SFG-surface vibrational spectroscopy studies of structure sensitivity and insensitivity in catalytic reactions: cyclohexene dehydrogenation and ethylene hydrogenation on Pt (1 1 1) and Pt (1 0 0) crystal surfaces

Keith R. McCrea, Gabor A. Somorjai*

Department of Chemistry, University of California at Berkeley, Berkeley, CA 94720, USA

Abstract

The effect of the surface structure of Pt (1 1 1) and Pt (1 0 0) has been investigated for cyclohexene hydrogenation and dehydrogenation, and ethylene hydrogenation by using sum frequency generation. Cyclohexene dehydrogenation is a structure sensitive reaction, and the rate was found to proceed more rapidly on the Pt (1 0 0) crystal surface than on the Pt (1 1 1) crystal surface. On Pt (1 0 0), the major reaction intermediate during cyclohexene dehydrogenation was 1,3-cyclohexadiene, whereas on Pt (1 1 1), both 1,3- and 1,4-cyclohexadiene were present. Both 1,3- and 1,4-cyclohexadiene can dehydrogenate to form benzene, although the reaction proceeds more rapidly through the 1,3-cyclohexadiene intermediate. Because of this, the structure sensitivity of cyclohexene dehydrogenation is explained by noting that there are both a fast and slow reaction pathway for Pt (1 1 1), whereas there is only a fast reaction pathway on Pt (1 0 0). Ethylene hydrogenation is a structure insensitive reaction. Both ethylidyne and di-σ-bonded ethylene are present in both Pt (1 1 1) and Pt (1 0 0) under reaction conditions, although the ratio of the concentrations of the two species are different. The rate of the reaction was found to be 11 ± 1 and 12 ± 1 molecules per site per second for Pt (1 1 1) and Pt (1 0 0), respectively. Since the reaction rate is essentially the same on the two surfaces, while the concentration of ethylidyne and di-σ-bonded ethylene are different, these species must not be the active species which turnover under catalytic ethylene hydrogenation. The most likely species which turnover are π-bonded ethylene and ethyl, and their concentrations are near the detection limit of SFG. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Boudart's classification of catalytic reactions as structure sensitive and structure insensitive survived the tests of time and became a focus of research in several laboratories. The experimental data that was the basis of the classification correlated the turnover rates for a given reaction with catalyst particle size; if the reaction rate stayed constant the reaction was insensitive to the catalyst structure [1]. This was the case for most hydrogenation processes including that of ethylene [2]. If the reaction rate varied with changes of particle size the reaction was structure sensitive. This was the case for ammonia synthesis and

* Corresponding author. Tel.: +1-510-642-4053;
fax: +1-510-643-9668.
E-mail address: somorjai@cchem.berkeley.edu (G.A. Somorjai).

the dehydrogenation of cyclohexene and cyclohexane as well as for hydrogenolysis of alkanes [3,4].

Molecular surface science studies of catalytic reactions using single crystal surfaces confirmed these correlations. As the surface structure of the single crystal was altered, if the reaction rates remained unchanged, the reaction was structure insensitive. If the reaction rates changed, the reaction was structure sensitive. Recently, sum frequency generation (SFG) vibrational spectroscopy permitted the detection of surface reaction intermediates while also monitoring reaction turnover using single crystal surfaces of metal catalysts [5–8]. This way the molecular species that turnover could be detected and their chemical behavior as the surface structure was changed could be monitored. A correlation with the nature and concentration of surface reaction intermediates with surface structure could be obtained during the catalytic reaction turnover under steady state conditions.

In this paper, we used the (1 1 1) and (1 0 0) crystal faces of platinum to monitor, at high reactant pressures (0.1–1 atm) the rates of ethylene hydrogenation and cyclohexene dehydrogenation to benzene and its hydrogenation to cyclohexane. Simultaneously, SFG vibrational spectroscopy was utilized to monitor the surface species, some of which were surface reaction intermediates. We found that strongly bound ethylidyne and di-σ-bonded ethylene are not the active species which turnover during ethylene hydrogenation. The reaction rate was the same for ethylene hydrogenation on both Pt (1 1 1) and Pt (1 0 0) indicating the reaction is structure insensitive. Weakly bound species such as π-bonded ethylene and ethyl are the most likely species which turnover, although they are not readily detected under the conditions discussed below. Since the concentration of both adsorbed ethylidyne and di-σ-bonded ethylene is relatively high, leaving few sites for the active intermediates, SFG is most likely not sensitive enough to detect these species under the conditions discussed below. Cyclohexene dehydrogenation and hydrogenation occurred through 1,3-cyclohexadiene and 1,4-cyclohexadiene surface intermediates whose relative concentration changed with platinum surface structure. Since the rate of cyclohexene dehydrogenation was faster through 1,3-cyclohexadiene, and 1,3-cyclohexadiene was the dominant species on the (1 0 0) crystal face of platinum, the rate of benzene

formation was greater on that catalyst surface. The Pt (1 1 1) surface had both 1,3-cyclohexadiene and 1,4-cyclohexadiene present under reaction conditions.

2. Sum frequency generation (SFG)-surface specific vibrational spectroscopy

Sum frequency generation is a surface specific vibrational spectroscopy with sub-monolayer sensitivity. During an SFG scan, a visible laser beam at a fixed wavelength and a tunable infrared beam are overlapped on a surface. As the IR beam is scanned over the frequency range of interest, a vibrational spectrum of molecules adsorbed on the surface is obtained. SFG is an excellent technique for studying molecules adsorbed on single crystal surfaces under high-pressure catalytic reaction conditions. It is a surface specific technique in that only a medium that lacks inversion symmetry may generate SFG signal under the electric dipole approximation. Because of this selection rule, the gas phase and bulk metal of the single crystal do not generate SFG signal, therefore, the signal is generated specifically at the surface.

