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Flash Hydrogenation of Ethylene on Tungsten Single Crystal Surfaces

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The production of ethane accompanying the thermal decomposition of ethylene on bare and hydrogen covered (110), (100), (112) and (111) tungsten surfaces has been studied. The fraction of ethylene converted to ethane is found to vary from face to face, but in no case does the amount of ethane produced correspond to hydrogenation of more than 1.5% of the chemisorbed ethylene; the remainder decomposes to a carbon residue and gaseous hydrogen. With no preadsorbed hydrogen (i.e., self-hydrogenation) the order of activity, as given by the fraction of ethylene converted to ethane, is as follows:

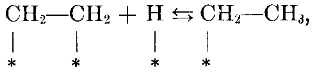
$$(110) < (100) \sim (112) < (111).$$

With preadsorbed hydrogen (hydrogenation) the order of activity is approximately the same.

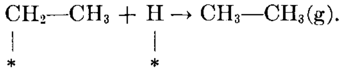
$$(110 < (100) < (111) < (112).$$

The inversion in the order for the (112) and (111) planes is due to a concentration effect. The increase in the fraction of ethylene hydrogenated over the fraction self-hydrogenated increases as the ratio of chemisorbed hydrogen to chemisorbed ethylene increases, and in the case of the (112) plane this ratio is a factor of 7 larger than the same ratio for the (111) plane. When D_2 is substituted for H_2 in the hydrogen predose, the extent of incorporation of D atoms in the ethane product, as indicated by the amount of d_5- and d_6-ethane relative to d_2-ethane, is ordered approximately in the inverse of the self-hydrogenation activity.

The amount of ethane produced is shown to be inconsistent with a Rideal–Eley mechanism, but consistent with the Horiuti–Polyani or half-hydrogenated state mechanism.



$$\underset{\overset{|}{*}}{CH_2}—\underset{\overset{|}{*}}{CH_2} + \underset{\overset{|}{*}}{H} \leftrightarrows \underset{\overset{|}{*}}{CH_2}—CH_3, \qquad (1)$$



$$\underset{\overset{|}{*}}{CH_2}—CH_3 + \underset{\overset{|}{*}}{H} \rightarrow CH_3—CH_3(g). \qquad (2)$$

The crystallographic dependence for hydrogenation and deuteration is a consequence of the reverse of Eq. (1). The probability of this step occurring decreases with increasing metal–metal spacing. A high density of short spacings as on the (110) plane would yield the observed small amounts of ethane but extensive incorporation of D atoms, while a high density of long spacings as on the (111) plane would yield the observed larger amounts of ethane with less extensive incorporation of D atoms.

INTRODUCTION

The role played by surface structure in catalytic reactions is not well defined. Discussion of a geometric factor in catalysis dates to before Balandin (1) in 1929, yet little experimental evidence exists about its effect. Although the geometric factor is usually associated with the lattice spacing of the surface atoms, Gwathmey and Cunningham (*2*) have pointed out that lattice spacing is only one aspect of the geometric factor and is by no means the only measure of surface structure. But regardless of the question as to the specifics of a geometric factor, recent studies of the chemisorption of N_2 (*3, 4*), H_2 (*5, 6*) and C_2H_4 (*7*) on the low index planes of tungsten have shown that the surface chemistry of these species is different on each of the single crystal planes. Thus, one way to probe a geometric factor in catalysis is to study a reaction catalyzed by a group of different single crystal surfaces. This has been done for the decomposition of NH_3 on W(*110*), W(*100*) and W(*111*) (*8*). Each surface was found to follow the same decomposition mechanism, but with differing rates for each. Other studies of a catalytic reaction on 2 or more single crystal faces of a fcc metal include H_2 and C_2H_4 on the (111), (110), (100) and (321) faces of Ni (*9*), the interaction of H_2 and O_2 (*10*) and the decomposition of formic acid (*11*) on copper single crystals, the decomposition of CO over Ni(111) and Ni(100) (*12*), and a study of the dehydrocyclization of *n*-heptane on several platinum surfaces (*13*). None of the results of these studies were explained in terms of simple crystal geometry except for the general conclusion that open surfaces are the most reactive (*8, 9, 13*).

This study of the reaction of H_2 and C_2H_4 on tungsten single crystals to form ethane differs in method from those studies mentioned above. The ethane is not produced in a flow system, but instead both reactants are sequentially adsorbed on the surface below the reaction temperature thereby establishing a known coverage of each species prior to reaction. The surface is then heated and the appearance of ethane in the gas phase followed. The amount of ethane produced is small, on all surfaces ~99% of the chemisorbed ethylene decomposes yielding H_2 in the gas phase. The results of the decomposition study have been reported elsewhere (*14*). The amount of ethane produced will be shown to depend on the reactivity of the surface, and the relative surface concentrations of H_2 and C_2H_4.

