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A COMPARISON OF GAS PHASE AND ELECTROCHEMICAL
HYDROGENATION OF ETHYLENE AT PLATINUM SURFACES

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ABSTRACT

Rates of hydrogenation of ethylene to ethane under gas-solid (G-S) and liquid-solid (L-S) (i.e. electrochemical) conditions at well-defined Pt(111) and smooth polycrystalline Pt surfaces are reported. The activation energies are 5.9 kcal/mole for the L-S reaction and 10.8 kcal/mole for the G-S reaction. Comparison of the rate laws under appropriate conditions shows that the hydrogenation proceeds by different reaction mechanisms at the two different interfaces. We have used surface science techniques (low-energy electron diffraction, Auger electron spectroscopy, high-resolution electron energy loss spectroscopy, temperature programmed desorption), and electrochemistry (a combination of solution and ultra-high vacuum procedures) to characterize the adsorbed species formed under G-S and L-S reaction conditions and to gain insight into the reaction mechanisms. We propose that in hydrogenation at the L-S interface, ethylene is reduced on the Pt surface by adsorbed H atoms, while during hydrogenation at the G-S interface, H atoms must be transferred from the Pt surface through a layer of irreversibly adsorbed ethylene to ethylene that is adsorbed on top of this layer.

INTRODUCTION

One of the fundamental questions of surface chemistry is how chemical changes that occur at gas-solid (G-S) interfaces compare with those at the liquid-solid (L-S) interface. These two heterogeneous processes are intrinsically similar -- both involve mass transfer to and from the surface, adsorption, desorption, and chemical reactions at the surface (Figure 1). However, the molecular structures and chemical reactions in the interfacial regions are possibly quite different due to the effects of higher molecular flux, solvent, and electrode potential at the L-S interface. Consequently, changes of atomic surface structure, adsorption, and chemical rearrangements should all be investigated at G-S and L-S interfaces on the same surface and using the same adsorbate or reactant molecules under similar experimental conditions to establish correlations between the reaction mechanisms at these interfaces.

There are a few catalytic reactions that occur under very similar experimental conditions at the G-S and L-S interfaces. Ethylene hydrogenation to ethane is one of them. This facile reaction readily occurs on platinum and other transition metal surfaces in both gas and solution phases at 300 K [1-4(G-S), 5-12(L-S)]. There are further similarities between ethylene hydrogenation in these two phases. Recent work shows that at both G-S and L-S interfaces the hydrogenation rate is not sensitive to the crystallographic orientation of the Pt surface (4,5). Studies of deuterium scrambling in L-S ethylene hydrogenation over polycrystalline Pt surfaces (6) show a deuterium distribution similar to that found for hydrogenations at the G-S interface over Pt(111) crystal faces (4): the product distribution of deuterium displays maximum yield at 1-2 deuteriums per ethane, although products all the way to C_2D_6 are observed. The rate of ethylene

H-D exchange in both cases is estimated to be 10-20% of that for hydrogenation.

This reaction, then, appears to be an excellent choice to explore the similarities and differences of the kinetics and mechanisms at the G-S and L-S interfaces, and platinum is a good choice to serve as a catalyst.

In this paper we present the results of our studies of ethylene hydrogenation over single-crystal and annealed, polycrystalline platinum surfaces at the G-S and L-S interfaces at 300 K. As far as we know, this is the first attempt to compare catalytic reactions at these two interfaces.

Our data on the structure and reactivity of chemisorbed ethylene under ethylene hydrogenation reaction conditions at the G-S and L-S interfaces were obtained over single crystal Pt surfaces. Surface science techniques [Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), temperature programmed desorption (TPD), and high-resolution electron energy loss spectroscopy (HREELS)] were utilized in ultra-high vacuum (UHV) to characterize adsorbed species before and after reactions in microreactors that were constructed in combination with the UHV chambers. Electrochemical techniques (cyclic voltammetry and chronoamperometry) and a ^{14}C radiotracer technique were used to characterize the reactivity of the adsorbed species.

Our results show that the structure and reactivity of ethylene chemisorbed on Pt under G-S and L-S conditions are different. As a result, the L-S and G-S hydrogenation processes occur via different pathways. Ethylene in the L-S hydrogenation is reduced directly on the Pt surface by adsorbed H atoms. In the G-S hydrogenation hydrogen atoms must be transferred from the surface to ethylene that is adsorbed on top of a layer of irreversibly adsorbed hydrocarbon fragments. The activation energy for the L-S hydrogenation is substantially lower than that for G-S

hydrogenation (5.9 vs. 10.8 kcal/mole). TPD results in ultra-high vacuum for the G-S hydrogenation of C_2H_4 over a deuterium-covered surface support the fact that the lower activation energy for the L-S hydrogenation is related to a process where ethylene is adsorbed directly on a hydrogen-saturated platinum metal surface. Based on the experimental evidence, we have proposed molecular models for the different reaction mechanisms that occur at the two interfaces.

EXPERIMENTAL

We briefly describe here the techniques and procedures used to study the structure and reactivity of chemisorbed ethylene. The UHV chamber/reactor systems for G-S (4,13-15,43) and L-S (16-18) reaction studies have been described. Two such systems are shown in Figure 2. With several surface science techniques (AES, TPD, LEED, and HREELS) in the UHV chambers, we characterize the clean or adsorbate-covered Pt surfaces before and after reactions in solution or at atmospheric gas pressures. The Pt(111) single crystal surfaces were cut and mounted to minimize the amount of polycrystalline Pt (4,16-18). G-S and L-S adsorbate characterization procedures are described below.

Reactions of the G-S chemisorbed ethylene were carried out by isolating the Pt single crystal in a "high pressure" cell after cleaning in vacuum, Figure 2-A. The cell was then pressurized with the reactant gases. After the reaction in the batch reactor had proceeded to the desired extent (while the amounts of ethylene and ethane were monitored by gas chromatography), the gases were pumped from the loop with sorption and diffusion pumps. Pumping and return to UHV took 10-15 minutes.