A brief discussion of SFG is presented here, and more detailed descriptions can be found in the literature [9–14]. Sum frequency generation is a second order non-linear optical process. The polarization of a material is described by

$$P = P^{(0)} + P^{(1)} + P^{(2)} + P^{(3)} + \cdots \qquad (1)$$

where $P^{(0)}$ is the static polarization, $P^{(1)}$, $P^{(2)}$, and $P^{(3)}$ are the first, second and third order polarizations. Since SFG is a second order process, we are concerned with the second order polarization

$$P_i^{(2)} = \varepsilon_0 \sum_{j,k} \chi_{ijk}^{(2)} \vec{E}_j(r) \cos(\omega_1 t) \vec{E}_k(r) \cos(\omega_2 t) \qquad (2)$$

where $\chi_{i,j,k}^{(2)}$ is the second order non-linear susceptibility, $\vec{E}(r)\cos(\omega t)$ describes the electric fields, the subscripts i, j, and k refer to the axes of the coordinate system. If ω_1 and ω_2 are oscillating at different frequencies, then Eq. (2) rearranges to the form

$$P_i^{(2)} = \tfrac{1}{2}\varepsilon_0 \sum_{j,k} \chi_{ijk}^{(2)} \vec{E}_j(r) \vec{E}_k(r) [\cos(\omega_1 + \omega_2)t$$
$$+ \cos(\omega_1 - \omega_2)t] \qquad (3)$$

In the brackets of Eq. (3), we see that there is now the possibility of frequencies at the sum and difference of ω_1 and ω_2 being generated by an oscillating dipole. These two processes are known as sum frequency generation (SFG) and difference frequency generation (DFG), respectively. In this work, we will focus on SFG although DFG also occurs.

The intensity of the SFG signal is proportional to the absolute square of the second order non-linear susceptibility ($|\chi^{(2)}|$) which is made up of both a resonant term and a non-resonant term.

$$\chi^{(2)} = \chi^{(2)}_{NR} + \chi^{(2)}_{R} \qquad (4)$$

The non-resonant term originates from the substrate surface and is typically invariant as the IR beam is scanned and is called the non-resonant background. The resonant susceptibility originates from the vibrational modes of molecules adsorbed on the surface and is described by

$$\chi^{(2)}_{R} = \chi^2_{i,j,k} \sum_{l,m,n} \langle (\hat{i} \cdot \hat{l})(\hat{j} \cdot \hat{m})(\hat{k} \cdot \hat{n}) \rangle \frac{A_q}{\omega_{IR} - \omega_q i \Gamma_q} \qquad (5)$$

where A_q is the strength of the qth vibrational mode, ω_{IR} is the frequency of the infrared laser beam, ω_q is the frequency of the qth vibrational mode, and Γ_q is the damping constant of the qth vibrational mode. The subscripts l, m, and n, refer to the axes for the molecular coordinate system. It is important to note that as the IR beam is scanned, when the frequency of the IR beam is the same as the frequency of a surface vibrational mode, $\chi^{(2)}_{R}$ reaches a maximum. Therefore, as the IR beam is scanned, a vibrational spectrum is acquired.

The selection rules for the SFG process are inferred from the equation

$$A_q = \frac{1}{2\omega_q} \frac{\partial \mu_n}{\partial q} \frac{\partial \alpha^{(1)}_{lm}}{\partial q} \qquad (9)$$

where μ_n is the dipole moment and $\alpha^{(1)}_{lm}$ the linear polarizability. In order to generate a SFG signal, both the IR and Raman selection rule must be met. Hence, there must be a change in the dipole and a change of polarizability. Under the electric dipole approximation, only a media without inversion symmetry can satisfy both selection rules. Centrosymmetric bulk materials and isotropic gas phases have centrosymmetry and are SFG forbidden. Therefore, only surfaces or interfaces may generate SFG signal.

The intensity of an SFG signal is also dependent on the ordering of the surface or interface. If molecules on the surface are randomly oriented, then $\chi^{(2)}$ becomes zero and SFG signal will not be generated. Therefore, when examining a SFG spectrum, strong SFG features indicate that the surface adsorbates are well ordered.

By using different polarization combinations for the IR, visible, and generated SFG light, information about molecular orientation on the surface may be obtained for non-metal surfaces [15]. For each polarization combination used during a SFG experiment, different susceptibility components are measured. By modeling these susceptibility components, it is then possible to determine the orientation of surface molecules. However, this technique is not possible for characterization of metal surfaces. Because of the metal-surface-selection rules (MSSR), an s-polarized IR beam is cancelled out due to the image field of the electrons in the metal. Therefore, an s-polarized IR beam cannot excite a dipole along a metal surface, and so when performing SFG experiments on a metal surface, the IR beam is always p-polarized. The visible beam may be either s- or p-polarized, but the signal is almost 40 times weaker for s-polarized visible light. Therefore, in the experiments reported here, both the IR and visible light were p-polarized, resulting in p-polarized SFG output.

3. Experimental

3.1. Laser systems

Two different laser systems were used to generate the IR and visible laser beams for the experiments covered in this paper. Both systems utilized the output of a Continuum Nd:YAG laser operated at 20 Hz with a 20 ps pulse at the fundamental frequency of 1064 nm with 35 mJ of energy per pulse. In the first laser system, the fundamental beam was split into two separate beams. The first beam passed through a KD*P non-linear crystal which doubled the frequency of the fundamental beam to 532 nm. This beam was then used for the visible portion of the experiment and had an output energy of 400 μJ per pulse. The

second portion of the fundamental beam was then sent to an optical parametric generation/optical parametric amplification stage (OPG/OPA) utilizing two counter rotating $LiNbO_3$ to generate a tunable infrared beam between 2700 and $3600\,cm^{-1}$ [16]. The maximum output of this stage was at $2850\,cm^{-1}$ with $200\,\mu J$ of energy and a full width at half maximum (fwhm) of $12\,cm^{-1}$. This laser system was used for cyclohexene dehydrogenation on both Pt (1 1 1) and Pt (1 0 0), and for ethylene hydrogenation on Pt (1 1 1).

