

Ethylene Hydrogenation on Pt(111) Monitored in Situ at High Pressures Using Sum Frequency Generation

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Abstract: Infrared–visible sum frequency generation (SFG) has been used to monitor the surface vibrational spectrum *in situ* during ethylene hydrogenation on Pt(111). Measurements were made near 1 atm of total pressure of ethylene and hydrogen and at 295 K. Kinetic information was obtained simultaneously with the surface vibrational spectroscopy by monitoring the reaction rate with gas chromatography. The macroscopic turnover rate and surface adsorbate concentration could then be correlated. During the reaction ethylidyne, di- σ -bonded ethylene, ethyl, and π -bonded ethylene were observed on the surface in various amounts depending on conditions. Ethylidyne, a spectator species during hydrogenation, competed directly for sites with di- σ -bonded ethylene and its surface concentration could be shown to be completely uncorrelated with the rate of hydrogenation. In contrast, π -bonded ethylene did not compete for sites with the ethylidyne overlayer and was observed on the surface regardless of the surface concentration of ethylidyne. Evidence points to the π -bonded species as being the primary intermediate in ethylene hydrogenation on Pt(111). The surface concentration of this species is about 0.04 ML (ML = monolayer) during reaction. Thus, the turnover rate per reaction intermediate is 25 times faster than the turnover rate if measured per surface platinum atom.

Introduction

A mechanism for the hydrogenation of the simplest olefin, ethylene, over a platinum surface was first proposed in the 1930's by Horiuti and Polanyi (Figure 1).¹ According to their model, ethylene chemisorbs on the clean metal surface by breaking one of the carbon–carbon double bonds. This species, which forms two σ bonds with the underlying metal substrate, is then stepwise hydrogenated through an ethyl intermediate to ethane. Evidence for an ethyl intermediate was found in the 1950's by Kemball et al. using deuterium labeling that showed ethylene molecules readily exchange hydrogen atoms during the hydrogenation process.² Kinetic studies showed that the rate at which ethylene hydrogenates is independent of the structure of the underlying metal atoms and therefore it is called a structure-insensitive reaction.³ The reaction has been observed to vary between half order and first order in hydrogen (depending upon temperature) and to be zero or slightly negative order in ethylene.⁴

Surface science investigations of the mechanism for ethylene hydrogenation began in the 1970's with model studies of ethylene adsorption on low miller index faces of platinum under ultrahigh vacuum (UHV) conditions. Ethylene adsorbed on Pt(111) in the absence of hydrogen was monitored with a variety of techniques that revealed the presence of several distinct surface species. Ultraviolet photoemission spectroscopy (UPS) showed that ethylene physisorbs through its π -orbital on clean Pt(111) below 52 K.⁵ This species is referred to as π -bonded

ethylene (Figure 2a). Its binding site has yet to be determined by low-energy electron diffraction (LEED) surface crystallography, but analogy to organometallic cluster chemistry tends to favor an atop site.^{6,7}

When heated above 52 K, ethylene irreversibly breaks the π bond and forms two σ bonds to the surface metal atoms and is called di- σ -bonded ethylene (Figure 2b). This species is sp^3 hybridized⁸ and resides in an fcc 3-fold hollow site on the Pt(111) surface as determined by LEED.⁹ Saturation coverage is 0.25 monolayers (ML),¹⁰ which means there is one di- σ -bonded ethylene molecule for every four underlying platinum surface atoms.

Above 240 K di- σ -bonded ethylene dehydrogenates to ethylidyne ($M\equiv CCH_3$) by transferring one hydrogen from one carbon to the other and losing a hydrogen (Figure 2c).¹¹ The dehydrogenation is accompanied by hydrogen atom recombination to H_2 , which then desorbs from the surface as molecular hydrogen near room temperature and can be readily monitored by thermal desorption mass spectrometry. Like di- σ -bonded ethylene, ethylidyne is also adsorbed in an fcc 3-fold hollow site as determined by LEED; however, its C–C bond axis is normal to the surface.¹² Scanning tunneling microscopy (STM) reveals that ethylidyne cannot be imaged unless the surface is cooled to 220 K.¹³ This suggests that the species is highly

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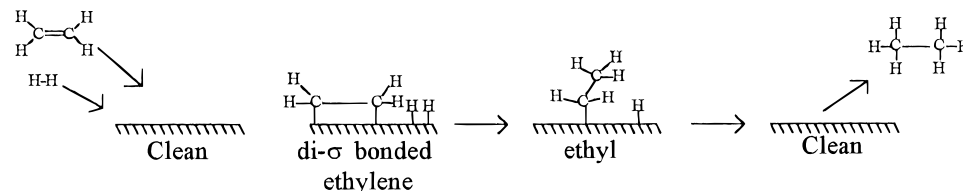


Figure 1. Horiuti–Polanyi mechanism for ethylene hydrogenation on platinum.

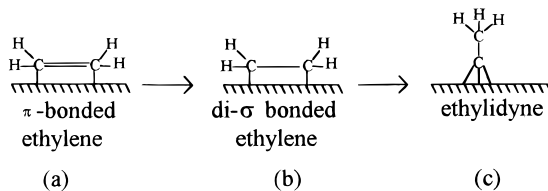


Figure 2. The thermal evolution of adsorbed ethylene on Pt(111). The dehydrogenation proceeds from (a) π -bonded ethylene at low temperature through (b) di- σ -bonded ethylene to (c) ethylidyne.

mobile on the surface at room temperature, most likely moving between 3-fold sites. Ethylidyne has a saturation coverage of 0.25 ML¹⁰ and upon annealing the ethylidyne/Pt(111) system above 500 K further dehydrogenation to graphitic precursors (such as C₂H and CH) takes place. Finally, above 700 K the hydrocarbon fragments decompose to graphite.¹³

In order to determine the role of each of the surface species in ethylene hydrogenation, their chemistry has been studied in the presence of hydrogen under reaction conditions. Several groups have investigated the role of ethylidyne. Davis et al. hydrogenated ¹⁴C-labeled ethylidyne on Pt(111) with near atmospheric pressure of H₂. Their results indicated that the rate of hydrogenation of the ethylidyne was several orders of magnitude slower than the overall turnover rate of hydrogenation of ethylene to ethane indicating that ethylidyne was not directly involved in the reaction.¹⁴ Beebe et al. monitored ethylene hydrogenation over a Pd/Al₂O₃ supported catalyst *in situ* by using transmission infrared spectroscopy. By varying the ratio of ethylene to hydrogen it was observed that hydrogenation occurred over surfaces both with and without an ethylidyne (\equiv CCH₃) overlayer.¹⁵ Rekoske et al. have repeated the transmission infrared work on Pt/Cab-O-Sil and concluded that the ethylidyne was not involved in the reaction in the case of a supported platinum catalyst.¹⁶ All evidence strongly suggests that ethylidyne is a spectator species not involved in ethylene hydrogenation.

