<table>
<thead>
<tr>
<th>Title</th>
<th>HYDROGENATION OF ETHYLENE ON METALLIC CATALYSTS: Part 9 - The Reaction over Evaporated Tungsten Films</th>
</tr>
</thead>
<tbody>
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<td>Author(s)</td>
<td>MIYAHARA, K.; OKI, S.; HARADA, K.; NAGAI, K.</td>
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HYDROGENATION OF ETHYLENE ON METALLIC CATALYSTS

Part 9—The Reaction over Evaporated Tungsten Films

By

K. MIYAHARA,*) S. OKI*, K. HARADA* and K. NAGAI*)

(Received April 10, 1968)

Abstract

Hydrogenation of ethylene catalyzed by evaporated tungsten film was observed at temperatures between −45°C and 100°C with regard to its rate, adsorbed amounts of hydrogen and ethylene in course of the reaction and deuterium distribution in hydrogen and ethylene at the early stage of deuteration of light ethylene.

Observations of the adsorption and the deuterium distribution indicate, unlike the case of evaporated nickel film, that the hydrogenation is attended with dehydrogenated adsorption of ethylene of a considerable extent even at −45°C irrespective as to whether the tungsten film is freshly evaporated, once used for the reaction and evacuated at room temperature or reduced by deuterium after the latter treatment and evacuated similarly at 300°C. Deuterium preliminarily adsorbed was actively exchanged with protium in gaseous hydrogen or ethylene.

The deuterium was found randomly distributed in hydrogen, but not in ethylene both at −45°C and 100°C, which indicates that the step of hydrogen chemisorption is kept in equilibrium, but the set of steps leading to hydrogen exchange of ethylene is not.

The optimum temperature, ca. 20°C, was observed over reduced tungsten film with regard to the hydrogenation of ca. 0.4 mmHg light ethylene by equimolar protium and its activation heat was found 8.2 kcal/mole at temperatures below the optimum.

The number of sites of the critical system of the rate-determining step of ethane formation was found to be \(10^3\) per unit surface area of reduced tungsten film, indicating that the whole surface is active in catalyzing the ethane formation, in spite of a pronounced dehydrogenated adsorption of ethylene, which possibly results in an appreciable coverage of the surface with acetylenic complex or carbonic deposit rendering more or less sites incompetent.

Introduction

Tungsten is known to catalyze hydrogenations and hydrogen exchanges of several hydrocarbons, but its behaviour as a catalyst differs considerably

*) Research Institute for Catalysis, Hokkaido University. S. O. was a domestic scholar from the Faculty of Education, Utsunomiya University.
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from those of transition metals; for instance, the rate and the activation heat of ethylene hydrogenation on tungsten at 0°C was, as observed by Beeck, extraordinarily small as compared with those on transition metals. Considerable amount of deutoethylenes including \( d_1 \)-ethylene, \( i.e. \) \( \text{C}_2\text{D}_4 \), was formed in course of catalyzed deuteration of light ethylene at \(-100^\circ\text{C}\) on Rh, Ni or Fe, but not on W, where there was formed just a small amount of \( d_1 \)-ethylene, \( i.e. \) \( \text{C}_2\text{H}_4\text{D}_2 \), but none of \( d_n \)-ethylene of \( n>1 \). Tungsten was found much less active than transition metals in catalyzing hydrogenolysis of amines at \(200^\circ\text{C}\).

Tungsten is, on the other hand, most active in catalyzing the hydrogen exchange between deuterium and light methane, ethane or catalytic hydrogenolyses of paraffins. Another peculiarity of tungsten as catalyst is the lower limit of the number, \( i.e. \) \( 10^6 \text{cm}^{-2} \), of sites of critical system of the rate-determining step as derived from the statistical mechanical analysis of kinetic data of the exchange reaction between methane and deuterium, which is exceptionally small as compared with its average, \( ca. 10^{15} \text{cm}^{-2} \), derived from 66 available cases of experimental data.