The second laser system was a commercially built OPG/OPA system provided by Laservision. The fundamental beam was passed through a KTP crystal to generate a 532 nm beam. This beam was then split, with a portion being used for the visible portion of the experiment and the second portion was sent to a OPG/OPA stage utilizing two counter rotating KTP crystals to generate a near IR beam between 720 and 870 nm. This near IR beam was then difference frequency mixed with a portion of the fundamental beam through two counter rotating KTA non-linear crystals. This then generated a tunable IR beam between 2000 and $4000\,cm^{-1}$. The energy at $2875\,cm^{-1}$ was $400\,\mu J$ with a fwhm of $10\,cm^{-1}$. This laser system was used for ethylene hydrogenation on Pt (1 0 0).

Both the IR and visible beams are p-polarized and are both spatially and temporally overlapped on a single crystal mounted in a UHV chamber. The visible beam makes an angle of $50°$ with respect to surface normal while the IR beam is at $55°$ with respect to surface normal. The generated SFG beam is then sent through a monochromater and the signal intensity is detected by a photomultiplier tube and integrated by a gated integrator.

3.2. UHV/high-pressure reaction chamber

Single crystal samples were mounted in a UHV/reaction chamber pumped by a turbomolecular pump and an ion pump to a base pressure of 2×10^{-10} Torr. The experimental apparatus has been described in detail elsewhere [17]. The chamber was equipped with a retarding field analyzer (RFA) for Auger electron spectroscopy and low energy electron diffraction (LEED). By use of resistive heating, the sample could be heated up to a temperature of 1200 K, and cooled under vacuum with liquid nitrogen to 140 K. The samples were cleaned in UHV by

repeated cycles of Ar^+ bombardment and annealing at temperatures up to 1200 K. After the sample was clean, gases were introduced through a gas manifold system. During high-pressure catalytic reactions, the sample was isolated from the vacuum pumps by a gate valve. A recirculation pump was used to mix the gases in the chamber, and a septum in the recirculation line was used to sample the gas for analysis by gas chromatography. For SFG experiments, the chamber had input and output windows made of CaF_2 to allow the IR light to enter the chamber.

To identify vibrational peaks in the high-pressure catalytic reaction experiments, low-pressure experiments were first performed in which possible intermediate species were introduced into the chamber. Not only do the low-pressure experiments help in the assignment of high-pressure intermediate species, they also allow the correlation of the SFG spectra with results of previous low-pressure vibrational studies of these systems.

3.3. Cyclohexene hydrogenation and dehydrogenation: a structure sensitive reaction

Before the advent of SFG, there have been many different types of spectroscopies used to study the adsorption of cyclohexene on Pt surfaces. These spectroscopic methods include EELS, HREELS, and IRAS [18–22]. The results of these studies show that cyclohexene dehydrogenates to form benzene through a C_6H_9 intermediate. The techniques used in these studies are limited to low-pressure studies and it is possible that there are different reactive intermediates on Pt surfaces under high-pressure catalytic reaction conditions. Because of this limitation, it was not possible to investigate the effect of the surface structure during cyclohexene dehydrogenation under reaction conditions. In order to determine the effect of structure, a high-pressure technique such as SFG is needed.

Using SFG, a comparison between cyclohexene hydrogenation and dehydrogenation over Pt (1 1 1) and Pt (1 0 0)(5 × 20) single crystals at high pressures and temperatures is made to determine how the surface structure influences these reactions. As a reference to high-pressure experiments, similar cyclohexene on Pt UHV experiments were performed in this laboratory using SFG. The vibrational spectroscopic results

from these UHV studies agree with the observations of others [7].

After the single crystal was cleaned, the bell jar was sealed off from the pumps, and 10 Torr of cyclohexene, 100 Torr of hydrogen, and 650 Torr of He were introduced into the chamber. After the initial room temperature SFG spectra and GC data were acquired, the sample was then heated in 25 degree increments up to 600 K while monitoring spectroscopic changes of surface species using SFG and monitoring the gas composition. Turnover rates were calculated at each temperature using the GC data and are plotted in Fig. 1a and b for cyclohexene on Pt (1 1 1) and Pt (1 0 0), respectively. Both the hydrogenation and dehydrogenation rates are negligible on both surfaces at 300 K. As the crystals are heated, the hydrogenation rate rises, and reaches a maximum of 78 molecules per site per second at 400 K for Pt (1 1 1), and a maximum of 38 molecules per site per second at 425 K for Pt (1 0 0). The rate of dehydrogenation of cyclohexene becomes measureable around the temperature for the maximum hydrogenation turnover rate on both crystals. As the dehydrogenation rate increases with temperature, the hydrogenation rate decreases. The rate of dehydrogenation increases on Pt (1 1 1) until it reaches a maximum of 58 molecules per site per second at 475 K, while on the Pt (1 0 0) surface, the maximum dehydrogenation rate is determined to be 75 molecules per site per second at 500 K.

Assuming that the dehydrogenation turnover rate is negligible in the region of increasing hydrogenation turnover rate, the activation energy for cyclohexene hydrogenation is calculated to be 8.9 and 15.5 kcal mol^{-1} for Pt (1 1 1) and Pt (1 0 0), respectively. Considering the fact that the cyclohexene hydrogenation rate decreases after it increases to a maximum while the dehydrogenation process increases, indicates that the two processes must be related to a change in the active surface sites for the two processes. Otherwise, the hydrogenation reaction would obey the Arrhenius law over the entire temperature range.