EXPERIMENTAL METHODS

The crystals, crystal mounting and experimental system have been described previously (*6, 7*). The surfaces were normally cleaned by flashing to temperatures >2400 K; however, each surface was O_2 cleaned prior to the hydrogenation experiments. Hydrogen desorption spectra were used as a check of this cleaning procedure. As C_2H_4 decomposes above 200 K the crystals were flashed to ~1700 K to remove adsorbed gases and then cooled to below 150 K in a vacuum of at least 5×10^{-10} Torr prior to admission of C_2H_4. When hydrogen was predosed, the required cooling period was adequately supplied by the hydrogen dosing period. Temperatures were measured by a W 5% Re/W 26% Re thermocouple welded to the center of the crystal.

The number of molecules of type x, n_x, appearing in the gas phase in a thermal desorption experiment is proportional to the area under the desorption spectrum.

$$n_x \alpha \int \Delta i_{\mathrm{M}}^+ \, dt = A_{\mathrm{M}}. \qquad (1)$$

Δi_{M}^+ is the change in mass spectrometer ion current due to the molecular ion M of species x, t is time and the value of the integral is obtained from A_{M}, the area under the mass M thermal desorption spectrum (*15*). For ethylene the main reactions that occur during the flash are decomposition leading to production of gaseous hydrogen and hydrogenation yielding ethane (*16*). The number of ethane molecules is proportional to A_{30}, for among the C_1 and C_2 hydrocarbons a charge to mass ratio of 30 is unique to ethane. The number of hydrogen molecules produced is proportional to A_2, but as 2 hydrogen molecules are produced for each ethylene decomposed the number of ethylene molecules is proportional to $0.5\,A_2$. The ratio of the number of ethane molecules produced to the number of ethylene molecules decomposed is

$$\frac{n_{C_2H_6}}{n_{C_2H_4}} = \frac{K_{C_2H_6}}{0.5}\frac{A_{30}}{A_2} = K\frac{A_{30}}{A_2}. \qquad (2)$$

To determine the exact value of the ratio, the factor $K_{C_2H_6}$ must be known, but a comparison of the relative amount of ethane produced from plane to plane can be based only on A_{30}/A_2 ratios on each plane as K contains only ratios of pumping speeds and mass spectrometer sensitivities, factors which should vary little from plane to plane.

In order to get an approximate idea of the amount of ethane produced a value of $K_{C_2H_6}$ can be estimated. Following Ref. (*17*),

$$K_{C_2H_6} = \frac{S_{C_2H_6}}{S_{H_2}}\frac{Z_2}{Z_{30}}. \qquad (3)$$

$S_{C_2H_6}/S_{H_2}$, the ratio of pumping speeds is assumed to be given by the ratio of the mean molecular speeds of C_2H_6 and H_2, $(2/30)^{1/2}$; this assumption was shown to be approximately valid for the hydrogen isotopes (*17*). We have no calibration for Z_2/Z_{30} but we can estimate it from ion gauge sensitivities by assuming that differences in mass spectrometer ion currents arise only in the ionization process. For ionization gauges the sensitivity, Z, is defined as follows:

$$i_{\text{total}}^{+} = i^{-}(Z_{\text{total}})P, \qquad (4)$$

i^{-} is the current of ionizing electrons. The cracking pattern of ethane (*18*) shows that the total ion current is $\sim 7.7\, i_{30}^{+}$. Inserting this for i_{total}^{+} in Eq. (4) leads to $Z_{30} = (1/7.7)(Z_{\text{total}})_{C_2H_6}$. Since mass 2 is the major ion from H_2, $Z_2 \sim (Z_{\text{total}})_{H_2}$. Thus, $Z_2/Z_{30} \simeq 7.7(Z_{\text{total}})_{H_2}/(Z_{\text{total}})_{C_2H_6}$, and use of Young's values of ionization gauge sensitivities (*19*) and the value for $S_{H_2}/S_{C_2H_6}$ in Eq. (3) yields $K_{C_2H_6} = 0.3$.

RESULTS AND INTERPRETATION

A. Hydrogenation and Self Hydrogenation

Rapid heating of a monolayer of ethylene adsorbed on tungsten at $\sim$135 K leads to decomposition as the major reaction with hydrogen as the principal gas phase product. Ethane in small amounts is the only other gas phase product detected. Figures 1 and 2 contain the spectra obtained on the (110), (100), (112), and (111) planes of tungsten. For each plane the sequence of curves is the same: curve a, hydrogenation, is the mass 30 spectrum resulting from a surface presaturated with hydrogen and then exposed to a saturation dose of ethylene; curve b, self-hydrogenation, is the mass 30 spectrum resulting from a surface saturated with ethylene; and curve c, decomposition, is the mass 2 spectrum resulting from a surface saturated with ethylene.

