Hydrogenation of the alpha,beta-Unsaturated Aldehydes Acrolein, Crotonaldehyde, and Prenal over Pt Single Crystals: A Kinetic and Sum-Frequency Generation Vibrational Spectroscopy Study

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Acrolein, Crotonaldehyde, and Prenal over Pt Single Crystals: A Kinetic and Sum-Frequency Generation Vibrational Spectroscopy Study

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TITLE RUNNING HEAD: Hydrogenation of $\alpha,\beta$-unsaturated aldehydes over Pt(111)/Pt(100)

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ABSTRACT.

Sum-frequency generation vibrational spectroscopy (SFG-VS) and kinetic measurements using gas chromatography have been used to study the surface reaction intermediates during the hydrogenation of three $\alpha,\beta$-unsaturated aldehydes, acrolein, crotonaldehyde, and prenal, over Pt(111) at Torr pressures (1 Torr aldehyde, 100 Torr hydrogen) in the temperature range of 295K to 415K. SFG-VS data showed that acrolein has mixed adsorption species of $\eta_2$-di-$\sigma$(CC)-trans, $\eta_2$-di-$\sigma$(CC)-cis as well as highly coordinated $\eta_3$ or $\eta_4$ species. Crotonaldehyde adsorbed to Pt(111) as $\eta_2$ surface intermediates. SFG-VS during prenal hydrogenation also suggested the presence of the $\eta_2$ adsorption species, and became more highly coordinated as the temperature was raised to 415K, in agreement with its enhanced C=O hydrogenation. The effect of catalyst surface structure was clarified by carrying out the hydrogenation of crotonaldehyde over both Pt(111) and Pt(100) single crystals while acquiring the SFG-VS spectra in situ. Both the kinetics and SFG-VS showed little structure sensitivity. Pt(100) generated more decarbonylation “cracking” product while Pt(111) had a higher selectivity for the formation of the desired unsaturated alcohol, crotylalcohol.

1. Introduction

The selective hydrogenation of an unsaturated C=C bond in the presence of a C=O carbonyl group of the same molecule has been a subject of much research in recent years.
Both experimental and theoretical work has been devoted to this topic and comprehensive reviews of the subject have been published\textsuperscript{1,2}. One product of this reaction, the unsaturated alcohol, is an important intermediate in both the pharmaceutical and fragrance industries. However, it is quite difficult to achieve a high selectivity and activity for the unsaturated alcohol product because the hydrogenation of the C=C is thermodynamically preferred by roughly 35 kJ/mol\textsuperscript{2}.

The platinum group metals are the catalysts most frequently employed during this reaction, but the selectivity for the desired unsaturated alcohol is relatively low for these catalysts. Over platinum, the selectivity for unsaturated alcohol has been shown to improve upon alloying with another metal, for instance Fe\textsuperscript{3} or Sn\textsuperscript{4}, as well as upon the addition of various promoters\textsuperscript{5}, such as potassium on the surface. Catalyst structure, such as the (111) or (100) crystal face of a metal, has also been suggested to play a role in the reaction selectivity\textsuperscript{6}.

Also effecting the selectivity in the hydrogenation of α,β-unsaturated aldehydes is the amount of steric hindrance to adsorption added to the C=C bond by the placement of bulky groups, such as phenyl or methyl groups, on this side of the molecule. Hoang-Van et al\textsuperscript{7} reported on the hydrogenation of acrolein over various platinum catalysts. Each of the widely used Pt based catalysts (Pt black, Pt-Al, Pt-Si) showed greater than 99\% selectivity for the hydrogenation of the C=C to yield propionaldehyde (Scheme 1). In comparison, for the hydrogenation of prenal, the same molecule as acrolein with two methyl groups added to the C=C bond, Birchem et al\textsuperscript{4} show at 353K the dominant product to be the unsaturated alcohol, a complete reversal of the selectivity seen for acrolein hydrogenation.
In this work, the hydrogenation of acrolein, crotonaldehyde, and prenal (Schemes 1-3) was carried out over Pt(111) while using sum frequency generation vibrational spectroscopy (SFG-VS) to monitor the surface reaction intermediates. These spectra are then compared to published DFT calculations to assist in the interpretation. Crotonaldehyde, with a reaction selectivity intermediate between prenal hydrogenation and acrolein hydrogenation, was chosen to elucidate the effect that catalyst structure has on this reaction. Reaction kinetics using gas chromatography and SFG-VS spectra were taken for crotonaldehyde hydrogenation over Pt(111) and Pt(100) in the temperature range from 150K to 415K.

