On the other hand, the first example of an ET chain reaction that can be initiated in either way also illustrates the problem of side reactions. Electron-reservoir ligands should be helpful in switching the mode of initiation of the ET chains.

An application of the suitably initiated electrocatalytic ligand exchange reaction is the coupling between ECE and organometallic catalysis with the aim of improving the reaction conditions, yields, and selectivities of transition-metal catalysis. Exemplified here by the facile induction of the polymerization of terminal alkynes, this principle should find considerable extension in the near future to other types of catalytic reactions. In more general terms, the coupling between several types of catalysis, some of which involve ET, is one of the keys for future achievement and improvement of technological processes.[41]

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Identification of Molecular Adsorbates by LITD/FTMS: A Breakthrough for Surface Chemistry

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Introduction

During the last 20 years, enormous progress has been made in the development of new and more precise probes of the solid–gas interface. Techniques such as low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) provide information about the elemental composition and structure of the surface layer, and X-ray photoelectron spectroscopy (XPS) is a sensitive method for determining the elemental composition and oxidation state of surface adsorbates. These methods are of only limited usefulness to a chemist, however, because they reveal little about the *molecular* composition of the surface species. Electron energy loss spectroscopy (EELS) and infrared spectroscopy can be used to identify simple molecular adsorbates, but identifying complex species, such as are encountered in problems related to catalysis, lubrication, adhesion, corrosion, and microelectronics fabrication, remains a difficult problem. Part of the difficulty results because very high detection sensitivity is required. For example, one monolayer of adsorbed material corresponds to about 3 pmol distributed over a surface area of 1 mm². Another difficulty is that small signals from the adsorbate can be overwhelmed by those arising from the bulk substrate.

In this Account we describe an exciting new surface analysis method called LITD/FTMS.[1–4] Laser-induced thermal desorption (LITD) utilizes a pulsed laser beam to rapidly heat the surface and remove intact neutral molecular species. These are then ionized by an electron beam, trapped in a magnetic field, and detected by Fourier transform mass spectrometry (FTMS).[5–8] FTMS has two distinct advantages: high mass resolution and the ability to record all masses simultaneously from a *single* laser shot. LITD/FTMS is a highly sensitive and rapid method for identifying complex molecular species adsorbed on surfaces. Intermediates in catalytic reactions can be observed, and rate constants for surface-catalyzed reactions can be measured.

Principles of LITD/FTMS

The sequence of events for a LITD/FTMS experiment is shown in Figure 1.[9–12] Figure 1a shows a pulsed

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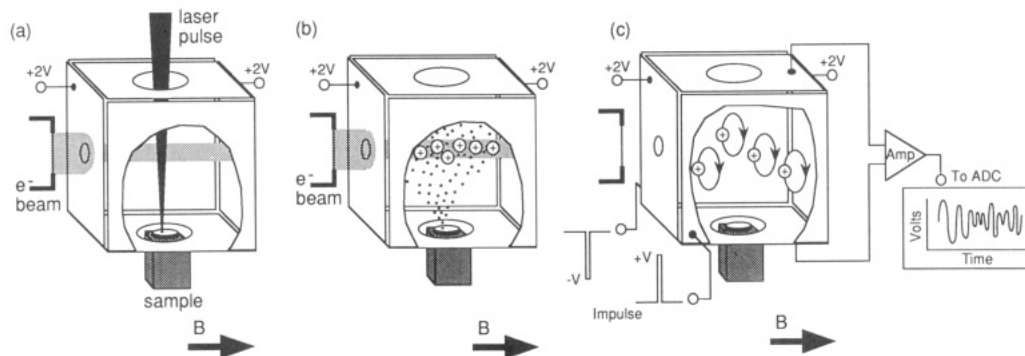
Figure 1. The sequence of events in a LITD/FTMS experiments: (a) a laser beam pulse passes across the FTMS analyzer cell, strikes the surface of the sample, and desorbs neutral molecules; (b) desorbed molecules are ionized by a 70-eV electron beam and are trapped inside the analyzer cell by the magnetic field; (c) impulse excitation accelerates all the ions to larger cyclotron orbits, and the coherent cyclotron motion is detected, to produce a mass spectrum of the ions.