By analyzing the SFG data at each temperature during the reaction, the turnover rates can be correlated with the features in the SFG spectra. The SFG spectra for the temperature at which the gases were introduced, the temperature at which the hydrogenation rate is at the maximum, and the temperature at which the dehydrogenation rate is at a maximum are
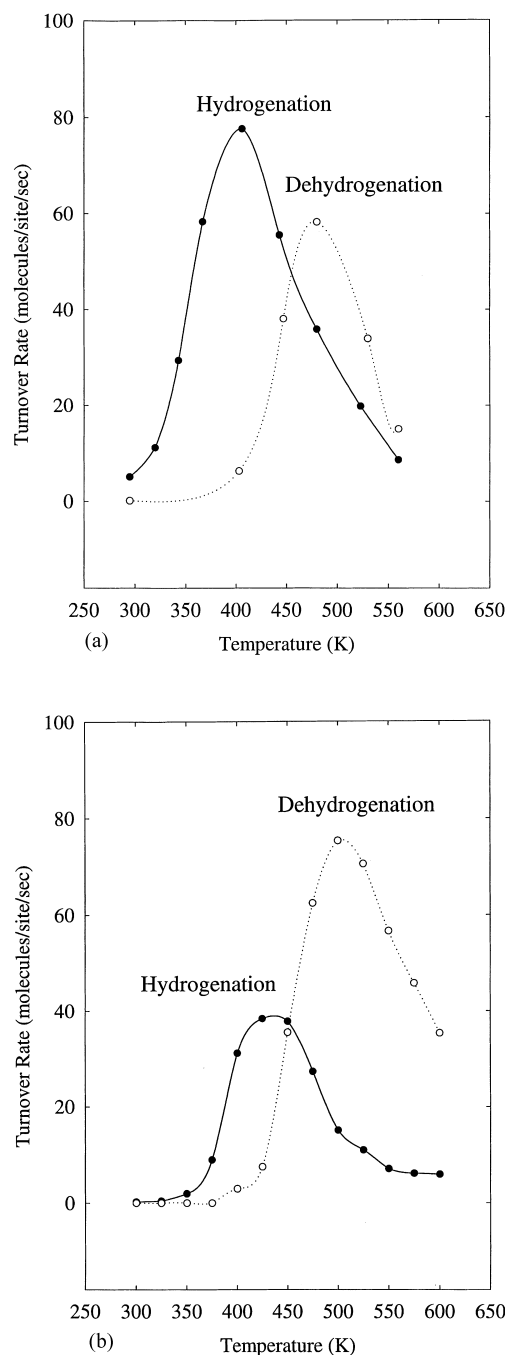

Fig. 1. The temperature dependence of cyclohexene hydrogenation and dehydrogenation turnover rates under 10 Torr cyclohexene, 100 Torr of H$_2$, and 650 Torr He. (a) Pt (1 1 1); (b) Pt (1 0 0).

shown in Fig. 2a and b for Pt (1 1 1) and Pt (1 0 0), respectively. On Pt (1 1 1), a sharp feature at 2755 cm^{-1} is observed at 295 K, which can be assigned to 1,4-cyclohexadiene [8]. The weaker features at higher frequencies are attributed to 1,3-cyclohexadiene. It is important to note that there is no evidence of a c-C$_6$H$_9$ intermediate as observed under UHV conditions. At 300 K on Pt (1 0 0), there is a weak feature corresponding to 1,4-cyclohexadiene. Larger features at higher frequency are observed on Pt (1 0 0) which are assigned to 1,3-cyclohexadiene.

At the maximum hydrogenation rate at 403 and 425 K for Pt (1 1 1) and Pt (1 0 0), respectively, the two similar SFG spectra indicate the presence of 1,3-cyclohexadiene as the major species on the surface. This spectral evidence indicates that cyclohexene hydrogenation proceeds through a 1,3-cyclohexadiene intermediate. As the temperature is increased to the maximum rate for the dehydrogenation process, differences between the two spectra are observed once again. Both 1,3- and 1,4-cyclohexadiene are observed on Pt (1 1 1) at 475 K. Unlike Pt (1 1 1), the Pt (1 0 0) surface at 500 K shows only 1,3-cyclohexadiene. Considering the differences in the two SFG spectra and the difference of the turnover rates for the maximum dehydrogenation, a reaction pathway is proposed for cyclohexene dehydrogenation on both Pt surfaces. On Pt (1 1 1), dehydrogenation can proceed through either a 1,3 or 1,4-cyclohexadiene intermediate whereas on Pt (1 0 0), dehydrogenation only occurs through a 1,3-cyclohexadiene intermediate. Fig. 3 shows schematically the reaction pathways for both surfaces.

Because cyclohexene dehydrogenation occurs faster on Pt (1 0 0) than on Pt (1 1 1) and because 1,4-cyclohexadiene is absent from the Pt (1 0 0) surface, it is believed that 1,4-cyclohexadiene formation is a competing reaction pathway for dehydrogenation which essentially inhibits the overall rate of the dehydrogenation process. This is reasonable considering that 1,4-cyclohexadiene must isomerize to 1,3-cyclohexadiene before it can completely dehydrogenate to form benzene.