The roles of chemisorbed and physisorbed ethylene have also been examined. Using transmission infrared spectroscopy, Moshin et al. have shown that both π -bonded and di- σ -bonded ethylene are hydrogenated when H₂ is flowed over a Pt/Al₂O₃ catalyst precovered with these species.¹⁷ Further, they found that upon annealing a surface covered with π -bonded and di- σ -bonded ethylene in the absence of hydrogen only the di- σ -bonded species was converted to ethylidyne while the π -bonded ethylene remains unaffected.

None of the infrared spectroscopy studies described above, however, allowed the monitoring of surface intermediates of ethylene hydrogenation when ethylene was flowing. This is because gas-phase ethylene greatly interferes with the infrared spectroscopy experiments.¹⁶ Hence, all experiments in which di- σ - and π -bonded ethylene were monitored required that

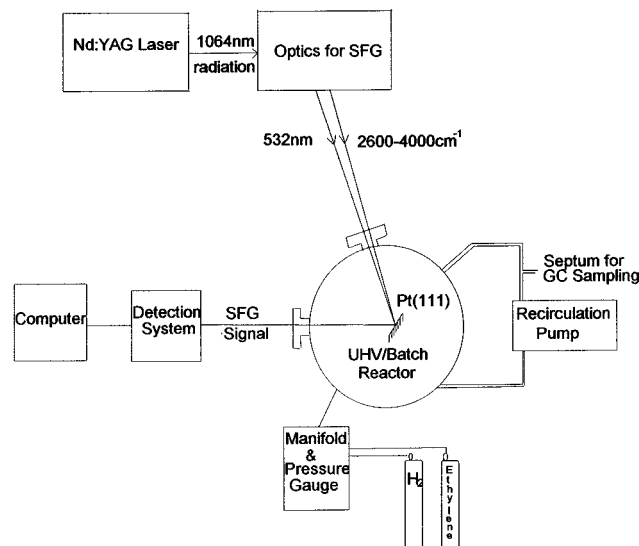


Figure 3. The UHV/batch reactor apparatus for *in situ* catalysis.

ethylene be removed from the gas phase in order to make observations. In order to avoid this problem, nonlinear optical methods are employed in this study. Sum frequency generation (SFG) as a *surface specific* vibrational spectroscopy is an ideal choice, because it generates virtually no signal from the gas phase.^{18–20} Therefore, it can be used to obtain surface vibrational spectra *in situ* under steady state reaction conditions when all the reactants and products are present over a wide range of pressures and temperatures.

In this paper we report SFG studies carried out simultaneously with gas phase turnover rate measurements of ethylene hydrogenation to ethane on the Pt(111) crystal surface near room temperature and atmospheric pressure. These studies permit the identification of the molecular species present on the surface at different hydrogen to hydrocarbon ratios and provide insight into how the turnover rate depends on the nature of the species that are present. A mechanism for ethylene hydrogenation is proposed with the molecular details of the process that greatly amplify the model proposed by Horiuti and Polanyi.

Experimental Section

(1) UHV, Reactor, and SFG Apparatus. All experiments were performed in a UHV/batch reactor system on a Pt(111) single crystal (Figure 3). The crystal was cut, polished, and oriented using the normal procedures. The UHV system was pumped by a turbo pump and an ion pump and had a base pressure of less than 1×10^{-10} Torr. The crystal could be heated resistively to over 1300 K and cooled with liquid nitrogen to approximately 115 K. The UHV system was equipped with an electron gun for argon ion bombardment, a retarding field analyzer for LEED and Auger, and a mass spectrometer. In addition, the chamber has two CaF₂ windows which were used to allow tunable IR and green light into the chamber as well as to allow sum frequency light to go out to a photomultiplier tube.

The light used for SFG was generated by a passive, active mode locked Nd:YAG laser with a 20 ps pulse width. A portion of the output was sent to an optical parametric generator/amplifier stage where infrared light between 2600 and 4000 cm⁻¹ was generated. This light was then combined at the Pt(111) sample with 532-nm light that was

