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Laboratories and Demonstrations

A Laboratory Study of Heterogeneous Catalysis in Ultrahigh Vacuum

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…the mechanistic pathway of a basic surface reaction can be determined… with hands-on experience in the techniques of ultrahigh vacuum.

A surface science experiment has been developed that can be used in both the undergraduate and graduate curriculum. Students study the mechanism of carbon monoxide oxidation using a platinum foil catalyst, and they also get hands-on experience with ultrahigh vacuum equipment. Using temperature programmed desorption, students study the desorption of carbon monoxide and oxygen from platinum foil in vacuum. The study allows students to determine that the Langmuir-Hinshelwood reaction mechanism operates in this catalytic system.

Introduction

The study of surfaces can be approached from many perspectives. On one hand, most interesting phenomena at solid

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surfaces occur in ambient atmosphere (e.g. corrosion), at elevated pressures (e.g. heterogeneous catalysis), or in liquid environments (e.g. electrocatalysis). On the other hand, clear insights into the atomic- and molecular-level events which give rise to these phenomena can often be achieved only by performing experiments under the rigorously well-defined conditions provided by ultrahigh vacuum (UHV, $P < 10^{-9}$ torr). This has spawned a vigorous field of academic research devoted to studies of surfaces in ultrahigh vacuum. Preparation of ultra-pure and ultra-perfect materials, as required for the modern microelectronics industry, also can require manufacturing processes to be carried out in the vacuum environment. Nonetheless, it is rare to find this important, modern-day aspect of surface science represented in undergraduate or graduate laboratory curricula.

In this paper, we describe a relatively simple experiment which is used regularly by undergraduates in our physical chemistry laboratory and by graduate students taking our surface chemistry course. It shows how the mechanistic pathway of a basic surface reaction can be determined, and it provides the students with hands-on experience in the techniques of ultrahigh vacuum. The reaction chosen for study is the surface-catalyzed oxidation of carbon monoxide, a reaction which has been the subject of much research, and for which the the mechanistic pathway was debated in the literature until the early 1980s [1].

Overview of the Experiment

The purpose of the experiment is to determine which mechanism operates in the catalytic oxidation of carbon monoxide over platinum foil. Briefly, the Langmuir-Hinshelwood (LH) mechanism [2] requires adsorption of both species involved in the reaction. The Eley-Rideal (ER) mechanism [2] involves adsorption of only one reactant with subsequent reaction by impingement of the other from the gas phase. The goal is to distinguish between these two mechanisms.

Four experiments are performed: (a) desorption of carbon monoxide in vacuum, (b) desorption of oxygen in vacuum, (c) desorption of CO in the presence of flowing O_2 gas, and (d) desorption of O_2 in the presence of flowing CO gas. The levels of gaseous CO, O_2,and CO_2 are monitored in each experiment using a mass spectrometer, while the sample is heated; this technique is termed Temperature Programmed Desorption (TPD) [3]. The first two experiments establish the two (very different) temperature regimes in

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which CO and O_2 desorb. The third experiment illustrates that oxygen must adsorb for reaction to occur, and the fourth that CO must do the same. Taken together, they allow the student to conclude that the LH mechanism operates. An alternative approach (but one which we have not explored) would be to give instructions on performing experiments (a) and (b), and let the students design experiments (c) and (d), or something analogous, for themselves.

In our program the experiment serves four educational objectives:

1. It lets students use modern surface science instrumentation.
2. It illustrates the interfacing between instrumentation and computers.
3. It gives students an appreciation for the relationship between the sample temperature and the strength of the adsorbate-surface bond.
4. It gives students an opportunity to examine experimental data critically and draw conclusions from their results.

In order to illustrate broader chemical principles, this exercise may be used in several ways. For instance, the kinetic theory of gases can emphasized by explaining—or by asking the students to explain—why vacuum is necessary to perform this type of work. Kinetics and catalysis can be emphasized by focusing on why the surface is necessary at all for reaction to occur. Instrumentation can be emphasized by discussing the principles of mass spectrometry.

This experiment has been used in our curriculum for eight years, and has been improved many times in that period. The version reported here works very well, and the student response is positive.

Equipment

The equipment required for this experiment is relatively sophisticated from the point of view of an undergraduate laboratory. In setting up the experiment initially, it is helpful to work with someone with experience in ultrahigh vacuum technology. The time period, from initial design to laboratory use, will be a few months under reasonable circumstances.