laser beam striking the surface of a sample. The sample is supported on a probe and positioned adjacent to one of the plates of a FTMS analyzer cell. The analyzer cell is simply a box with six square stainless steel electrodes.[13,14] It is mounted inside an ultrahigh-vacuum chamber and centered between the pole caps of an electromagnet. The laser pulse rapidly heats the surface and causes adsorbed material to be vaporized. Very low laser power levels (about 10^6 W/cm^2) are used in our experiments so that only neutral species are desorbed by the laser. Figure 1b shows that the desorbed neutrals are ionized by a pulsed electron beam, and the ions thus produced are trapped inside the FTMS analyzer cell. The applied magnetic field causes the ions to move in small circular orbits. The frequency of this *cyclotron* motion is $w = qB/m$, where B is the magnetic field strength and m/q is the mass-to-charge ratio of the ions. The last step, shown in Figure 1c, is mass analysis and detection of the ions. This is accomplished by accelerating them with a high-voltage impulse and digitizing the transient signal that is produced by their coherent cyclotron motion.[15–17] The transient signal is a composite of all the various ion cyclotron frequencies, and a mass spectrum is extracted from it by a fast Fourier transform (FFT) calculation. This whole sequence of events is controlled by a computer and can be repeated as fast as 10 times per second. The final result is an electron ionization (EI) mass spectrum of the desorbed neutral molecules, which can be used to infer information about the original species present on the surface.

Even though the ionization efficiency of the electron beam is very low (about $10^{-4}\%$), LITD/FTMS has very high sensitivity for detection of surface species. For example, Figure 2a is a LITD/FTMS mass spectrum for 0.03 monolayer of cyclohexane adsorbed on Pt at 160 K. This mass spectrum was produced from just *one*
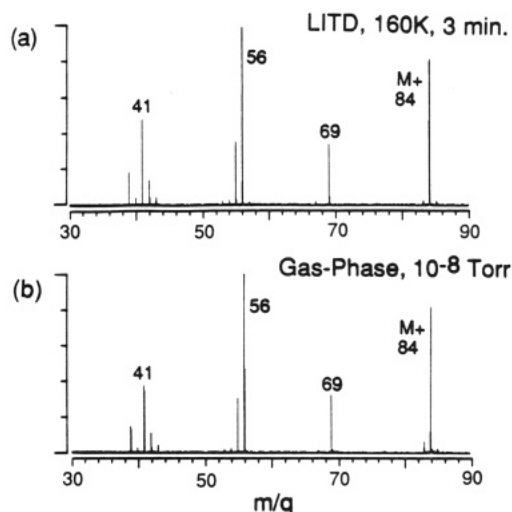
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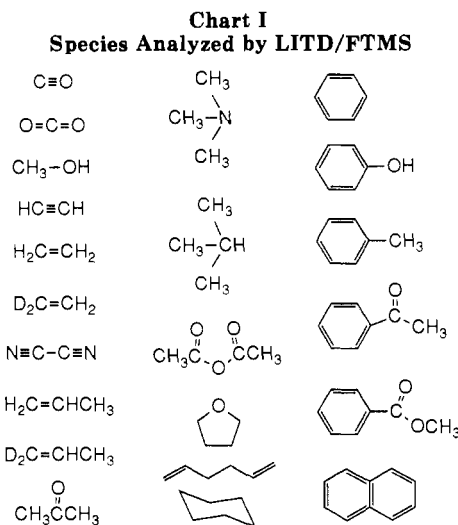(13) McIver, R. T., Jr. *Rev. Sci. Instrum.* **1970**, *41*, 555.
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Figure 2. (a) LITD/FTMS mass spectrum obtained from 0.03 monolayer of cyclohexane adsorbed on Pt(111) at 160 K, using a single laser shot. Data from m/z 10–800 were acquired, but only the portion of the mass spectrum between m/z 30 and 90 is displayed. (b) EI mass spectrum obtained by backfilling the vacuum chamber with cyclohexane at 2×10^{-8} Torr. The same conditions as in spectrum a were used except that no laser pulse was fired.