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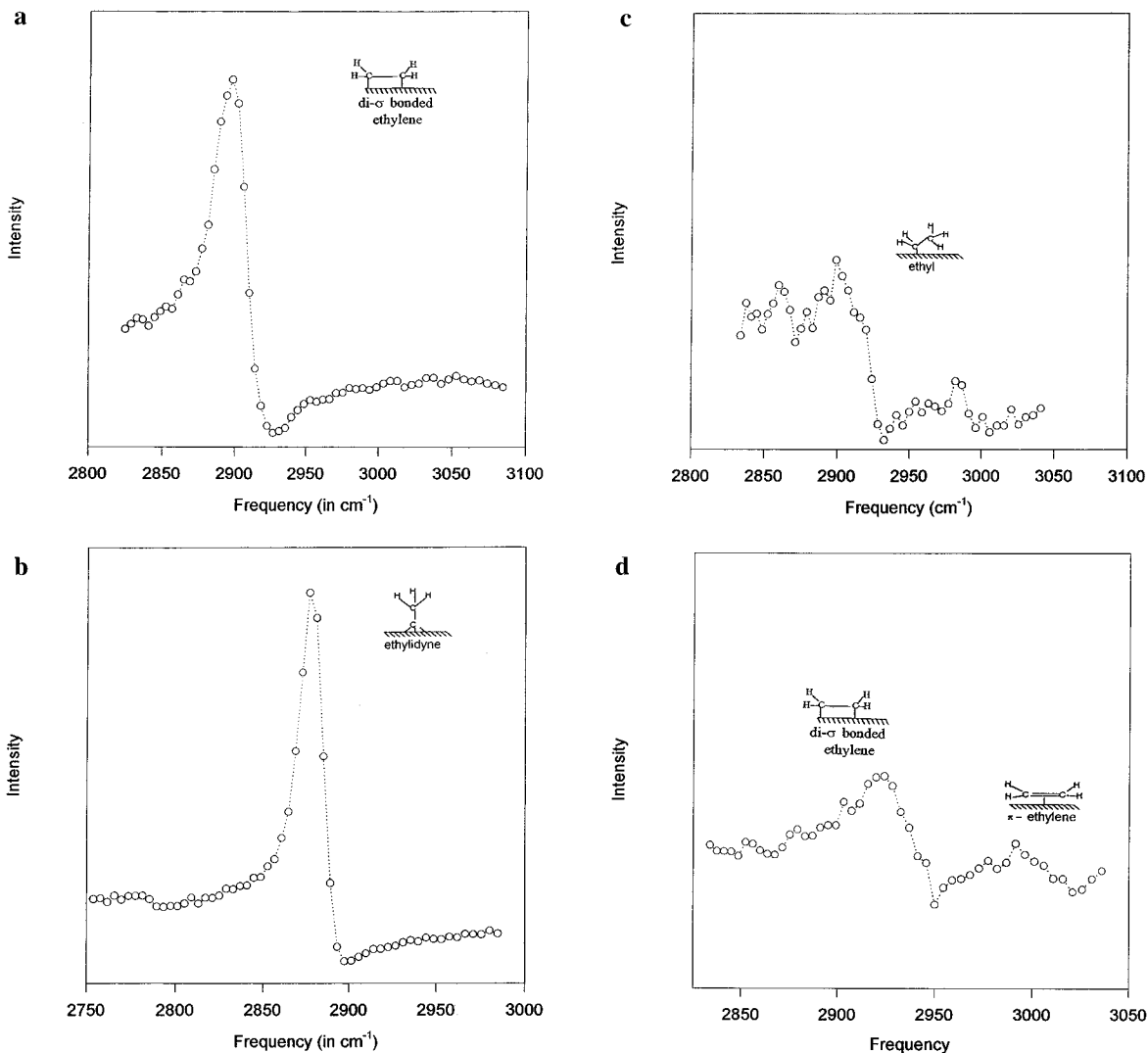


Figure 4. UHV spectra of saturation coverages of (a) di- σ -bonded ethylene at 202 K on Pt(111), (b) ethylidyne at 300 K on Pt(111), (c) ethyl groups at 193 K on Pt(111), and (d) a mixture of di- σ - and π -bonded ethylene at 120 K on O/Pt(111).

frequency doubled from the 1064-nm Nd:YAG fundamental. Although both the apparatus used in this experiment¹¹ to perform the sum frequency generation experiments and the technique itself^{18–20} have been described elsewhere, it should be noted that for vibrational modes to be active in SFG they must obey both the Raman and IR selection rules. Only modes which lack centrosymmetry can in the dipole approximation simultaneously obey both rules. In the experiments described in this paper the gas phase (which is isotropic) and the fcc lattice of the bulk platinum sample possess inversion symmetry and give nearly zero contribution to the signal. The dominant contribution is generated at the platinum surface, where inversion symmetry is always broken.

Atmospheric pressure experiments were undertaken in a batch reactor which could be isolated from the turbo pump and the ion pump via a gate valve (Figure 3). Gas pressures were monitored by a Baratron gauge that was capable of measuring pressures between 100 mTorr and 1000 Torr. The gases in the reactor were constantly mixed by a recirculation pump and samples could be withdrawn from the reaction loop and analyzed in an HP 5890 series II gas chromatograph equipped with a 115-3432 GSQ column for the separation of ethylene from ethane.

(2) UHV Calibration Experiments To Identify Various Adsorbates. To aid in the assignment of the spectroscopic features from surface adsorbates present during catalysis, several high-vacuum analogs

were prepared on the pristine platinum surface with which to compare. Figure 4a shows the SFG vibrational spectrum of a saturation coverage of di- σ -bonded ethylene on Pt(111) in the CH stretch region. The peak at 2904 cm⁻¹ is the $\nu_s(\text{CH}_2)$ of the methylene groups. The system was prepared by exposing the clean Pt(111) surface to 4 langmuirs of ethylene at 200 K. The dip of the baseline below its initial level following the spectral feature is due to the interference between the nonresonant background from the platinum metal and the resonant signal from the di- σ -bonded species. All vibrational spectra in this paper contain this artifact of the sum frequency generation experiment. Because of the interference between the resonant and the nonresonant signals, the background signal may be suppressed for several hundred wavenumbers following a major peak. Also, the resonant features are slightly red shifted and their exact frequencies must be determined by fitting.

The di- σ -bonded species is stable on the surface in UHV up to 240 K at which temperature it dehydrogenates to ethylidyne ($\text{M}\equiv\text{CCH}_3$). Ethylidyne can also be formed by directly exposing ethylene to Pt(111) between 240 and 450 K. The spectrum of a saturated coverage of ethylidyne/Pt(111) formed at 300 K in UHV is shown in Figure 4b. The major spectral feature is the $\nu_s(\text{CH}_3)$ peak of ethylidyne's terminal methyl group at 2884 cm⁻¹.

Ethyl groups can be formed on Pt(111) by exposing the clean surface to ethyl iodide and then annealing the surface above 170 K to begin breaking some of the C–I bonds.²¹ The spectrum of ethyl/Pt(111) at 193 K is shown in Figure 4c. Several CH stretch features are observable

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on the surface. The two lower frequency features (2860 and 2920 cm^{-1}) have been assigned to a fermi resonance and the $\nu_s(\text{CH}_3)$, respectively. The higher frequency peak near 2970 cm^{-1} is the $\nu_s(\text{CH}_3)$ of undissociated $\text{CH}_3\text{CH}_2\text{I}$.²²

UHV calibrations of the π -bonded species were made by exposing the clean Pt(111) surface to a near saturation coverage of O_2 at 300 K. This surface was then further exposed to ethylene at 120 K to yield a mixture of π -bonded and di- σ -bonded ethylene.^{23,24} The SFG spectra of the adsorbates is shown in Figure 4d. The larger peak at 2915 cm^{-1} corresponds with di- σ -bonded ethylene and the 2995- cm^{-1} feature is associated with the $\nu_s(\text{CH}_2)$ of π -bonded ethylene. This is in good agreement with transmission infrared data on supported platinum catalysts showing intensity for π -bonded ethylene near 3000 cm^{-1} .^{17,25,26} The intensity of the $\nu_s(\text{CH}_2)$ is fairly weak in the SFG experiment because the surface metal dipole selection rule requires the presence of a surface normal component of the dynamic dipole for the species to be observable. In the case of π -bonded ethylene, the $\nu_s(\text{CH}_2)$ is nearly in plane with the metal surface; hence, the signal observed is small. The total coverage of ethylene from both species is roughly 0.16 ML.²³ Fitting the peaks suggests that approximately 0.10 ML is from di- σ -bonded ethylene and 0.06 ML from π -bonded ethylene. All calibration results for ethyl, ethylidene, di- σ -bonded ethylene, and π -bonded ethylene are in good agreement with infrared values in the literature.