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The turbomolecular-pumped stainless steel vacuum chamber used is purchased and assembled piece-wise. It is shown schematically in Figures 1–3. The main elements are a turbomolecular pump assembly, a six-way cross (the heart of the chamber), and a small manifold for introducing gases into the chamber. The entire apparatus is supported by a metal framework. The chamber pressure can be reduced from atmosphere to about 10^{-2} torr using the mechanical pump behind the 110 L s^{-1} Balzer's turbomolecular pump, and the turbomolecular pump can be used to evacuate the system further, typically into the 10^{-8} torr range. A manual gate valve (Figure 1) is available for isolation of the turbomolecular pump from the chamber. This is useful, in principle, for venting the chamber while keeping the pump in operation, although the valve is seldom used in practice and could be eliminated. This figure also shows one of the glass gas bulbs (the other bulb is hidden in this view). The glass bulbs containing CO and O_2 are purchased from Matheson Gas Products. The bulbs are connected via glass-to-metal seals to variable leak valves purchased from Varian Vacuum Products.

Figure 2 is an enlarged drawing of the sample mount. The mount consists of a 2 3/4 in Conflat flange with two 1/4 in copper rods and two chromel-alumel thermocouple pairs electrically isolated from the flange. Only one thermocouple pair is shown in Figure 2. This mount was obtained from Insulator Seal, Inc., Hayward, CA. The 0.002 in by l in diameter platinum foil is spot welded to two 0.050 in tantallum wires, which are, in turn, held to the copper rods with 3/8 in copper clamps and 2-56 stainless steel set screws. The thermocouple pairs are spot welded to the back of the platinum foil. One is located near the top of the foil; the other is located near the bottom of the foil. Since two thermocouple pairs are available, students can determine whether a thermal gradient exists along the length of the sample. The sample temperature is raised by passing current through the sample. About 40 A is required to raise the sample temperature to 1000 °C. The sample is visible through the viewport.

The platinum foil is cleaned by heating to 1000 °C in 5×10^{-8} torr O_2 for several 1 hr periods [4, 5]. Reproducible results are obtained by holding the sample at 1000 °C in vacuum for 30 s between experiments.

The Dycor 100 quadrupole mass spectrometer and the ion gauge are shown in Figure 3. The mass spectrometer monitors the partial pressures of desorbing gases as the platinum sample is heated as described below. The ion gauge reads the total chamber pressure.

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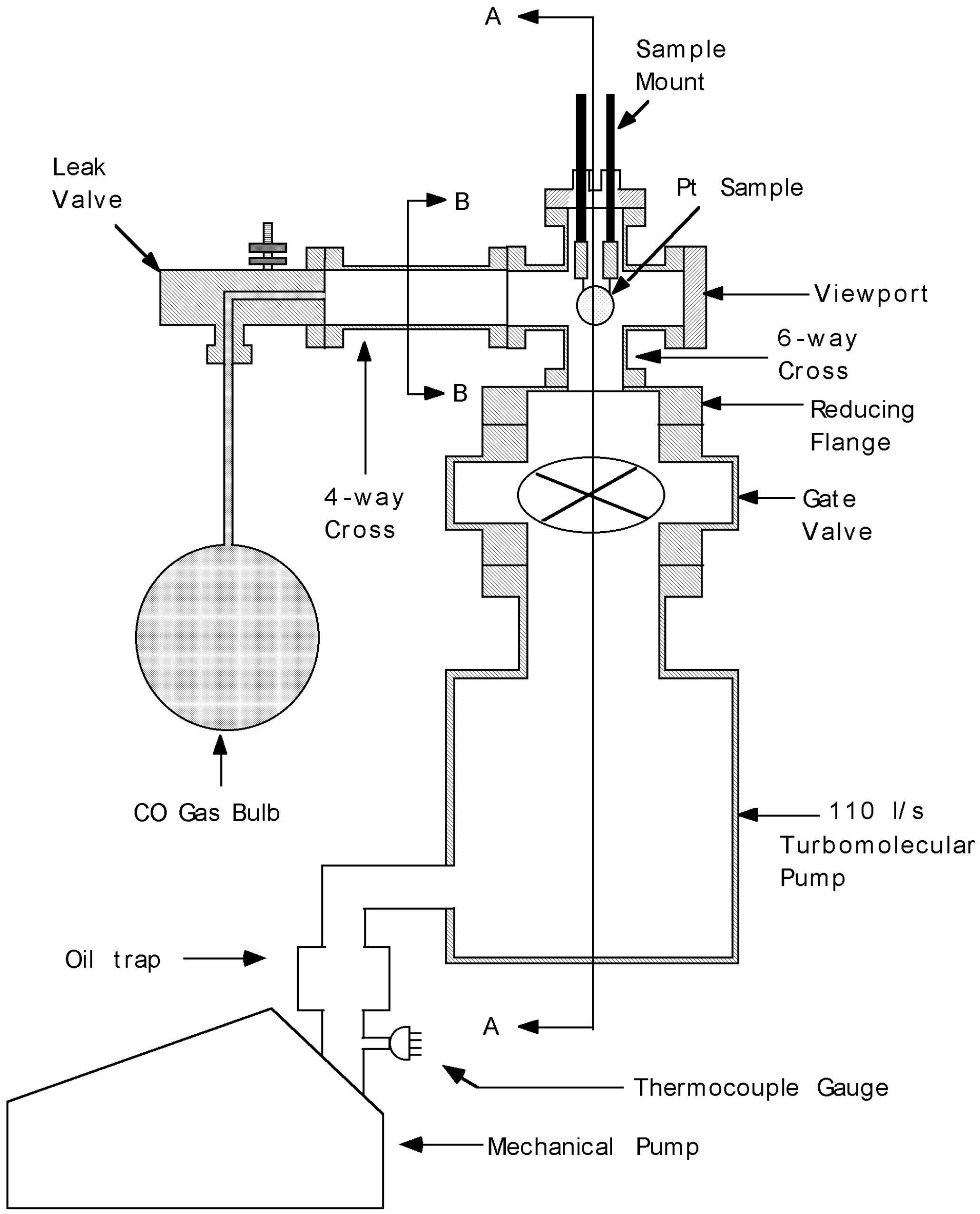