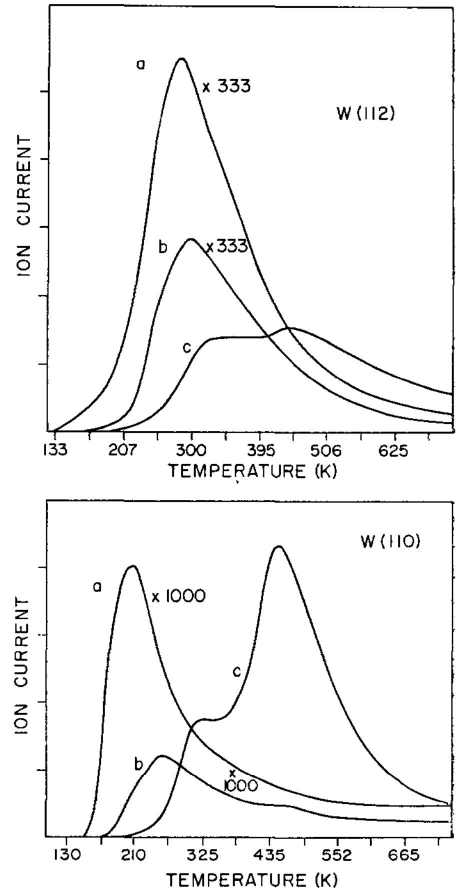


FIG. 1. Isotope spectra from W(112) and W(110): (a) mass 30 (ethane partial pressure) spectra resulting from sequential adsorption of H_2 and C_2H_4; (b) mass 30 spectra resulting from a monolayer of C_2H_4; (c) mass 2 (hydrogen partial pressure) resulting from a monolayer of C_2H_4.

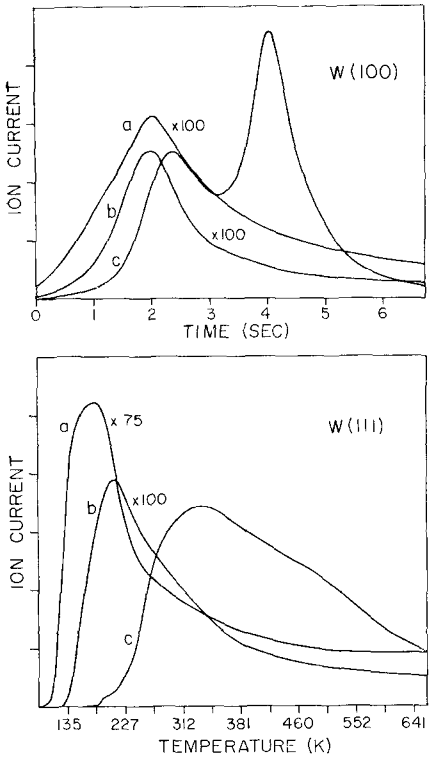


FIG. 2. Isotope spectra from W(100) and W(111): (a) mass 30 (ethane partial pressure) spectra resulting from sequential adsorptions of H_2 and C_2H_4; (b) mass 30 spectra resulting from a monolayer of C_2H_4; (c) mass 2 (hydrogen partial pressure) resulting from a monolayer of C_2H_4.

On all four planes, ethane production, with or without preadsorbed hydrogen, reaches its maximum rate at a temperature below the temperature of the peak maximum for ethylene decomposition. As ethylene must decompose at temperatures at or below that at which hydrogen appears in the gas phase, and undecomposed ethylene is required for hydrogenation, the upper limit for hydrogenation is determined by the stability of chemisorbed ethylene as reflected by the respective mass 2 spectra. While the upper limit for flash hydrogenation is determined by ethylene stability, the lower limit is apparently determined by the availability of hydrogen. With no preadsorbed hydrogen the hydrogen for ethane production is furnished by ethylene decomposition. As a result production of ethane is constrained to occur in the temperature region corresponding to the initial portion of the ethylene decomposition spectra. With predosed hydrogen the lower limit for hydrogenation would be governed by hydrogen mobility (*17*), and in general the effect of predosed hydrogen is to increase the amount of ethane produced and shift this production to lower temperatures.

On each plane the size of the mass 30 spectrum is at least a factor of 75 smaller than the mass 2 spectrum indicating that hydrogenation is a minor reaction compared to decomposition. For comparison from plane to plane consider the fraction, f, of adsorbed ethylene molecules that are converted to ethane. In terms of the area under the mass 2 spectrum, A_2, from an ethylene monolayer, and the area under the mass 30 spectrum, A_{30}, f is given by

$$f = \frac{n_{C_2H_6}}{n_{C_2H_4} + n_{C_2H_6}} = \frac{KA_{30}}{\theta_{C_2H_4}A_2 + KA_{30}}. \qquad (5)$$

