Using Fractional Desorption Spectroscopy To Determine Kinetic Parameters for Surface Processes

Aleksander J. Franz,[†] Jeffrey T. Ranney,[‡] Warren B. Jackson,[§] and John L. Gland*,[∥]

Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan 48109, and Xerox Palo Alto Research Center, Palo Alto, California 94304

Received: February 24, 1999

Fractional desorption spectroscopy (FDS) is an interesting new approach for the determination of activation energies for a large range of surface processes. The activation energy can be determined over a wide coverage range using a single experiment. The FDS method utilizes a modulated temperature program during the desorption experiment by applying a modified Arrhenius analysis to extract kinetic parameters from desorption rate vs temperature data. FDS improves on other differential approaches in two important aspects. First, it enables determination of the activation energy over a range of accessible surface concentrations in a single adsorption/desorption experiment. This is particularly useful for studying surface reactions involving multiple species or in cases where complex surface preparations are required prior to the temperature-programmed desorption (TPD) experiment. Second, the FDS method possesses unique self-diagnostic and system-diagnostic abilities. The self-diagnostic aspect of the method enables a more systematic approach to eliminating errors from baseline drift. Like other differential approaches, the FDS method does not require assumptions about the reaction order, frequency factor, or the dependence of activation energy on surface concentrations. In this paper, the FDS method is shown effective in estimating concentration-dependent activation energies for first-order desorption, second-order desorption, and binary surface reaction processes, using straightforward desorption models. We experimentally validate the FDS method by applying the technique to determine the activation energy for CO desorption, O atom recombination and desorption, and CO_2 formation from adsorbed CO and O atoms, all on the Pt(111) surface. The FDS-determined activation energies for these systems are in excellent agreement with values established in the literature.

Introduction

The objective of many temperature-programmed desorption (TPD) studies is to determine the activation energy (E_a), order (n), and frequency factor (ν) for the process of interest. These parameters describe the temperature and concentration dependence of the reaction rate and enable comparison of low-pressure surface studies with high-pressure reaction processes. A number of approaches have been developed for the extraction of these parameters from experimental data. Several excellent reviews of these methods in surface science, and generalized for other thermally activated processes, are available.[1−6]

The TPD methods for extraction of kinetic parameters can generally be divided into two categories: the integral and the differential approaches.[7] The integral approach, primarily developed for TPD by Redhead,[8] solves the classic Polanyi−Wigner rate equation,

$$\frac{d\theta}{dt} \, \nu \exp\left(\frac{-E_a}{RT}\right)\theta^n \qquad (1)$$

assuming a constant reaction order. The activation energy and frequency factor can then be determined from TPD desorption peak properties, such as width, and peak temperature, assuming that the activation energy, reaction order, and frequency are independent of concentration and temperature. The integral approach has the advantage of utilizing a single desorption curve but requires knowledge or estimates of the reaction order. Furthermore, this approach can lead to large errors in the estimated parameters when the activation energy is varying with the surface concentration (except at very low coverages).[7]

The differential approaches derive the activation energy and frequency factor information from Arrhenius plots of the TPD data, using

$$\ln\left(\frac{d\theta}{dt}\right) = \frac{-E_a}{RT} + \ln(\nu\theta^n) \qquad (2)$$

The differential approach does not require assumptions about the reaction order and can accurately determine the concentration dependence of the activation energy. The concentration dependence of the activation energy is determined by generating Arrhenius plots at constant coverages (the isosteric approach), using multiple desorption spectra with varying heating rates and/or initial coverages.[9] Alternatively, the threshold approach can be used.[10] In the threshold approach, data from the leading edge of a desorption peak are used directly to generate an Arrhenius plot, assuming a constant surface concentration in the region of analysis. The differential approach requires fewer assumptions than the integral approach and potentially provides more information. However, differential methods are experimentally intensive, typically requiring variations of 1 order of magnitude

---

* To whom correspondence should be addressed.
[†] Current address: Department of Chemical Engineering, MIT, Cambridge, MA 02139.
[‡] Current address: Department of Chemistry, University of Washington, Seattle, WA 98195.
[§] Xerox Palo Alto Research Center.
[∥] University of Michigan.

in heating rate to achieve reasonable results. These variations are often difficult to accomplish experimentally, and at faster heating rates, temperature gradients in the sample may distort the results.[11] Finally, the integral approach can be affected by experimental variations for sequential TPD spectra in system parameters, such as sample position relative to the measurement device, reproducibility of heating rates, and instrumental drift. Several excellent reviews describe the methodology and theory of the various TPD methods, presenting relative advantages and disadvantages.[1−5]

On the basis of a fractional approach to TPD experiments, we have developed a novel method for determining kinetic parameters for surface reactions. The fractional desorption spectroscopy (FDS) method is capable of extracting activation energies of comparable accuracy to more experimentally intensive differential approaches *from a single* TPD-like experiment. No assumptions about the surface processes are required, and both concentration independent and concentration dependent activation energies can be determined reliably. The FDS method is further distinguished by its self-diagnostic and system-diagnostic capabilities.

During the FDS experiment, instead of employing a single linear heating ramp, the temperature of the sample is modulated using a triangular wave form. Like other differential approaches, and unlike the Engstrom and Weinberg thermal modulation method,[12] FDS relies on straightforward Arrhenius-like analysis of the data. Engstrom and Weinberg had previously used sinusoidal surface temperature variation to study reaction rate parameters, based on wave frequency variation and response phase and amplitude analysis.[11] The fractional approach has been successfully used previously to study other thermally activated processes, such as thermoluminescence[13] and thermally driven evolution.[14] In this paper, we develop the fractional approach for TPD studies. The FDS method is demonstrated theoretically and validated experimentally for three different, previously characterized processes on the Pt(111) surface. Although the FDS method is developed herein to study surface processes, it can be easily generalized to determine kinetic parameters for a variety of physical phenomena.

Fractional Desorption Spectroscopy

Experimental Procedure. The FDS utilizes temperature modulation of the sample during the desorption/reaction experiment. In contrast, classic TPD employs a single linear temperature ramp. Figure 1 shows temperature and evolution rate histories for a simulated FDS experiment. The temperature initially is ramped linearly to the specified cycle point, and then the sample is cooled linearly until the desorption rate can no longer be measured. The alternating heating and cooling cycles are repeated, with each heating ramp reaching a temperature higher than the previous heating ramp by a specified increment. The desorption rate is measured during both the heating and cooling ramps throughout the experiment. The resulting rate vs temperature plot is compared to a traditional TPD experiment in Figure 2. The inherent advantage of this experimental approach is the ability to determine the kinetic parameters for a surface rate process over the entire range of surface coverages, using a single experiment and sample preparation. The FDS method can, therefore, be particularly advantageous in experiments, where extensive sample preparation is required.