FIGURE1. A SCHEMATIC DRAWING OF THE EXPERIMENTAL VACUUM CHAMBER (FRONT VIEW).

The mass spectrometer must measure the partial pressures of several gases, effectively simultaneously, as a function of sample temperature. To do this, the spectrometer samples each gas briefly, then the next, and the next, in cyclical fashion. This is accomplished using a commercial package (which includes the Dycor 100 mass spectrometer, data acquisition card, and data system for the sample thermocouple)

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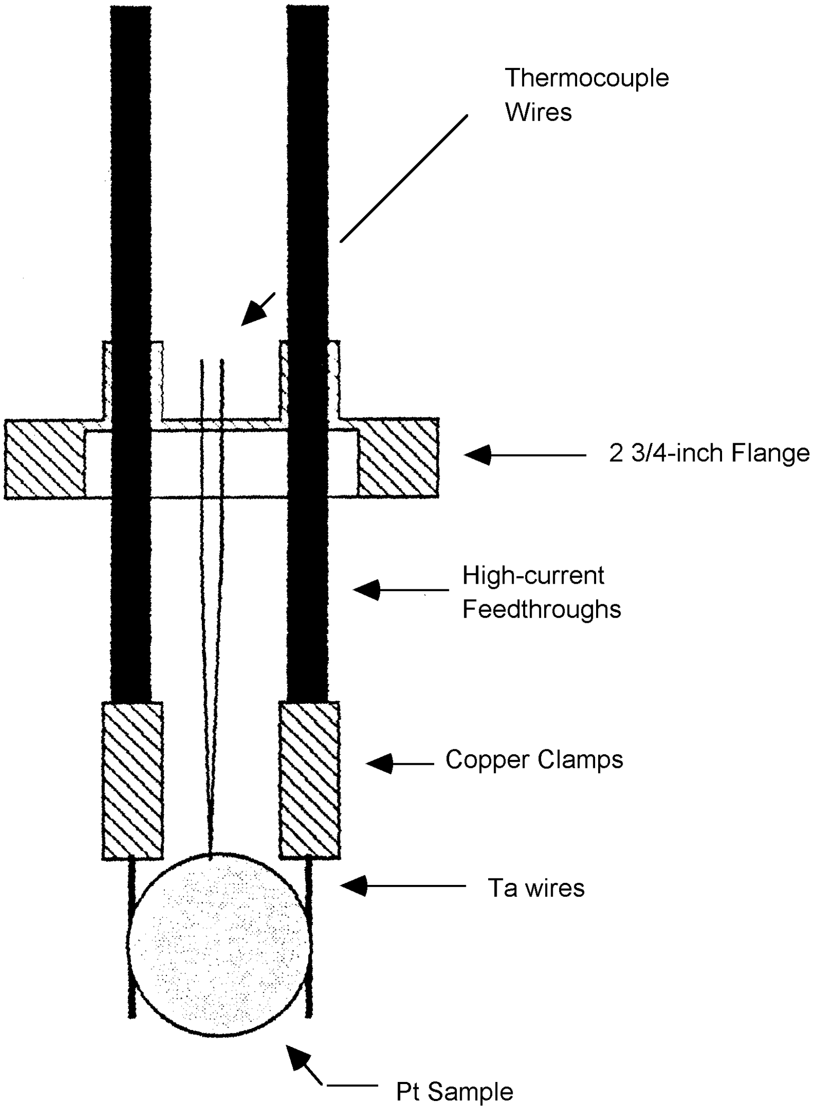

FIGURE 2. A SCHEMATIC DRAWING OF THE EXPERIMENTAL VACUUM CHAMBER (SAMPLE MOUNT).

marketed by Ametek. The system interfaces directly to a personal computer. The data are manipulated using Microsoft Excel, and are plotted on a commercial printer.