2. Experimental Section

Materials

Crotonaldehyde (99.5%, Fluka) and 3-methylcrotonaldehyde (97%, Sigma-Aldrich Inc.) were subjected to several freeze-pump-thaw cycles prior to use and the purities were checked by means of gas chromatography and quadrupole mass spectroscopy. Acrolein was obtained in gas phase from Airgas with balance of research grade argon and purity verified with quadrupole mass spectroscopy to be 99%.

The high-pressure/ultra-high vacuum system

All experiments reported here were carried out in a high-pressure/ultrahigh-vacuum (HP/UHV) system. The UHV chamber is operated at a base pressure of $2 \times 10^{-10}$ Torr and is isolated from the HP cell by a gate valve. The UHV system is equipped with an Auger electron spectrometer (AES), a quadrupole mass spectrometer (Stanford Research Systems) and an ion bombardment gun (Eurovac). The HP cell consists of two CaF$_2$ conflat windows that allow transmission of infrared (IR), visible (VIS) and sum frequency radiation for sum frequency generation (SFG) experiments. The product gases in the HP cell are constantly
mixed via a recirculation pump and kinetic data is acquired by periodically sampling the reaction mixture and analyzing the relative gas phase composition in a flame ionization detector (FID) of a gas chromatograph (Hewlett Packard HP 5890 on a 5% Carbowax 20M packed column).

**Sample preparation**

Prior to each experiment, the Pt(111) and Pt(100) crystal surfaces were cleaned in the UHV chamber by Ar\(^+\) (1 keV) sputtering for 20 min at approximately 3 x 10\(^{-5}\) Torr of Ar. After sputtering, the crystals were heated to 1103 K in the presence of O\(_2\) of 5 x 10\(^{-7}\) Torr and annealed at the same temperature for 2 min. The cleanliness of the crystal surfaces was verified by AES and the crystallographic structure verified with low energy electron diffraction (LEED). The samples were then transferred into the HP cell for SFG and kinetic studies.

**Sum Frequency generation vibrational spectroscopy**

For SFG measurements, an active/passive mode-locked Nd:YAG laser (Leopard D-20, Continuum) with a pulse width of 20 ps and a repetition rate of 20 Hz was used. The fundamental output at 1064 nm was sent through an optical parametric generation/amplification (OPA/OPG) stage where a tunable IR (2300-4000 cm\(^{-1}\)) and a second harmonic VIS (532 nm) beam were created. The IR (150 μJ) and VIS (200 μJ) beams were spatially and temporally overlapped on the crystal surface at angles of incidence of 55 and 60°, respectively, with respect to the surface normal. The generated SFG beam was collected and sent through a motorized monochromator equipped with a photomultiplier tube to detect the SFG signal intensity. The signal-to-noise ratio was further increased by using a gated integrator while the IR beam was scanned through the spectral region of interest. The
SFG signal, $I_{\text{SFG}}$, is related to the incoming visible ($I_{\text{VIS}}$) and infrared ($I_{\text{IR}}$) beam intensities, and second-order susceptibility of the media ($\chi^{(2)}$), according to eq 1:

$$I_{\text{SFG}}(\omega_{\text{SFG}}) \propto |\chi^{(2)}| I_{\text{VIS}}(\omega_{\text{VIS}}) I_{\text{IR}}(\omega_{\text{IR}}) \quad (1)$$

($\chi^{(2)}$) is enhanced when $\omega_{\text{IR}}$ is at resonance with a vibrational mode of the molecules, $q$, according to eq 2:

$$I_{\text{SFG}} \propto |\chi_{\text{NR}}^{(2)} e^{i\delta_{\text{NR}}} + \sum_{q} A_{q} (\omega_{\text{IR}} - \omega_{q} + i\Gamma_{q}) e^{i\phi_{q}}|^2 \quad (2)$$

where $\chi_{\text{NR}}^{(2)}$ is the nonresonant nonlinear susceptibility, $e^{i\delta_{\text{NR}}}$ is the phase associated with the nonresonant background, $A_{q}$ is the strength of the $q$th vibrational mode, $\omega_{\text{IR}}$ is the frequency of the incident IR laser beam, $\omega_{q}$ is the frequency of the $q$th vibrational mode, $\Gamma_{q}$ is the natural line width of the $q$th vibrational transition, and $e^{i\phi_{q}}$ is the phase associated with the $q$th vibrational transition. All SFG-VS spectra reported are data fit to a form of eq 2.