3.4. Ethylene hydrogenation: a structure insensitive reaction

Unlike cyclohexene dehydrogenation, which is a structure sensitive reaction, ethylene hydrogenation is
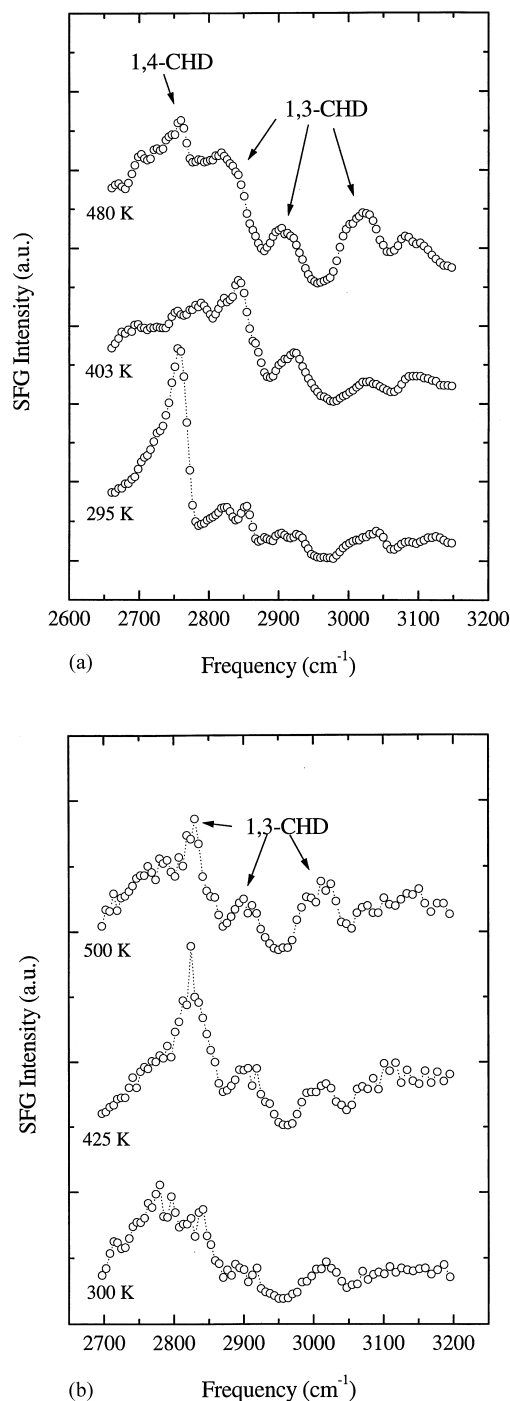

Fig. 2. SFG spectra of reaction intermediates adsorbed on the surface during cyclohexene hydrogenation and dehydrogenation under 10 Torr cyclohexene, 100 Torr of H$_2$, and 650 Torr He. (a) Pt (1 1 1); (b) Pt (1 0 0).

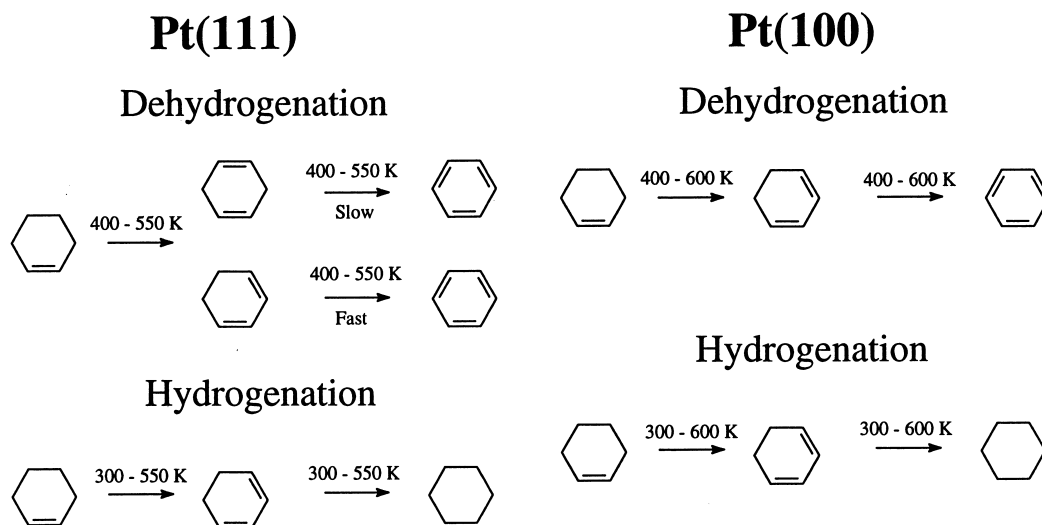# Pt(111) Pt(100)

Dehydrogenation Dehydrogenation

Fig. 3. Proposed reaction pathways for cyclohexene hydrogenation and dehydrogenation on Pt (1 1 1) and Pt (1 0 0).

a structure insensitive reaction in which the reaction rate is independent on the surface structure of platinum particles. SFG is an excellent technique to study ethylene hydrogenation by comparing the results between two different crystal faces of Pt to determine whether or not the surface species are the same on the two faces.

During the 1930s, Horiuti and Polyani proposed the first mechanism for the hydrogenation of the simplest olefin, ethylene, on a platinum surface [23]. Their model proposed ethylene adsorbs to a clean platinum surface by first breaking one of the double bonds and then forming two s-bonds with the metal surface. This intermediate is known as di-σ-bonded ethylene. This di-σ-bonded species would then hydrogenate stepwise to ethane through an ethyl intermediate.

Surface techniques such as ultraviolet photoemission spectroscopy (UPS) have since been used under UHV conditions to study the mechanism of ethylene hydrogenation on platinum single crystals. It was shown that below 52 K, ethylene physisorbs through the π-bond, referred to as π-bonded ethylene [24]. As the temperature is heated above 52 K, the π-bond is broken, and di-σ-bonded ethylene is formed [25]. As the temperature is further increased, di-σ-bonded ethylene dehydrogenates to ethylidyne ($MC\equiv CH_3$) by transferring a hydrogen atom from one carbon atom

to the other [26]. At higher temperatures, ethylidyne decomposes into graphitic precursors [27].

Ethylidyne is not believed to be a reaction intermediate in ethylene hydrogenation. Davis and coworkers showed using ^{14}C labeling that ethylidyne hydrogenation was several orders of magnitude slower than the overall hydrogenation of ethylene to ethane [28]. Further, Beebe and Yates, using in situ infrared transmission spectroscopy, showed that the reaction rate was the same on a Pd/Al_2O_3 supported catalyst whether the surface was covered with or without ethylidyne [29]. These studies indicate that ethylidyne is a spectator species, and not an active participant in ethylene hydrogenation.

To determine the importance of π-bonded ethylene and di-σ-bonded ethylene, Mohsin and coworkers, using transmission infrared spectroscopy, showed that both species are hydrogenated on a supported Pt/Al_2O_3 catalyst as hydrogen is flowed over the surface [30]. In addition, Mohsin and coworkers showed that only di-σ-bonded ethylene is converted to ethylidyne in the absence of hydrogen when the catalyst is heated. These studies, however, were not performed under actual high-pressure reaction conditions because gas phase ethylene interferes with infrared experiments. Since gas phase ethylene does not generate SFG signal, SFG is an excellent technique to study ethylene hydrogenation in situ under high-pressure

reaction conditions. In this work, ethylene hydrogenation studies were performed on Pt (1 0 0) and Pt (1 1 1).