With special reference to these peculiar catalytic behaviours of tungsten the catalyzed reaction between ethylene and hydrogen in its presence was investigatied in the present work in comparison with the previous results of nickel catalyst, on which basis the mechanism of the reaction was discussed.

**Experimental**

The apparatus, materials and experimental procedure were similar to those in the previous works excepting the preparation of evaporated tungsten film.

A tungsten wire of \( 0.2 \text{ mm} \phi \) and \( ca. 30 \text{ cm} \) in length was mounted in the reaction vessel of 130 cc capacity, heated at \(500^\circ\text{C} \) by an electric furnace in \( ca. 40 \text{ mmHg} \) deuterium gas for \( ca. 14 \text{ hr} \) and evacuated for 15 hr as far as \( 5 \times 10^{-7} \text{mmHg} \), while the wire was heated with \( ca. 4.5 \text{ A a.c.} \); the wire was now evaporated for 40 min by passing \( 6.0 \text{ A a.c.} \) through the wire, immersing the reaction vessel in a salt bath at \(300^\circ\text{C} \). The wire was subjected to the above treatment and evaporated for 10 min in case where the wire was evaporated to coat the film previously evaporated. A film thus freshly evaporated either directly on the glass wall or on a previously evaporated film is denoted by \( F \) and that once used for reaction and evacuated to \( 5-7 \times 10^{-7} \text{mmHg} \) at room temperature by \( S \) in what follows. \( R \) similarly signifies film \( S \) used for the reaction, evacuated to \( 5-7 \times 10^{-7} \text{mmHg} \) at room temperature, reduced at \(300^\circ\text{C} \) in \( ca. 15 \text{ mmHg} \) deuterium gas for an hour or longer and finally evacuated to \( 5 \times 10^{-7} \text{mmHg} \) for 30 min at \(300^\circ\text{C} \).
A run of reaction on film F, S or R was conducted, similarly as in the
previous work, by immersing the reaction vessel in a bath kept at a desired
temperature, by introducing into it a known amount of one to one mixture
of light ethylene and protium, deuterium or their mixture. The bath of
water or melting monochlorobenzene was used for the reaction at 0°C and
above or at −45°C respectively. Course of the total pressure was now
recorded by means of a Pirani gauge and a pen-recorder, usually for the first
short period, and after a recorded time of the reaction a part of the reacted
gas was diffused into a sampling vessel for mass spectrometric analysis; the
negative initial inclination of the total pressure derived from the record was
taken for a measure of the initial rate of deuteration or hydrogenation. The
course of deuterium distribution in hydrogen and ethylene was observed by
a series of runs at ca. 0.7 mmHg total pressure and at −45°C, each conducted
for a different time over one and the same tungsten film reduced prior to the
run by deuterium at 300°C and evacuated to 5×10⁻⁷ mmHg.

The mass spectrometric analysis was conducted quite similarly to the
previous work; the relative amounts of ¹H₂, ¹HD and D₂ in reacted gas were
approximated by the relative heights of peaks of mass numbers, 2, 3 and 4
respectively at the electron accelerating voltage, Vₑ, of 70 volt and those of
dₙ-ethylenes (n=0, 1, ⋯, 4) by the relative heights of peaks of mass numbers,
28, 29, ⋯, 32, obtained at Vₑ=13.5 volt, where the mass spectrum of ethylene
consists of parent peaks alone. The deuterium distribution in ethane was not
observed on account of its insufficient yield for the mass spectrometric analysis.

**Results**

Table 1 shows the deuterium distribution in hydrogen and ethylene in
course of deuteration of light ethylene at −45°C on films, F, S and R respectiv­
ely; the “Reacted %” is the percentage of the observed total pressure
decrease at the moment of sampling on the initial partial pressure of ethylene
calculated to be a half of the initial total pressure, Pₒ. Vₒ the initial rate of
the observed total pressure decrease and the parenthesized figures the relative
amounts for random distribution of deuterium atoms in hydrogen or ethylene
respectively calculated on the base of observed deuterium atomic fraction, yₜ
or yₜ, of hydrogen or ethylene.