The factor $\theta_{C_2H_4}$ must be included since different fractions of a monolayer of ethylene adsorb on each plane when the surfaces are presaturated with hydrogen (*14*). Since K, as estimated in the experimental section, is approximately 0.6 and $A_{30} \ll A_2$, the second term in the denominator can be neglected to yield

$$f = \frac{KA_{30}}{\theta_{C_2H_4}A_2}. \qquad (6)$$

Values of f/K along with the ethylene and hydrogen coverages from Ref. (*14*) are given in Table 1. f_h, hydrogenation, and f_s, self-hydrogenation, are used to distinguish between those cases where hydrogen is or is not preadsorbed. The relatively large error limits on the values of f are due to two factors: one is the small number of data points involved, only two for the (112) and (110), and the second is the small amount of ethane involved. The latter is especially a problem for self-hydrogenation considering the possibility of co-adsorption of hydrogen produced by ethylene decomposition in the ion pump and at hot filaments. The largest conversion of ethylene to ethane occurs on the (112) plane and with K equal

TABLE 1
HYDROGENATION DATA[a]

	(110)	(100)	(112)	(111)	Polycrys-talline
θ_{H_2}	0.98	0.67	0.96	0.36	0.86
$\theta_{C_2H_4}$	0.24	0.52	0.37	0.86	0.41
$\frac{f_s}{K}$ ($\times 10^3$)	0.4 ± 0.1	4.5 ± 0.9	3.8 ± 1	7.5 ± 2	1.5
$\frac{f_h}{K}$ ($\times 10^3$)	3.4 ± 0.3	11.9 ± 3.4	24.6 ± 4.3	13.1 ± 0.9	10.3
$n_{H_2}/n_{C_2H_4}$	6.5	2.4	5.4	0.76	4.1

[a] Hydrogen and ethylene coverages from Refs. (*14*) and (*17*), rows 1 and 2; fraction of chemisorbed ethylene self-hydrogenated and hydrogenated, rows 3 and 4; and the ratio of hydrogen to ethylene, row 5. The polycrystalline values are taken from data presented in Ref. (*17*).

to 0.6 corresponds to hydrogenation of 1.5% of the chemisorbed ethylene.

As indicated by the values of f_s, the (110) plane is the least active and the (111) plane the most active for self-hydrogenation. The order of activity is

$$f_s\text{: } (110) < (100) \sim (112) < (111).$$

Comparison of the f_s and f_h values in Table 1 shows that the effect of preadsorbed hydrogen on all four planes is to increase the fraction of ethylene converted to ethane. Direct comparison of hydrogenation activity as given by the f_h values shows the (110) plane to still be the least active, but the order for the (112) and (111) planes is inverted

$$f_h\text{: } (110) < (100) \sim (111) < (112).$$

Comparison of the hydrogenation results is complicated by differing ratios of hydrogen molecules to ethylene molecules on the four planes. This ratio, $n_{H_2}/n_{C_2H_4}$, can be determined from the hydrogen and ethylene coverages and the areas under the mass 2 spectra resulting from monolayers of hydrogen and ethylene (*14*). Values for the four planes are given in the fifth row of Table 1, and the order is as follows:

$$n_{H_2}/n_{C_2H_4}\text{: } (111) < (100) < (112) < (110).$$

With the exception of the (112) plane the order of hydrogenation activity is the reverse of the ratio of hydrogen to ethylene. When this ratio is considered the inactivity of the (110) plane is especially pronounced; the (110) plane is the least active despite having the largest ratio of hydrogen to ethylene, indicating *that the inactivity of the (110) plane is a property of the surface.*

Although the approximate ordering of the planes as to hydrogenation activity is a property of the surface, the increase in the amount of ethane produced by hydrogenation over self-hydrogenation shows a clear dependence on concentration. This enhancement is approximately given by $(f_h - f_s)/f_s$. These values are shown plotted in Fig. 3 vs the ratio of the number of hydrogen molecules to the number of ethylene molecules. In addition to the points for the four planes and polycrystalline tungsten (*17*) there is an additional point for the (112) that results from preadsorbing hydrogen in only the β_2 state. With only the β_2 state filled one is able to adsorb a full monolayer of ethylene so that $\theta_{H_2} = 0.48$, $\theta_{C_2H_4} = 1$, and $n_{H_2}/n_{C_2H_4} = 1$. Given these six data points the data can be approximated by a linear relationship between the enhancement of hydrogenation over self-hydrogenation and the ratio of hydrogen to ethylene molecules on the surface.

