from the laser pulses used in heat signal calibration. The laser pulses used for calibration must have the same temporal and spatial distribution on the sample as the molecular beam pulse. This is accomplished in our experiments by directing a laser into the beam path and allowing it to pass through the same series of apertures and mechanical chopper as the molecular beam [11]. If the response lineshapes match, the total heat from the molecular pulse can be determined from the ratio of the intensity of the heat signal upon adsorption to that from the laser pulse that deposits a known amount of heat. This heat signal intensity ratio has been measured using various methods (e.g., comparison of peak heights [7,10] or slopes on the rising side of the peaks [21]).

The detector response signal to an instantaneous pulse at time t' of a unit amount of heat onto the single crystal sample (i.e., a delta function input of a unit amount of heat) is by definition the instrument response function, $R(t - t')$. It has been shown [26] that the lineshape of $R(t - t')$ in SCAC using our type of heat detector (a pyroelectric polymer ribbon pressed against the back of the single crystal) is dictated by system parameters such as the time constants of heat transfer between the sample and detector ribbon and within the sample holder assembly, thermal conductivities,