Data Analysis. The fractional desorption spectra can be analyzed using two different approaches, the threshold approach and a modified Arrhenius analysis, each described below. The classic threshold analysis can be applied to the low-rate area of
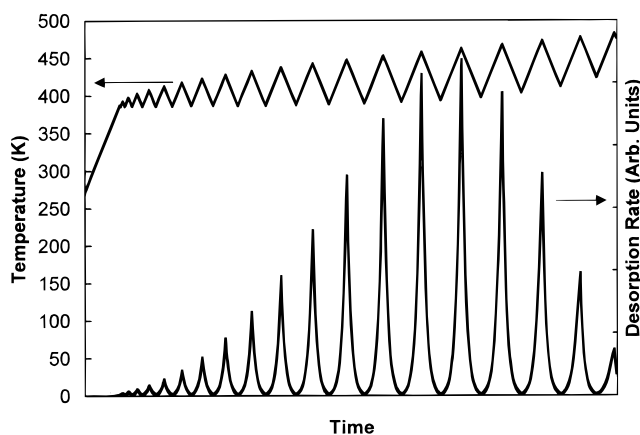

Figure 1. Temperature and desorption rate history during a model FDS experiment. The sample is heated to a higher temperature with each successive heating ramp and cooled until the desorption signal is too small to measure. The overall or average heating rate is much slower that the heating rate used during the individual heating/cooling cycles.
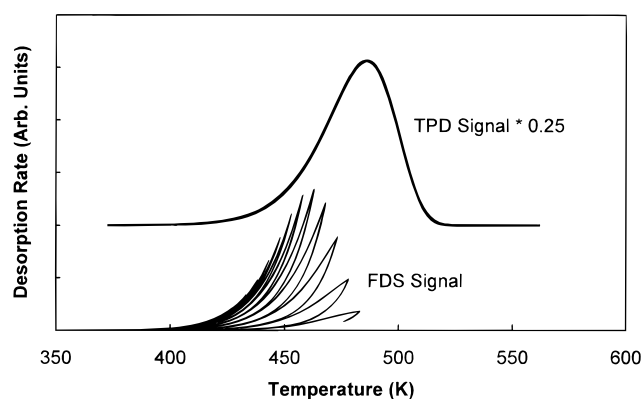

Figure 2. Comparison of TPR and FDS spectra for a first-order model system. The basic shape of the TPD spectrum is preserved during the FDS experiment. The desorption during an FDS experiment shifts to a lower temperature because of the lower average heating rate.

the spectrum, where the constant surface concentration assumption may be reasonable.[9] The threshold approach generates an Arrhenius plot directly from the initial rise of a TPD peak. The fractional approach improves on the traditional threshold analysis of a single TPD peak by providing additional information. The initial rise rate data for each heating ramp are complemented by the data from the preceding cooling ramp. In the region where the surface concentration is not changing significantly, the rates at the end of each cooling ramp and start of the subsequent heating ramp should be nearly identical (Figure 2). Therefore, in contrast to the classic threshold method, the region of accuracy for the threshold analysis is identified experimentally as the region of overlap in the cooling/heating ramp desorption data. In the classic threshold approach, TPD experiments at multiple exposures are required to analyze the coverage dependence of the activation energy. The fractional approach provides data for the threshold analysis at multiple surface coverages, using a single sample preparation experiment.

The threshold analysis is, however, extremely sensitive to the behavior of the baseline.[7] (All of the differential methods assume that the pumping rates are much higher than the desorption rates in the experimental system.) Accurate experiments require either the background pressures for masses of interest to be very low compared to the partial pressures during desorption or a very steady and well-behaved baseline. If the assumption of large pumping speed is not valid, the changing baseline can result in substantial errors in the estimated kinetic
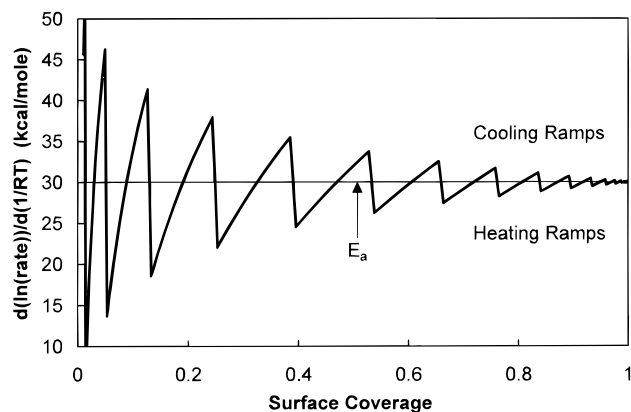
Kinetic Parameters for Surface Processes

J. Phys. Chem. B, Vol. 103, No. 21, 1999 **4459**

Figure 3. Slope of an Arrhenius plot of the FDS data. The changing surface concentration results in deviations from the desorption activation energy E_a. The deviations are large for higher desorption rates but oscillate around the true E_a because of the changing sign of the heating rate.

parameters.[7] Baseline drift in the classic TPD experiments is not easy to diagnose experimentally. As discussed later, the fractional approach allows for experimental diagnosis and correction of baseline drift.

Instead of relying on the threshold analysis (low rate data), we have developed an alternative approach to FDS data analysis. This alternative approach utilizes the rate data in the maximum rate region for each heating and cooling ramp set, greatly reducing the effect of noise and baseline drift on the estimated activation energy. We start by analyzing the behavior of the slope of the Arrhenius plot during a typical FDS experiment. By taking the natural logarithm of both sides of eq 1 for $n = 1$ and differentiating with respect to $1/RT$, we obtain an analytical expression for the slope of an Arrhenius plot

$$\frac{d \ln\left(\frac{d\theta}{dt}\right)}{d(1/RT)} = -E_a + \frac{1}{\theta}\frac{d\theta}{d(1/RT)} \tag{3}$$