The chamber base pressure after a 48 hr bakeout at 180 °C is ca. 1×10^{-10} torr. During the course of an experiment the base pressure typically rises to 1×10^{-9} torr. The primary residual gases are H_2 and CO.

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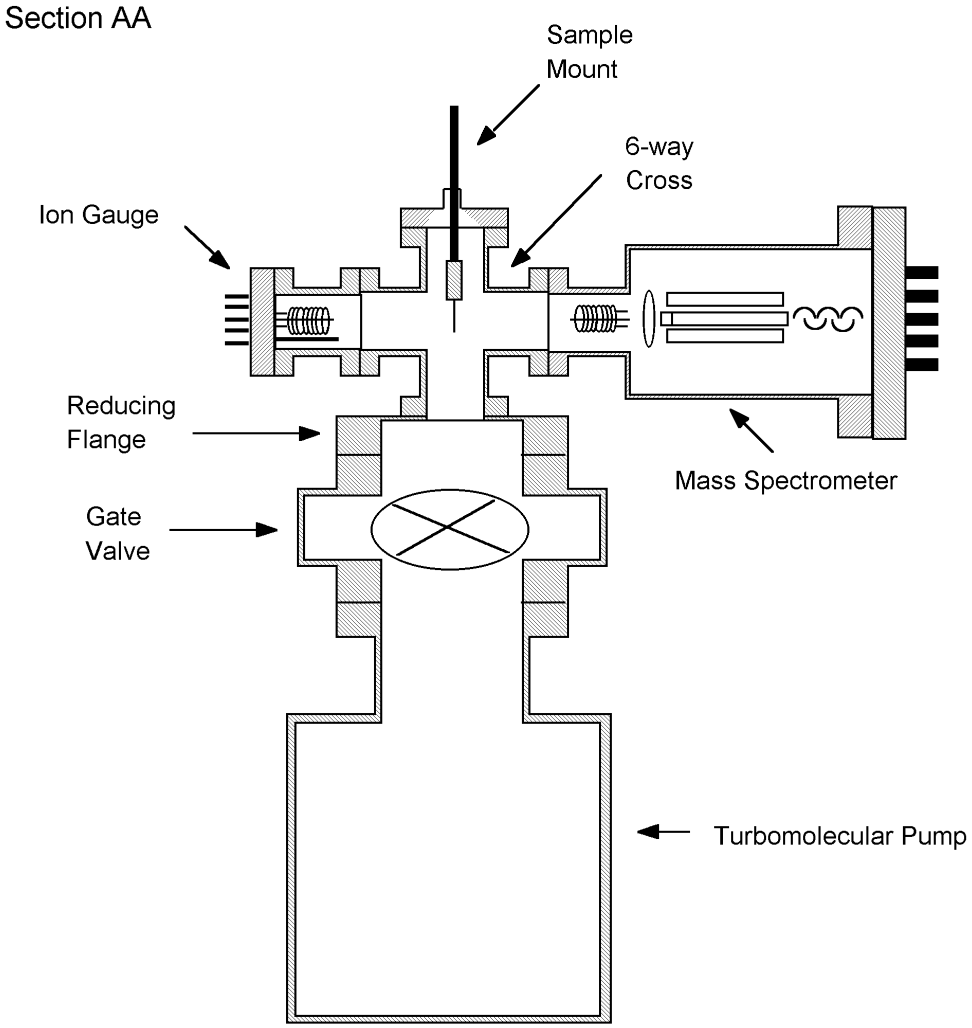

FIGURE 3. A SCHEMATIC DRAWING OF THE EXPERIMENTAL VACUUM CHAMBER (SECTION AA).

The total cost of the system is ca. $38,000. This figure covers not only the chamber, but also all major accessories, such as a computer and printer. The two single most expensive items are the Ametek package at $12,000 and the Balzer's turbomolecular pump at $7,000. We note that industrial laboratories are often willing to donate vacuum hardware which could be suitable for partially establishing this experiment. The cost of the instrument may be additionally justified by adapting it to research-level projects.