(3) Sample Preparation. Before performing high-pressure studies, the Pt(111) crystal was cleaned with cycles of Ar^+ sputtering and annealing, after which sample cleanliness was checked by Auger electron spectroscopy. The sample was then isolated from vacuum via a gate valve at which time pure hydrogen was introduced into the reactor. Hydrogen was always introduced first, followed by ethylene. This ensured that hydrocarbon contaminants did not poison the crystal.

Results

(1) High-Pressure Ethylene Hydrogenation. Ethylene hydrogenation experiments were carried out over a range of hydrogen pressures from less than 2 Torr of H_2 to over 700 Torr of H_2 . The ethylene pressure was kept lower than that of hydrogen under all circumstances. However, the absolute partial pressure of ethylene was not critical to the experiment because the reaction was conducted in the regime where it is known to be zero order in ethylene (except where noted). Control experiments were performed to verify that this was indeed the case. It was at intermediate pressures that the richest surface chemistry was observed (100 Torr of H_2). The SFG spectrum obtained during ethylene hydrogenation at 295 K with 100 Torr of H_2 , 35 Torr of ethylene, and 625 Torr of He is shown in Figure 5a. The dominant feature in the spectrum was the CH_3 symmetric stretch of ethylidene at 2878 cm^{-1} . The intensity of the peak corresponded to a coverage of 0.15 ML or 60% of saturation coverage. Just above the ethylidene peak the CH_2 symmetric stretch of di- σ -bonded ethylene was observed at 2910 cm^{-1} . The peak from the di- σ -bonded ethylene represented approximately 0.08 ML.

In addition to these two prominent features a weak and broad hump around 3000 cm^{-1} from π -bonded ethylene was observed. The intensity is weak because the dynamic dipole of the molecule's $\nu_s(\text{CH}_2)$ is nearly in plane with the metal surface. Although this feature is weak, it was consistently reproducible over numerous experimental trials. The coverage of this species was about 0.04 ML based on the calibration coverage of Figure 4d. The spectrum in Figure 5a remained unchanged for hours

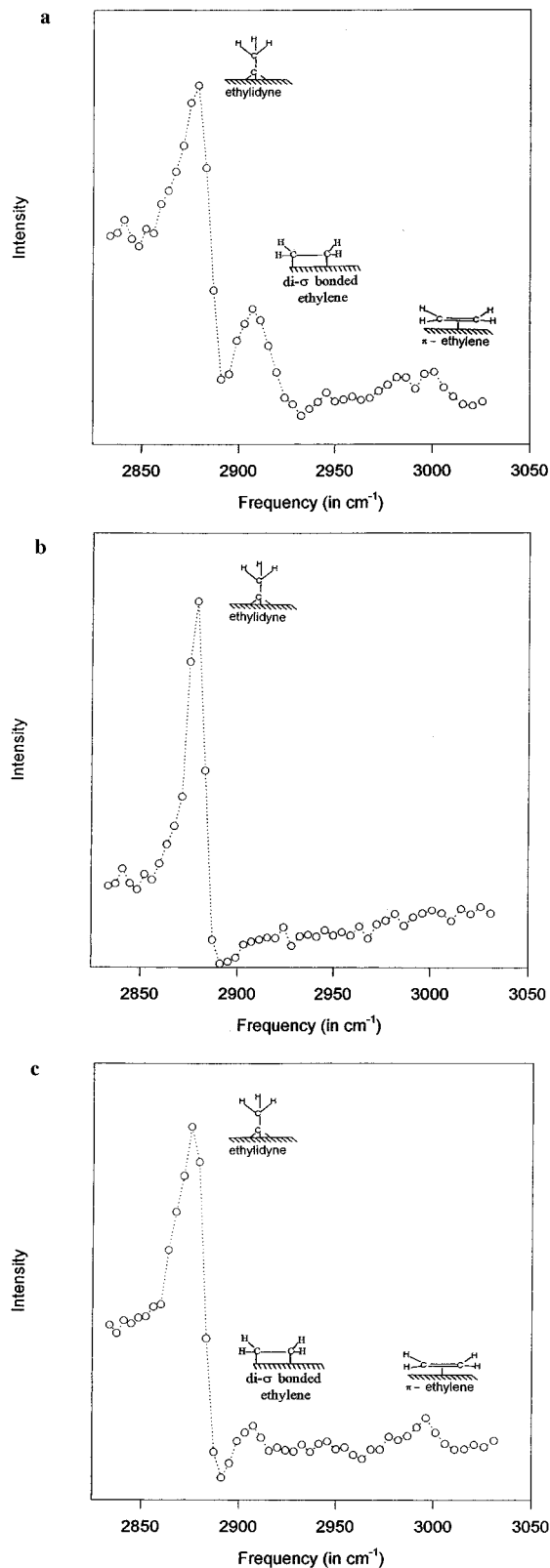


Figure 5. (a) SFG spectrum of the Pt(111) surface during ethylene hydrogenation with 100 Torr of H_2 , 35 Torr of C_2H_4 , and 615 Torr of He at 295 K. (b) The vibrational spectrum of the same system after the evacuation of the reaction cell. (c) The SFG spectrum under the same conditions as (a), but on a surface which was precovered in UHV with 0.25 ML of ethylidene.

showing that the composition of adsorbates on the surface remained unchanged over the lifetime of the experiment.

While vibrational spectra were being recorded, the gas-phase composition was monitored by gas chromatography (GC). GC

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measurements of ethane production revealed a turnover rate (TOR) of 11 ± 1 ethylene molecules per surface platinum atom per second; this means 11 ethylene molecules were converted to ethane per second for every exposed platinum atom.

