JOURNAL OF CATALYSIS 12, 198–206 (1968)

Hydrogenation of Olefins on Alumina

II. Deuteration and Exchange Reactions of Ethylene*

Y. AMENOMIYA

From the Division of Applied Chemistry, National Research Council, Ottawa 7, Canada

Received August 6, 1968

The hydrogenation of ethylene with deuterium has been carried out, respectively, on the weaker and the stronger active sites of alumina, which had been found previously with hydrogen to give different activity and kinetics for the reaction. It has been found that, on the weaker sites at low temperature, the main product is 1,2-ethane-d_2 with a small amount of ethane-d_3, while on the stronger sites at higher temperature, H–D exchange of ethylene occurs much more quickly than hydrogenation and all deutero-ethanes are produced. The results on the weaker sites have been successfully explained by a Twigg-Rideal mechanism. For the reactions on the stronger sites, however, a different mechanism is proposed, involving reaction of ethyl carbonium ions with hydrogen atoms formed by the dissociative adsorption of hydrogen on the weaker sites.

INTRODUCTION

It has been reported in Part I of this series (1) that the hydrogenation of ethylene occurs on alumina at relatively low temperatures if ethylene is preadsorbed on the catalyst. It has also been found that the reaction takes place in different manner on two groups of active sites of alumina which were previously found by Amenomiya and Cvetanovic for olefin chemisorption (*2*): the hydrogenation readily occurs even at room temperature or lower on the weaker sites (sites I); on the stronger sites (sites II), on the other hand, the reaction is negligible at room temperature and becomes measurable when the temperature is raised above 60°.

The kinetics of the reaction have been studied on these active sites with respect to both hydrogen pressure and the surface concentration of ethylene. Two possible mechanisms, the molecular addition of hydrogen and the Twigg-Rideal mechanism, were postulated for the hydrogenation on sites I (*1*), but the experimental results could not provide a definite proof for either of these mechanisms. The results also suggested that sites I were homogeneous but sites II heterogeneous.

Use of hydrogen isotopes, in addition to the kinetic information, has been very valuable in providing a deeper insight into the mechanism of olefin hydrogenation on metal catalysts. In view of this, the hydrogenation of ethylene with deuterium has been carried out on both sites I and II of alumina in an attempt to obtain further information on the mechanism of the reaction, and the results are reported in this paper.

EXPERIMENTAL

Apparatus. The same apparatus as was employed in the previous work (*1*) was used in the present study with minor modifications. A small circulation pump of a single plunger type operated by an electromagnet was added to the reaction system, so that hydrogen could be circulated during reaction through the pump, a liquid nitrogen trap, and the reactor. Thus any hydrocarbon (mainly ethane) desorbed from the catalyst was condensed in the trap ahead of the reactor without recontacting with the catalyst. The volume of the circulation system including the reactor was about 140 cc. A

---

* Contribution No. 10469 from the National Research Council, Ottawa, Canada.

Toepler-type pump was also attached to the circulation system and used to collect hydrogen gas for analysis.

The circulation pump was made of glass with two small polyethylene springs. It was verified that neither hydrogenation nor exchange reaction occurred in the pump under the conditions employed in this study.

Materials. Alumina catalyst was taken from the same batch as was used for the previous work, and the preparation and pretreatment have already been described (*1*). The surface area of the alumina after the treatment was 206 m^2/g as determined by BET with nitrogen; 0.976 g of catalyst was loaded in the reactor. The catalyst was usually evacuated for 2 to 3 hr at 650° after each run. After several runs, however, the catalyst was treated with light hydrogen at 600° prior to the evacuation to prevent the catalyst from being deuterated.

The purification of ethylene and hydrogen was also described before. Matheson's CP grade deuterium was passed through a spiral type liquid nitrogen trap, and stored in a reservoir. HD at a concentration of 0.5% was the only impurity detected by gas chromatograph, and no further purification was attempted. The amount of HD reported in this paper was corrected for this impurity.

Procedure. For the hydrogenation of ethylene on sites I at low temperatures, an approximately constant amount of ethylene was preadsorbed at reaction temperature (mostly 0°). The amount was about 0.39 cc/g and it adsorbed on both sites I and II. The final pressure after 10 min adsorption was less than 5×10^{-3} torr, and the catalyst was subsequently evacuated for 5 min to remove the gas-phase ethylene. Deuterium was then introduced in the circulation system excluding the reactor and the amount was measured manometrically. After the trap has been immersed in liquid nitrogen and the circulation pump set in operation, the reaction was started by opening the stopcocks at both ends of the reactor. The hydrogen pressure during the reaction was pulsating due to the circulation pump, but the fluctuation did not exceed 5% of the total pressure.