Points of the result are summarized below.

(1) Table 1 shows that Vₒ over R lies intermediate between those over
F and S irrespective of the period of reduction, and slightly decreases by
repetitions of run of the reaction each followed by reduction and evacuation
### Table 1. Deuterium distribution in gaseous hydrogen and ethylene formed by reactions of equimolar mixture of D₂ and light ethylene at −45°C over freshly evaporated (F), once used (S) and reduced (R) tungsten films.

<table>
<thead>
<tr>
<th>$P_0$ (mmHg)</th>
<th>State of film</th>
<th>Reacted (%</th>
<th>$V_0$ (mmHg/min)</th>
<th>$d_n$-Hydrogen (%)</th>
<th>$d_n$-Ethylenes $\equiv E_n$ (%)</th>
<th>D-atomic fraction</th>
<th>$y_H$</th>
<th>$y_E$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>F</strong></td>
<td>0.07</td>
<td>63</td>
<td>0.782</td>
<td>1.3</td>
<td>4.4</td>
<td>94.3</td>
<td>39.0</td>
<td>19.5</td>
</tr>
<tr>
<td><strong>S</strong></td>
<td>0.07</td>
<td>41</td>
<td>0.441</td>
<td>0.2</td>
<td>3.9</td>
<td>96.0</td>
<td>61.6</td>
<td>15.4</td>
</tr>
<tr>
<td><strong>R, 1.0 hr</strong></td>
<td>0.07</td>
<td>47</td>
<td>0.561</td>
<td>1.5</td>
<td>3.9</td>
<td>94.5</td>
<td>48.6</td>
<td>17.1</td>
</tr>
<tr>
<td><strong>F</strong></td>
<td>0.07</td>
<td>54.5</td>
<td>0.752</td>
<td>1.8</td>
<td>6.7</td>
<td>91.5</td>
<td>35.5</td>
<td>16.0</td>
</tr>
<tr>
<td><strong>S</strong></td>
<td>0.07</td>
<td>38.3</td>
<td>0.481</td>
<td>1.2</td>
<td>4.5</td>
<td>94.3</td>
<td>55.0</td>
<td>15.0</td>
</tr>
<tr>
<td><strong>R, 1.3 hr</strong></td>
<td>0.07</td>
<td>50.0</td>
<td>0.516</td>
<td>1.2</td>
<td>5.1</td>
<td>93.6</td>
<td>50.0</td>
<td>18.5</td>
</tr>
<tr>
<td><strong>R, 2.5 hr</strong></td>
<td>0.07</td>
<td>41.7</td>
<td>0.511</td>
<td>1.5</td>
<td>4.9</td>
<td>93.6</td>
<td>72.5</td>
<td>10.9</td>
</tr>
<tr>
<td><strong>R, 15.0 hr</strong></td>
<td>0.07</td>
<td>32.7</td>
<td>0.500</td>
<td>1.9</td>
<td>3.5</td>
<td>95.6</td>
<td>84.2</td>
<td>7.9</td>
</tr>
<tr>
<td><strong>F</strong></td>
<td>0.57</td>
<td>8.6</td>
<td>0.274</td>
<td>0.7</td>
<td>3.1</td>
<td>96.2</td>
<td>86.7</td>
<td>9.2</td>
</tr>
<tr>
<td><strong>R, 1.0 hr</strong></td>
<td>0.57</td>
<td>10.5</td>
<td>0.256</td>
<td>0.8</td>
<td>3.9</td>
<td>95.4</td>
<td>84.0</td>
<td>10.4</td>
</tr>
<tr>
<td><strong>R, 18.5 hr</strong></td>
<td>0.57</td>
<td>11.6</td>
<td>0.155</td>
<td>0.6</td>
<td>3.3</td>
<td>96.1</td>
<td>87.5</td>
<td>8.9</td>
</tr>
</tbody>
</table>

*) $P_0$ is the pressure derived from the amount of gas initially introduced and the volume of the reaction vessel assuming the ideal gas law; $0.100$ mmHg of $P_0$ corresponds to $6.33 \times 10^{17}$ molecules at −45°C.