The slope of the Arrhenius plot yields the desorption activation energy, modified by a term reflecting changing surface concentration. When the second term is small (low rates), it can be neglected, resulting in the threshold analysis method. The thermal oscillation of the surface during FDS results in interesting behavior of the second term in eq 3, which leads to the alternative analysis approach. During the desorption experiment, the surface concentration is always decreasing ($d\theta < 0$). However, the temperature is decreasing or increasing (d $(1/RT)$ > 0 or <0), and the second term on the right side of eq 3 changes sign, depending on the sign of the heating rate. As a result, the slope of the Arrhenius plot during the FDS experiment oscillates around the desorption activation energy, as shown in Figure 3. Averaging the Arrhenius slope over a single heating and cooling cycle,

$$\left\langle \frac{d \ln\left(\frac{d\theta}{dt}\right)}{d(1/RT)} \right\rangle_{T_o \to T_{max} \to T_o} \approx -E_a \tag{4}$$

should approximately cancel out the contribution from the second term in eq 3 and provide a good approximation of the activation energy. Although eq 4 was developed herein for a first-order desorption process, it can easily be derived more generally.
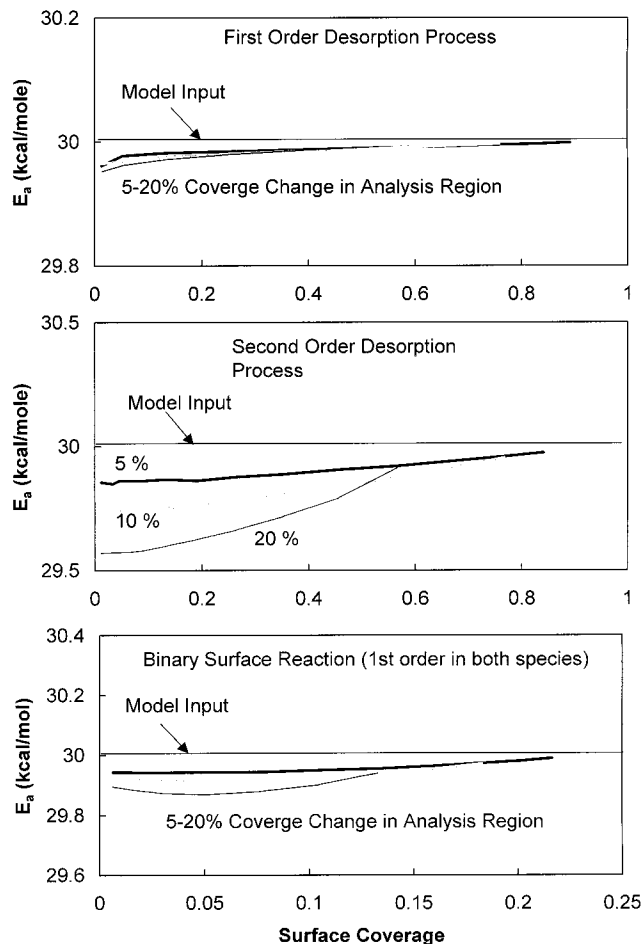

Figure 4. Estimated and input activation energies for model FDS experiments. The modified Arrhenius analysis results in very good estimates of the input activation energies for a first-order desorption process, second-order desorption process, and a surface reaction first order in both reactants. The accuracy of the estimates depends on the temperature range over which the analysis is carried out.

We tested the quality of the approximation in eq 4 by applying the modified Arrhenius analysis to simulated FDS spectra for several different desorption/reaction systems. Excellent estimates of the activation energy (within 2% or less of model input) were obtained over the entire range of surface coverages (Figure 4). A straightforward numerical model, with sample temperature history and surface kinetic parameters as inputs, was used to simulate the desorption rate during an FDS experiment. In Figure 4, we compare the activation energies estimated using eq 4 with model input for a first-order desorption process, a second-order desorption process, and a binary surface reaction. Estimated values agree very well with model inputs for all three processes.

The accuracy of the approximation in eq 4 is a function of the temperature range over which the averaging is carried out. The activation energies are estimated using different temperature ranges (varying T_o) around the peak temperature, with larger temperature ranges (lower T_o) corresponding to larger changes in surface coverage in the analyzed region. The changes in the surface coverage are reported as percent of the coverage at the peak temperature T_{max}, for which the activation energy is estimated. Figure 4 shows the estimated activation energies for coverage changes of 5, 10, and 20%. As expected, taking the average slope of the Arrhenius plot for larger changes in the surface coverage results in slightly larger estimate errors. However, even for large coverage changes of 20%, the estimated parameters agree very well with the model input. At higher
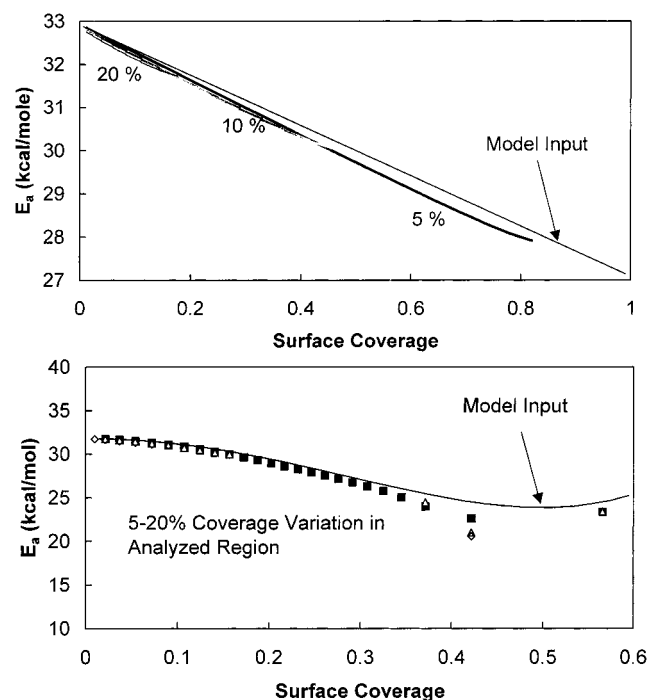
Figure 5. Estimated and input activation energies for model FDS experiments with coverage-dependent activation energies. The modified Arrhenius analysis yields good estimates of the behavior of the activation energy with changing surface coverage in a single experiment.

coverages in the beginning of an FDS experiment, less than 5% of surface species desorbs in each thermal cycle, and estimated activation energies match the model input almost exactly. The coverage change during a single heating/cooling cycle can be controlled during the experiment, as described in the discussion section below.

The FDS method is shown effective also in determining the dependence of desorption activation energy on surface coverage using the model. Figure 5 shows the application of the FDS analysis to two different cases, where the activation energy varied with surface coverage for a first-order desorption process. In Figure 5a, the activation energy varies linearly with the coverage. In Figure 5b:

$$E/R = 16000(1 - 2\theta^2 + 4\theta^4) \tag{5}$$

This relation has been used previously by Miller et al. to compare the effectiveness of integral and differential methods.[7] As with the constant activation energy cases, the FDS method using the modified Arrhenius approach yields very good estimates of the activation energy, for both the linear and more complex dependence of the activation energy on surface concentration. Miller et al. show that the integral approaches result in very large errors for coverage-dependent activation energies (except for very low coverages). Furthermore, the threshold method results in significant errors when applied over a region where 5% of the surface coverage is desorbing. In theory, only the isosteric differential approaches, which completely eliminate the coverage dependence using a large number of classic TPD experiments, and threshold experiments for very small changes in coverage (0.2%), result in good estimates of coverage-dependent activation energy. These approaches are time intensive and are susceptible to experimental errors associated with multiple TPD experiments, as discussed earlier. Figure 5 demonstrates that FDS and the modified Arrhenius approach can accurately determine the coverage dependence of

the activation energy from a single experiment. The FDS experiment is not susceptible to the errors associated with multiple TPD experiments in the isosteric and threshold approaches, and the modified Arrhenius approach greatly reduces the effect of baseline noise on the estimated activation energy, when compared to threshold methods. In the following sections, we demonstrate experimentally the validity and utility of the FDS method for several desorption and reaction systems on the Pt(111) surface.