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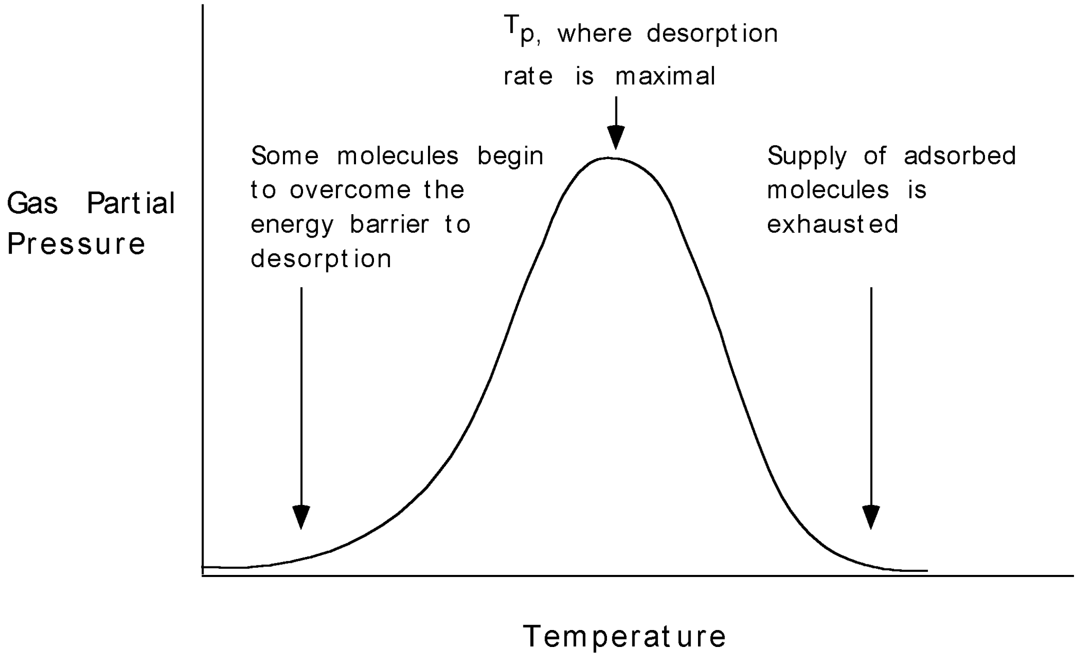

FIGURE 4. EXAMPLE OF A THERMAL DESORPTION SPECTRUM. AS THE SAMPLE TEMPERATURE INCREASES ADSORBED MOLECULES BECOME MORE ENERGETIC AND DESORB. ON FURTHER HEATING MOLECULES CONTINUE DESORBING, AND A PEAK IN THE SPECTRUM IS OBSERVED AT THE TEMPERATURE OF MAXIMUM DESORPTION RATE. FINALLY, THE SUPPLY OF MOLECULES ON THE SURFACE IS DEPLETED AND THE DESORPTION RATE FALLS OFF.

Principles of Temperature Programmed Desorption

Temperature Programmed Desorption (TPD) is a procedure by which the desorption bond energy and decomposition products of adsorbed molecules are measured [3]. The experiment has two steps. First, a clean metal sample is dosed with the gas of interest. Then, the sample is heated while the mass spectrometer monitors the gas composition in the vacuum chamber. As the temperature of the sample increases, the adsorbed molecules become more energetic and eventually desorb. The desorbing molecules cause the partial pressure of that gas in the vacuum chamber to increase up to a point which reflects the maximum rate of depletion of molecules on the surface. Analysis of the resulting spectrum (Figure 4) yields the desorption bond energy which can usually—and particularly in this experiment—be equated to the strength of the chemical bond between the molecule and the surface. The rate of desorption, $N(t)$, in units of monolayers s^{-1}, can be expressed by the equation

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$$N(t) - \frac{d\Theta}{dt} = v_n \Theta^n e^{-E/RT} \tag{1}$$

where n is the reaction order, Θ is surface coverage in monolayers, v_n is the pre-exponential rate constant in units which depend on n, T is the surface temperature in Kelvin, and E is the desorption energy, whose units depend on the units of R, the gas constant [6]. The surface coverage, Θ, is defined as the ratio of adsorbed particles to surface metal atoms; thus, if half the surface metal atoms are covered by adsorbed particles, the surface coverage is 0.5 monolayer.

Some simplifying assumptions are made to use equation 1. These assumptions include: (1) the change in temperature is linear in time ($T = T_o + \beta t$); and (2) both desorption energy and preexponential factor are independent of the number of molecules on the surface. With these assumptions, equation 1 can be solved for the temperature of maximum desorption rate, T_p (peak temperature):

$$\frac{E}{RT_p^2} = \frac{v_1}{\beta} e^{-E/RT_p} \qquad \text{for n = 1} \tag{2a}$$

$$= \frac{v_2 \Theta_0}{\beta} e^{-E/RT_p} \qquad \text{for n=2} \tag{2b}$$

where Θ_0 is the initial coverage. (The solutions are basically achieved by realizing that at T_p the second derivative of the coverage with respect to time is zero.) The first order case ($n = 1$) applies to molecules which do not dissociate upon adsorption, such as CO on Pt. In this case T_p is independent of Θ_0 To find the desorption energy from equation 2a, iterative techniques must be used.