**) Initial deuteration rate derived from decrease of total pressure.

***) Time of reduction with ca. 15 mmHg deuterium at 300°C.

to $5 \times 10^{-7}$ mmHg.

(2) The deuterium distribution in hydrogen and ethylene, i.e., the relative amounts of $^1$H₂, $^1$HD and D₂ in hydrogen and those of $d_n$-ethylenes, are respectively nearly the same in every case of films F, S and R.

(3) Table 1 shows that the deuterium distribution in ethylene of runs of $P_0=0.07$ mmHg at −45°C over film F is wide of random one and $d_n$-ethylenes are alternately abundant at $n=0, 2$ and 4. The similar tendency of $d_n$-ethylenes is potentially perceptible in cases of films S and R at $P_0=0.07$ mmHg. At higher $P_0$ as shown in Fig. 1 a, the relative amounts of $d_2$- and $d_4$-ethylenes on film R, are constantly larger than that of $d_3$-ethylene from the initial stage of the reaction and $d_2$-ethylene predominates over $d_4$-ethylene after the elaspe of ca. 40 sec of reaction time, revealing the similar deuterium
Hydrogenation of Ethylene on Metallic Catalysts, Part 9

Fig. 1 a. Courses of relative amounts of respective $d_n$-ethylenes formed by reaction between equimolar light ethylene and deuterium catalyzed by tungsten film R at $-45^\circ$C and $P_0=0.7$ mmHg.

Fig. 1 b. Courses of relative amounts of $^1H_2$, $^1$HD and $D_2$ formed by reaction between equimolar light ethylene and deuterium catalyzed by tungsten film R at $-45^\circ$C and $P_0=0.7$ mmHg.
distribution to that in case of film F mentioned above. Table 2 shows that at 100°C and \( P_0 = 0.8 \text{ mmHg} \) on film R, \( d_3 \)-ethylene never exceeds \( d_1 \)- and \( d_4 \)-ethylenes similarly to the case of the result in Fig. 1a.

(4) The deuterium distribution in hydrogen is practically random as seen from Tables 1, 2 and 3; Table 3 indicates that the equilibration of the mixture of \( D_2 \) and \( ^1H_2 \) is immediately attained on its contact with film R at \(-45°C\) in the presence of light ethylene.

(5) In runs of \( P_0 = 0.07 \text{ mmHg} \) the observed initial pressure was much less than \( P_0 \) on any of films F, S and R, which indicates that a considerable adsorption sets in immediately after the introduction of the reactant mixture over the film. Table 4 shows the amount of hydrogen or ethylene adsorbed on film R at \(-45°C\), which was derived as the excess of the amount of hydrogen (or ethylene) initially introduced into the reaction vessel over the sum of those of hydrogen (or ethylene) and ethane existing in reacted gas;

**Table 2.** Deuterium distribution in hydrogen and ethylene derived from equimolar mixture of light ethylene and \( D_2 \) kept over film R at 100°C.