Experimental Validation

Procedure. The experimental apparatus used in these experiments was a stainless steel UHV system described elsewhere.[15] The base pressure in the UHV (ultrahigh vacuum) system was typically in the low 10^{-10} Torr range after system bake-out. The Pt(111) sample was mounted to a liquid-nitrogen-cooled sample manipulator by tantalum support wires, which allowed for resistive heating of the sample and cooling to ca. 110 K. Standard sample cleaning procedures for Pt(111) were followed to generate a clean surface. Prior to each series of experiments, oxygen adsorption/desorption or oxygen cleaning at 650 K and annealing at 1000 K were typically sufficient to generate a clean surface.

Carbon monoxide (99.9999%) and oxygen (99.998%) were used as supplied by Matheson. Adsorbate exposures were accomplished using variable leak valves connected to stainless steel directional dosing arrays. The Pt(111) sample was positioned to within 2 cm of the direction doser outlets for all gas exposures. During thermal desorption, the sample was located within 0.5 cm of the quadrupole mass spectrometer (QMS) collimator, in a direct line of sight configuration. In this configuration, contributions from the heating wires and background pressure are minimized during the desorption experiments.

For standard TPD experiments, linear heating rates could be varied over a wide range (0.1−10 K/s) without difficulty. However, for FDS experiments, it is desirable to have the same heating and cooling rates. The cooling rates can be limiting because of slow conduction of heat away from the crystal through tantalum wires. We have limited the maximum heating rate in the FDS experiments to match the maximum controllable cooling rate. The maximum controllable cooling rate changes with the crystal temperature, requiring slower heating/cooling rates at lower temperatures. For temperatures near 180 K, the maximum controllable cooling rate for our experimental setup was 1.5 K/s, while at 800 K cooling rates in excess of 5 K/s were easily controlled. A temperature increment of 20−25 K between subsequent heating ramps was typically used, and the total time of the temperature cycling for a single FDS experiment was about 10 min.

Results. To demonstrate the utility of the FDS method, we have investigated several previously characterized systems. Herein, we present results for the desorption of carbon monoxide, recombinative desorption of oxygen atoms, and the reaction of CO and O(a) to CO_2, all on the Pt(111) surface. Good estimates of the activation energies exist in the literature for all three surface processes. The three processes span a wide range of mechanisms. CO desorption is generally agreed to be a first-order process, and O(a)/Pt(111) a second-order desorption process, allowing us to demonstrate the effectiveness of the FDS method for desorption processes, obeying different apparent reaction orders. We also demonstrate the FDS method for a surface reaction system. The formation of CO_2 by the reaction of coadsorbed CO and O(a) has been previously characterized
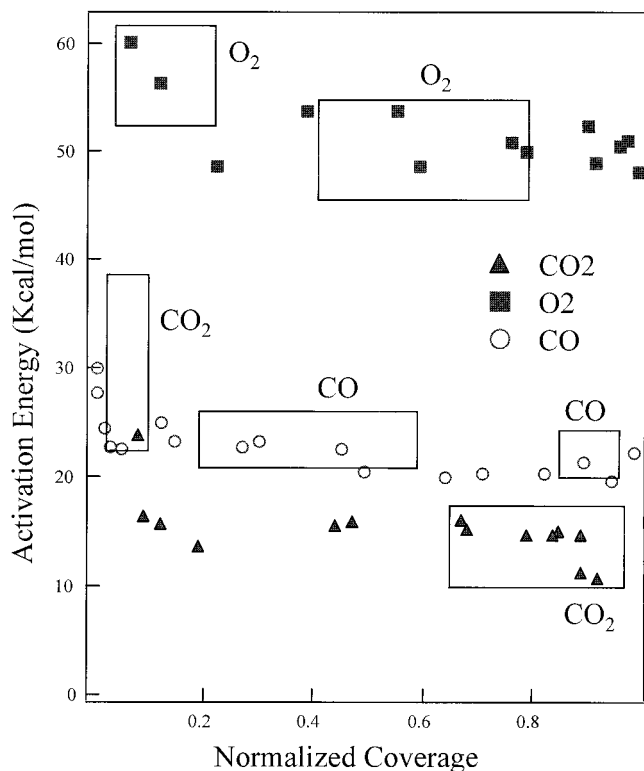
Kinetic Parameters for Surface Processes

J. Phys. Chem. B, Vol. 103, No. 21, 1999 **4461**

Figure 6. Estimated activation energies as a function of surface coverage for CO desorption, O atom recombination and desorption, and CO_2 desorption from the CO + O reactions, all from the Pt(111) surface. The estimated activation energies are in excellent agreement with published values for these systems. The ranges for published values are indicated with boxes. The surface coverages have been normalized to unity in each case.

on the Pt(111) surface, providing a good system for validation of the FDS method.

Plots of the activation energies derived from FDS experiments vs coverage for CO desorption, O_2 desorption, and CO_2 formation from CO and O(a) on Pt(111) are presented in Figure 6. The saturation coverages have been normalized to 1.0. The results are in excellent agreement with previously reported activation energy values for these systems. A brief discussion of the results and comparison to previously reported activation energies are presented below.

The adsorption/desorption of CO on Pt(111) has been previously characterized in detail using a combination of techniques.[16−20] Adsorbed CO initially occupies on top sites on the Pt(111) surface. As the CO coverage increases, bridge sites become populated and the surface saturates at a coverage of 0.68 monolayer (ML).[17] The reported desorption activation energy for CO from Pt(111) varies somewhat between reports. However, in general, activation energies at low coverage tend to approach 30 kcal/mol, with the activation energy decreasing to the 23−28 range at moderate coverages. At coverages higher than about 0.5 ML, activation energy in the 20−24 kcal/mol range is reported. Similar desorption activation energies are also observed for desorption from the (111) terraces of stepped Pt surfaces.[21]