Since the gas phase in the HP cell absorbs some of the incoming IR radiation, the SFG signal was then normalized by using the following expression (eq 3):

$$I_{\text{SFG, norm}} = \frac{I_{\text{SFG}}}{\sqrt{I_{\text{IR, before}} I_{\text{IR, after}}}} \quad (3)$$

where $I_{\text{IR, before}}$ and $I_{\text{IR, after}}$ define the IR beam intensities measured before and after the HP cell. More information on the HP/UHV system and SFG measurement can be found elsewhere.8-12

3. Results and Discussion

3.1. Sum Frequency Generation Vibrational Spectroscopy of Acrolein, Crotonaldehyde, and Prenal Hydrogenation over Pt(111)

3.1.1. Acrolein Hydrogenation on Pt(111) – SFG-VS Results
Acrolein is the simplest $\alpha,\beta$-unsaturated aldehyde which makes it attractive for surface science study. As can be seen in Scheme 1, it contains only the conjugated carbonyl and alkene groups with no side groups. Using density functional theory analysis, Loffreda et al.\textsuperscript{13} examined possible adsorption modes of acrolein on Pt(111) at various coverages and determined adsorption energies and predicted a vibrational spectrum for each of the possible stable structures.

There are seven stable adsorption modes presented in the work mentioned above. First, the $\eta_1$ adsorption mode has the oxygen atom as the only part of the acrolein molecule which interacts with the Pt(111) surface. The $\eta_2$-cis and $\eta_2$-trans modes involve a di-$\sigma$ bond to two Pt atoms originating from the C=C of the acrolein. Clearly, the cis conformer being the one with the oxygen of the carbonyl pointing back towards the acrolein molecule, while in the trans form it points away. The $\eta_3$-cis and $\eta_3$-trans are the same as the $\eta_2$ adsorption modes with the exception that the oxygen atom of the carbonyl is pointing down to and bonding with the metal surface. Finally the $\eta_4$-cis and $\eta_4$-trans adsorption modes are bound to the surface via two di-$\sigma$ bonds, one originating from the C=C and one from the C=O.

Figure 1 shows the SFG vibrational spectrum of 1 Torr acrolein with no hydrogen added over a Pt(111) single crystal at 295K. Five vibrational resonances are seen in this C-H region. The “softest” vibrational resonance is present at 2785 cm$^{-1}$ which can be assigned to the aldehyde C-H stretch. The aldehyde C-H in gas phase acrolein is at 2800 cm$^{-1}$, so a 15 cm$^{-1}$ red-shift of this clearly identifiable mode occurs upon adsorption. To gain insight into the true bonding characteristics of the acrolein to the Pt(111) surface the vibrational spectra are compared to those predicted with DFT. Although there are often several structures that correspond to a given vibrational frequency, one can only accept structures if the other peaks
in the predicted spectrum are also present. In the DFT work of Loffreda et al\textsuperscript{13}, the only chemisorption mode of acrolein with a vibrational mode near this value is the \( \eta_2 \)-trans species. The rest of the resonances are seen at 2850 cm\(^{-1}\), 2930 cm\(^{-1}\), 3020 cm\(^{-1}\), and 3060 cm\(^{-1}\). The \( \eta_1 \) adsorption species, interacting with the Pt surface solely through the oxygen atom, may be ruled out due to the absence of any modes above 3100 cm\(^{-1}\) in the SFG-VS spectrum, likewise the \( \eta_4 \)-cis can be eliminated as an option. The mode observed at 2850 cm\(^{-1}\) corresponds best with the \( \eta_2 \)-cis C-H aldehyde vibrational mode. The two “soft” aldehyde peaks at 2850 cm\(^{-1}\) and 2785 cm\(^{-1}\) are quite indicative of the \( \eta_2 \) di-\( \sigma \)(CC) adsorption mode as none of the more highly coordinated surface species have C-H resonances that far to the red.