<table>
<thead>
<tr>
<th>( P_0 ) (mmHg)</th>
<th>State of film</th>
<th>Reacted (%)</th>
<th>( V_0 ) (mmHg/min)</th>
<th>Hydrogen (%)</th>
<th>( d_\alpha )-Ethylene ( \equiv ) ( E_n ) (%)</th>
<th>D-atomic fraction</th>
<th>( \gamma_H )</th>
<th>( \gamma_E )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>R, 56.0 hr</td>
<td>12.1</td>
<td>2.27</td>
<td>1.7</td>
<td>14.6837</td>
<td>56.5</td>
<td>24.0</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>R, 1.0 hr</td>
<td>10.5</td>
<td>2.00</td>
<td>1.6</td>
<td>13.2852</td>
<td>65.3</td>
<td>22.3</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>R, 2.0 hr</td>
<td>5.6</td>
<td>1.71</td>
<td>1.4</td>
<td>10.4882</td>
<td>69.1</td>
<td>19.3</td>
<td>6.9</td>
</tr>
</tbody>
</table>

**Table 3.** Deuterium distribution in gaseous hydrogen and ethylene formed by reactions of equimolar mixture of light ethylene and \( D_2 + ^1H_2 \) at \(-45°C\) over film R.

<table>
<thead>
<tr>
<th>( P_0 ) (mmHg)</th>
<th>State of film</th>
<th>Reacted (%)</th>
<th>( V_0 ) (mmHg/min)</th>
<th>Hydrogen (%)</th>
<th>( d_\alpha )-Ethylene ( \equiv ) ( E_n ) (%)</th>
<th>D-atomic fraction</th>
<th>( \gamma_H )</th>
<th>( \gamma_E )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7</td>
<td>R, 1.0 hr</td>
<td>6.70</td>
<td>0.133</td>
<td>9.1</td>
<td>35.0559</td>
<td>88.6</td>
<td>7.2</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>R, 1.0 hr</td>
<td>7.70</td>
<td>0.136</td>
<td>9.1</td>
<td>35.0559</td>
<td>88.6</td>
<td>7.2</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Initial mixture 16.8 1.781.5 97.8 2.2 0 0 0 0.823 0.006

*) The percentage of \(^1H_2\) may be too large on account of the mass spectrometric superposition of \( D^+ \).
TABLE 4. Adsorption of protium and light ethylene in course of their reaction at $-45^\circ$C over film R.

<table>
<thead>
<tr>
<th>Number of molecules initially introduced</th>
<th>State of film</th>
<th>Reacted (%)</th>
<th>$^1H_2$ adsorbed (molecules)</th>
<th>$C_2H_4$ adsorbed (molecules)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.31 \times 10^{18}$</td>
<td>R, 1.0 hr</td>
<td>37.2</td>
<td>$1.61 \times 10^{16}$</td>
<td>$1.45 \times 10^{16}$</td>
</tr>
<tr>
<td>$1.71 \times 10^{18}$</td>
<td>&quot;</td>
<td>79.3</td>
<td>$-1.27 \times 10^{17}$</td>
<td>$0.32 \times 10^{17}$</td>
</tr>
<tr>
<td>$1.71 \times 10^{18}$</td>
<td>&quot;</td>
<td>33.3</td>
<td>$-0.44 \times 10^{17}$</td>
<td>$2.85 \times 10^{17}$</td>
</tr>
<tr>
<td>$1.71 \times 10^{18}$</td>
<td>&quot;</td>
<td>30.4</td>
<td>$-1.57 \times 10^{17}$</td>
<td>$3.10 \times 10^{17}$</td>
</tr>
<tr>
<td>$1.71 \times 10^{18}$</td>
<td>&quot;</td>
<td>20.0</td>
<td>$-1.71 \times 10^{17}$</td>
<td>$3.80 \times 10^{17}$</td>
</tr>
<tr>
<td>$1.71 \times 10^{18}$</td>
<td>&quot;</td>
<td>28.1</td>
<td>$-1.58 \times 10^{17}$</td>
<td>$3.55 \times 10^{17}$</td>
</tr>
<tr>
<td>$1.71 \times 10^{18}$</td>
<td>&quot;</td>
<td>8.2</td>
<td>$-1.96 \times 10^{17}$</td>
<td>$4.56 \times 10^{17}$</td>
</tr>
<tr>
<td>$1.71 \times 10^{18}$</td>
<td>&quot;</td>
<td>11.9</td>
<td>$-1.96 \times 10^{17}$</td>
<td>$3.49 \times 10^{17}$</td>
</tr>
<tr>
<td>$1.71 \times 10^{18}$</td>
<td>&quot;</td>
<td>13.3</td>
<td>$-1.96 \times 10^{17}$</td>
<td>$3.10 \times 10^{17}$</td>
</tr>
<tr>
<td>$2.44 \times 10^{18}$</td>
<td>&quot;</td>
<td>70.0</td>
<td>$-1.30 \times 10^{17}$</td>
<td>$1.04 \times 10^{17}$</td>
</tr>
</tbody>
</table>