In Figure 7 the fractional desorption results for CO/Pt(111) are presented. Figure 7a shows the desorption (QMS signal) of CO as a function of time and the temperature history of the sample corresponding to the desorption spectrum. Excellent control of the temperature was achieved, even around the discontinuity associated with the change in the sign of the heating rate. The good temperature control results in sharply
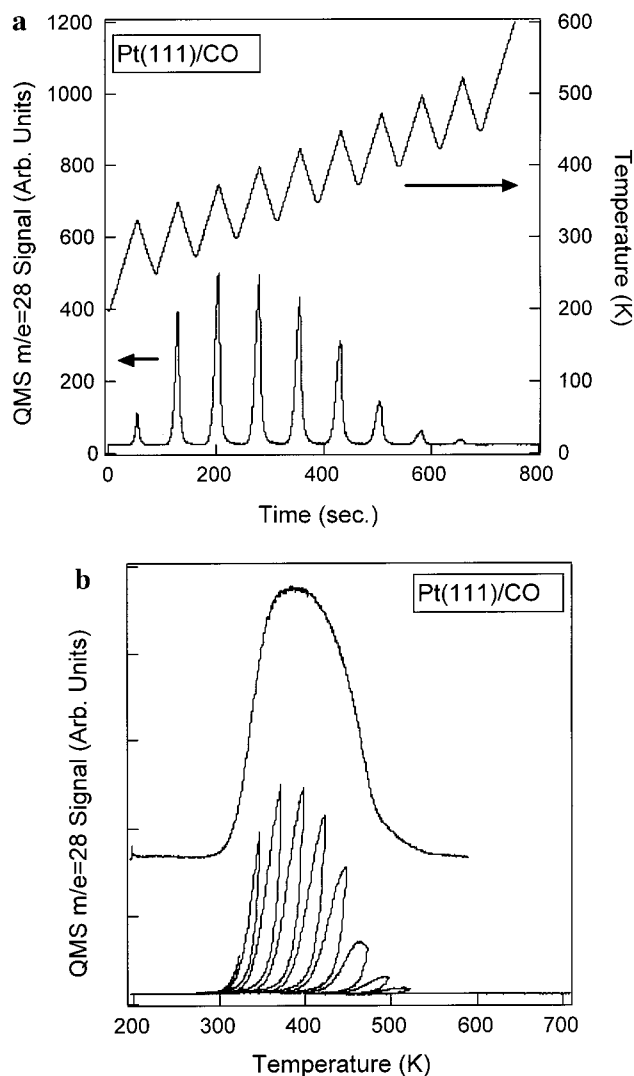

Figure 7. The FDS spectra for CO desorption from Pt(111). Initially, the surface was saturated with CO resulting in a 0.67 ML coverage. Part a shows the desorption CO and the sample temperature as a function of time. The desorption of CO corresponds to the maximum temperature for each heating/cooling cycle as shown. Part b shows the fraction desorption of CO as a function of surface temperature and compares FDS with a linear TPD spectra for CO/Pt(111) demonstrating that the peak shape for CO desorption is retained by the FDS data. The heating/cooling rate for FDS and the linear heating rate for the TPD spectra are 2.5 K/s.

defined desorption features. In Figure 7b, the desorption of CO is presented as a function of the sample temperature, along with a standard linear heating rate TPD spectrum for comparison. Clearly, the fractional desorption data retain the peak shape of the TPD spectrum, although for the same linear heating rate, the desorption peak is shifted to a lower temperature. The shift to a lower temperature during FDS is due to a lower average heating rate, which results in a lower peak desorption temperature. In Figure 8 a plot of the Arrhenius slope vs surface coverage is shown for the experimental data. As predicted by the desorption model in the Data Analysis section (Figure 3), the slope of the Arrhenius plot for an FDS experiment has an oscillatory behavior.

From the analysis of these data, using eq 4, we arrive at a high coverage activation energy of 21 kcal/mol. As the coverage decreases, the activation energy increases to 23−25 kcal/mol, increasing with decreasing coverage. Finally, near zero coverage, we find an activation energy of 27 kcal/mol. These results are
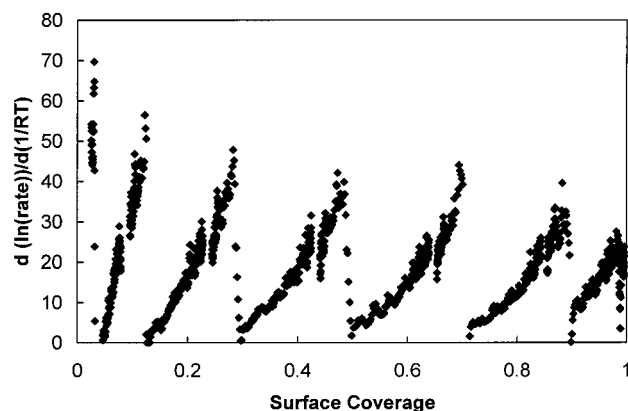
Figure 8. Arrhenius slope during the CO/Pt(111) FDS experiment. The experimental Arrhenius slope exhibits a behavior similar to the model predicted behavior in Figure 3.

in excellent agreement with previous studies, falling neatly within the range of activation energies reported for CO desorption from the Pt(111) surface.[16−19] In addition, assuming a first-order desorption process, we have used eq 2 and the modified Arrhenius analysis to estimate a frequency factor for CO desorption of $10^{12}-10^{13}$ s^{-1}. This frequency factor agrees very well with values predicted by kinetic theory, further validating this analysis. Consistent with previous studies of the CO/Pt(111) system, FDS yields a desorption activation energy that increases with decreasing coverage. The activation energy was derived for this nominally first-order process over the entire coverage range in a single experiment, and no assumptions were needed regarding the reaction order or frequency factor in determining the activation energy.

Oxygen desorption from Pt(111) was studied to confirm the FDS method for determination of the activation energy for a system generally accepted as second-order desorption. Previous studies of oxygen atom desorption from Pt(111) estimate the desorption activation energy at 60 kcal/mol for low coverage, with the E_a decreasing to about 40 kcal/mol at saturation coverage.[22−24] In Figure 9, we show the FDS and TPD spectra for the recombination and desorption of a saturated layer of adsorbed oxygen atoms on Pt(111). At coverages greater than about 75% of saturation, an activation energy for desorption of approximately 49 kcal/mol is estimated from the FDS data analysis. Below 20% of the saturation coverage, the E_a increases rapidly approaching 60 kcal/mol at very low oxygen coverage. These results are in excellent agreement with previous studies of the O−Pt(111) system, where the estimated E_a rapidly increased at coverages below 20% of saturation, approaching 60 kcal/mol at near zero coverage.[23] Just as for first-order CO desorption, the FDS method gives good agreement with previously estimated activation energies for the second-order recombinative desorption of oxygen atoms on the Pt(111) surface.