Figure 2 displays the SFG spectra as 100 Torr hydrogen is added and the temperature is raised to 415K. Upon the addition of hydrogen at room temperature the spectrum undergoes two changes. The soft aldehyde peak at 2785 cm\(^{-1}\), corresponding to the \( \eta_2 \)-trans surface species, disappears as well as the peak at 3020 cm\(^{-1}\). Due to the fact that those two modes disappear together, as well as the fact that DFT predicts the \( \eta_2 \)-trans adsorption mode to have absorptions in both those regions, the 3020 cm\(^{-1}\) peak is also assigned to a C-H vibration off of the di-\( \sigma \) bond of the \( \eta_2 \)-trans species (Figs. 1,2). Upon heating the Pt(111) crystal to 370K, a strong new peak appears at 2867 cm\(^{-1}\). The other resonances become very weak and the only one with appreciable signal remains at 2930 cm\(^{-1}\). Upon further heating the Pt(111) crystal to 415K, the only remaining peak is the 2867 cm\(^{-1}\) resonance corresponding to ethylidyne on the surface resulting from the decarbonylation of acrolein. The ethylidyne is red-shifted by about 10 cm\(^{-1}\) from its usual location on a clean Pt(111) crystal, but the coadsorption of CO and ethylidyne on Pt(111) has been previously reported to cause a slight
red-shift in the ethylidyne peak$^{14}$. The observation of ethylidyne on Pt(111) after acrolein adsorption was also noted by de Jesus and Zaera$^{15}$ using RAIRS.

According to the Gibbs free adsorption energy curves reported by Loffreda et al$^{16}$ for acrolein adsorption to Pt(111) the experimental conditions used here (1 Torr acrolein, 295-415K) likely crosses the 0 Gibbs free adsorption energy line as the temperature is raised, thus favoring desorption of the acrolein molecule. This is in agreement with the SFG-VS spectra, as by 415K the only species remaining on the surface is ethylidyne. Lastly, the peak observed at 2930 cm$^{-1}$ is indicative of a more highly coordinated $\eta_3$-cis or $\eta_4$-trans surface species. In relation to the DFT calculations, it is most closely matched with the $\eta_3$-cis species. Clearly, then, for acrolein adsorption and hydrogenation over Pt(111) there exists a mixed state of adsorption mode surface species.

In a later paper Loffreda et al$^{17}$ study the hydrogenation reaction pathway with DFT over the Pt(111) surface. Their conclusion was that the reaction actually favors the attack of the C=O carbonyl, but the desorption step of the resulting allyl alcohol has a very high barrier height compared to the reaction pathway involving the attack of the C=C and desorption of the propionaldehyde product. Thus, they conclude the surface will build up a high concentration of allyl alcohol, but the gas phase will show a high selectivity for the formation of propionaldehyde. In this work the frequency range from 2500-4000 cm$^{-1}$ was studied and there was no evidence found for the unsaturated alcohol on the surface as was proposed by Loffreda et al$^{17}$, although a species with the OH bond perfectly parallel to the surface cannot be ruled out due to the metal surface selection rule$^{18,19}$.

3.1.2. Crotonaldehyde Hydrogenation on Pt(111)– SFG-VS Results
The hydrogenation of crotonaldehyde (Scheme 2) has a selectivity intermediate between that of acrolein and prenal hydrogenation (Sec. 3.2). The addition of the methyl group improves the selectivity for the unsaturated alcohol, but it also adds complexity to the vibrational spectrum, especially in the C-H region. Figure 3 shows the spectrum for a multilayer of crotonaldehyde on Pt(111) at 150K in the absence of hydrogen, followed by the temperature dependent spectra of 1 Torr crotonaldehyde and 100 Torr hydrogen reacting over a Pt(111) single crystal from 295 to 415K. In the multilayer (bottom) at 150K, four vibrational resonances are seen. At 2750 cm$^{-1}$ a strong peak is seen for the trans aldehyde C-H vibration. The analysis of the other three peaks at 2830 cm$^{-1}$, 2935 cm$^{-1}$, and 2995 cm$^{-1}$ requires comparison to gas phase DFT calculations for interpretation. In this context, the peak at 2830 cm$^{-1}$ corresponds to the aldehyde C-H stretch of E-(s)-cis crotonaldehyde, the 2935 cm$^{-1}$ corresponds to the symmetric stretching in the methyl side group and the 2995 cm$^{-1}$ corresponds to both the asymmetric methyl stretch and the vinylic C-H stretches off the C=C bond.