B. Deuteration

When D_2 is substituted for H_2 in the hydrogen predose, the complete range of deuterated ethanes up to d_6-ethane is obtained. As an example Fig. 4 contains the isotope spectra for masses 32 through 36 obtained from the (100) plane. These were

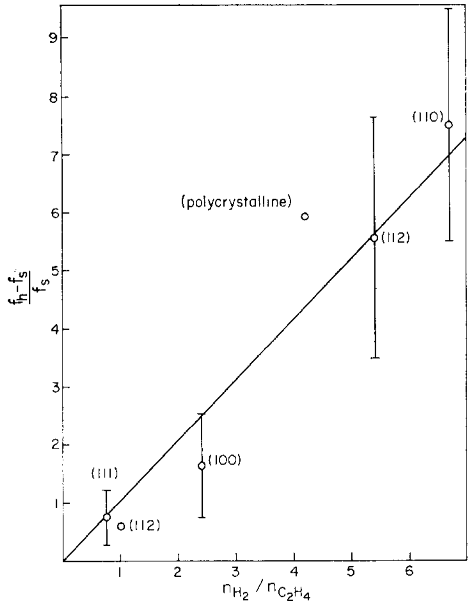


FIG. 3. Enhancement in the fraction of ethylene hydrogenated due to an increase in the ratio of the number of chemisorbed hydrogen molecules to the number of chemisorbed ethylene molecules.

obtained by recording that portion of the mass spectrum containing masses 32 through 36 at a rate of four scans a second and then replotting the amplitudes as a function of time. On all four planes the same general trend is observed; there is a general decrease in size with increasing extent of deuteration with a sharp break in the size of the spectra occurring between the mass 32 and 33 spectra. This break might indicate, as found by Kemball (*20*) for deuteration of ethylene over tungsten films, the production of a large amount of d_2-ethane. However, as the 70 eV ionizing electrons used in this study lead to extensive fragmentation of ethane, all the higher deuteroethanes yield ions with a charge to mass ratio of 32. As a result the area under the mass 32 spectrum can only be taken as proportional to an upper limit for the amount of d_2-ethane produced. This is not the case for the areas under the mass 36 and 35 spectra, for their only contributions are from the d_6- and d_5-ethane molecular ions.

Table 2 contains a summary of the areas under the isotope spectra relative to the area under the mass 32 spectra for the four planes and for polycrystalline tungsten (*17*). If the relative amount of mass 35

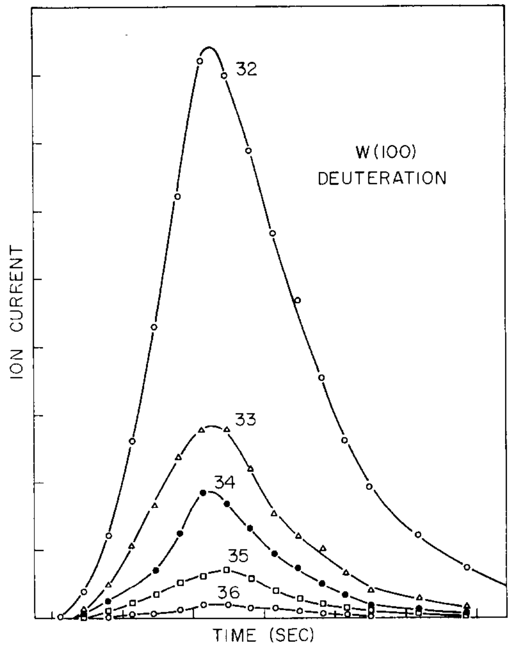


FIG. 4. Deuteration: mass 32 through 36 isotope spectra resulting from sequential adsorption of D_2 and C_2H_4 on W(100). Spectra from the remaining three planes are similar in shape. The areas under the isotope spectra from the four planes are given in Table 2.

TABLE 2

DEUTERATION: THE AREAS UNDER THE ISOTOPE SPECTRA FOR MASSES 33 THROUGH 36 RELATIVE TO THE AREA UNDER THE MASS 32 SPECTRUM[a]

	(111)	(100)	Polycrystalline	(112)	(110)
$\frac{A_{36}}{A_{32}}$	0	0.03	0.05	0.06	0.05
$\frac{A_{35}}{A_{32}}$	0.06	0.07	0.13	0.08	0.11
$\frac{A_{34}}{A_{32}}$	0.20	0.17	0.21	0.14	0.22
$\frac{A_{33}}{A_{32}}$	0.40	0.32	0.29	0.17	0.39

[a] The polycrystalline values are from data partially presented in Ref. (*17*).

and 36 from this table is compared with the ratio of hydrogen to ethylene in Table 1, it appears that the amount of d_5- and d_6-ethane increases as this ratio increases. However, it is possible that this trend is only apparent since the values in Table 2 are based on the amount of mass 32 not the amount of d_2-ethane. As the amount of mass 32 depends both on the amount of d_2-ethane and contributions from higher deuteroethanes there is the possibility that differing isotopic distributions on each plane are responsible for the trend. To explore this possibility we have calculated the contribution (expressed as a fraction of the parent amount) that each deuteroethane makes to mass 32 in a manner identical to that used by Kemball (*20*). These fractions are calculated using a reported cracking pattern (*18*) for d_6-ethane and assuming that the loss of one and two hydrogen atoms occurs to the same extent in all the deuterated species, but that the probability for loss of an H-atom is 1.17 times that of a D-atom. Subtraction of the contributions of the higher deuteroethanes from the observed amount of mass 32 gives the amount of mass 32 directly proportional to d_2-ethane. Figure 5 shows a plot of the calculated d_6/d_2 and d_5/d_2 ratios vs the ratio of D_2 to C_2H_4 on the surface. Figure 5 shows that production of d_6- and d_5-ethane increases as the D_2 to C_2H_4 ratio increases, so correction applied to the mass 32 data leaves the trends unchanged. This is of course dependent on the cracking pattern, but independent variation of the mass peaks corresponding to the loss of one and two hydrogens relative to the parent by ±25% did not reverse any of the trends.