Figure 5b shows the vibrational spectrum of the catalytic Pt(111) surface immediately after evacuation of the reactor. The only spectral feature which remained was from ethylidyne. Further, the intensity of the ethylidyne peak increased to that of saturation coverage (0.25 ML). This increase in the ethylidyne peak was due to the dehydrogenation of di- σ -bonded ethylene to ethylidyne after the hydrogen had been removed from the gas phase (analogous to what has been shown to occur under UHV conditions). The π -bonded species might also dehydrogenate to form ethylidyne, but presumably needs to go through a di- σ -bonded intermediate first in order to do so. This clearly demonstrates that at 300 K π -bonded ethylene and di- σ -bonded ethylene are only present on the surface in the presence of hydrogen and ethylene. As soon as the reactant gases are removed the species either decompose or desorb.

In order to determine the effect of a saturation coverage of ethylidyne on the reaction, experiments were carried out on a surface that was precovered with ethylidyne. The ethylidyne Pt(111) system was prepared by dosing the clean platinum surface with 4 L of ethylene in UHV at 295 K. The crystal was then exposed to similar experimental conditions as in Figure 5a. Figure 5c shows the vibrational spectrum for the UHV prepared ethylidyne/Pt(111) system exposed to 100 Torr of H_2 , 35 Torr of ethylene, and 625 Torr of He at 295 K. The measured turnover rate under these conditions was 12 ± 1 molecules per platinum site per second. This rate is almost identical to the previous conditions; however, the vibrational spectrum looks quite different. The ethylidyne peak at 2878 cm^{-1} is much stronger than in the previous case, while the $\nu_s(\text{CH}_2)$ from di- σ -bonded ethylene is much smaller. Curve fitting the small di- σ -bonded ethylene feature revealed that it represented less than 0.02 ML. This corresponds to more than a factor of 4 drop in the di- σ -bonded ethylene concentration from the previous case without ethylidyne preadsorption. By contrast, the feature from π -bonded ethylene was present and appeared to be quite similar in intensity to the previous case.

The decrease in the concentration of di- σ -bonded ethylene without a decrease in the rate of hydrogenation argues strongly against di- σ -bonded ethylene being an important intermediate in ethylene hydrogenation. It appears the di- σ -bonded species compete directly for sites with ethylidyne. Once ethylidyne species are formed they apparently block the adsorption sites for di- σ -bonded ethylene. Because it is known from previous studies on supported catalyst surfaces that the presence or absence of ethylidyne has no effect on the rate of ethylene hydrogenation,^{15,16} di- σ -bonded ethylene also can be ruled out as an important intermediate in ethylene hydrogenation. Indeed, if di- σ -bonded ethylene had been an important intermediate, then ethylidyne would be a poison for ethylene hydrogenation.

In contrast to the behavior of the di- σ -bonded species, the concentration of π -bonded ethylene was unaffected by the ethylidyne concentration. Therefore, *the π -bonded species is likely to be a key intermediate in ethylene hydrogenation.*

(2) Effects of Higher and Lower Hydrogen Pressures. The ethylene hydrogenation reaction was also carried out at higher pressures of hydrogen and ethylene (Figure 6). These conditions (723 Torr of H_2 , 38 Torr of ethylene, and 295 K) gave rise to a surface that was not saturated by ethylidyne or other hydrocarbon species in contrast to what was observed using 100 Torr of H_2 . It is significant to note that there is little change in intensity of the peak corresponding to π -bonded ethylene;

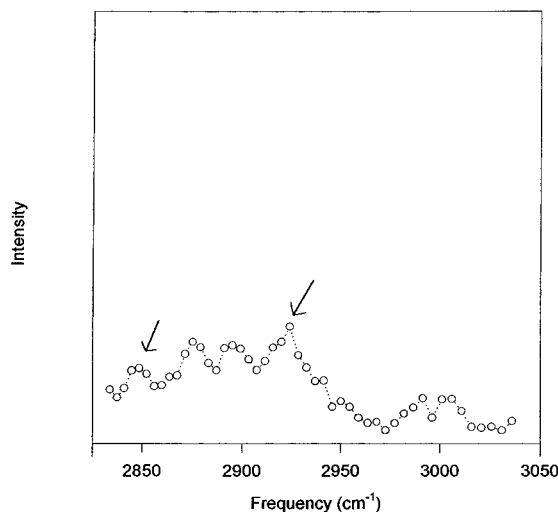


Figure 6. The hydrogenation of ethylene on Pt(111) with 727 Torr of H_2 and 60 Torr of C_2H_4 at 295 K. The two peaks marked with arrows are features characteristic of an ethyl species.

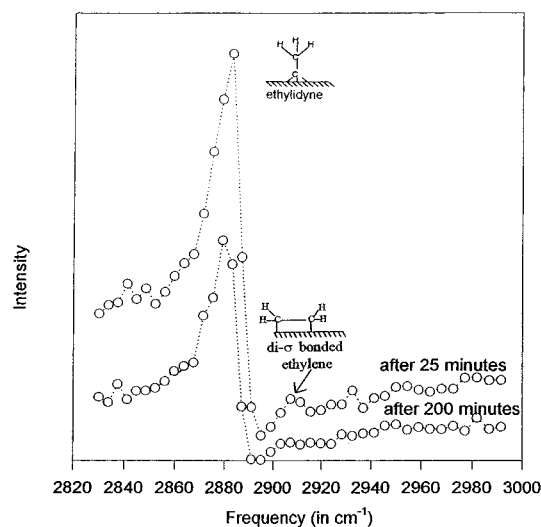


Figure 7. The hydrogenation of ethylene on Pt(111) with 1.75 Torr of H_2 , 0.25 Torr of C_2H_4 , and 758 Torr of Ar at 295 K. The upper SFG spectrum was taken after 25 min and the lower spectrum after 200 min.

however, there is a drop in intensity of other spectral features as compared with Figure 5a and 5c. Some di- σ -bonded ethylene and ethylidyne were observable under these conditions, but two additional peaks (marked with arrows) at 2850 and 2925 cm^{-1} were also visible. These features correspond quite well with those seen in the calibration measurements for ethyl/Pt(111) and can be assigned to the presence of the half-hydrogenated ethyl intermediate on the surface in large enough quantity to be observed. The turnover rate measured for ethane formation was 61 ± 3 molecules per platinum site per second under these conditions reflecting 0.81 order of this reaction with respect to hydrogen. This is in excellent agreement with literature values at this temperature.⁴

At lower pressures of hydrogen and ethylene (1.75 Torr of H_2 , 0.25 Torr of ethylene, and 758 Torr of Ar) the spectrum observed showed that the surface had nearly a saturation coverage of ethylidyne from the onset of reaction with only a small concentration of di- σ -bonded ethylene present (Figure 7). As the reaction continued, the di- σ -bonded ethylene peak slowly disappeared and after 200 min the only spectroscopic feature present was from ethylidyne. The turnover rate was 1.6 molecules per platinum site per second and remained unchanged

over the course of the reaction (i.e. did not change with the observed decrease in concentration of di- σ -bonded ethylene). It should also be noted that the π -bonded ethylene species could not be observed under these circumstances presumably because its concentration was too low. Due to the low reactant pressures used in this case, the reaction order is somewhat negative in ethylene, which is consistent with the surface not being saturated with the hydrocarbon intermediate species, π -bonded ethylene. Despite this, the surface remained saturated with the spectator species, ethylidyne.