pulse of the laser, and the excellent mass resolution and sensitivity are typical for FTMS detection. Since a coverage of one monolayer corresponds to about 10^{14} molecules/cm^2, a simple calculation shows that the mass spectrum in Figure 2a was produced by desorption of about 18 fmol (10^{-15}) of material!

Another important feature of LITD/FTMS is that the mass spectra it produces are readily interpretable. For example, a mass spectroscopist can easily recognize that Figure 2a is for cyclohexane (parent mass m/z 84) because it is practically identical with the normal EI mass spectrum of cyclohexane (Figure 2b), which was obtained by admitting gaseous cyclohexane into the vacuum chamber, firing the electron beam, and acquiring a FTMS mass spectrum under the same operating conditions. The agreement between these two spectra is excellent and demonstrates that, to a first approximation, LITD/FTMS can be thought of as providing an EI mass spectrum of the molecules originally on the surface.

Most of the early experiments with laser desorption mass spectrometry utilized high-power lasers and detected the ions produced by the "spark" of the laser

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Chart I
Species Analyzed by LITD/FTMS

C≡O

O=C=O

CH₃-OH

HC≡CH

H₂C=CH₂

D₂C=CH₂

N≡C-C≡N

H₂C=CHCH₃

D₂C=CHCH₃

$$CH_3\overset{O}{\overset{\|}{C}}CH_3$$

$$CH_3-\overset{CH_3}{\underset{}{\overset{|}{N}}}$$

$$CH_3-\overset{CH_3}{\underset{}{\overset{|}{CH}}}$$

$$CH_3\overset{O}{\overset{\|}{C}}\overset{}{\underset{O}{\,}}\overset{O}{\overset{\|}{C}}CH_3$$

(benzene ring)

(phenol — OH)

(toluene — CH₃)

(acetophenone)

(furan)

(methyl benzoate)

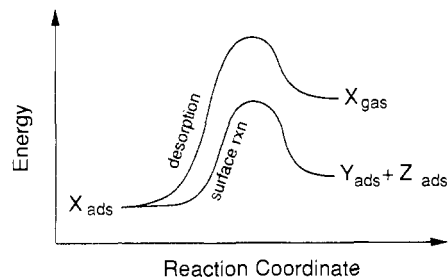(pentene)

(cyclohexene)

(naphthalene)

Figure 3. Simple model for two competing, thermally activated reaction channels. Species X adsorbed on the surface (X$_{ads}$) can either desorb into the gas phase (X$_{gas}$) or react to give new surface species Y$_{ads}$ and Z$_{ads}$.

hitting the surface. A key element that distinguishes LITD/FTMS is that the desorption and ionization steps are performed separately. This allows much lower laser power levels to be used and avoids the nonlinear effects that result from high power laser desorption experiments. Most of our experiments have utilized a 70-eV electron beam for ionization of the desorbed neutrals. The advantage of this is that EI is a general, nonspecific ionization method and the fragmentation it produces can be used to identify the desorbed species. Other ionization methods can also be used. For example, the desorbed neutrals can be ionized by a second laser pulse[18-20] or chemical ionization (CI) can be accomplished by reacting the desorbed neutrals with reagent ions such as CH₅⁺.[21]