Ethylene adsorption studies were first performed on both crystal surfaces to help in the assignment of peaks observed under high-pressure reaction conditions [5]. Di-σ-bonded ethylene was formed on Pt (1 1 1) by exposing the surface to 4 L of ethylene at 220 K (Fig. 4a). As this surface is annealed to higher temperatures, di-σ-bonded ethylene converts to ethylidyne (Fig. 4b) [6]. Both di-σ-bonded ethylene and ethylidyne will form on Pt (1 0 0) if the surface is exposed to a static pressure of 1×10^{-7} Torr of ethylene (Fig. 5). On both Pt (1 1 1) and Pt (1 0 0), the ethylidyne stretching frequency was observed around 2880 cm^{-1} and the di-σ-bonded ethylene stretching frequency was observed at 2910 cm^{-1}. Both ethylidyne and di-σ-bonded ethylene were previously found to sit in fcc three-fold hollow sites LEED with molecular axis of di-σ-bonded ethylene is tilted with respect to the surface plane by about 22° [31,32]. The surface of the Pt (1 0 0) crystal face reconstructs to a pseudo-hexagonal structure, known as Pt (1 0 0)(5 × 20), resembling the hexagonal structure of Pt (1 1 1) when properly cleaned. As the Pt (1 0 0)(5 × 20) surface was exposed to 1×10^{-7} Torr of ethylene, the surface structure was monitored with LEED, and the surface was observed to reconstruct back to the 1 × 1 structure. This is interesting considering ethylidyne and di-σ-bonded ethylene sit in fcc three-fold sites. Because it appears that the C–H bond of di-σ-bonded ethylene is unperturbed on the Pt (1 0 0) surface as compared with the Pt (1 1 1) surface, it is likely that ethylidyne and di-σ-bonded ethylene hold the three-fold site in place as it first adsorbs on the Pt (1 0 0)(5 × 20) surface.

High-pressure ethylene hydrogenation reactions were performed on both the Pt (1 1 1) and Pt (1 0 0) surfaces by introducing 100 Torr of H$_2$, 35 Torr of ethylene, and 625 Torr of He. The temperature of the crystal was maintained at room temperature as SFG spectra were acquired and gas phase analysis was measured using GC. The measured turnover rates were measured to be 11 ± 1 and 12 ± 1 molecules per site per second for Pt (1 1 1) and Pt (1 0 0), respectively. The fitted SFG spectra for ethylene hydrogenation on Pt (1 1 1) and Pt (1 0 0) are shown in Fig. 6a and b, respectively. Both ethylidyne and di-σ-bonded ethylene are the main features on both crystal faces.
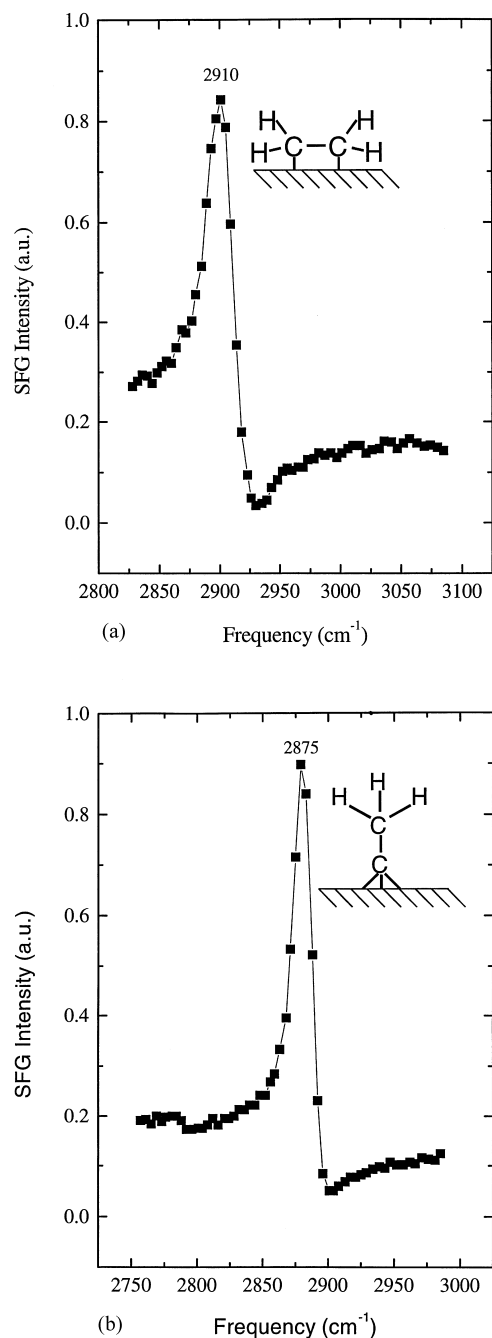

Fig. 4. (a) SFG spectrum of di-σ-bonded ethylene adsorbed on Pt (1 1 1) at 200 K. (b) SFG spectrum of ethylidyne adsorbed on Pt (1 1 1) at 300 K.
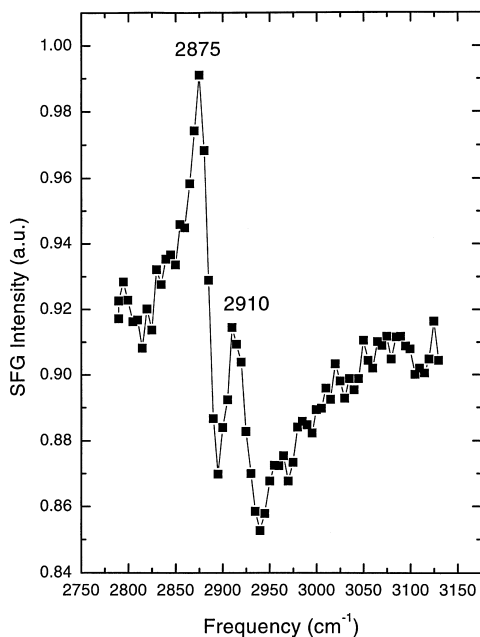
Fig. 5. SFG spectrum of di-σ-bonded ethylene and ethylidyne formed on Pt (1 0 0) at 300 K under a static pressure of 1×10^{-7} Torr of ethylene.