To find a first order desorption energy the values of T_p, ν_1, and β are needed. The preexponential factor, ν_1, is assumed as 10^{13} s^{-1}, corresponding to a typical vibrational frequency and consistent with values reported for CO desorption from surfaces believed similar to our Pt foil [7]. The linear heating rate, β, and peak temperatures of the desorbing gases are determined experimentally.

For second order kinetics ($n = 2$) the case is more complex. This case applies often to molecules which dissociate when adsorbed, such as oxygen on Pt. For second order kinetics, T_p depends on Θ_0. To find the desorption energy from equation 2b, again,

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iterative techniques must be used. To solve for E we must know values for T_p, ν_2, β, and Θ_0. T_p and β are found experimentally, as in the $n = 1$ case. We assume ν_2 is 10^{13} s^{-1} monolayer^{-1}, again consistent with the literature value [8]. The initial coverage, Θ_0, for a particular adsorbate depends on the metal surface substrate, as well as the conditions of exposure. The surface used in this experiment is polycrystalline platinum. Most of this surface is small (111) facets bordered by steps and kinks [9]. Saturation coverage for oxygen on Pt (111) is 0.25 monolayers [8, 10]. Step and kink atoms increase the number of adsorption sites; therefore, as an approximation for initial coverage we assume $\Theta_0 = 0.3$ monolayers.

The students calculate the desorption bond energy by iteratively solving equation 2a and 2b. In the course of this experiment both CO and O_2 adsorb on the metal surface. CO adsorbs intact, while O_2 adsorbs dissociatively.

The Procedure

Four experiments are performed: (a) desorption of CO in vacuum, (b) desorption of O_2 in vacuum; (c) desorption of CO in the presence of flowing O_2 gas; and (d) desorption of O_2 in the presence of flowing CO gas. In each experiment, the goal is to use the mass spectrometer to measure the partial pressures of three gases as a function of sample temperature. The three gases are: CO (m/e = 28), O_2 (m/e = 32), and CO_2 (m/e = 44). For example, see Figure 5. No correction is made for the contribution to intensity at m/e = 28 from fragmentation of CO_2.

The sample heating rate is controlled manually. The students draw a line on a piece of graph paper corresponding to a heating rate of 10 K s^{-1}. This paper is placed on an *XY* recorder set up with a time scale in the *X* direction and the sample temperature (thermocouple output in mV) in the *Y* direction. The time sweep is started when the sample heating power supply begins passing current through the sample. The students increase the current to the sample by manually controlling the power supply's potentimeter so the temperature rises at the prescribed rate.

Each experiment begins by saturating the surface with a gas. Fifty Langmuir (1 Langmuir (L) = 10^{-6} torr × s) exposures are used in each experiment. A 50 L exposure of CO is achieved, for example, by opening the leak valve above the CO bulb until the chamber pressure, measured by the ion gauge, reads 5×10^{-7} torr. If the pressure is maintained at

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this level for 100 seconds, the surface is exposed to 50 L (5×10^{-7} torr × 100 s) of CO. The pressures of flowing CO and O_2 for parts c and d of the experiment are 3×10^{-8} and 3×10^{-7} torr, respectively. (The gases are flowing between the glass bulbs and the turbomolecular pump, which removes them from the system.)

For a well-prepared student, the laboratory takes about 3 hours including the time spent plotting data. The most typical problem occurs when a student tries to close a leak valve but accidentally opens it instead. In the worst case, this can empty the gas reservoir into the chamber and require replacing the glass bulb, plus baking out the system to regain good vacuum. It can also burn out, or shorten the lifetime of, the filaments in the mass spectrometer and ion gauge. This accident can make the apparatus unavailable to students who were scheduled to use it in the near future.

Results

Sample spectra for CO and O_2 desorption from Pt foil are shown in Figures 5 and 6, respectively. In each panel, the molecule of interest is shown by the bottom curve, and levels of the other two gases, which are due to background gas and reactions with background gas, are shown by the top curves. Our results are in good agreement with those of Collins, Lee and Spicer [5]. Two desorption maxima are observed for CO at ca. 110 and 225 °C. The corresponding desorption bond energies, calculated from equation 2a, are 23 and 30 kcal mol^{-1}. Oxygen desorption is maximized at ca. 510 °C. The desorption bond energy of oxygen, calculated from equation 2b, is 50 kcal mol^{-1}. From these two experiments the students conclude that oxygen bonds much more strongly to Pt than does CO and that adsorbed oxygen is stable on the Pt surface to a much higher temperature than is adsorbed CO.

Sample spectra for the desorption of CO in the presence of flowing O_2 are shown in Figure 7. As the sample temperature increases, CO begins to desorb. When the CO in the low temperature state desorbs, the partial pressure of oxygen drops and the evolution of CO_2 begins. After all the CO desorbs, the O_2 partial pressure returns to its initial level and CO_2 evolution ceases. By comparing Figures 5 and 7, the students can see that the high-temperature desorption state for CO is depressed in the presence of flowing O_2. This illustrates the competing processes: CO desorption and CO oxidation.