The generality of LITD/FTMS for detecting molecular adsorbates is demonstrated by Chart I, which is a list of compounds investigated after low-temperature adsorption at near-monolayer coverages on Pt. In all these cases the intact neutral species are desorbed and the LITD/FTMS mass spectra are identical with their conventional EI mass spectra. This is an important observation because Pt is a very reactive surface and most of these molecules decompose when the surface is heated. For example, when a Pt crystal covered with a monolayer of naphthalene is heated, the naphthalene decomposes completely to give gaseous H₂ and a layer of carbon on the surface.[22] There are many examples of this, and generally it is found that under the very rapid heating conditions provided by the laser pulse (1000 K in 20 ns) direct desorption of the intact molecules from the surface is faster than surface decomposition. If the surface is slowly heated, however, thermal decomposition dominates. This can be explained by a simple two-channel model, shown in Figure 3, in which species X on the surface either desorbs to give gaseous X or decomposes to form Y and Z. The rate coefficients for these two channels can be modelled by Arrhenius equations, $k = Ae^{-E_a/RT}$, with characteristic activation energies (E_a) and frequency factors (A). As the tem-

perature of the surface is raised, molecules initially react via the decomposition pathway because it typically has the lowest activation energy. Under the conditions of rapid laser heating, however, the temperature increases so fast that the exponential terms in the Arrhenius equations approach their high-temperature limits, $e^{-E_a/RT}$ approaches 1, and the rate coefficients are dominated by the frequency factors. This usually means that the desorption channel becomes faster than the decomposition channel. The A factors for desorption are typically much faster than those for decomposition because entropic factors, such as increased degrees of freedom in the transition state for desorption, are more favorable for desorption.[23-30] In order to enhance desorption, the surface must reach this high-temperature limit in nanoseconds or less, so that the adsorbate molecules do not undergo surface reactions during the temperature jump. This requires heating rates in excess of 10⁹ K/s, which can be achieved with nanosecond pulsed lasers.

Surface Chemical Studies

In surface science studies, great care is taken to operate under controlled conditions with well-characterized surfaces. The surface for study is a single crystal of a transition metal that has been carefully cut and finely polished to expose a specific crystallographic plane. Our studies have been performed primarily on the (111) plane of Pt single crystals. The surface is cleaned in vacuum using standard surface cleaning techniques in order to obtain an atomically smooth, pure Pt surface. The surface is characterized by AES, LITD/FTMS, and LEED to verify the cleanliness and surface structure.[12] Great care must be taken to obtain a clean crystal because it has been found that impurities and defects at levels as low as 1% can profoundly influence the chemistry on the surface.

Reaction Surveys. Kinetic data for surface reactions can be obtained in LITD/FTMS by slowly varying the crystal temperature and firing the laser at fixed intervals to monitor the molecular adsorbates. Only a single laser pulse is required to get a good quality mass

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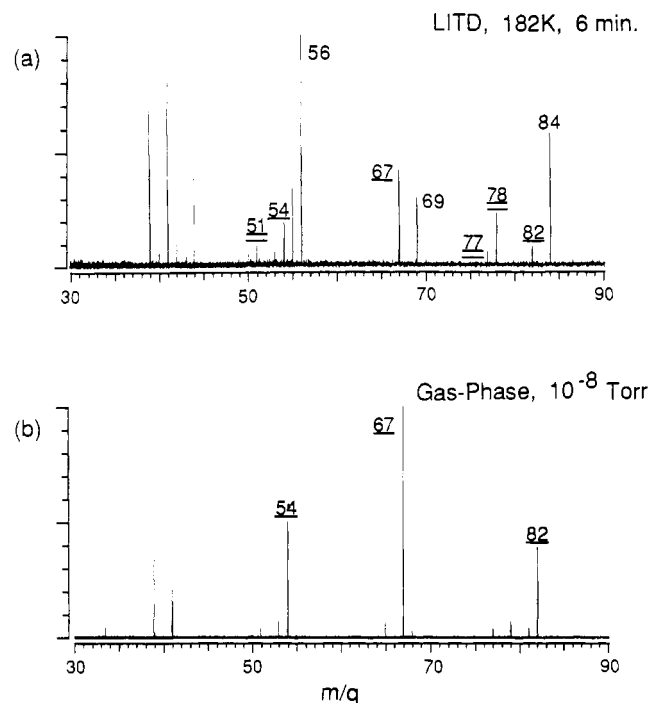
Identification of Molecular Adsorbates