This excess gives the adsorbed amount exactly, provided that the hydrogenation of ethylene to ethane is only reaction that takes place and that ethane is not at all adsorbed in the presence of ethylene as verified in a previous work. The amount of adsorbed hydrogen thus derived presents, with its sign reversed, the lower limit to the amount of hydrogen gas evolved by the dehydrogenated adsorption of ethylene. The latter lower limit decreases with rise of temperature as seen from Table 5.

(6) In case where tungsten film was preliminarily reduced by deuterium and evacuated to $2-3 \times 10^{-6}$ mmHg, considerable amount of deuterated hydrogen and hydrocarbons, inclusive of $D_2$ and $C_2D_6$, were found at the early stage of reaction between light ethylene and protium conducted over the same film at $P_0=0.07$ mmHg and $-45^\circ$C; hydrogen gas was completely equilibrated also in this case with regard to the deuterium distribution. Deuterosubstitution product was not at all found in the case where a film reduced by $D_2$ was preliminarily evacuated to $5 \times 10^{-7}$ mmHg for 30 min.

(7) Table 5 presents the hydrogenation rate, the composition of reacted gas and "the adsorbed amounts of hydrogen and ethylene" at the early stage of the reaction between light ethylene and protium over film R at $P_0=0.8$ mmHg at different temperatures. We see from the Table that the excess of hydrogen in reacted gas over ethylene is the greater, the lower the reaction temperature.

*) Cf. point (5).
<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>Temp. (°C)</th>
<th>Number of molecules ($\times 10^{18}$)</th>
<th>Composition of reacted gas (%)</th>
<th>Adsorbed amount ($\times 10^{17}$ molecules)</th>
<th>Hydrogenation rate ($10^{18}$ molecules/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Introduced</td>
<td>Decrease*</td>
<td>$C_2^1H_6$ formed**</td>
<td>$H_2$</td>
</tr>
<tr>
<td>25.0</td>
<td>-45</td>
<td>4.91</td>
<td>0.71</td>
<td>0.57</td>
<td>50.8</td>
</tr>
<tr>
<td>7.0</td>
<td>-25</td>
<td>4.91</td>
<td>0.76</td>
<td>0.64</td>
<td>44.5</td>
</tr>
<tr>
<td>10.0</td>
<td>-25</td>
<td>4.91</td>
<td>0.76</td>
<td>0.72</td>
<td>48.2</td>
</tr>
<tr>
<td>2.4</td>
<td>0</td>
<td>4.72</td>
<td>0.79</td>
<td>0.70</td>
<td>43.9</td>
</tr>
<tr>
<td>2.2</td>
<td>20</td>
<td>4.42</td>
<td>1.11</td>
<td>0.92</td>
<td>40.5</td>
</tr>
<tr>
<td>3.4</td>
<td>50</td>
<td>4.37</td>
<td>1.23</td>
<td>1.14</td>
<td>31.3</td>
</tr>
<tr>
<td>4.4</td>
<td>74</td>
<td>4.32</td>
<td>1.41</td>
<td>1.16</td>
<td>30.4</td>
</tr>
<tr>
<td>4.4</td>
<td>97</td>
<td>4.12</td>
<td>1.35</td>
<td>0.91</td>
<td>34.6</td>
</tr>
</tbody>
</table>