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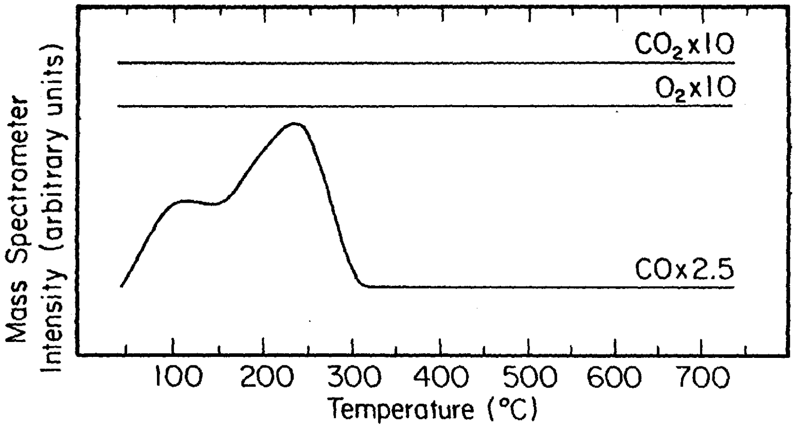

FIGURE 5. THERMAL DESORPTION SPECTRA FOR SATURATED LAYER OF CO ON PT FOIL. O_2 DESORPTION IS COMPLICATED BY ADSORPTION OF RESIDUAL CO GAS. SOME OF THIS ADSORBED CO REACTS WITH THE ADSORBED OXYGEN TO FORM CO_2.

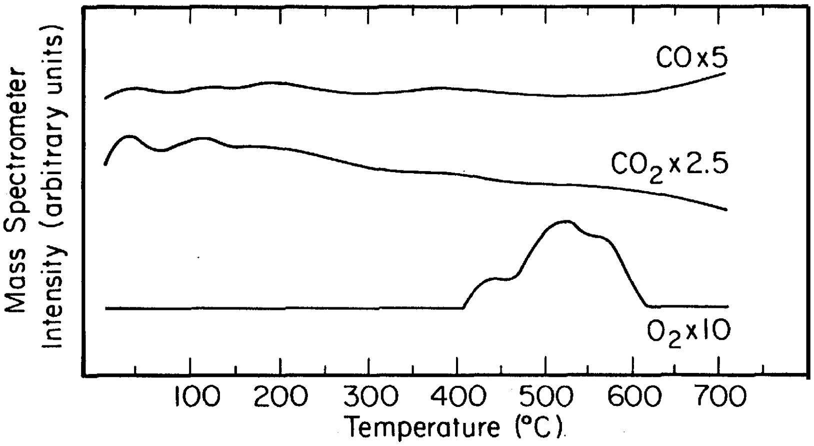

FIGURE 6. THERMAL DESORPTION SPECTRA FOR SATURATED LAYER OF O_2 ON PT FOIL. O_2 DESORPTION IS COMPLICATED BY ADSORPTION OF RESIDUAL CO GAS. SOME OF THIS ADSORBED CO REACTS WITH THE ADSORBED OXYGEN TO FORM CO_2.

Figure 8 illustrates data for the desorption of O_2 in the presence of flowing CO gas. Carbon dioxide production begins immediately after CO is admitted to the chamber and ceases when the sample temperature reaches ca. 300 °C. By referring back to Figures 5–7, the students can see that the end of CO_2 production is correlated with CO desorption, not with O_2 desorption. (Note, also, that since CO is a prominent residual gas in the

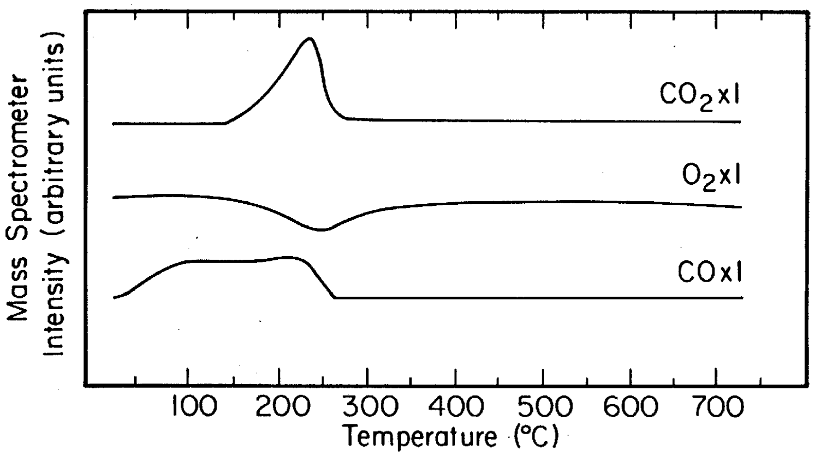

FIGURE 7. THERMAL DESORPTION SPECTRA FOR ADSORBED CO IN THE PRESENCE OF 3 X 10^{-7} TORR OXYGEN. CARBON MONOXIDE, OXYGEN, AND CARBON DIOXIDE WERE MONITORED SIMULTANEOUSLY USING A PERSONAL COMPUTER INTERFACED TO THE MASS SPECTROMETER.