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Figure 4. (a) LITD/FTMS mass spectrum obtained from about 0.02 monolayer of cyclohexane adsorbed on Pt, after warming the crystal from 160 to 182 K. This spectrum indicates that a mixture of species is present on the surface. Peaks at m/z 84, 69, and 56 are due to cyclohexane, and benzene is evidenced by peaks at m/z 78, 77, and 50. (b) EI mass spectrum of cyclohexene obtained by backfilling the chamber with 1×10^{-8} Torr. Characteristic peaks at m/z 82, 67, and 54 are also seen in spectrum a.
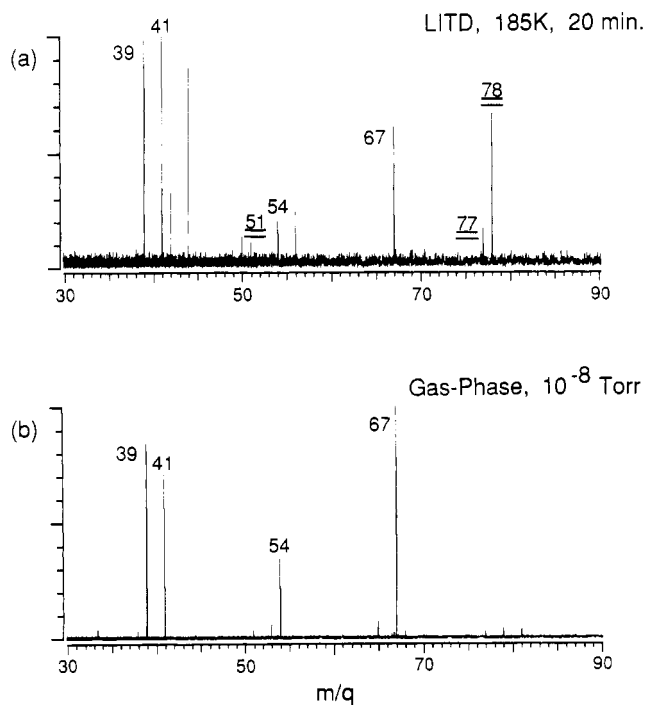
Figure 5. (a) LITD/FTMS mass spectrum obtained for cyclohexane adsorbed on Pt, after reacting at 185 K for several minutes. Benzene is the main species on the surface, as indicated by the large peaks at m/z 78, 77, and 51. Also, a reaction intermediate, possibly 1,6-hexanediylidene, is indicated by the peaks at m/z 67, 54, and 41, which are characteristic of 1,5-hexadiene. (b) EI mass spectrum obtained by backfilling the chamber with 1×10^{-8} Torr of 1,5-hexadiene.

spectrum, and the laser spot is well localized (typically 1.8 × 0.2 mm), leaving the rest of the sample unperturbed. As a result, as many as 50 nonoverlapping spots can be sampled on a 1-cm^2 crystal. After cleaning and characterizing of the metal surface, it is cooled, typically to 115 K, and the adsorbate molecule of interest is dosed onto the surface at submonolayer coverage. Next, the laser is fired at the sample to desorb the surface species and a FTMS mass spectrum is recorded. Then the laser is redirected at a fresh spot, the sample temperature is increased a few degrees, and the process is repeated. In this way, the changes in adsorbate composition as a function of temperature are mapped out.