Surface structure and composition were analyzed upon return of the crystal to UHV by TPD, HREELS, and a ^{14}C radiotracer technique. TPD [monitoring $\text{amu}=2(4)$, $\text{H}_2(\text{D}_2)$ desorption] was used to determine the temperatures (activation energies) for decomposition of the adsorbed ethylene. ^{14}C ethylene was chemisorbed and the surface radioactivity measured before and after treatments with one atmosphere of hydrogen (19,20) to establish the identity and stability of the surface carbon. HREEL spectroscopy [reviewed (21)] was used to get a vibrational "fingerprint" of the surface structure. HREEL spectra before and after treatment of chemisorbed ethylene with 1 atmosphere of H_2/D_2 were used to

confirm adsorbate structure and stability.

In the L-S studies the well-defined Pt(111) clean surface, or the surface pretreated with G-S adsorbed ethylene, was positioned in the electrochemical cell compartment, valved off from the LEED chamber (Fig. 2-B) and brought to atmospheric pressure with argon. Solution was introduced into the cell and electrochemical characterization carried out using conventional potentiostatic circuitry and procedures (22). After electrolysis, the liquid was drained, and after brief sorption, cryogenic, ionization and getter pumping, the crystal was characterized by LEED, AES, and TPD.

Electrochemistry using thin-layer cells has been reviewed (23,24). The thin-layer electrode (TLE) employed for this study was described in reference 25. An annealed, polycrystalline Pt electrode in a semi-infinite system was used for kinetic study under chronoamperometric (26) conditions.

1 M HClO_4 solution was used in the L-S study as supporting electrolyte and nitrogen (Linde, oxygen-free grade) as inert gas. If not otherwise stated, the concentration of ethylene in the supporting electrolyte was 4×10^{-3} M. Potentials are reported with respect to AgCl/Ag half-cell prepared with 1 M NaCl. Reagents used in both the G-S and L-S studies were the same as in previous work (ref. 4 for G-S and ref. 5 for L-S). The concentration of ethylene was varied in the L-S reactions by passing a mixture of ethylene and nitrogen through the solution.

RESULTS AND DISCUSSION

1. Rates and Kinetic Parameters

Throughout this comparison of G-S and L-S hydrogenations, we will address the question of how best to compare gas phase and solution reaction data. We already noted the qualitative similarities of these two heterogeneous processes in the introduction (Fig. 1). In this section we first present and discuss some new results on the rates and kinetic parameters of L-S hydrogenation of ethylene. Next we compare the rate laws for L-S and G-S hydrogenation processes over the Pt surfaces.

L-S ethylene hydrogenation kinetic parameters can be extracted from chronoamperometric (current vs. time) data (26). Such data obtained at -0.15 V are shown for contrasting cases in Figure 3 and Table I: reduction of chemisorbed ethylene, Figure 3-A; reduction of ethylene from solution at an I-pretreated surface, 3-B; reduction of ethylene at a Pt surface pretreated with ethylene at 0.2 V, 3-C; and, reduction of ethylene at an H-covered surface, 3-D. From Figure 3-D we see that L-S ethylene reduction occurs three-fold more rapidly on a surface which has not had opportunity to acquire a layer of adsorbed hydrocarbon (of the type which forms spontaneously at open circuit or at 0.2 V, Fig. 3-C). Comparison of 3-B with 3-D reveals that a layer of chemisorbed I-atoms decreases the rate of reduction more than ten-fold relative to the clean Pt surface. This is as expected because the iodine atomic layer prevents adsorption of ethylene and greatly attenuates the amount of adsorbed hydrogen (5). Ethylene acts as a blocking agent toward its own reduction, but adsorbed iodine blocks (although not completely) the reaction even more severely.

Referring to Table I, the kinetic isotope effect of D_2O on L-S reduction of ethylene from the bulk solution is relatively large ($K_H/K_D=2$ to 2.2)

compared with that for the chemisorbed layer ($K_H/K_D=1.3$). Large isotopic dependences are indicative of mechanisms involving breakage or formation of a specific H-X bond in the rate-determining step (27). (Previous electrochemical examples of this phenomenon have been discussed in Ref. 28.) Accordingly, L-S reduction of ethylene from the bulk solution must involve breaking or forming a specific C-H or Pt-H bond. The latter possibility, breakage of a Pt-H bond, seems more likely as discussed below.

It should be noted that ethylene electroreduction at Pt is zero-order in ethylene concentration (pressure). Also, the dependence of the rate on electrode potential [as measured by the Tafel slope, $dE/d(\log \text{ rate})$] is less than the 120 mV value expected for rate-determining electron transfer reactions, implicating a reaction mechanism involving one or more reversible electron transfer steps, followed by rate-determining chemical reactions (29).

We now compare the rate law for L-S ethylene hydrogenation at polycrystalline Pt with that for G-S hydrogenation over Pt(111) single-crystal surfaces. Comparison of these G-S and L-S hydrogenations requires that the rate data not be mass transfer limited. In the G-S reaction, the reaction rate (about 25 molecules/Pt atom/s) is orders of magnitude less than the molecular flux at the surface (about 10^6 molecules/Pt atom/s). Likewise under L-S conditions, the initial rate (10^2 molecules/Pt atom/s) is much less than the collision rate. At potentials approaching the onset of hydrogen evolution, the limiting influence of diffusional transport was avoided by stirring the solution. The Pt(111) surface, as shown in Table II, behaves catalytically like polycrystalline Pt catalysts.

The G-S hydrogenation rate law at atmospheric pressures over either a clean or ethylene-pretreated surface has the form:

$$\text{Rate} = 8 \times 10^8 P_{\text{C}_2\text{H}_4}^{-0.6} P_{\text{H}_2}^{1.3} \exp(-E_a/RT) \quad (1)$$

where the rate is in molecules/Pt atom/s and $E_a = 10.8 \pm 0.1$ kcal/mole (4).