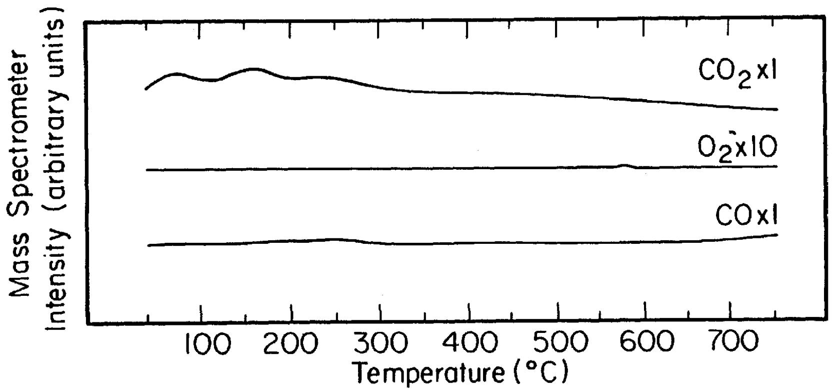

FIGURE 8. THERMAL DESORPTION SPECTRA FOR ADSORBED OXYGEN IN THE PRESENCE 3 X 10^{-8} TORR CO. CARBON MONOXIDE, OXYGEN, AND CARBON DIOXIDE WERE MONITORED SIMULTANEOUSLY USING A PERSONAL COMPUTER INTERFACED TO THE MASS SPECTROMETER.

chamber, oxidation of CO to CO_2 occurs to some extent in the oxygen desorption experiment illustrated in Figure 6.)

Discussion

Successful use of these experiments to establish the LH mechanism requires, first, that the students identify the two different temperature regimes in which CO and O_2 desorb.

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This is done in the experiments illustrated in Figure 5 and 6 and is usually straightforward. In interpreting the next two experiments, illustrated in Figures 7 and 8, the students must simultaneously implement two criteria. These are that in ER (1) the reaction should start immediately when the gaseous reactant begins flowing through the chamber, and (2) it should only stop when the coverage of adsorbed reactant drops to zero. The first criterion is not met in the experiment of Figure 7, showing that oxygen must adsorb for reaction to occur; the second is not met in the experiment of Figure 8, showing that CO must adsorb for reaction to occur. However, interpretation of these last two experiments can be complicated by the different site-blocking effects of CO and O_2, and we find it helpful to tell the students explicitly that adsorbed CO blocks O_2 adsorption, but not vice-versa, thus making the correct interpretation unambiguous. Overall, careful analysis of the data allows the conclusion that the LH mechanism operates, as the literature currently supports[11-13].

More specifically, Figure 7 shows that about half of the adsorbed CO desorbs before CO_2 evolution begins. At the same time the oxygen pressure dips, supporting the idea that oxygen is consumed in this reaction. CO_2 evolution and O_2 uptake by the surface stop after all the CO desorbs. This leads to the conclusion that at the beginning of the experiment the surface is saturated with CO, and this prevents O_2 adsorption. Once some CO desorbs, oxygen can adsorb at free sites on the surface. This oxygen adsorbs, dissociates, and reacts with adsorbed CO to form CO_2, which is evolved into the gas phase. If the reaction proceeded by the ER mechanism, the reaction should commence immediately before any CO desorbs.

For the desorption of O_2 in the presence of CO (Figure 8), CO is not blocked from adsorbing on the oxygen saturated surface; thus, once the leak valve is opened, CO immediately adsorbs on the oxygen-covered surface and reacts to form CO_2. For this reason, time is of the essence for this part of the experiment. As the sample temperature increases to 300 °C, CO from the gas phase can no longer adsorb on the surface because the sample temperature is too high. If the ER mechanism operated for this system, impinging CO would continue to react with adsorbed oxygen up to the oxygen desorption temperatures. The students should thus be able to deduce the LH mechanism for these conditions as well.

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Conclusions

This experiment gives undergraduate and graduate students of chemistry hands-on experience with sophisticated ultrahigh vacuum laboratory equipment. The students perform experiments to determine the catalytic mechanism of carbon monoxide oxidation over platinum. This experiment exposes a student to the type of laboratory equipment which is used today in many advanced technologies, including microelectronics, surface analysis, and catalysis characterization.

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