The spectrum recorded at 295K in the presence of hydrogen in Figure 3 shows five vibrational resonances much different from the multilayer condensed onto Pt(111). First, the trans aldehyde C-H stretch around 2750 cm$^{-1}$ disappears by 295K. Four more resonances are seen at 2865 cm$^{-1}$, 2915 cm$^{-1}$, 2965 cm$^{-1}$, and 2995 cm$^{-1}$. The 2995 cm$^{-1}$ resonance has flipped from a positive going peak to a negative going peak due to a change in its relative phase as seen in the fit to eq. 2. Further, the absence of any peak at 2750 cm$^{-1}$ or below suggests that the $\eta_2$-di-$\sigma$(CC)-E-(s)-trans species is not present in significant surface concentration at 295K in 100 Torr H$_2$. Although the trans adsorbed species disappears as the temperature is raised and hydrogen is added, this does not necessarily mean it is no longer
participating in the reaction mechanism. The trans species could react more quickly than the cis surface species, in which case no appreciable surface concentration of the trans species would build up.

At 295K, once again in comparison to the DFT calculated frequencies\textsuperscript{20}, the frequencies agree quite well with the η\textsubscript{2}-di-σ(CC)-E-(s)-cis crotonaldehyde species (Fig. 3). As the Pt(111) crystal is heated to 415K the only notable change is the disappearance of the negative going peak at 2995 cm\textsuperscript{-1}.

### 3.1.3 Prenal Hydrogenation on Pt(111) – SFG-VS Results

Figure 4 displays the SFG-VS spectra of 1 Torr prenal both with and without 100 Torr hydrogen over Pt(111). A striking difference between these spectra and those discussed for acrolein and crotonaldehyde is the broad –OH hydrogen bonded peak centered around 3380 cm\textsuperscript{-1} present even before hydrogen is added to the system. The hydrogenation of prenal has been shown to be quite selective for the formation of the desired unsaturated alcohol\textsuperscript{3}. The buildup of –OH on the surface would indeed indicate that the desorption step of the alcohol is a rate limiting step as was proposed for acrolein hydrogenation by Loffreda et al.\textsuperscript{17} Upon heating, the –OH vibration is red-shifted, indicating a more electron donating interaction with the surface.

Once again, by comparing the observed spectra with the DFT calculated spectra for the various adsorption modes is informative. For the spectra (Figure 4, bottom) taken prior to the addition of hydrogen, a peak is visible at 2720 cm\textsuperscript{-1} which should clearly correspond to an intact aldehyde C-H. Other than the –OH peak discussed, vibrational peaks are observed at 2845 cm\textsuperscript{-1}, 2915 cm\textsuperscript{-1}, and 3015 cm\textsuperscript{-1}. Upon the addition of 100 Torr hydrogen, the 2720 cm\textsuperscript{-1} peak vanishes and the 3015 cm\textsuperscript{-1} peak becomes much weaker. The only changes in the
spectra as the crystal is heated to 415K is that the –OH band becomes more intense, and red-shifted, and a new peak grows in at 2945 cm\(^{-1}\). The peak growing in at 2945 cm\(^{-1}\) agrees well with the growing presence of either the \(\eta_3\)-di-\(\sigma\)(CC)-\(\sigma\)(O)-(s)-cis, corresponding to the asymmetric stretching in one of the methyl groups, or to the aldehyde C-H stretch of the \(\eta_4\)-di-\(\sigma\)(CC)-di-\(\sigma\)(CO)-(s)-trans species on the surface at higher temperatures. The high temperature spectrum is reversible. After heating to 415K and then returning the crystal to 295K the peak at 2945 cm\(^{-1}\) disappears again. This is proof that it is not a cracking product or poison on the surface, but a reversible change in surface intermediate.