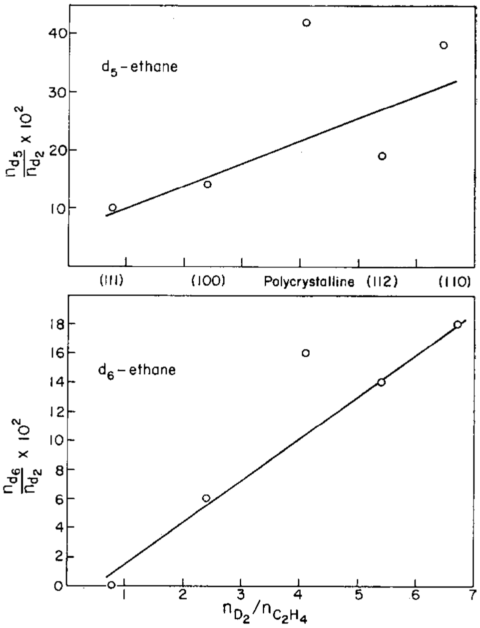


FIG. 5. The amount of d_6- and d_5-ethanes relative to the amount of d_2-ethane plotted vs the ratio of the number of chemisorbed D_2 to the number of chemisorbed C_2H_4.

C. Comparison with Polycrystalline Tungsten

For comparison with the flash hydrogenation observed on polycrystalline tungsten a better measure of the hydrogenation would be the number of ethane molecules produced per square centimeter. The ratio of the number of ethane molecules produced per square centimeter ($\bar{n}_{C_2H_6}$) to the number of molecules per square centimeter in a monolayer of hydrogen ($\bar{n}_{H_2}$) is proportional to the area under the mass spectrum divided by the area under the mass 2 spectrum from a monolayer of hydrogen (A_{H_2}).

$$\frac{\bar{n}_{C_2H_6}}{\bar{n}_{H_2}} \propto \frac{A_{30}}{A_{H_2}}. \qquad (7)$$

A_{H_2} is introduced to facilitate comparison between planes as the relative hydrogen densities from plane to plane have been reported (*5*, *6*). The ratio of the number of density of ethane molecules on any plane x to the number produced on the (100) plane is equal to

$$\frac{(\bar{n}_{C_2H_6})_x}{(\bar{n}_{C_2H_6})_{(100)}} = \frac{(A_{30}/A_{H_2})_x}{(A_{30}/A_{H_2})_{(100)}} \cdot \frac{(\bar{n}_{H_2})_x}{(\bar{n}_{H_2})_{(100)}}. \qquad (8)$$

Table 3 lists values of number of molecules of hydrogen per square centimeter on each plane relative to the number of W(100) determined by us and others from the areas under flash desorption curves and the geometric areas of the crystals studied. Our results are in good agreement with the published values except for

TABLE 3
Surface Densities (No./cm^2) of Hydrogen on Each Plane Relative to W(100)

	W(110)	W(100)	W(112)	W(111)
This work	0.76	1	0.79	1.1
Tamm and Schmidt (*5*)	0.70	1	—	1.75
Other[a]			0.80	0.6

[a] Absolute densities obtained from chemical evidence, W(112) (*6*), and from the area under the desorption spectra and knowledge of the pumping speed, W(111) (*22*), relative to the absolute density reported for the (100) plane reported by Madey (*21*).

W(111), where our value is low compared to that of Tamm and Schmidt (*5*) and high compared to the values given by Madey (*22*). In evaluation of Eq. (8) we have used our values, since W(111) is assumed to make only a small contribution to polycrystalline tungsten the choice is not a critical one.

In a study of the sequential adsorption of D_2 and C_2H_4 on the same four planes of tungsten we were able to synthesize the D_2 and C_2H_4 coverages for sequential adsorption of D_2 and C_2H_4 on polycrystalline tungsten (*17*) from the coverages obtained on the single crystal surfaces by assuming the polycrystalline surface to be composed of reasonable, but not unique, percentages of these four planes: 40% (110), 35% (100), 20% (112) and 5% (111) (*14*). The single crystal self-hydrogenation and hydrogenation spectra given in Figs. 1 and 2 were scaled to those for the (100) plane using these assumed percentages for the various planes, and the ratio of ethane densities given by Eq. (8). The results are shown plotted on a linear temperature scale in Fig. 6. Included for reference are spectra obtained on polycrystalline tungsten (*17*). The (112) and (100) planes make the largest contribution to flash hydrogenation on polycrystalline tungsten. This is obviously true for our assumed composition of polycrystalline tungsten, but the conclusion would still be valid unless one assumed a very large fraction of (110) or (111) planes.