Unlike the medium pressure case (100 Torr of H₂), preadsorbing ethylidyne had very little effect on the nature and concentration of surface species seen in Figures 6 and 7. Under the highest pressure conditions (> 700 Torr of H₂) preadsorbed ethylidyne was quickly hydrogenated off the surface under reaction conditions in agreement with supported catalyst work under similar conditions. At low pressures of hydrogen, ethylidyne was present at saturation coverage regardless of whether it was preadsorbed or not.

(3) Hydrogenation of Di- σ -Bonded Ethylene at Low H₂ Pressure ($\sim 10^{-5}$ Torr) and Low Temperature (240 K). Although it was determined under high-pressure conditions that di- σ -bonded ethylene was not responsible for the observed rate of ethylene hydrogenation, it remained unclear as to whether this species was merely hydrogenating at a very slow rate or completely static on the surface. To answer this question UHV experiments were conducted on the hydrogenation rate of a saturated coverage of di- σ -bonded ethylene at 235 K, a temperature at which this molecule is stable on the Pt(111) surface.

Figure 8a shows spectra for increasing coverages of di- σ -bonded ethylene at 200 K on Pt(111) up to saturation coverage. As the exposure of ethylene is increased, the CH₂ symmetric stretch feature increased in intensity and shifts in frequency from 2924 cm⁻¹ for low exposure to 2904 cm⁻¹ as the saturation coverage of 0.25 ML is reached.

Figure 8b shows spectra of an initial saturation coverage of di- σ -bonded ethylene and after exposure to increasing dosages of hydrogen at 235 K. As the exposure to hydrogen is increased, the CH₂ symmetric stretch at 2904 cm⁻¹ begins to attenuate and shift to higher frequency. The feature could be almost completely removed at 235 K after exposure to 30 000 langmuirs of hydrogen. The attenuation of the signal with increasing exposure to hydrogen demonstrates the hydrogenation of di- σ -bonded ethylene under UHV conditions. The blue shift in the peak is due to the coverage dependence of the frequency as shown in Figure 8a. No other features appeared during UHV hydrogenation of ethylene. This result clearly demonstrates that although di- σ -bonded ethylene is not hydrogenating fast enough to be responsible for the turnover rate seen under atmospheric conditions, it indeed is hydrogenating on the surface under conditions where it is present.

Discussion

Vibrational spectroscopy using sum frequency generation permits the detection of submonolayer quantities of species under reaction conditions even in the presence of high reactant and product pressures in the gas phase. Specifically, the vibrational spectra taken during ethylene hydrogenation reveal the presence of ethylidyne, di- σ -bonded ethylene, π -bonded ethylene, and ethyl groups at various concentrations depending upon specific reaction conditions.

(1) Ethylidyne and Di- σ -Bonded Ethylene. The lack of any direct role of ethylidyne (M \equiv CCH₃) in the mechanism for ethylene hydrogenation has already been well documented,¹⁴⁻¹⁶

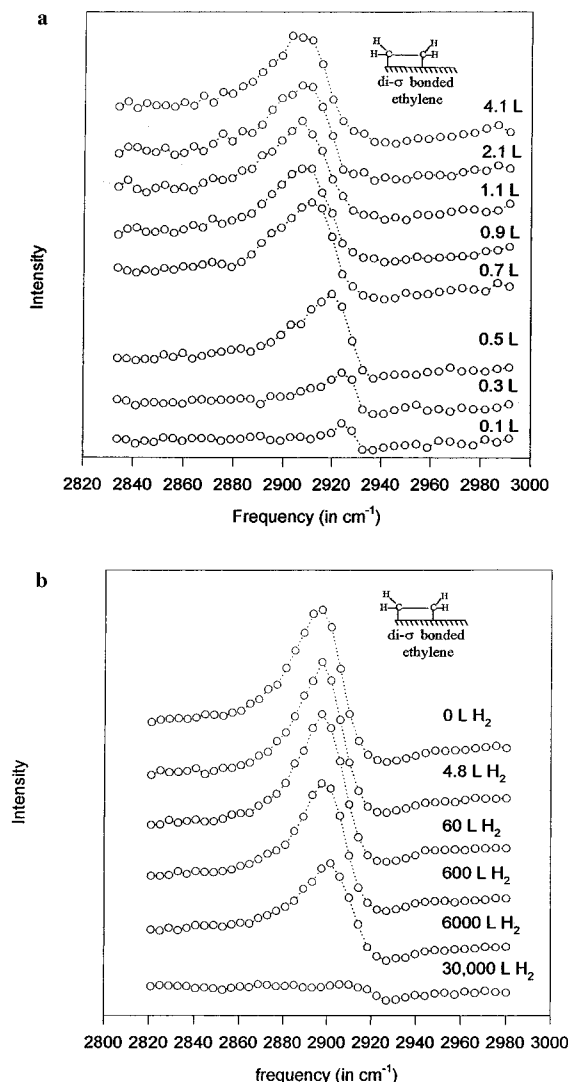


Figure 8. (a) SFG spectra of di- σ -bonded ethylene on Pt(111) as a function of ethylene exposure. The 0.1-langmuir exposure represents low coverage while the 4.1-langmuir spectrum is of a saturation coverage. (b) SFG spectra of a saturation coverage of di- σ -bonded ethylene on Pt(111) at 235 K as a function of hydrogen exposure. (Note: 1 langmuir = 10^{-6} Torr s).

however the SFG results suggest that stagnant ethylidyne blocks the sites for di- σ -bonded ethylene adsorption on the catalytic Pt(111) surface. This result corresponds well with LEED surface crystallography which has shown that di- σ -bonded ethylene and ethylidyne reside in the same surface site, the fcc 3-fold hollow.^{9,12}