The first LITD studies of surface-catalyzed reactions were reported in 1984 by Hall and DeSantolo for the decomposition of methanol on Ni.[24] They used a quadrupole mass spectrometer instead of FTMS and were limited, therefore, to monitoring a single mass for each laser shot. Since then several other such studies have been performed, including ethylene on Ni,[31] and methanol on Ru, ammonia, water, and hydrogen, each on Si(111), all performed by George et al.[32] Hydrogen and propylene on Si(100) and CO coadsorbed with potassium on Ni(111) has also been studied by Janda et al., using these techniques.[33-36] LITD with quadrupole

mass spectrometry detection has also been used to study surface diffusion.[37-40]

Reactions of C$_6$ Hydrocarbons on Pt(111). One of the most important areas of catalysis relates to the reactions of hydrocarbons on transition metals. For example, although it has been known for years that cyclohexane dehydrogenates on Pt(111) to form benzene, the intermediates in this reaction were not known, despite studies by a myriad of surface techniques. Our results for this system are shown in Figure 4.[41] The mass spectrum in Figure 4a is a LITD/FTMS spectrum for cyclohexane on Pt(111) after warming to 182 K. In addition to the peaks at m/z 84, 69, and 56 due to cyclohexane (see Figure 2), there are also peaks at m/z 78, 77, and 51, which are due to benzene. Most surprising are the peaks at m/z 82, 67, and 54, which we believe are due to cyclohexene on the surface. This assignment is confirmed by comparison with the cyclohexene EI mass spectrum shown in Figure 4b. This

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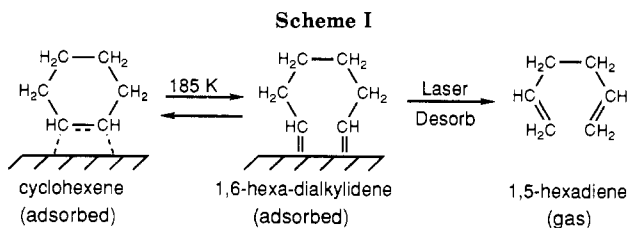
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Scheme I

cyclohexene   1,6-hexa-dialkylidene   1,5-hexadiene
(adsorbed)   (adsorbed)   (gas)

Figure 6. Natural logarithm of the ethylene ion signal $(C_2H_4^+)$ as a function of time at five different isothermal reaction temperatures. The lines through the points are linear least-squares fits to the data. The linearity of these plots indicates that a first-order process occurs, and the observed temperature dependence was used to calculate the activation energy and frequency factor for the formation of ethylidyne on Pt.

is the first direct observation of cyclohexene as an intermediate in this reaction.

The experiments above were repeated under conditions of higher adsorbate coverage with interesting results. Once again at about 185 K cyclohexene was observed, but after several minutes the mass spectrum in Figure 5a was obtained. This mass spectrum shows the expected peaks for benzene at m/z 78, 77, and 51, but peaks at m/z 67, 54, and 41, which are not due to benzene, are also observed in conjunction with a complete lack of peaks in the range m/z 80–84. This indicates that another intermediate is present on the surface. A search of EI mass spectra gave only one stable gas-phase species, 1,5-hexadiene, which produces these characteristic peaks. The FTMS mass spectrum of 1,5-hexadiene is shown for comparison in Figure 5b. The formation of the intermediate is believed to occur by olefin metathesis of cyclohexene, which involves a rearrangement of bonding electrons (as shown in Scheme I) to give 1,6-hexanediylidene on the surface. Upon desorption, this species would be expected to undergo facile 1,2 hydrogen shifts to form 1,5-hexadiene by the time the species is ionized, thus producing the mass spectrum seen in Figure 5b.

Additional experiments at lower cyclohexane coverages show no evidence for the alkanediylidene or cyclohexene. This points at a phenomenon common to many surface systems: a coverage dependence in the relative rates of surface reactions. There are several identified causes for this coverage dependence. These include repulsive interactions between adsorbed species which may decrease the barrier for desorption, attractive interactions, such as hydrogen bonding, which may increase the desorption energy barrier, and site blocking. Surface catalytic reactions are believed to require specific "active" sites for reaction to occur. These sites might be positions between two or three adjacent surface atoms or comprise ensembles of many surface atoms for each reactive interaction. At moderate to high coverages, the decomposition of molecules on the surface can lead to occupation of active sites needed for further reaction. This results in a self-poisoning of the catalytic activity of the surface.