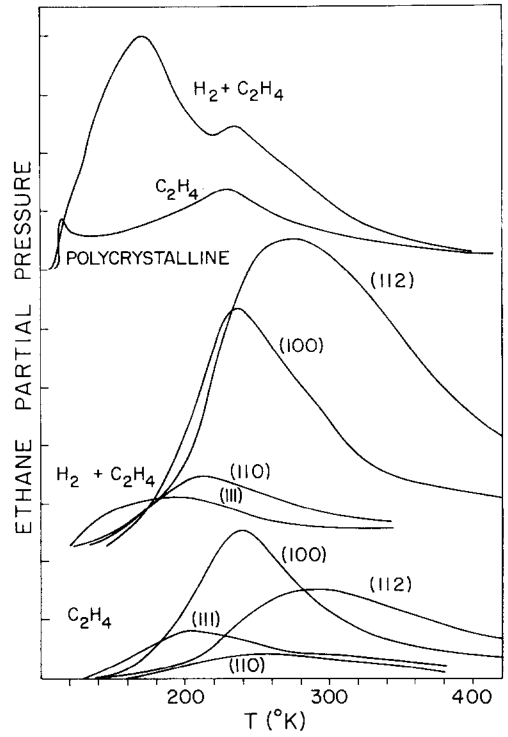


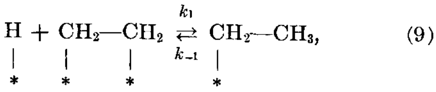
Fig. 6. Flash hydrogenation and self-hydrogenation from the four planes scaled according to the number of ethane molecules produced per square centimeter and the percentage contribution of each plane to polycrystalline tungsten as given in Ref. (*14*). The polycrystalline results are included for comparison.

A second consequence of Fig. 6 is that the polycrystalline results cannot be understood as simply a composite of results from this simple set of planes even though the f_h and f_s values, Table 1, for polycrystalline fall inside the extremes of the single crystal values. The major features in the polycrystalline spectra to be understood are the enhancement of hydrogenation over self-hydrogenation and the observation that this enhancement occurs predominantly in a peak at ~160 K while self-hydrogenation occurs predominantly in a peak at ~230 K. Direct comparison of temperatures for the polycrystalline results with temperatures for the single crystal results can not be made due to the different methods used for temperature measurement in the two cases, but temperatures between the individual single crystal planes should be comparable. Comparison of the four sets of single crystal results can not lead to a synthesis of the main features in the polycrystalline results. Such a synthesis might be possible if we assumed, for example, that the temperatures recorded for the spectra obtained on the (112) plane were in error by approximately 100 K relative to the temperatures for the other planes. But, as this is highly unlikely, we must conclude that the hydrogenation activity observed on polycrystalline tungsten can not be understood simply as a composite of results obtained on these four planes.

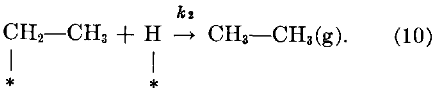
DISCUSSION

There have been many mechanisms proposed for the hydrogenation of ethylene. These belong to one of two groups: either Langmuir–Hinshelwood mechanisms where the reaction occurs between chemisorbed ethylene and chemisorbed hydrogen; or Rideal–Eley mechanisms where one reactant is chemisorbed and the second is either physically adsorbed or in the gas phase. Gardner and Hansen (*23*) have proposed a Rideal–Eley mechanism for hydrogenation of ethylene on tungsten in which gas phase ethylene collides with "*trans*-diadsorbed" ethylene, captures two hydrogen atoms and is converted to ethane. The amount of ethane observed during the flash is such that its production by impact of gaseous ethylene is highly unlikely. Although we close the ethylene supply valve and pump for 1 min before flashing, the ethylene pressure at the time of flash is ~5 × 10^{-9} Torr. This pressure of ethylene gives a rate of impact per ethylene on the surface such that slightly more than one ethane per incident ethylene would have to be produced on some surfaces. This does not take into account the fact that ethylene molecules are decomposing at the same time. In addition, their mechanism could in no way produce the extensive incorporation of D atoms that we observe in our deuteration experiments.

One widely accepted mechanism for hydrogenation is the Horiuti–Polanyi mechanism proposed in 1934 (*24*).