For similar surfaces, the L-S hydrogenation rate law for the clean (H-covered surface, Fig. 3-D) is:

$$\text{Rate} = 8.6 \times 10^6 a_{\text{H}^+} \exp\{[E_a + 1.5F(E - E_0)]/RT\} \quad (2)$$

where $E_a = 5.9 \pm 0.6$ kcal/mole and E_0 is defined below (equation 3). Over an ethylene-pretreated surface (Fig. 3-C) the rate law for the initial rate is the same, but the activation energy has a larger value of 6.6 ± 0.6 kcal/mole.

To compare equations (1) and (2), the potential dependence in the L-S reaction must be converted to an equivalent H_2 pressure. For that purpose, the Nernst equation is used, since the H_2/H^+ equilibrium is rapid:

$$E = E_0 + (2.3/RT) \log(a_{\text{H}^+}/P_{\text{H}_2}^{0.5}) \quad (3)$$

where E_0 is the standard potential of the hydrogen electrode (N.H.E.) vs. AgCl/Ag reference ($E_0 = -0.204$ V at 323 K). Combining eqns. (2) and (3), with $a_{\text{H}^+} = 1$:

$$\text{Rate} = 8.6 \times 10^6 P_{\text{H}_2}^{0.75} \exp(-E_a/RT) \quad (4)$$

Since the reaction rates are not mass transfer limited, we conclude that the different rate laws (especially the differing activation energies) for G-S and L-S hydrogenation of ethylene indicate different reaction mechanisms. The mechanisms will be discussed in section 3.

2. Adsorbed Species

Having summarized and compared the macroscopic kinetic parameters, we present here new data on molecular aspects of the surface reaction in ethylene hydrogenation. In particular, we have characterized, before and after ethylene hydrogenations, the surfaces of single crystal Pt catalysts using LEED, TPD, HREELS, AES, cyclic voltammetry, chronoamperometry, and a ^{14}C radiotracer technique. We present the results of these adsorbed species studies in three sections: (1) the structure of chemisorbed ethylene, (2) its reactivity with hydrogen and (3) its reactivity with ethylene. In each section we present first the G-S data, then the L-S data, and finally a comparison of the two.

2.1 Structure of Chemisorbed Ethylene

2.1a Gas-Solid Conditions

Chemisorption studies in UHV [LEED (30,31), UPS (32), TPD (33-35), and HREELS (33,36)] have shown that ethylene adsorbs dissociatively on clean Pt(111) surfaces to form ethylidyne (CCH_3 , Fig. 4) at temperatures conducive to ethylene hydrogenation. In the conversion of ethylene to ethylidyne, a hydrogen atom from the ethylene bonds to the surface, recombines with another hydrogen atom, and desorbs as H_2 . The remaining C_2H_3 fragment undergoes a hydrogen atom shift to form a methyl group which sits above the dehydrogenated carbon in a three-fold hollow site on the Pt(111) surface. The activation energy for this UHV process is about 18 kcal/mole (35).

These ethylidyne (CCH_3) moieties also form on clean Pt(111) surfaces during ethylene hydrogenation at atmospheric pressures. Three separate techniques support this fact -- TPD, LEED, and HREELS. The results of these three techniques for a Pt(111) surface after ethylene hydrogenation are

compared with the "fingerprint" results for ethylidyne in Figure 5. The LEED pattern of the Pt(111) surface [a (2x2)] and the temperatures of hydrogen desorption in TPD from adsorbate decomposition after ethylene hydrogenation (4), both match those for ethylidyne on this surface (30-33). The diffuseness of the 1/2 order spots in LEED and the shaded shoulder in the TPD are probably due to minority C_xH_y fragments on the surface. In addition, HREEL vibrational spectra of the Pt(111) surface after ethylene hydrogenation, as shown in Figure 5, show peaks mostly attributable to ethylidyne. C_xH_y species are again the most probable reason for the extra features. There is also a small amount of coadsorbed carbon monoxide. Finally, hydrogenation reactions begun over either clean or ethylidyne-saturated Pt(111) surfaces prepared in UHV have identical rates. Consequently, we conclude that ethylene chemisorbed as ethylidyne is present on the Pt surface during G-S ethylene hydrogenation at atmospheric pressures.

2.1b. Liquid-Solid Conditions

In the present work, LEED observations were made in UHV on ethylene adsorbed under L-S conditions. Such experiments were preceded, as usual, by blank runs to determine whether accidental contamination of the surface occurred during transfer between vacuum and solution (16,17); Auger spectra following the blank runs indicated a trace of carbon, $\theta_C < 0.03$, presumably due to residual ethylene, and no change in the Pt(111) (1x1) LEED pattern. In contrast to the G-S result which produced a (2x2) LEED pattern (4), adsorption of ethylene from solution at open circuit (rest potential about 0.02 V vs. Ag/AgCl) produced a (1x1) LEED pattern with noticeable diffuse scattering, Figure 6-A.

Based upon integration of Auger spectra of this surface, Figure 7, the

carbon packing density (Θ_C) was about 1.5 times the packing density for saturation ethylidyne coverages. However, determination of Θ_C in vacuum clearly underestimates the amount of ethylene present when the Pt surface was in contact with solution: the anodic charge for electrochemical oxidation of the adsorbed ethylene decreased by 23% when the Pt surface was subjected to vacuum (as in Auger spectroscopy) prior to electrolysis in ethylene-free electrolyte, as discussed below. Adding this fraction to the amount observed by Auger spectroscopy places the packing density at saturation in L-S conditions at $\Theta_{C \text{ L-S}} \approx 2\Theta_{C \text{ G-S}}$.