The measured strengths of the vibrational mode (A_q) are shown in parenthesis at the end of the indicated species names next to the peaks. From the values of A_q, it is observed that the ratio of ethylidyne to di-σ-bonded ethylene is different on the two crystal surfaces. On Pt (1 1 1), the values of A_q for ethylidyne (4.0) and di-σ-bonded ethylene (5.0) are roughly the same, whereas the value of A_q for di-σ-bonded ethylene (2.1) on Pt (1 0 0) is roughly three times as large as ethylidyne (5.7). This indicates that the relative concentration of ethylidyne and di-σ-bonded ethylene are different on the two surfaces, essentially indicating that there is a higher concentration of ethylidyne on the Pt (1 1 1) surface. Noticing that the relative concentrations of these species are different for the two crystal faces while their turnover rates are essentially the same, indicates that neither ethylidyne nor di-σ-bonded ethylene are the reactive intermediates on the surface.

The most likely reactive intermediates for ethylene hydrogenation are weakly bound species such as π-bonded ethylene and ethyl. Under the conditions reported above, the only evidence of a weakly bound
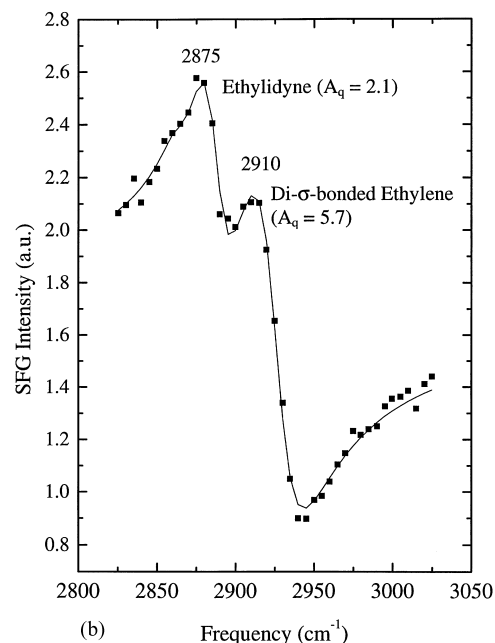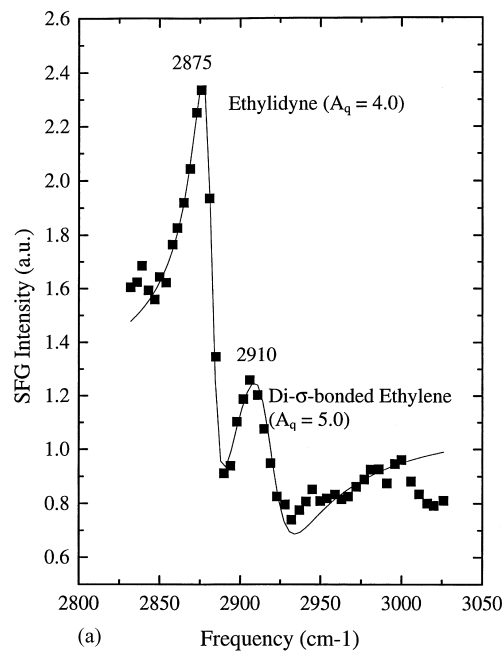

Fig. 6. SFG spectra of adsorbed species during ethylene hydrogenation under 35 Torr of ethylene, 100 Torr of H_2, and 625 Torr of He. (a) Pt (1 1 1); (b) Pt (1 0 0).

species is a shoulder at $2850\,cm^{-1}$ on both surfaces which corresponds to the fermi resonance of an ethyl species. SFG spectra during ethylene hydrogenation with high pressures of H_2 show stronger evidence that ethyl species exist under reaction conditions [33]. The combined coverage of ethylidyne and di-σ-bonded ethylene is approximately 35% of a monolayer, or between 60 and 70% of a saturation coverage. Because there is a high concentration of ethylidyne and di-σ-bonded ethylene, the concentration of the active surface intermediates may be at the detection limits of SFG. It is important to note that the concentration of the reactive intermediates are most likely the same on both surfaces since the reaction rate for ethylene hydrogenation is the same on both surfaces.

4. Summary and conclusions

In the results discussed above, it is clear that SFG is a unique tool that allows the detection of vibrational spectra of adsorbed molecules present on single crystal surfaces under catalytic reaction conditions. Not only is it possible to detect active surface intermediates, it is also possible to detect spectator species which are not responsible for the measured turnover rates. By correlating high-pressure SFG spectra under reaction conditions and GC kinetic data, it is possible to determine which species are important under reaction intermediates.

Because of the flexibility of this technique for studying surface intermediates, it is possible to determine how the structures of single crystal surfaces affect the observed rates of catalytic reactions. As an example of a structure sensitive reaction, the hydrogenation and dehydrogenation of cyclohexene was explored using SFG. Under UHV conditions, cyclohexene dehydrogenates to benzene through a c-C_6H_9 intermediate that is not observed under high-pressure reaction conditions. By comparing the SFG spectra and GC kinetic data for cyclohexene hydrogenation and dehydrogenation, it was determined that 1,3-cyclohexadiene is the important reaction intermediate for cyclohexene hydrogenation on both surfaces. For cyclohexene dehydrogenation, it was observed that both 1,3-cyclohexadiene and 1,4-cyclohexadiene are present on Pt (1 1 1), whereas only 1,3-cyclohexadiene was present on the Pt (1 0 0)

surface. Dehydrogenation has been shown that it can proceed through either 1,3- or 1,4-cyclohexadiene, but it proceeded faster through 1,3-cyclohexadiene. Because 1,4-cyclohexadiene is not present on the surface of Pt (1 0 0) under dehydrogenation conditions, dehydrogenation can proceed faster on Pt (1 0 0) than on Pt (1 1 1). Essentially, there are two competing reactions on Pt (1 1 1), one fast and one slow, whereas there is only a fast reaction pathway on Pt (1 0 0). The structure sensitivity can be explained by the predominance of one of the two reaction intermediates, which provides a more rapid reaction pathway than the other reaction intermediate.