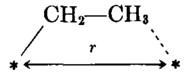


$$\underset{*}{\underset{|}{H}} + \underset{*}{\underset{|}{CH_2}}-\underset{*}{\underset{|}{CH_2}} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \underset{*}{\underset{|}{CH_2}}-CH_3, \tag{9}$$



$$\underset{*}{\underset{|}{CH_2}}-CH_3 + \underset{*}{\underset{|}{H}} \xrightarrow{k_2} CH_3-CH_3(g). \tag{10}$$

The asterisks in these expressions represent bonds to the surface. The crystallographic dependence for flash hydrogenation and flash deuteration that we have observed is in agreement with such a mechanism. The step of major importance is the reverse of Reaction 9, the conversion of the half-hydrogenated state back to a chemisorbed ethylene. This reaction should occur through a transition state of the form



with the probability of formation of this transition state decreasing with increasing tungsten–tungsten distance, r (*25*). As a result of a lower probability for formation of this transition state leading to the reverse reaction, the lifetime of the half-hydrogenated state will be longer and there will be a greater chance for production of ethane via Reaction 10. This dependence on tungsten–tungsten distance is clearly evident from a comparison of self-hydrogenated activity. On both the most active plane, W(111), and the least active, W(110), each surface tungsten atom is surrounded by six nearby tungsten atoms, but on the (111) plane the tungsten–tungsten distance is 4.47 Å, and on the (110) plane four are at 2.78 Å and two are at 3.14 Å. Thus in agreement with our observation there should be a larger amount of ethane produced on the (111) plane as a consequence of a slow reverse step in Eq. (9). The (100) and (112) planes with spacings intermediate between these two extremes produce an intermediate amount of ethane.

The same dependence on spacing must also exist in the case of hydrogenation. And again the (110) plane is the most inactive, but the order for the (112) and (111) planes have been reversed due to a concentration dependence. As seen in Fig. 3 the increase in hydrogenation over self-hydrogenation increases with increasing ratio of hydrogen to ethylene. Production of ethane by the Horiuti–Polanyi mechanism requires reaction of two successive hydrogen atoms with the same ethylene molecule. On a given plane the probability of this occurring will increase as the ratio of hydrogen to ethylene increases, i.e., the most favorable case for hydrogenation on a given plane would occur when that surface was rich in hydrogen and poor in ethylene. In the case of hydrogenation the (112) plane is relatively rich in hydrogen while the (111) plane is relatively rich in ethylene. Thus, the reversal in the activity of the (112) and (111) planes is simply due to this concentration effect being a greater factor on the (112) plane than on the (111) plane.

Extensive incorporation of deuterium in the product ethane molecule depends on the reverse step in Eq. (9). And we observe the most extensive incorporation of deuterium occurs on the (110) plane where this reverse step should be most rapid, and the least incorporation occurs on the (111) plane where the reverse step should be the slowest. However, in this case it is not possible to separate the effect of spacings from the concentration effects (*26*) indicated by Fig. 5. But it should be possible by choice of proper ethylene exposures to produce the same ratio of deuterium to ethylene on each plane. Any resulting differences in the distribution of deuterated ethanes would then be due to differences in the rate of the reverse step of Eq. (9).

Kemball (*20*), in an investigation of the deuteration of ethylene on evaporated tungsten films at 174 K, reported a $d_6:d_2$ ratio of 0 and a $d_5:d_2$ ratio of 0.003 for the initial distribution of deuterated ethanes. Only slightly higher ratios were observed for the final distributions. On all surfaces except the (111) plane the relative amount of d_6- and d_5-ethane produced is at least an order of magnitude greater than that reported by Kemball even for his final distribution. We have noted before that the difference between our results and Kemball's probably results from a differing ratio of deuterium to ethylene (*17*). Since ethylene is observed to block the adsorption of deuterium (*14, 17*), the surface in Kemball's case would rapidly become rich in ethylene and poor in deuterium yielding a low average deuterium content given that his first data point was not taken until approximately 3 min after the start of the reaction. Given that hydrogenation decreases as the ratio of hydrogen to ethylene decreases, blocking of hydrogen adsorption by ethylene would partially explain the low activity of tungsten for hydrogenation (*27*). In a normal hydrogenation reaction the surface would rapidly become rich in ethylene and poor in hydrogen. However, since hydrogenation reactions are normally run at temperatures above room temperature where the decomposition reaction is rapid (*16*), the major cause of the low reactivity is the rapid ethylene decomposition which rapidly converts chemisorbed ethylene to a carbon residue. Kemball (*20*) has reported that at 173 K, where we know the decomposition reaction to be slow, tungsten is relatively a much better catalyst for ethylene hydrogenation.

Although we can understand the hydrogenation activity observed on the single crystal surfaces in terms of the structural implications in the Horiuti–Polanyi mechanism, the hydrogenation observed on polycrystalline tungsten apparently can not be described in terms of the single crystal results. It may be possible that a major contribution to hydrogenation on polycrystalline tungsten comes from either stepped surfaces, or from imperfections such as dislocations or grain boundaries. Joyner, Lang, and Somorjai has observed on platinum surfaces that high catalytic activity occurs on stepped surfaces.

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