The FDS method can be particularly useful in studying surface reactions, where the additional degrees of freedom in concentration make isosteric approaches arduous. To demonstrate the ability of the FDS method to obtain activation energies for surface reactions, the formation of carbon dioxide on Pt-(111) was investigated. In Figure 10, the FDS and TPD of CO$_2$ from the reaction of CO with O(a) are shown. Again good qualitative agreement in peak shape is observed between the TPD spectra and the "overall shape" of the FDS data. Analysis of these data yields activation energies for the formation of CO$_2$ ranging from 14 to 23 kcal/mol, with the activation energy increasing with decreasing coverage. In addition, at very high coverages, the FDS method derived an initial activation energy
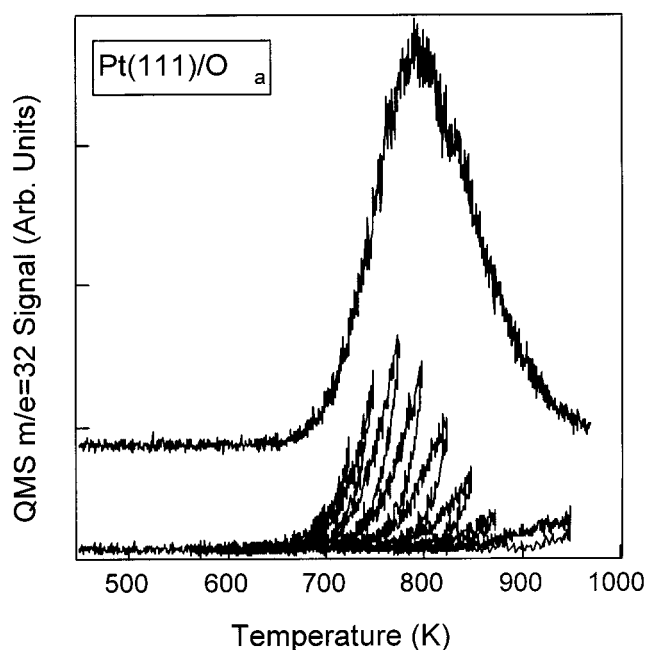

Figure 9. The FDS and TPD curves for the recombination and desorption of oxygen atoms adsorbed on the Pt(111) surface. These data were used to estimate the desorption activation energy presented in Figure 6 and in the text. The heating/cooling rate for these experiments was 5 K/s.
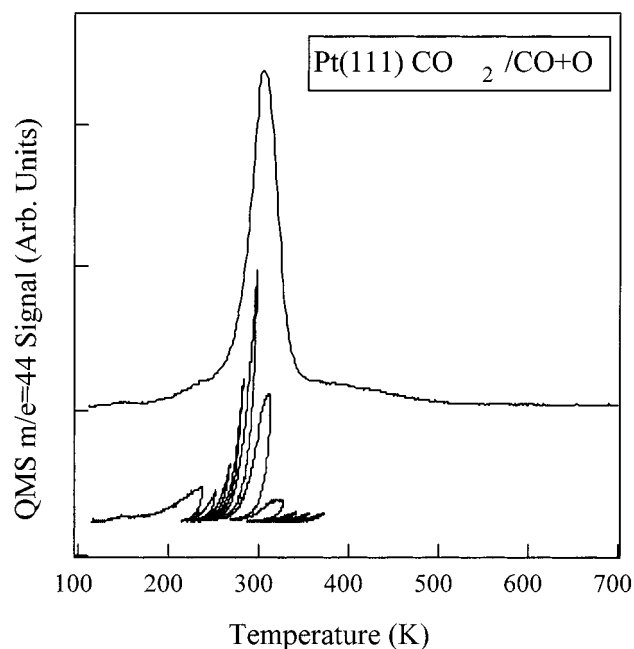

Figure 10. The FDS and TPD spectra for carbon dioxide desorption from the reaction of adsorbed CO and O(a) on the Pt(111) surface. The heating/cooling rate during FDS was 2 K/s and during TPD the heating rate was 2.5 K/s.

of 10.5 kcal/mol, which corresponds to the broad leading edge shoulder in the TPD.

The formation of CO$_2$ by the reaction of coadsorbed CO and O(a) on Pt(111) has been characterized in detail previously.[25−27] Numerous studies of CO oxidation on Pt(111) have unambiguously demonstrated that the reaction occurs via the reaction of chemisorbed CO with oxygen atoms. For the CO + O(a) reaction, typically reported activation energies range from 12 to 17 kcal/mol at high surface coverages to 24−40 kcal/mol at lower reactant coverages. TPRS (temperature-programmed reaction spectrometry) isostere studies give activation energies

Kinetic Parameters for Surface Processes

J. Phys. Chem. B, Vol. 103, No. 21, 1999 **4463**

from 17 to 40 kcal/mol, decreasing with increasing coverage.[25] Molecular beam studies yield slightly lower activation energies ranging from 12 to 24 kcal/mol, again with lower values at higher coverages.[27] The activation energies determined from the FDS data are within the range of literature values. The leading shoulder that results in the low activation energy we observed at high coverages is seen elsewhere for CO_2 formation;[25] however, the isostere method did not resolve the activation energy of this small shoulder. The low activation energy we find at high coverage may correspond to the lower E_a (12 kcal/ mol) derived from molecular beam studies. The formation of CO_2 studied by FDS demonstrates the utility of this novel method for investigating surface reactions. No conjecture on the order of the surface reaction is needed to derive the activation energy using this method. Additionally, this method was able to estimate the activation energy for the low-temperature shoulder on the TPD peak, which previously had not been resolved using the isosteric approach. The low-temperature CO_2 formation activation energy is in excellent agreement with the high coverage activation energy reported elsewhere.[27]

The experiments discussed herein validate the FDS method for three different kinetic processes on the Pt(111) surface. The utility of the FDS approach is illustrated by the method's ability to accurately determine the activation energy over a large coverage range in a single experiment. The advantages of this method are further discussed in the next section.

Discussion of the FDS Method

In a single adsorption/desorption experiment, the FDS method is able to estimate the activation energy for a variety of surface processes as a function of surface coverage, over the entire coverage range. As with other differential methods, no assumptions about the reaction order and the frequency factor are made in determining the activation energy. This is particularly useful when the reaction order for desorption is unknown and when the activation energy and order change as a function of coverage, as can often be the case. Using FDS to probe the surface reaction between CO and O(a), we are able to determine the activation energy for a surface reaction over a range of surface coverages in only one experiment. The isosteric methods give similar resolution of coverage dependence of the activation energy but are much more experimentally intensive, may require unattainably large variations in heating rate, and are susceptible to variations in the experimental system between sequential TPD experiments. The ability to determine activation energies for a desorption/reaction process as a function of coverage, independent of reaction order, in a single experiment is one of the major strengths of the FDS method.