As an example of a structure insensitive reaction, ethylene hydrogenation was explored on both Pt (1 1 1) and Pt (1 0 0). The rates were determined to be essentially the same. It was observed that both ethylidyne and di-σ-bonded ethylene were present on the surface under reaction conditions on both crystals, although in different concentrations. This result shows that these two species are not responsible for the measured turnover rate, as it would be expected that one of the two crystals would be more active than the other, since the concentration of the surface intermediate would be different on the two crystals. The most likely active intermediates are weakly adsorbed molecules such as π-bonded ethylene and ethyl. These species are not easily detected because their cocentration lies at the detection limit of SFG. The SFG spectra and GC data essentially show that ethylene hydrogenation is structure insensitive for Pt (1 1 1) and Pt (1 0 0).

SFG has proven to be a unique and excellent technique for studying adsorbed species on single crystal surfaces under high-pressure catalytic reactions. Coupled with kinetic data obtained from gas chromatography measurements, it can give much insight into how the structure of a single crystal surface affects the chemistry of a catalytic reaction by detecting surface species under reaction conditions.

References

[1] M. Boudart, Adv. Catal. 20 (1969) 153.

[2] F. Zaera, G.A. Somorjai, J. Am. Chem. Soc. 106 (1984) 2288.

[3] N.O. Spencer, R.C. Schoonmaker, G.A. Somorjai, Nature 294 (5842) (1981) 643–644.

[4] R.K. Herz, W.D. Gillespie, E.E. Petersen, G.A. Somorjai, J. Catal. 67 (1981) 371.

[5] P.S. Cremer, X. Su, Y.R. Shen, G.A. Somorjai, J. Am. Chem. Soc. 118 (1996) 2942.

[6] P.S. Cremer, X. Su, Y.R. Shen, G.A. Somorjai, J. Phys. Chem. 100 (40) (1996) 16302.

[7] X. Su, K. Kung, J. Lahtinen, Y.R. Shen, G.A. Somorjai, Catal. Lett. 54 (1998) 9.

[8] X. Su, Y.R. Shen, K.Y. Kung, J. Lahtinen, G.A. Somorjai, J. Mol. Catal. A 141 (1999) 9.

[9] Y.R. Shen, Surf. Sci. 299/300 (1994) 551.

[10] Q. Du, R. Superfine, E. Freysz, Y.R. Shen, Phys. Rev. Lett. 70 (1993) 2313.

[11] Y.R. Shen, Nature 337 (1989) 519.

[12] Y.R. Shen, The Principles of Nonlinear Optics, Wiley, New York, 1984.

[13] P. Guyot-Sionnest, J.H. Hunt, Y.R. Shen, Phys. Rev. Lett. 59 (1987) 1597.

[14] C.D. Bain, J. Chem. Soc., Faraday Trans. 91 (1995) 1281.

[15] C. Hirose, H. Yamamoto, N. Akamatsu, K. Domen, J. Chem. Phys. 97 (1993) 10064.

[16] D. Zhang, J. Huang, Y.R. Shen, C. Shen, J. Opt. Soc. Am. 10 (1993) 1758.

[17] P.S. Cremer, X. Su, Y.R. Shen, G.A. Somorjai, J. Am. Chem. Soc. 118 (1996) 2942.

[18] M.E. Bussell, F.C. Henn, C.T. Campbell, J. Phys. Chem. 96 (1992) 5965.

[19] J.A. Rodriguez, C.T. Campbell, J. Phys. Chem. 93 (1989) 826.

[20] C.L.A. Lamont, M. Borbach, R. Martin, P. Gardner, T.S. Jones, H. Conrad, A.M. Bradshaw, Surf. Sci. 374 (1997) 215.

[21] D.P. Land, W. Erley, H. Ibach, Surf. Sci. 289 (1993) 773.

[22] R. Martin, P. Gardner, M. Tushaus, C.H. Bonev, A.M. Bradshaw, T.S. Jones, J. Electron. Spectrosc. Relat. Phenom. 54/55 (1990) 773.

[23] I. Horiuti, M. Polanyi, Trans. Faraday Soc. 30 (1934) 1164.

[24] A. Cassuto, J. Kiss, J. White, Surf. Sci. 255 (1991) 289.

[25] H. Ibach, S. Lehwald, Surf. Sci. 117 (1982) 685.

[26] P. Cremer, C. Stanners, J. Niemantsverdriet, Y. Shen, G. Somorjai, Surf. Sci. 328 (1993) 111.

[27] T. Land, T. Michely, R. Behm, J. Hemminger, G. Comsa, J. Chem. Phys. 97 (9) (1992) 6774.

[28] S. Davis, F. Zaera, B. Gordon, G. Somorjai, J. Catal. 92 (1985) 250.

[29] T. Beebe, J. Yates, J. Am. Chem. Soc. 108 (1986) 663.

[30] S. Mohsin, M. Trenary, H. Robota, J. Phys. Chem. 92 (1988) 5229.

[31] U. Starke, A. Barbieri, N. Materer, M.A. Van Hove, G.A. Somorjai, Surf. Sci. 286 (1993) 1–14.

[32] R. Döll, C.A. Gerken, M.A. Van Hove, G.A. Somorjai, Surf. Sci. 374 (1997) 151–161.

[33] K.M. McCrea, J.S. Parker, G.A. Somorjai, in preparation.