We have investigated the structure of L-S adsorbed ethylene to compare with CCH_3 . Auger spectra indicated that the nature of the adsorbed species formed under L-S conditions varies with electrode potential. Adsorption of C_2H_4 at potentials between 0 and 0.3 V (vs. AgCl/Ag) yielded surfaces relatively free of oxygenous species as judged from the Auger spectra, as seen for instance in Figure 7-C. However, when adsorption was carried out either under more reducing ($E < 0$ V) or more oxidizing ($E > 0.3$ V) conditions, oxygen Auger signals appeared (510 eV, Figure 7-D). Under oxidizing conditions, the oxygen signal results simply from the onset of oxidation of the Pt surface (18,37), but the presence of oxygen signals under reducing conditions is surprising. A clue as to the origin of this oxygen signal was provided by the electrochemical data for this adsorbed layer: linear scan voltammograms for a smooth polycrystalline thin-layer electrode (38,39) in ethylene-free 1 M $HClO_4$ after treatment with ethylene solution at midrange ($E = 0.2$ V), Figure 8-A, and reducing potentials ($E = -0.1$ V and -0.2 V), Figures 8-B and 8-C, show the emergence of an oxidizable species (peak potential 0.5 V) under reducing adsorption conditions. While the identity of

this species is unknown, it undergoes oxidation at potentials where species adsorbed from aqueous alcohol solutions react (40). Voltammograms obtained for progressively more positive adsorption potentials, Figures 8-D and 8-E, illustrate the full course of this transition in reactive behavior.

It is interesting that disorder introduced into the Pt(111) surface by electrochemical oxidation (18,41) substantially altered the electrochemical behavior of adsorbed ethylene, particularly oxidation. These differences are illustrated by the voltammetric curves in Figures 9-C and 9-D.

Besides changes in the structure of L-S adsorbed ethylene with potential, there are also changes in coverage. Figure 10 shows the dependence of the charge involved in the oxidation of the L-S ethylenic moieties as a function of the electrode potential during adsorption. Provided that surface coverage is proportional to Q_{ox} , this plot represents the potential dependence of the surface coverage of the adsorbed organic material. As expected, ethylene packing density displays a maximum at potentials (0 to 0.2 V) intermediate between oxidation and reduction of adsorbed ethylene.

2.1c Comparison of Gas-Solid and Liquid-Solid Conditions

The structure of L-S adsorbed ethylene within this potential window between oxidation and reduction of ethylene (0 to 0.2 V) is the most appropriate structure to compare to the ethylidyne structure of G-S adsorbed C_2H_4 . Comparison of Auger spectra, Figures 7-B and 7-C, illustrates the consistent difference in carbon peak morphology for G-S and L-S adsorbed ethylene. The G-S carbon peak exhibits a hump on the low energy side and is broader than the L-S carbon peak. This spectral difference together with the integrated Auger electron spectra showing that L-S adsorbed ethylene was twice as densely packed on the Pt surface as ethylidyne, suggest a structural dif-

ference in L-S and G-S chemisorbed ethylene. To confirm that the G-S and L-S chemisorbed ethylene structures are different and to see if either is a hydrogenation reaction intermediate, we investigated the reactivity of G-S and L-S adsorbed ethylene with hydrogen and ethylene.

2.2 Reaction with Hydrogen

2.2a Gas-Solid Conditions

Reaction of G-S chemisorbed ethylene (ethylidyne) with $\text{H}_2(\text{g})$ was studied by a ^{14}C radiotracer technique (20) and by high-resolution electron energy loss spectroscopy. Figure 11 shows the HREELS and ^{14}C results of the reaction of G-S chemisorbed ethylidyne with 1 atm. of H_2 . In both experiments a saturation coverage of CCH_3 remains close to one monolayer coverage ($\Theta/\Theta_0 \approx 1$) at near room temperature. Only at temperatures above 330 K are the ^{14}C fragments appreciably hydrogenated and removed from the surface (Fig. 11-A). The complementary HREEL spectra in Figure 11-B prove that the structure of this strongly adsorbed ethylidyne is the same before and after 1 atm. H_2 treatments, since these spectra are virtually identical. The increase in the CO (ν_{CO}) band intensity is the result of CO adsorption from background gases when a small fraction of the CCH_3 is hydrogenated and removed from the surface, but since CO has a large cross section for vibrational excitation, this increased peak intensity corresponds to less than 5% of a monolayer of chemisorbed CO . We estimate the rate of ethylidyne rehydrogenation to be 10^{-4} molecules/Pt atom $\cdot$ s (Table III), over 4 orders of magnitude slower than the rate of ethylene hydrogenation at the same temperature and H_2 pressure.

2.2b Liquid-Solid Conditions

Reaction of L-S chemisorbed C_2H_4 with $\text{H}_2(\text{g})$ was studied by cyclic

voltammetry and by monitoring the coverage as measured by Q_{ox} . In contrast to the stability of G-S adsorbed ethylidyne to 1 atm. of H_2 at 300 K, the L-S adsorbed species reacted with H_2 dissolved in aqueous electrolyte at 1 atm. external pressure, both at open circuit and when the electrode potential was held at 0.200 V (Figure 12-A). The reaction led to partial desorption (Table III), as well as to a change in chemical properties of the adsorbate, as evidenced by emergence of a new oxidative voltammetric peak near 0.5 V, Figure 12-A as compared with Figure 8-A; the size of this new peak increased with increasing exposure to H_2 , Figures 12-B,C. The surface species produced by this transformation have not been identified, although the oxidative voltammetric peak is suggestive of adsorbed alcohols (40), and the Auger spectra display an oxygen signal, Figure 7-D.

2.2c Comparison of G-S and L-S conditions

The lack of reactivity of G-S adsorbed ethylene with H_2 as compared with L-S adsorbed ethylene reactivity is not due to a blocking of sites for H_2 adsorption as shown by temperature programmed desorption. Figure 13 shows TPD results for coadsorption of $H_2(D_2)$ on an ethylidyne-saturated surface (coverage typical for ethylene hydrogenation). H(D) atoms coadsorbed on the Pt surface desorb as $H_2(D_2)$ at below 300K, while CCH_3 decomposes to evolve H_2 at >500K. While no coadsorption was possible with low pressure exposures of H_2 (less than 10^{-5} torr), coadsorption of $H_2(D_2)$ was possible with 1 atm. exposures of these gases as shown by the presence of the 300 K desorption peak in Figure 13 (42).