The FDS method is flexible and can easily be adapted to different experimental needs and systems. The FDS experimental procedure described in this paper increases the maximum temperature of each heating ramp by a specified increment. This approach to FDS experiments results in variation of the peak desorption rate from cycle to cycle and an uneven distribution of estimated activation energies with respect to coverage (Figure 6). Higher data density is achieved at the beginning and end of each FDS experiment, since each heating and cooling cycle results in small coverage changes. In contrast, only a few activation energy data points are obtained at intermediate coverages because of higher desorption rates and corresponding larger coverage changes for each cycle. The FDS experimental protocol can easily be modified by either changing the size of the temperature increment between cycles or using the desorption rate to control the heating ramp increment. Alternatively,
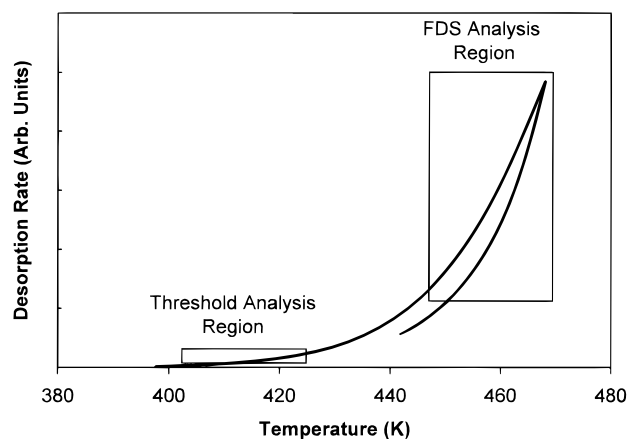

Figure 11. Comparison of analysis regions for the threshold and modified Arrhenius analysis. The low rates in the threshold analysis region result in higher sensitivity to baseline offsets and drift.

TABLE 1: Effect of Baseline Error on Activation Energies Estimated Using FDS and Threshold Analyses

		baseline		
analysis	model input	ideal	offset	drift
FDS	30 (kcal/mol)	30.0	29.7	30.0
threshold	30 (kcal/mol)	29.9	24.6	28.8

additional data points can be obtained by performing multiple FDS experiments with different maximum temperatures for the initial heating ramp. A tradeoff exists between the maximum number of data points achievable with a single experiment and the error associated with these data points. Increasing the number of cycles for a given experiment increases the data density, but it results in lower peak desorption rates, thus, decreasing the signal-to-noise ratio. In addition, too many cycles can result in prohibitively long experiments, where readsorption from background gases may affect the results. The maximum number of cycles is, therefore, limited by the system signal-to-noise ratio and experiment duration. Since the basic experimental setup for FDS is the same as for a TPD experiment, an FDS experiment can be easily optimized for an existing experimental TPD setup and chemical system of interest by simply modifying and optimizing the temperature program.

As shown in Figure 11, the modified Arrhenius approach used in the FDS method improves on threshold analysis by using the high desorption rate, as opposed to the low-rate data region. The FDS method, therefore, takes advantage of the better signal-to-noise ratio associated with higher rates. In addition to better signal-to-noise ratio, the FDS analysis is less sensitive to baseline offset and drift than other methods. This advantage is illustrated in Table 1 by comparing activation energies derived for the heating and cooling cycle, shown in Figure 11, using threshold and FDS analysis. Without any baseline offset or drift, both threshold and FDS analyses result in good agreement with the model input. A baseline offset of only 0.5% of the maximum rate in Figure 11 does not affect FDS analysis, but results in a large error (18%) in threshold analysis. Baseline drift, corresponding to a change of 2% of the maximum rate over the course of the heating and cooling cycle, has a similar effect on both types of analysis. The comparable effect is due to the threshold analysis taking place closer to the known baseline, where both the desorption rates and the net error because of drift are smaller. However, unlike the threshold approach, the FDS method can identify and compensate for baseline drift by extending the cooling ramp to locate the baseline. A much more precise estimate of the activation energy can, therefore, be
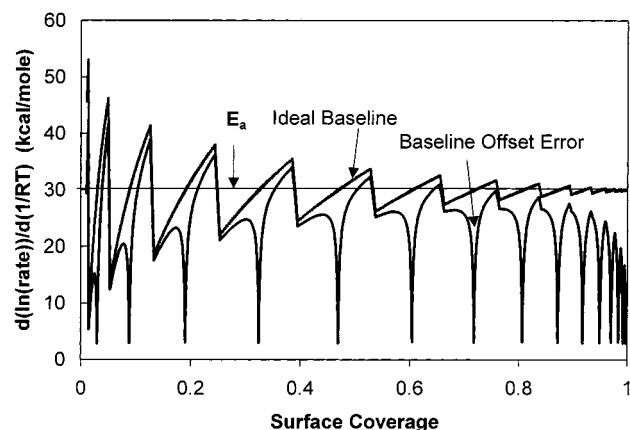
Figure 12. Effect of baseline offset on the behavior of the Arrhenius slope during an FDS experiment. The ideal baseline behavior from Figure 3 is shown for comparison. The drastically different behavior of the Arrhenius slope can be used to diagnose a baseline offset error and to fine tune the baseline for an FDS experiment.
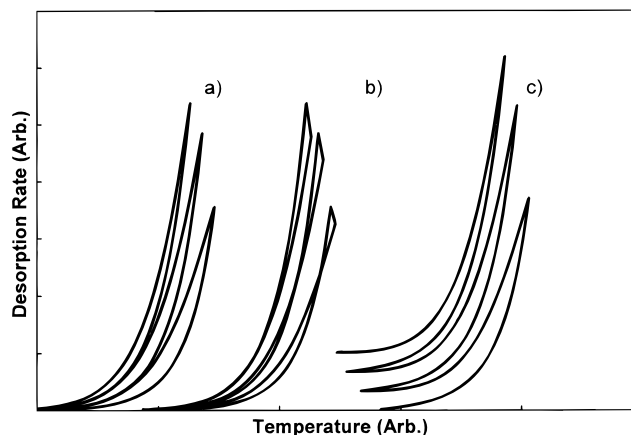

Figure 13. Unique diagnostic abilities of the FDS experimental method: (a) ideal behavior of an FDS spectrum; (b) loops form in an FDS spectrum because of time lags in the system; (c) baseline drift causes offsets between consecutive cooling and heating ramps in the low rate region.

obtained using the FDS method to compensate for the experimentally monitored baseline drift, as shown in Table 1.

The ability to compensate for baseline drift also distinguishes the FDS approach from other experimental methods. All of the differential approaches are sensitive to baseline drift. The FDS method provides more data on the behavior of the baseline during the experiment than classic TPD experiments, where baseline data are available only prior to and following main desorption features. More importantly, only the FDS approach can diagnose if the correct baseline has been subtracted from the measured rate. In Figure 12 we show the behavior of the slope of the Arrhenius plot for first-order model desorption with a baseline error. This behavior is radically different from the ideal behavior shown in Figure 3. Understandably, the deviation from ideal behavior is especially large for low evolution rates, with large spikes developing in the Arrhenius slope vs coverage plot. Therefore, the plot of the Arrhenius slope vs coverage in an FDS experiment can be used to estimate the optimal baseline for the desorption data.