*) In gas phase derived from the total pressure decrease.  
**) In gas phase derived from the total pressure and the composition of reacted gas sampled.
Fig. 2. Arrhenius plot of the rate of hydrogenation of light ethylene by equi-molar protium (○ and △) or deuterium (●) at \( P_0 = 0.8 \) mmHg over tungsten film R; curve A or B is that of the rate of the total pressure decrease, \( V_0 \) (○) or of the rate of ethane formation, \( V'_0 \) (△) respectively in the hydrogenation by protium (Cf. Table 5).

(8) Fig. 2 shows the Arrhenius plots of the hydrogenation rates; curve A or B is the Arrhenius plot of \( V_0 \) or the rate, \( V'_0 \), of ethane formation. They nearly coincide with each other at lower temperatures giving practically the same values of optimum temperature, ca. 20°C, and of activation heat, 8.2 kcal/mole, over the temperature below the optimum.

(9) The ratio of hydrogenation rate, \( V_0 \), of light ethylene to its deuteration rate is derived from the result of Fig. 2 as ca. 2.1 at \(-45°C\) and 1.1 at 97°C over film R as observed with one to one mixture of ethylene and protium or deuterium at \( P_0 = 0.8 \) mmHg.
Discussions

It has been known that hydrogen was irreversibly adsorbed up to full coverage of the surface\(^{10}\) and hydrogen thus adsorbed was capable of being exchanged to any extent with gaseous hydrogen.\(^{31}\) Point (6) of the foregoing section states, on the other hand, that the hydrogen irreversibly adsorbed is very active in hydrogenation of ethylene as well as in hydrogen exchange with gaseous hydrogen. The random distribution of deuterium in gaseous hydrogen stated in point (4) verifies, in conjunction with point (6), that the chemisorption of hydrogen

\[
\text{H}_2 \rightarrow 2 \text{H(a)}
\]  

is in equilibrium in course of ethylene hydrogenation over the temperature range from \(-45^\circ\text{C}\) to \(100^\circ\text{C}\), which amply embraces the optimum temperature, \(\text{ca. } 20^\circ\text{C}\).

The negative value of “the amount of adsorbed hydrogen”\(^*)\) in Tables 4 and 5 indicates a pronounced evolution of hydrogen by dehydrogenated adsorption of ethylene over film R; this contrasts with the case of nickel film,\(^9\) where “the amount of adsorbed hydrogen”\(**)\) was positive throughout in conformity with the observed absence of dilution of deuterium gas by protium in course of deuteration of light ethylene on either of nickel films S and R.

Large amount of deuteroethylene of every extent of deuterosubstitution was formed at \(-45^\circ\text{C}\) in the present experiments as shown in Table 1 and Fig. 1 a, in contrast with the result of Kemball\(^2\) that deuteroethylene was scarcely formed in deuteration of light ethylene over tungsten film at \(-100^\circ\text{C}\).

As regards point (3) the exchange through step

\[
\text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_2(a) + 2\text{H(a)}
\]  

and its reverse ought to be taken into account. \(^3\)H(a) formed by the forward act of step (2) are immediately replaced by D(a) through step (1) in equilibrium in the initial stage of the reaction between D\(_z\) and C\(_2\)H\(_4\), so that \(d_1\) and \(d_3\)-ethylenes are preferentially formed by the backward act of step (2), provided that \(cis\) hydrogen atoms of ethylene molecule are removed or restored by the forward or the backward act of step (2) respectively. The formation of \(d_2\) and \(d_4\)-ethylenes may be assigned to the appearance of \(^3\)H(a) in the later stage of reaction and/or to the concurrent “stepwise hydrogen exchange” of ethylene,

\[
\text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_3(a) + \text{H(a)}
\]  

and/or

\(^*)\) Cf. point (5).
\(**) Cf. point (5).
None of steps (2), (3) and (4) ought to be in equilibrium on account of the wide deviation of the deuterium distribution in ethylene from random one and of the considerable difference between \( y_H \) and \( y_E \) as seen in Tables 1, 2 and 3, since, if otherwise, any of these steps in equilibrium would work with step (1) in equilibrium to render the deuteroethylene a random distribution and the value of \( y_E \) coincident with \( y_H \).