Furthermore, while the reaction of ethylidyne with $H_2(g)$ showed none of the irreversible structure changes seen for L-S chemisorbed $C_2H_4 + H_2$, there were reversible structure changes as evidenced by reactions with D_2 . HREELS studies (not shown here) of ethylidyne reaction with 1 atm. of deuterium

show that there is a very small amount of H-D exchange in the methyl group. Similar results on Rh(111) have been reported and a mechanism proposed (43). Again, the rate of this process was estimated to be less than 10^{-5} molecules/Pt atom/s, orders of magnitude slower than ethylene hydrogenation (Table III).

G-S and L-S adsorbed C_2H_4 also react differently with electrogenerated hydrogen as shown by the linear scan voltammetric data in Figure 14. The ethylidyne species characteristic of G-S adsorption is much less reactive electrochemically, Figure 14-A, than the L-S adsorbed species, Figure 14-B, toward both reduction (dashed curves) and oxidation (solid curves). The lower reactivity of G-S adsorbed ethylene (ethylidyne) towards electrogenerated H atoms correlates with the slow rehydrogenation rate of CCH_3 under 1 atm. of gas phase H_2 (section 2.1a).

By comparing the rates of reaction of G-S and L-S chemisorbed C_2H_4 with $H_2(D_2)$ to the ethylene hydrogenation rates under similar conditions (Table III), we conclude that ethylene chemisorbed under G-S conditions as ethylidyne is too stable to be a hydrogenation intermediate at 300 K, but L-S chemisorbed C_2H_4 is a possible intermediate in the L-S hydrogenation.

2.3 Reaction with C_2H_4

2.3a Gas-Solid Conditions

It has already been noted (section 2.2a) that the ethylidyne (present on Pt(111) surfaces during the G-S hydrogenation of C_2H_4) is not a reaction intermediate. HREELS studies also show that C_2H_4 cannot be irreversibly adsorbed in an ethylidyne monolayer, even at 1 atm. pressure. HREEL studies in Figure 15

show the fingerprint spectra of CCD_3 (15-A), CCH_3 (15-C), and of a CCD_3 monolayer exposed to 1 atm. of C_2H_4 (15-B). This latter spectrum shows no sign of the intense $\delta_s \text{CH}_3$ mode (1340 cm^{-1}) for CCH_3 . This mode would appear if there were C_2H_4 coadsorption or replacement to form CCH_3 .

2.3b Liquid-Solid Conditions

Despite their lower electrochemical reactivity, ethylidyne-covered Pt(111) surfaces prepared in UHV catalyzed electrochemical reduction and oxidation of ethylene from solution identically to the clean Pt(111) surface (Figure 16). This surprising result is rendered more understandable by the observation that exposure of the ethylidyne layer to aqueous ethylene solution at open circuit converted the ethylidyne to a form apparently identical to the L-S adsorbed species as evidenced by the identical appearance of the LEED patterns [(1x1) with noticeable diffuse intensity, Fig. 6-A], identical Auger spectral morphology, Figure 7-C, and identical electrochemical behavior, Figure 14-B. That this interconversion is due to displacement of adsorbed ethylidyne by ethylene rather than to a reduction process of ethylidyne is indicated by the fact that interconversion does not occur in the absence of dissolved ethylene; voltammetric behavior identical to Figure 14-A was still obtained, and the LEED pattern was still (2x2) although sharpened somewhat, Figure 6-B. In other words, exposure of the ethylidyne-coated surface to aqueous ethylene in the appropriate potential window (0 to 0.2 V) regenerates the reactive ethylene intermediate by replacement. By contrast, as noted earlier, G-S ethylidyne reacted extremely slowly with molecular C_2H_4 in the gas phase (Figure 11).

2.3c Comparison of G-S and L-S conditions

While G-S adsorbed ethylidyne can be converted to the L-S adsorbed

form in solution, the reverse is not true. Exposure of L-S adsorbed ethylene to vacuum or ethylene vapor altered the behavior of the adsorbed layer somewhat, but did not produce adsorbed ethylidyne, as evidenced by voltammetric scans following vacuum treatment, Figure 9-B: smaller oxidative charges resulted for sample which had been evacuated, although the locations of the peaks were the same. Comparison of Figure 14-A with 9-B, for adsorbed ethylidyne, illustrates this vastly different behavior.

2.4 Summary of G-S and L-S Chemisorbed Ethylene Structure and Reactivity

In comparing the adsorbed ethylene species that cover these Pt surfaces during ethylene hydrogenation, we conclude from the preceeding data that:

- (1) Chemisorbed ethylene structures are different for G-S and L-S reactions; the gas phase structure is ethylidyne (CCH_3) and the L-S product is, most probably, densely packed, undissociated ethylene.
- (2) The G-S formed structure is stable in vacuum, and does not react with $\text{C}_2\text{H}_4(\text{g})$. It can be converted to L-S chemisorbed ethylene on exposure to aqueous ethylene at open circuit.
- (3) The L-S formed structure is stable in vacuum and more reactive electrochemically in acidic solution than the G-S structure; it does not convert to CCH_3 when transferred to vacuum.
- (4) The G-S adsorbate is inert towards molecular hydrogen (although H_2 can be adsorbed and dissociated on the surface), while the L-S material reacts actively with H_2 in the aqueous environment.
- (5) At potentials approaching the onset of hydrogen evolution, chemisorbed ethylene is reductively desorbed from the surface and partially converted to alcohol-related chemisorbed products.

- (6) G-S adsorbed ethylene is irreversibly adsorbed and is not a hydrogenation reaction intermediate at 300 K.
- (7) G-S and L-S adsorbates can be characterized in vacuum without altering their catalytic or electrochemical activity and with only partial desorption of the adsorbate.

3. Modelling the L-S Hydrogenation in G-S UHV Experiments

Since ethylene cannot be adsorbed on the catalytically active Pt(111) surfaces that are "saturated" with CCH₃ during C₂H₄ hydrogenation at 300 K, the steady state hydrogenation of ethylene at the G-S interface at this temperature (if a minority of "defect sites" are not the catalyst) occurs on top of this layer of ethylidyne. By contrast, the L-S hydrogenation of C₂H₄ may occur directly on a H-covered Pt surface since L-S chemisorbed ethylene can be hydrogenated and removed from the surface at 300 K. The possibility that the L-S hydrogenation occurs on the surface and the G-S hydrogenation in a second layer above the surface could explain the higher activation energy for the G-S reaction (10.8 as compared to 5.9 kcal/mole) and suggests that ethylidyne inhibits the G-S reaction.