Three distinct spectroscopic features were seen on the Pt(111) surface during ethylene hydrogenation at 295 K with 100 Torr of hydrogen and 35 Torr of ethylene: di- σ -bonded ethylene, π -bonded ethylene, and ethylidyne (Figure 5a). When the reaction was carried out on an initially clean surface, the concentration of di- σ -bonded ethylene that could be observed was about 8% of a monolayer. However, if the platinum surface was saturated with ethylidyne, very little di- σ -bonded ethylene was observed under catalytic conditions (Figure 5c) and the rate of hydrogenation, as measured by gas chromatography, was independent of the surface concentration of the di- σ -bonded ethylene species. Under reaction conditions of 1.75 and 100 Torr of H₂, the platinum 3-fold sites remained near saturation coverage of ethylidyne + di- σ -bonded ethylene. Hence the total concentration of these species was always near 0.25 ML. This means that both of these species were adsorbing far faster than

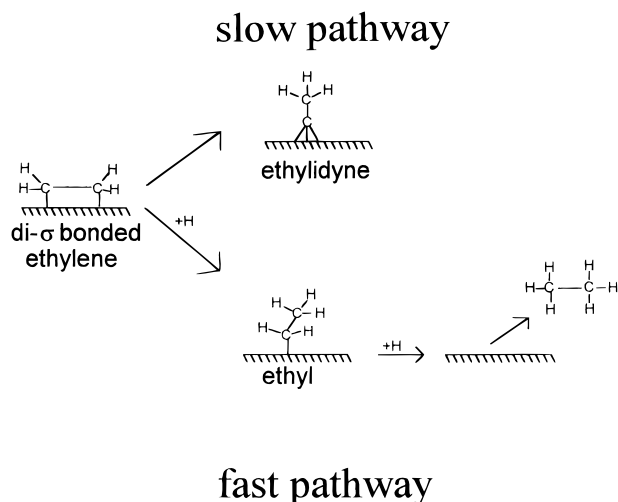


Figure 9. The schematic representation of the reaction channels for di- σ -bonded ethylene on Pt(111) during ethylene hydrogenation at 295 K.

they could be hydrogenated. At higher pressures of hydrogen (~ 700 Torr) the surface became mostly free of these adsorbates. However, this does not mean that ethylidyne and di- σ -bonded ethylene are hydrogenated at the same rate. UHV experiments (Figure 8b) clearly showed that the di- σ -bonded species can be hydrogenated under the relatively modest conditions of 235 K and 10^{-5} Torr of H_2 . By contrast, even under room temperature conditions with 1 atm of H_2 , previous authors have demonstrated that ethylidyne hydrogenates very slowly.¹⁴

The chemistry of di- σ -bonded ethylene can be modeled as follows (Figure 9): on a closed packed platinum surface, which is not saturated with ethylidyne, di- σ -bonded ethylene may adsorb. Di- σ -bonded ethylene is hydrogenated in the presence of hydrogen to ethane (fast pathway) or dehydrogenates to ethylidyne (slow pathway). Ethylidyne may also be hydrogenated, but does so much more slowly than di- σ -bonded ethylene. Under steady state conditions at 295 K with 100 Torr of H_2 and 35 Torr of C_2H_4 a near saturation coverage of ethylidyne is favored. At higher pressures of hydrogen (over 700 Torr), di- σ -bonded ethylene and ethylidyne are hydrogenated at a fast enough rate that the surface is not saturated with these species.

(2) π -Bonded Ethylene. Figure 5a reveals the presence of π -bonded ethylene on the platinum surface when the hydrogenation of ethylene to ethane was detectable. The π -bonded feature was present under reaction conditions (Figure 5a), but disappeared upon removal of the reactants (Figure 5b). Unlike di- σ -bonded ethylene the presence of this peak did not appear to be related to the ethylidyne coverage. It appears that this species was present at roughly the same intensity for the conditions displayed in both Figures 5a and 5c, where the rates of reaction are nearly identical. All experimental evidence indicates that π -bonded ethylene is the dominant reaction intermediate that hydrogenates to ethane.

The surface coverage of π -bonded ethylene under reaction conditions is about 4% of a monolayer. This means that the turnover rate per ethylene molecule is a factor of 25 higher if reported per surface intermediate than if reported per platinum atom. This is clearly significant, because it means that not all platinum atoms on the surface are active at any given time. However, the number of active sites is still far too high for this reaction to be primarily occurring at defect sites. Indeed, numerous studies have shown that ethylene hydrogenation is a structure-insensitive reaction and, therefore, the specific location at which key reaction steps take place must be at sites that are

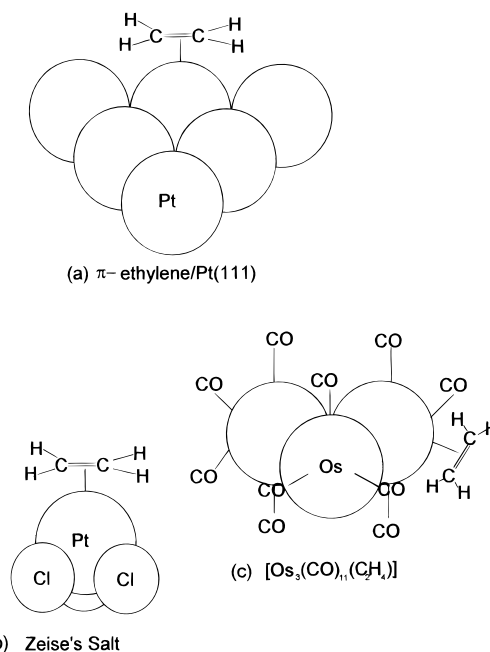


Figure 10. (a) The proposed bonding site for π -bonded ethylene on Pt(111) and the bonding site for two organometallic analogs, (b) Zeise's salt, $K[Cl_3Pt(C_2H_4)] \cdot H_2O$, and (c) an osmium complex.

available on all crystallographic planes of platinum. The π -bonded ethylene molecule, being of key mechanistic importance, must reside on such a site. We propose atop adsorption on the surface metal atoms (Figure 10). This is consistent with organometallic cluster analogs of the π -bonded surface species.^{6,7}

Bowker et al. suggested that there is a correlation between the atop site for hydrogenation on heterogeneous catalysts and the chemistry of the homogeneous phase Wilkinson's catalyst, $RhCl(PPh_3)_3$.²⁷ In the case of the homogeneous catalyst there is only one metal atom (in this case a rhodium atom) site available, which only allows for atop hydrogenation. Hence, the chemistry is quite similar in both the heterogeneous and homogeneous case.