The coverage dependence of the cyclohexane system leads one to speculate that the cyclohexene and alkanediylidene are only seen at high coverages because at low coverages, these intermediates can further dehydrogenate on the surface. At high coverages, however, the sites required for dehydrogenation of these intermediates species are blocked. Under these conditions, desorption of the intact intermediates competes more favorably and the species are observed in the LITD/FTMS mass spectra.

Kinetics of the Dehydrogenation of Ethylene on Pt(111). The dehydrogenation of ethylene on Pt(111) to form ethylidyne (CCH_3) provides an example of how LITD/FTMS can be used to monitor the kinetics of
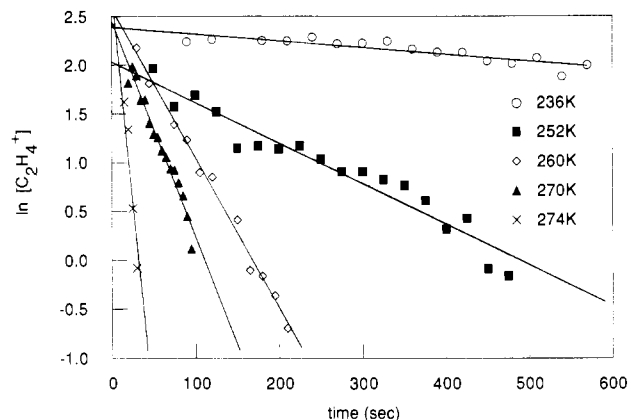
surface reactions. This system has been extensively studied, and data exist with which to compare our results.[42] Ethylene dehydrogenation is a well-studied system because of its importance as a model for olefinic dehydrogenation.[43-50]

The kinetics experiments are carried out as follows. Ethylene is adsorbed onto the clean Pt(111) surface at submonolayer coverage at a temperature of 200 K. First a LITD/FTMS mass spectrum is taken to ensure that the ethylene is present and intact. Then the temperature is ramped to and held at the desired isothermal reaction temperature, and successive LITD/FTMS mass spectra are taken at different spots to monitor the loss of ethylene as a function of time. Although ethylene undergoes both thermal desorption and surface decomposition over this temperature range, parallel experiments using AES indicate that surface decomposition is the only reaction pathway monitored by the LITD/FTMS experiments.[42]

Figure 6 is a plot of the decrease in the LITD/FTMS signal for $C_2H_4^+$ versus time at temperatures from 236 to 272 K. The straight lines indicate that the process is first order in C_2H_4. The slopes of these lines give the rates at each temperature, from which we obtain the preexponential factor $(A = 10^{10 \pm 1.2} \text{ s}^{-1})$ and activation energy $(E_a = 14 \pm 1 \text{ kcal/mol})$ for this reaction. These numbers correspond well with two recent studies of the same system which monitored the buildup of the dehydrogenation product, ethylidyne (by FTIR, $A = 10^{10 \pm 1}$

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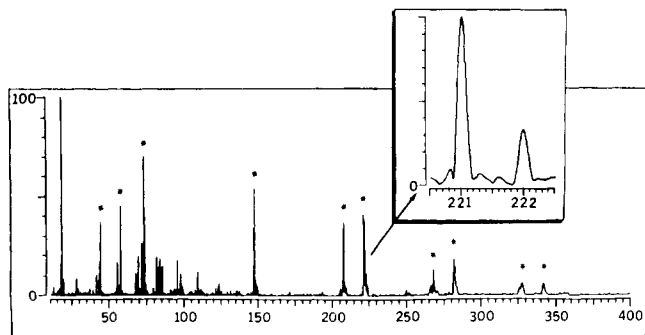
Figure 7. LITD/FTMS mass spectrum obtained for contaminants on the surface of a computer hard disk (248 nm, 15 MW/cm^2 laser pulse). Accurate mass measurement has been used to identify the starred peaks (*) as poly(dimethylsiloxane) compounds.