To test this hypothesis, we have modelled the proposed mechanism of L-S hydrogenation on the Pt surface in ultra-high vacuum using temperature programmed desorption. In these experiments, a clean Pt(111) single crystal surface is exposed in UHV at 150 K first to 30 L D₂ [1 langmuir (L) = 10⁻⁶ torr-sec] and then to 6 L C₂H₄. (Ethylidyne does not form below 270 K.) Upon heating the crystal at 30 K/s, ethane-d₂ (amu=32, Figure 17) is one of the desorption products. The low desorption peak temperature (250 K) and large peak width imply a low activation energy for this hydrogenation reaction.

Using the method of Chan and Weinberg (44), we obtain from this data an activation energy of 6 ± 1 kcal/mole (42). This activation energy is, to within experimental error, the same as was found for L-S ethylene hydrogenation, supporting the hypothesis that this reaction of ethylene with hydrogen occurs on the Pt surface.

4. G-S and L-S Ethylene Hydrogenation Mechanisms

Based upon the observations described in the text and summarized in Tables I-III, the following mechanism for the steady state G-S hydrogenation of ethylene at 300 K is proposed (Ref. 4, Figure 18):

The presence of ethylidene species ($CHCH_3$) that form reversibly under high pressures of H_2 has been suggested previously (4,35,43). This mechanism explains how hydrogen atoms adsorbed on the surface are transferred to ethylene on top of an irreversibly adsorbed layer of ethylidyne. The idea of an adsorbed hydrocarbon being the source of hydrogen for hydrogenations was first proposed by Thomson and Webb (3) to explain much of the literature G-S C_2H_4 hydrogenation data. The similarity between reduction rate data for single-crystal and supported Pt surfaces noted earlier can be attributed to masking of the surface structure by the carbonaceous (CCH_3) deposit (4).

According to the L-S results (Table I and Table III), the following mechanism is proposed for the steady state electroreduction of ethylene to ethane at 300 K (Figure 19):

This mechanism is consistent with the observed dependence of the rate on potential (Tafel slope). As mentioned previously, the 40 mV Tafel slope for reduction of ethylene from bulk solution can be attributed to two reversible electrochemical reduction steps [(8) and (9)], followed by a rate-determining chemical reaction. The hypothesis that ethylene does not actually chemisorb on the surface as an intermediate in the L-S hydrogenation to ethane is supported by the fact that chemisorbed ethylene has a different activation energy and larger Tafel slope for reduction to ethane (Table I). This latter reaction is probably the result of an initial rate-determining electron transfer to chemisorbed ethylene followed by hydrogenation steps. It is noteworthy that eqn. (10) is identical to that first postulated by Horiuti and Polanyi (45) and confirmed recently by Kita (8).

The primary reason for the activation energy difference in the G-S and L-S hydrogenations is that the interfering hydrocarbon layer is removed in the L-S reaction by electrochemical reduction of most of the chemisorbed ethylene. Owing to the absence of a blocking hydrocarbon layer, ethylene molecules can react directly with adsorbed hydrogen atoms in the L-S hydrogenation. The fact that the activation energy for L-S ethylene hydrogenation is the same as that determined by TPD for the reaction of gas phase ethylene with adsorbed H atoms supports this conclusion.

In comparing the G-S and L-S ethylene hydrogenation mechanisms, we

conclude:

- (1) G-S reduction of ethylene occurs by hydrogen atom transfer from the Pt surface through a chemisorbed C_2H_3 (ethynylidyne) layer to gas phase C_2H_4 .
- (2) L-S reduction of ethylene occurs by reaction of ethylene with electrogenerated H atoms on the platinum surface.

CONCLUSIONS

The structures and reactivity of ethylene chemisorbed on platinum under G-S and L-S ethylene hydrogenation reaction conditions at 300 K are different. As a consequence, the hydrogenation processes occur via different pathways and are limited by different rate-determining steps. L-S reduction of ethylene proceeds by reaction with hydrogen atoms adsorbed on the platinum surface, while G-S hydrogenation of ethylene requires transfer of hydrogen atoms from the surface via irreversibly chemisorbed ethylene to weakly adsorbed ethylene in a second layer. The activation energies for these processes are 5.9 and 10.8 kcal/mole respectively. Temperature programmed desorption experiments in ultra-high vacuum support this lower activation energy for reduction of ethylene in direct contact with hydrogen on the surface.

Our results also show that the G-S and L-S adsorbates can be characterized in vacuum without loss of their catalytic or electrochemical activity and with only partial desorption of the adsorbate. The voltammetric behavior of L-S adsorbed ethylene is more clearly resolved on Pt(111) than on polycrystalline or disordered Pt surfaces.