(3) Ethyl Groups. The ethyl species only becomes visible under the highest hydrogen pressure conditions in these experiments (Figure 6). This demonstrates the high degree of reversibility in the incorporation of the first hydrogen into adsorbed ethylene. Indeed UHV studies by Zaera et al. have shown that ethyl groups can readily undergo β -hydride elimination to yield di- σ -bonded ethylene and adsorbed hydrogen.²⁸ This may explain the difficulty in detecting ethyl species in transmission infrared experiments on supported platinum catalysts. In the only literature report of an ethyl group, Del La Cruz et al. present data for the introduction of 3×10^{-5} Torr of hydrogen onto ethylene-covered Pt/SiO₂ which led to several very weak features in the infrared transmission spectrum.²⁹ The authors tentatively assigned these to an ethyl group. Their study creates conditions that are the low-pressure equivalent of the present SFG work, where the increase in hydrogen pressure shifts the equilibrium for the addition of the first hydrogen into adsorbed π -bonded ethylene far enough toward the formation ethyl groups to permit their detection.

(4) Mechanism for Ethylene Hydrogenation. It has been observed that ethylene hydrogenation occurs at the same

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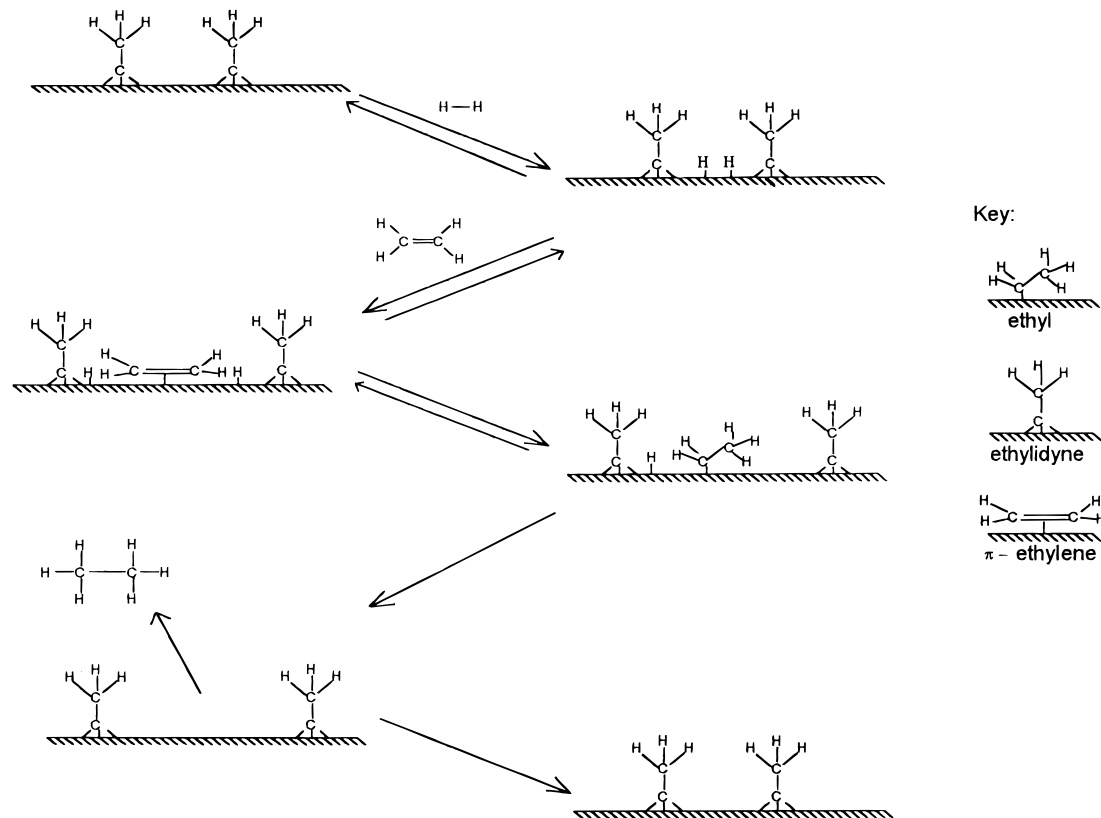


Figure 11. Proposed mechanism for ethylene hydrogenation on Pt(111).

rate regardless of whether ethylidyne is present or absent. Therefore, the ability of hydrogen and π -bonded ethylene to adsorb must be unaffected by the presence of this species. STM studies have demonstrated that ethylidyne is very mobile on Pt(111) at room temperature.¹³ Further, extended Hückel calculations carried out for an ethylidyne molecule on a platinum surface showed a low barrier for diffusion (~ 0.2 eV).³⁰ This suggests that, when present, ethylidyne may move far enough out of the way for ethylene to physisorb on a single platinum atom.

We propose a model in which hydrogen dissociately chemisorbs on a clean or ethylidyne covered platinum surface (Figure 11). This step is followed by the physisorption of ethylene on single atom sites to form π -bonded ethylene. If ethylidyne is present, it may move out of the way in order to accommodate the adsorption of the π -bonded ethylene. Although the two species reside in different sites, this may be necessary because of steric hindrance. Physisorbed ethylene is then stepwise hydrogenated through an ethyl intermediate onto ethane. All steps up to the incorporation of the second hydrogen are highly reversible.

(30) Nomikou, Z.; Van Hove, M.; Somorjai, G. *Langmuir* Submitted for publication.

Conclusion

Both π -bonded ethylene and di- σ -bonded ethylene are present on the Pt(111) surface under certain catalytic conditions where ethylene is being hydrogenated to ethane. However, the concentration of di- σ -bonded ethylene can be decreased dramatically by the presence of a spectator species, ethylidyne, without any corresponding decrease in the reaction rate. Therefore, the surface concentration of di- σ -bonded ethylene is uncorrelated with the rate of ethane formation and this species is not an important reaction intermediate in the hydrogenation of ethylene. A mechanism involving the hydrogenation of π -bonded ethylene is suggested instead. The relative hydrogenation rates of the species adsorbed on the surface during ethylene hydrogenation are as follows: π -bonded ethylene \gg di- σ bonded ethylene \gg ethylidyne.

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