The lower limit to the number of sites, \( N^* \), of the critical system of the rate-determining step of ethane formation over film R is now derived according to the procedure developed in the previous work 7) on the base of activation heat, 8.2 kcal/mole, of ethane formation at temperatures below the optimum, the rate, \( 3.26 \times 10^{16} \) molecules-sec\(^{-1}\), of ethane formation at \(-45^\circ\)C, and the proportionality of the rate of ethane formation to the partial pressure of hydrogen alone as derived from the observation of Beeck 13) over evaporated tungsten film at 0°C. The lower limit was thus found to be \( 5.0 \times 10^{19} \) to the total number of sites on the whole surface of film R. The lower limit to the number of sites per unit area is hence calculated at \( 10^{15} \) to \( 10^{16} \) on the base of the roughness factor, \( 10^{-10^2} \)* and ca. 150 cm\(^2\) apparent area of the film. The number of sites is in consequence \( 10^{15} \) cm\(^{-2}\), with reference to its upper limit, \( 10^{18} \) cm\(^{-2}\), defined by the crystallographic number of surface metal atoms. The whole surface of the film is hence active in catalyzing the ethane formation.

Azuma and Ishizuka 12) have found by field emmision microscopic study that ethylene adsorbed on tungsten was decomposed by evacuation at temperatures above 300°C to leave carbonic deposit on the surface, which was enhanced by contacting the adsorbed ethylene preliminarily with hydrogen. Taking this fact into consideration it may be conceived that ethane formation by the reaction of ethylene with gaseous hydrogen as well as with H(a)'s formed by steps (2) and (3) proceeds on tungsten surface covered by “acetylenic complex”, which leaves by evacuation some carbonic deposit on the surface which poisons further hydrogenation of ethylene. We thus understand point (1) on the differences among \( V_0 \)-values over the films F, S and R.

It is concluded from point (8) of the approximate coincidence of the rate

\[
\text{C}_2\text{H}_4(a) + \text{H}(a) \rightarrow \text{C}_2\text{H}_6(a). \tag{4}
\]

* According to the observation of Beeck (Advances in Catalysis 2, p. 151 (1950)) the roughness factor of a surface of tungsten film evaporated onto glass wall kept at liquid air temperature was \( 10^3 \) by order of magnitude and five times as large as that of nickel film evaporated under the same condition. We found the roughness factor 3 for nickel film evaporated on glass wall kept at 200°C, hence the roughness factor of the present tungsten film evaporated at 300°C was thus estimated on account of it being rather stable against sinter due ot its higher melting point.
of ethane formation with that of total pressure decrease, that ethane is formed by such reactions as

$$\text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6$$  \hspace{1cm} (5)

and

$$2\text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_4,$$  \hspace{1cm} (6)

but reactions consuming ethylene otherwise, e.g. polymerization or carbonization of ethylene, if any, do not matter at temperatures below the optimum.

We could not so far observe the steady hydrogenation of ethylene over tungsten film to the exclusion of dehydrogenated adsorption of ethylene; what is concluded for the present is that the rate-determining step of the hydrogenation of ethylene on W catalyst may, unlike the nickel catalyst, serve for that of formation of deuterioethylene as well throughout reaction temperatures below and above the optimum, on the ground that the deuterium distribution was random in hydrogen but not in ethylene.

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