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FIGURE CAPTIONS

- Figure 1. The intrinsic similarities between electrochemical reduction at a metal electrode in solution (A) and reaction of gas phase molecules at a metal surface (B). The presence of solvent molecules and the effect of the electrode potential in electroreductions are the main differences between these two processes.
- Figure 2. The UHV chamber/reactor systems used in the gas-solid (A) and liquid-solid (B) ethylene hydrogenation reaction studies. Crystal cleaning and adsorbate characterization is accomplished with surface science techniques in the UHV chambers. The crystal is transferred to and from the reactors without exposure to atmosphere by either (1) closing a tube around the crystal to form a batch reactor for gas phase reaction studies or (2) transferring the crystal through a gate valve to a thin layer electrochemical cell for electroreductions.
- Figure 3. Chronoamperometric current-time curves for reduction of ethylene at an annealed polycrystalline platinum electrode at -0.15 V. A: reduction of L-S chemisorbed ethylene. B: reduction of ethylene from solution at an I-pretreated surface. C: reduction of ethylene at a Pt surface pretreated with ethylene at 0.2 V. D: reduction of ethylene at an H-covered surface.
- Figure 4. The structure of ethylidyne, produced by ethylene chemisorption from gas phase on a Pt(111) single crystal surface in the temperature range 300 – 450 K. The bond lengths of this ethylidyne species were determined from low-energy electron diffraction analysis.
- Figure 5. Evidence for the presence of ethylidyne on the Pt(111) surface after hydrogenation of gas phase ethylene at atmospheric pressures over this surface. Temperature programmed desorption, low energy electron diffraction, and high-resolution electron energy loss spectroscopy data for ethylidyne are compared with the results of these techniques on Pt(111) after ethylene hydrogenation at atmospheric pressure and return of the crystal to vacuum.
- Figure 6. LEED patterns: (A) Pt(111) (1×1) - C_2H_4 , 75 eV, (B) Pt(111) (2×2) - C_2H_3 , 65 eV, after reduction in 1 M $HClO_4$.
- Figure 7. Auger electron spectra: (A) Pt(111) clean surface; (B) Pt(111) (2×2) - C_2H_3 ; (C) Pt(111) (1×1) - C_2H_4 , after L-S adsorption at open circuit (0.02 V); (D) Pt(111) (1×1) - C_2H_4 and oxygen-containing species adsorbed during a negative scan below 0 V. Experimental conditions: primary beam, 0.5 μA at $2,000$ eV, angle of incidence, $\alpha_i = 73^\circ$, modulation amplitude (CMA), 5.00 V.

- Figure 8. Cyclic current potential curves of polycrystalline Pt (TLE, refs. 38,39) electrode. L-S ethylene adsorbed: (A) at any potential between 0 and 0.3 V; (B) at -0.100 V; (C) at -0.200 V; (D) at +0.400 V and (E) at +0.600 V. (----) clean Pt surface, (....)Pt-C₂H₄ surface. Following ethylene adsorption, TLE cavity was rinsed with 1 M HClO₄. Experimental conditions: adsorption time = 2 min; scan rate = 10 mV/s
- Figure 9. Cyclic current-potential curves of Pt(111) electrode obtained in 1 M HClO₄ electrolyte following: (A) L-S adsorption of ethylene during negative scan (Fig. 16-A); (B) vacuum exposure of L-S ethylene adsorbed during the negative scan; (C) L-S adsorption of ethylene on Pt(111) at 0.35 V; (D) L-S adsorption of ethylene at 0.35 V on Pt(111) disordered by electrochemical oxidation. Scan rate = 10 mV/s.
- Figure 10. Anodic charge for L-S oxidation of adsorbed ethylene, and number of electrons per surface Pt atom, as a function of adsorption potential.
- Figure 11. Stability of ethylidyne species on Pt(111) under 1 atm. of H₂(g). (A) The Pt(111) surface is saturated with ¹⁴C₂H₄ and the surface radioactivity measured after 1 atm. of H₂ exposure for various times as a function of temperature. The fraction of the initial ¹⁴C remaining on the surface, θ/θ_0 , is determined. (B) HREEL vibrational spectrum of ethylidyne before (a) and after (b) 1 atm. of H₂ for 5 min. at 310 K.
- Figure 12. Cyclic current-potential curves for L-S adsorbed ethylene at polycrystalline Pt(TLE) electrodes. Ethylene adsorption at 0.2 V was followed by: (A) rinsing the C₂H₄ coated electrode with H₂-saturated electrolyte at 0.2 V; (B) and (C) gaseous hydrogen at 1 atmosphere; (D) negative-going potential scan (without hydrogenation). Scan rate = 10 mV/s.
- Figure 13. Temperature programmed desorption to show coadsorption of hydrogen with a monolayer of ethylidyne (CCH₃) on Pt(111) by 1 atm. exposure of H₂. (A) saturation coverage of CCH₃/ TPD amu=2 (B) saturation coverage of CCH₃ + 1 atm. of H₂/ TPD amu=2 (C) saturation coverage of CCH₃ + 1 atm. of D₂/ TPD amu=4. The desorption peak near 300 K corresponds to H₂(D₂) desorbing from the bare Pt(111) surface. The higher temperature H₂ desorption results from the decomposition of CCH₃ to give H₂ and surface carbon.
- Figure 14. Cyclic current-potential curves of Pt(111) electrode. (A) following G-S adsorption of ethylidyne: (—) positive going scan starting from rest potential (0.6 V), (....) negative going scan, and (----) subsequent cyclic scan characteristic of the "disordered" Pt(111) surface; (B) following L-S adsorption of ethylene at open circuit (0.20 V) and rinsing with pure electrolyte. Scan rate = 10 mV/s.
- Figure 15. High resolution electron energy loss vibrational spectra to show that ethylene cannot be irreversibly coadsorbed in an ethylidyne monolayer even under atmospheric pressure exposures. (A) Ethylidyne,

CCH_3 ; (B) Ethylidyne- d_3 + 1 atm. of C_2H_4 for 5 min.; (C) Ethylidyne- d_3 .

Figure 16. Cyclic current-potential curves of: (—) initially clean Pt(111) electrode and: (---) Pt(111)- C_2H_3 surface, recorded in 1 M HClO_4 saturated with ethylene. (A) Negative going scan; (B) positive going scan: (....) subsequent cyclic scan characteristic of the disordered Pt(111) surface. Scan rate = 10 mV/s.

Figure 17. Temperature programmed desorption of ethane- d_2 ($\text{amu}=32$) from a deuterium-covered Pt(111) surface exposed to ethylene at 150 K. The desorption peak maximum (250 K) and peak width were used to calculate an activation energy for this hydrogenation reaction of 6 ± 1 kcal/mole (see text).

Figure 18. Proposed mechanism for the steady state hydrogenation of gas phase ethylene at atmospheric pressures over the Pt(111) surface at 300 K. Other mechanisms are operative at higher temperatures and under nonsteady state conditions.

Figure 19. Proposed mechanism for the steady state electroreduction of ethylene to ethane over Pt surfaces at 300 K.