3.2. Hydrogenation of Crotonaldehyde over Pt(111) and Pt(100): Kinetic and SFG-VS Results

The hydrogenation of crotonaldehyde was carried out with 1 Torr crotonaldehyde and 100 Torr hydrogen over both the Pt(111) and Pt(100) crystal faces to elucidate the effect that catalyst structure plays in this reaction. The industrially desired product crotyl alcohol, the unsaturated alcohol, results from the hydrogenation of the C=O (Scheme 2), while the thermodynamically favored product, butyraldehyde, results from the hydrogenation of the C=C. Further, the temperature range from 295K to 415K was used and apparent activation energies calculated for the reaction products over both surfaces.

Figure 5 shows the Arrhenius plots and reaction selectivities over both metal surfaces, and Table 2 displays the apparent activation energies for all reaction pathways. The activation energy for the formation of crotyl alcohol is significantly less than that for the formation of butyraldehyde. This is evident also in the reaction selectivities of Figure 5 which show a significantly enhanced selectivity for the formation of the unsaturated alcohol at low temperatures (35\(^\circ\) C). At such low catalytic temperatures however the turnover frequencies
(TOF, product molecules/Pt site/sec) are very low for all products, on the order of $10^{-3}$, while as the temperature is raised to 130° C the TOF for the formation of butyraldehyde approaches ~$10^0$ over both surfaces.

Pt(111) shows a higher selectivity for the formation of the unsaturated alcohol, especially at low temperatures, while Pt(100) shows a higher selectivity for the formation of the decarbonylation “cracking” product propylene (Fig 5). The selectivity for the totally saturated product butanol remained low, less than 1%, on both surfaces at the temperatures studied.

Figure 6 compares a spectrum taken over Pt(111) to one taken over Pt(100) under 1 Torr crotonaldehyde and 100 Torr hydrogen at 295K. The vibrational features between the two crystal faces were identical here and for all temperatures studied. This argues that the dominant surface reaction intermediates are the same for both crystal faces for the hydrogenation of crotonaldehyde. This is in contrast to theoretical work done by Delbecq et al\textsuperscript{21} which demonstrated significantly different adsorption modes for crotonaldehyde between the Pt(111) and Pt(100) surfaces. However, it is consistent with the reaction selectivities and kinetics above which demonstrated very similar activities and selectivities for the two surfaces, the primary difference simply being in the barrier heights for the various reaction pathways evidenced by the differing activation energies calculated allowing for some kinetic control of the product distribution.


Using a combination of SFG vibrational spectroscopy and kinetic measurements, along with detailed comparison to DFT calculations, the surface species during the catalytic hydrogenation of acrolein, crotonaldehyde, and prenal have been clarified. The effect that catalyst structure has on the hydrogenation of crotonaldehyde has been elucidated by
comparing both the reaction kinetics and SFG-VS spectra over Pt(111) and Pt(100) single crystals.

In the case of acrolein, a mixed adsorption state existed including $\eta_2$-cis and $\eta_2$-trans species as well as more highly coordinated $\eta_3$ or $\eta_4$ species. However, upon the addition of hydrogen the $\eta_2$-trans surface species vanished. Further, as the Pt(111) crystal was heated to 415K all of the surface intermediate peaks vanished except that of ethyldyne, forming from the decarbonylation of acrolein.

The reaction kinetics for crotonaldehyde hydrogenation showed a lower activation energy for the formation of the industrially desired crotylalcohol than for the formation of the thermodynamically favored butyraldehyde. Thus, at lower temperatures the selectivity for the desired product was enhanced.

For the adsorption of crotonaldehyde to Pt(111) at 150K, both cis and trans species were found with SFG-VS. However, in the presence of hydrogen at 295K and hotter the only surface species observed was $\eta_2$-cis. This may be an indication that the $\eta_2$-trans species is not stable at the higher temperature, or is simply the fastest one to react and desorb, not allowing a significant surface concentration to build up. The SFG-VS data, then, agree nicely with the reaction kinetics, given that the $\eta_2$ adsorption modes do not have the carbonyl interacting with the surface and the selectivity for the hydrogenation of the C=O was low in the case of crotonaldehyde hydrogenation.