Table I
Structural Assignments for LITD/FTMS Mass Spectrum of a Magnetic Hard Disk Surface

proposed composition	calcd mass	measd mass
SiO^+	43.972	43.979
$CH_3SiCH_2^+$	57.016	57.065
$CH_3Si(CH_3)_2^+$	73.047	73.043
$CH_3Si(CH_3)_2OSi(CH_3)_2^+$	147.07	147.07
$CH_3(Si(CH_3)_2O)_2SiHCH_3^+$ or $H(Si(CH_3)_2O)_2Si(CH_3)_2^+$	207.07	207.04
$CH_3(Si(CH_3)_2O)_2Si(CH_3)_2^+$	221.08	221.10
$CH_3(Si(CH_3)_2O)_3SiH_2^+$ or $H(Si(CH_3)_2O)_3SiHCH_3^+$	267.07	266.99
$CH_3(Si(CH_3)_2O)_3SiHCH_3^+$ or $H(Si(CH_3)_2O)_3Si(CH_3)_2^+$	281.09	281.05
$H(Si(CH_3)_2O)_4SiH_2^+$	327.08	326.97
$CH_3(Si(CH_3)_2O)_4SiH_2^+$ or $H(Si(CH_3)_2O)_4SiHCH_3^+$	341.09	340.96

s^{-1}, E_a = 14 ± 1 kcal/mol,[51] and by T-NEXAFS, A = 3.6 × 10^{10} s^{-1}, E_a = 15 ± 1 kcal/mol).[53,54]

Analytical Applications

An important feature of the LITD/FTMS method is that the mass spectra closely match the normal EI mass spectra of the molecular species on the surface. We anticipate that this will lead to many new analytical applications. An example is our identification of lubricants used on the surface of a computer magnetic hard disk.[54,55] The magnetic hard disks investigated were multilayer metal structures with a 30-nm layer of carbon sputter deposited on top of the magnetic layer. It has been shown that adsorption of molecular species on the carbon layer greatly affects the performance characteristics of the magnetic disk.[56] Figure 7 shows a typical LITD/FTMS mass spectrum for a magnetic disk sample that was provided by a computer company. A single laser pulse (248 nm; 0.5 mJ in 20 ns, 0.004-cm^2 area) was used to heat the surface, and the desorbed neutrals were ionized by a 70-eV electron beam. Peaks labeled by a star have been identified, by accurate mass measurement, as poly(dimethylsiloxane) compounds, which are a common type of silicone oil. Table I lists possible structures for these compounds and shows that there is excellent agreement between the observed and calculated masses for the starred peaks. Also, there is evidence that the clusters of peaks between 30 and 110 amu are the fragments of an aliphatic alcohol. At an

incident power level of 5 MW/cm^2, essentially the same pattern of peaks is observed after as many as 600 laser shots at the same spot. This suggests that the laser beam is not significantly decomposing these surface species and is not ablating the carbon film. Using AES and XPS, we were able to determine only that a partially oxidized form of Si is present, but the LITD/FTMS data allowed unambiguous identification of the surface species.

Conclusions

The capability to accomplish surface characterization very rapidly and with excellent reproducibility makes LITD/FTMS a powerful technique for measuring reaction kinetics. The high sensitivity of the technique extends the range for kinetic studies and also provides a way to monitor reaction intermediates which may be present only in small concentrations or under limited conditions. We are currently pursuing kinetic studies on the cyclohexane system to better understand the details of the mechanism for dehydrogenation and are beginning studies of other related systems. Clearly, LITD/FTMS will be an important tool in the quest for a fundamental understanding of surface chemistry, especially for complex systems. Less is known about the analytical potential of the method for identifying adsorbed surface materials. We can imagine, however, many possible applications in the analysis of surface contaminants in semiconductor fabrication, biomolecules adsorbed on contact lenses or implanted materials, and surface contaminants that have fouled catalyst materials.

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