TABLE I

Kinetic Parameters for L-S Hydrogenation of Ethylene
On an Annealed Polycrystalline Pt Electrode

	H-Covered Pt ^a	C ₂ H ₄ -Pretreated Pt ^b	Chemisorbed C ₂ H ₄ ^c
Activation Energy (kcal/mole) ^d	5.9	6.6	3.3
Kinetic Isotope Effect (k _H /k _D)	2.0	2.2	1.2
Reaction Rate (molec/Pt surface atom·s) ^e	108	33	1.6
Reaction Order (C ₂ H ₄) ^f	0	0	---
pH Dependence d(log rate)/dpH	-1	-1	---
Tafel Slope dE/d(log rate)(mV) ^g	40	40	107

a) C₂H₄ in contact with a clean Pt surface at -0.200 V vs. AgCl/Ag reference
[H⁺] = 1 M

b) Chemisorption of C₂H₄ at +0.200 V; reduction of ethylene from bulk
solution at -0.200 V/ [H⁺] = 1 M.

c) Chemisorption of C₂H₄ at +0.200 V; reduction in ethylene-free electrolyte
at -0.200 V/ [H⁺] = 1 M.

d) Temperature was varied from 0 to 50 °C.

e) Temperature = 298 K. To convert these rates to currents (A), multiply by
2.1 x 10⁻⁴.

f) Pressure was varied from 10 to 760 Torr (from 4 x 10⁻⁵ to 3 x 10⁻⁴ M);
all L-S data refer to 760 Torr.

g) Potential region, -0.100 to -0.200 V vs. AgCl/Ag reference.

TABLE II

Comparison of Ethylene Hydrogenation Kinetic Parameters
For Different Platinum Catalysts

<u>Catalyst</u>	<u>Log Rate</u> ^a	<u>a</u> ^b	<u>b</u> ^b	<u>E_a</u> kcal/mole)	<u>Reference</u>
Platinized foil	1.9	-0.8	1.3	10	46
Platinum evaporated film	2.7	0	1.0	10.7	47
1% Pt/Al ₂ O ₃	---	-0.5	1.2	9.9	48
Platinum wire	0.6	-0.5	1.2	10	49
3% Pt/SiO ₂	1.0	---	---	10.5	50
0.05% Pt/SiO ₂	1.0	0	---	9.1	51
Pt(111)	1.4	-0.6	1.3	10.8	4
Pt(111) ^c	---	---	---	6	This work
Pt(polycrystalline) ^d	2.3	0	.75	5.9	This work

a) Rate in molecules/Pt surface atom/s, corrected for the following conditions:

$T = 323 \text{ K}$, $P_{C_2H_4} = 20 \text{ Torr}$, $P_H = 100 \text{ Torr}$.

b) Orders in ethylene (a) and hydrogen (b) partial pressures.

c) Temperature programmed desorption of ethane from a Pt(111) surface first saturated with deuterium and then exposed to ethylene at 150 K (Figure 17).

d) Annealed polycrystalline Pt electrode; electroreduction at $E = -0.200 \text{ V}$ vs. AgCl/Ag with $[H^+] = 1 \text{ M}$.

TABLE III

Rates of Hydrogen Transfer Processes at T = 323 K
On Pt(111) and Annealed Polycrystalline Pt electrode surfaces

Surface	Process	Conditions	Estimated Turnover Rate (reactions/Pt atom's)	Source
Pt(111)	C ₂ H ₄ Hydrogenation	P _{C₂H₄} = 20 torr P _{H₂} = 100 torr	25	a
Pt(polycrystalline)	C ₂ H ₄ Electroreduction from solution	P _{C₂H₄} = 20 torr ^f P _{H₂} = 100 torr	187	b
Pt(111)	Hydrogenation and removal of G-S chemisorbed ethylene from the surface by H ₂ (g)	P _{H₂} = 760 torr θ _{C₂H₄} = satn.	10 ⁻⁴	c
Pt(polycrystalline)	Hydrogenation and removal of L-S chemisorbed ethylene from the surface by H ₂ (g)	P _{H₂} = 760 torr θ _{C₂H₄} = satn.	>0.1	d
Pt(polycrystalline)	Hydrogenation and removal of L-S chemisorbed ethylene from the surface by electrogenerated H atoms	[H ⁺] = 1 M E = -0.176 V θ _{C₂H₄} = satn.	2.2	b
Pt(111)	H,D exchange in the methyl group of ethylidyne using D ₂ (g)	θ _{C₂H} = satn. P _{D₂} = 1 atm.	10 ⁻⁵	e

a) Reference 4.

b) This work.

c) ¹⁴C radiotracer studies -- this work and reference 21.

d) Extent of reaction monitored by total oxidation charge which is compared to Q_{ox} in Figure 12.

e) Estimated from HREELS data mentioned here and to be discussed more fully later. Similar data has been discussed for Rh(111), ref. (41).

f) The reaction was run in solution with [H⁺] = 1. The effect of potential has been converted to an effective H₂ pressure using eqns. 2-4.

A

B

Fig. 1

(A)

XBL 88-6930

(B)

Fig. 2

Fig. 3

Pt (III) + ethynidyne

XBL794-6167

Fig. 4

EVIDENCE FOR THE PRESENCE OF ETHYLIDYNE AFTER ATMOSPHERIC HYDROGENATION OF ETHYLENE OVER Pt (111)

Fig. 5

(A)

(B)

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

¹⁴C RADIOTRACER EXPERIMENTS

VIBRATIONAL SPECTRA

Fig. 11

Fig. 12

XBL 846-2491

Fig. 13

Fig. 14

Fig. 15

MICROAMPERE, CURRENT, MILLIAMPERE

POTENTIAL, VOLT VS. AgCl/Ag

-0.3 -0.2 -0.1 0.0 0.1 0.2 0.3

START

A

1.0mA

START

B

50 μ A

POTENTIAL, VOLT VS. AgCl/Ag

0.0 0.2 0.4 0.6 0.8 1.0 1.2

Fig. 16

Fig. 17

Fig. 18

Fig. 19

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