The need for symmetry in the temperature program introduces a potential small source of error to FDS analysis that is not associated with other experimental approaches. Ideally, as mentioned in the Experimental Procedure section, the heating and cooling rates during an FDS experiment should be identical. Since the cooling rate is relatively slow in our experimental system, it limits the ramping speeds that can be used. We have theoretically investigated the effect of asymmetric heating programs on the quality of estimated activation energies. A 20% variation between the heating and cooling rate in a given cycle results in small errors for most coverages. At low coverages the effect becomes magnified, with errors of up to 10%. Therefore, as long as reasonable care is taken in controlling the heating and cooling ramps, the effect of temperature peak asymmetry on the activation energy estimates should be negligible.

Finally, the FDS method improves on other approaches by providing several self-diagnostic and system-diagnostic features. For example, the FDS method is capable of diagnosing lags and nonideal pumping speeds in the TPD system. In Figure 13a, we show the ideal behavior of the desorption rate with temperature modulation for a first-order process. If thermal lags are present in the system, then the rate vs temperature plot would develop loops, as shown in Figure 13b.[13] The "loops" in the desorption curve correspond to physical lags in the system

between the measured sample temperature and desorption rate. Nonideal pumping behavior in the system results in rate vs temperature behavior shown in Figure 13c. Ideally, because of low surface concentration changes at low desorption rates, the heating and cooling ramps should overlap. Because of slow pumping speeds and corresponding baseline drift, however, the desorption rate for the cooling ramp will be higher than that for the heating ramp. Although these types of system-related problems are common to all TPD methods, only the FDS approach facilitates rapid diagnosis of system difficulties and identification of possible important sources of error.

Conclusions

In this paper, the FDS approach to determination of activation energies for surface processes was developed. The FDS method utilizes a modulated temperature program during the desorption experiment and a modified Arrhenius analysis to extract kinetic parameters out of the desorption rate vs temperature data. The method was shown effective in estimating both concentration dependent and independent activation energies for first-order desorption, second-order desorption, and binary surface reaction processes using straightforward desorption models. The FDS method was then validated experimentally by comparing the derived activation energies for three mechanistically different processes on the Pt(111) surface with the literature values. Like other differential approaches, the FDS method does not require assumptions about the reaction order, frequency factor, and activation energy dependence on surface concentrations. This method improves on other differential approaches, however, in two important aspects. First, it enables determination of the activation energy over a range of accessible surface concentrations in a single adsorption/desorption experiment. The single experiment greatly reduces the experimental effort associated with isosteric approaches and eliminates a source of error because of system variations between sequential TPD experiments. This is particularly useful in cases where long detailed surface preparations are required prior to the TPD experiment and for studying surface reactions, where isosteric approaches are particularly cumbersome. Second, the FDS method possess unique self-diagnostic and system-diagnostic abilities. The self-diagnostic aspect of the method enables a more systematic approach to eliminating errors from baseline drift. The system-diagnostic properties alert the experimenter to important potential sources of error. Although the fractional approach and

Kinetic Parameters for Surface Processes

J. Phys. Chem. B, Vol. 103, No. 21, 1999 **4465**

data analysis methods were developed herein for surface processes, they can be easily extended to determine the kinetic parameters of other physical processes.

References and Notes

(1) King, D. A. *Surf. Sci.* **1975**, *47*, 384.

(2) Schmidt, L. D. *Catal. Rev.−Sci. Eng.* **1974**, *9*, 115.

(3) Yates, J. T. Jr. *Methods Exp. Phys.* **1985**, *22*, 425.

(4) Madix, R. J. In *Chemistry and Physics of Solid Surfaces*; Vanselow, R., Tong, S. Y., Eds.; CRC Press: Cleveland, 1947; Vol. II.

(5) Falconer, J. L.; Schwarz, J. A. *Catal. Rev.−Sci. Eng.* **1983**, *25* (2), 141−227.

(6) Chen, R.; Kirsh, Y. In *Analysis of Thermally Stimulated Processes*; Pergamon Press: New York, 1981.

(7) Miller, J. B.; Siddiqui, H. R.; Gates, S. M.; Russell, J. N., Jr.; Yates, J. T., Jr.; Tully, J. C.; Cardillo, M. J. *J. Chem. Phys.* **1987**, *87* (11), 6725.

(8) Redhead, P. A. *Vacuum* **1962**, *12*, 203.

(9) Falconer J. L.; Madix, R. J. *J. Catal.* **1977**, *48*, 262.

(10) Habenschaden, E.; Kuppers, J. *Surf. Sci.* **1984**, *138*, L147.

(11) Carter, R. N.; Anton, A. B. *J. Vac. Sci. Technol., A* **1992**, *10* (2), 344.

(12) Engstrom, J. R.; Weinberg, W. H. *Surf. Sci.* **1988**, *201* (1−2), 145.

(13) Gobrecht, H.; Hoffman, D. *J. Phys. Chem. Solids* **1966**, *27*, 509.

(14) Franz, A. J.; Jackson, W. B.; Gland, J. L. To be published.

(15) Ranney, J. T.; Gland, J. L. *Surf. Sci.* **1996**, *360*, 112.

(16) Vannice, M. A. In *Catalysis*, 3rd. edition; Anderson, J. R., Boudart, M., Eds.; Cpringer-Verlag: Berlin, 1982.

(17) Ertl, G.; Neumann, M.; Streit, K. M. *Surf. Sci.* **1977**, *64*, 393.

(18) Norton, P. R.; Goodale, J. W.; Selkirk, E. B. *Surf. Sci.* **1979**, *83*, 189.

(19) McCabe, R. W.; Schmidt, L. D. *Surf. Sci.* **1977**, *66*, 101.

(20) Hopster, H.; Ibach H. *Surf. Sci.* **1978**, *77*, 109.

(21) McClellan, R.; Gland, J. L.; McFeeley, F. R. *Surf. Sci.* **1981**, *112*, 63.

(22) Gland, J. L. *Surf. Sci.* **1980**, *93*, 487.

(23) Gland, J. L.; Sexton, B. A.; Fisher, G. B. *Surf. Sci.* **1980**, *95*, 587.

(24) Gland, J. L. *Proceedings of the Robert A. Welch Conferences on Chemical Research XXV*, 1981.

(25) Gland, J. L.; Kollin, E. B. *J. Chem. Phys.* **1983**, *78* (2), 15.

(26) Gland, J. L.; Kollin, E. B. *Surf. Sci.* **1985**, *151*, 260.

(27) Campbell, C. T.; Ertl, G.; Kuipers, H.; Segner, J. *J. Phys. Chem.* **1980**, *73* (11), 5862.