Pt(111) and Pt(100) showed little structure sensitivity for this reaction. The Pt(111) had a somewhat higher selectivity for the formation of crotylalcohol, while Pt(100) had a higher selectivity for the decarbonylation “cracking” reaction. Further, the SFG-VS spectra of crotonaldehyde hydrogenation over both surfaces were identical.
For the hydrogenation of prenal over Pt(111), the SFG-VS results indicated the presence of an –OH group even without the presence of excess hydrogen. This is consistent with the flipped selectivity for the hydrogenation of prenal in which the dominant product is the unsaturated alcohol. SFG-VS spectra demonstrated the presence of the $\eta_2$ surface species definitively. Further, upon heating the Pt(111) crystal to 415K a highly coordinated $\eta_3$ or $\eta_4$ species grows in on the surface. This clear difference from crotonaldehyde also agrees with the difference in reaction selectivities. The C=O of prenal interacts with the surface at higher temperatures, unlike the case for crotonaldehyde, and the C=O is predominantly hydrogenated in prenal hydrogenation while the C=C is predominantly hydrogenated in crotonaldehyde hydrogenation.

ACKNOWLEDGMENT

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Scheme 1. The hydrogenation pathways for acrolein.

Scheme 2. The hydrogenation pathways for crotonaldehyde.

Scheme 3. The hydrogenation pathways for prenal.
Figure 5. Arrhenius plots (top) and reaction selectivities (bottom) for the hydrogenation of crotonaldehyde over Pt(111) (right) and Pt(100) (left). The major reaction products are butyraldehyde (□), crotylalcohol (○), propylene (♦), and butanol (▲).
<table>
<thead>
<tr>
<th>Product</th>
<th>Pt(111)</th>
<th>Pt(100)</th>
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<tr>
<td>Butyraldehyde</td>
<td>75</td>
<td>90</td>
</tr>
<tr>
<td>Crotylalcohol</td>
<td>35</td>
<td>38</td>
</tr>
<tr>
<td>Propylene</td>
<td>68</td>
<td>63</td>
</tr>
<tr>
<td>Butanol</td>
<td>59</td>
<td>79</td>
</tr>
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**Table 2.** Activation energies in kJ/mol for the various products of crotonaldehyde hydrogenation carried out over Pt(111) and Pt(100) with 1 Torr crotonaldehyde and 100 Torr hydrogen.
Figure 1. SFG vibrational spectrum of 1 Torr acrolein in the absence of hydrogen over Pt(111) at 295K. The “soft” aldehyde C-H modes at 2785 cm\(^{-1}\) and 2850 cm\(^{-1}\) clearly identify the presence of \(\eta_2\)-trans and \(\eta_2\)-cis adsorption modes respectively.
Figure 2. SFG-VS spectra of 1 Torr acrolein over the Pt(111) crystal surface. The bottom spectra was taken in the absence of hydrogen, then the subsequent spectra include the addition of 100 Torr hydrogen and heating the crystal to 415K. The acrolein peaks vanish and only ethylidyne remains as the crystal is heated.
Figure 3. SFG-VS spectra of crotonaldehyde hydrogenation over Pt(111). The bottom spectrum was taken at 150K after exposing the crystal to 15L crotonaldehyde to form a multilayer. The top three spectra were taken with 1 Torr crotonaldehyde and 100 Torr hydrogen over the Pt(111) crystal at the temperatures listed.
Figure 6. SFG-VS spectra of 1 Torr crotonaldehyde and 100 Torr hydrogen at 295K over Pt(100) (bottom) and Pt(111) (top). SFG-VS spectra over Pt(111) and Pt(100) showed identical features at all temperatures from 295-415K.
Figure 4. SFG-VS spectra of 1 Torr prenal over Pt(111) from 295K to 415K. The bottom one is before the addition of H$_2$, while the rest are with 100 Torr H$_2$. The –OH peak indicates alcohol on the surface at all temperatures. The “soft” modes at 2720 cm$^{-1}$ and 2845 cm$^{-1}$ are indicative of η$_2$ adsorption species. The 2945 cm$^{-1}$ peak is indicative of more highly coordinated η$_4$ or possibly η$_3$ adsorbed prenal species.