After a selected reaction time, a part of the reaction system including the pump (about 100 cc) was isolated by closing stopcocks for sampling the gas-phase hydrogen which was later transferred by means of a Toepler pump to a sampler for the gas chromatographic analysis. Simultaneously the reactor was pumped out through the liquid nitrogen trap for 30 min at temperatures between 0° and room temperature. Ethane and ethylene thus collected in the trap were measured by a gas chromatograph with a 2-m alumina column, and separated for mass spectrometric analyses at the same time.

The same procedure was also employed for the reaction on sites II at higher temperatures except for the conditions during the preadsorption of ethylene. About 0.12 cc/g of ethylene, i.e., slightly less than required to cover sites II (0.147 cc/g) was preadsorbed at 93° and at about 5×10^{-3} torr, followed by evacuation for a short period to assure that all ethylene adsorbed on sites II but not on sites I. The reactor was then cooled to the reaction temperature and the subsequent procedure was as described above.

In both reactions, unreacted ethylene remaining on the catalyst was later desorbed in a stream of helium by increasing the catalyst temperature (temperature-programmed desorption), and collected in a liquid nitrogen trap located downstream. The temperature-programmed desorption technique has been described in detail elsewhere (*1*). The ethylene thus collected was also subjected to mass spectrometric analysis after a trace of ethane was removed gas chromatographically.

Analyses. Hydrogen isotopes were analyzed by a gas chromatograph with a 2-m alumina column coated with manganese chloride according to the recipe of Yasumori and Ohno (*3*). The column was operated at liquid nitrogen temperature and hydrogen eluted from the column was converted into water on copper oxide to increase the sensitivity for detection.

Ethane and ethylene were analyzed by an Atlas CH4 mass spectrometer with an electron multiplier. Before subjecting them to mass spectrometric analysis, ethane and ethylene were separated gas chromatographically as already described, to avoid mutual interference of the mass spectra. The mass spectrum of ethylene was taken with the ionizing voltage (IV) of 14 or 15 V where no fragmental ion appeared.

In the case of ethane, however, the ionization potential does not significantly differ from the appearance potential of ethylene ion, and a complete elimination of fragmental ions was not possible without sacrificing sensitivity and stability. Therefore the mass spectrometry of deuteroethanes had been first studied with nine isotopic ethane molecules at IV = 70 V as well as at low IV's. The results have been published elsewhere (*4*). Thus it has become possible not only to analyze the composition of deuteroethanes in general, but to determine the position of deuterium atoms if an isotopic molecule is predominant.

The mass spectrometric analyses of ethane reported here were carried out at the standard ionizing voltage (70 V) and calculations were made according to the standard spectra and relative sensitivities for detection of molecular ions reported previously (*4*). The results were also checked by the spectra taken at IV = 12.8 V.

RESULTS

Reactions on Sites I

Results obtained on sites I (weaker sites) at 0° with 10 torr of deuterium are shown in Fig. 1, where the amounts of various gases formed are plotted against the total amount of ethane produced. Since the initial amount of ethylene preadsorbed was kept approximately constant, the abscissa is proportional to the conversion of ethylene on sites I and the largest amount of ethane shown in the figure corresponds to 34% conversion. It is seen in Fig. 1 that ethane formed by the reaction is mainly dideuteroethane (ethane-d_2) with a small amount of ethane-d_3, and that the ethane-d_2 increases almost linearly up to about 0.05 cc of ethane (20% conversion) and then starts bending slightly downwards at higher conversion. Ethane-d_1 was also found in the product at high conversion, but the amount was always much less than that of ethane-d_3. Neither more highly deuterated ethane than ethane-d_3 nor ethane-d_0 was found in the products obtained at 0°.

TABLE 1
COMPARISON OF MASS SPECTRA[a]

m/e	Product[b]	$CH_2D{\cdot}CH_2D$[c]	$CHD_2{\cdot}CH_3$[c]
32	100.0	100.0	100.0
31	64.7	64.2	64.2
30	238.8	258.1	206.6
29	201.0	201.6	239.7
28	98.4	98.5	100.1
27	57.8	59.7	53.3
26	22.3	25.9	19.8
25	3.4	4.9	2.6
17	0.4	0.4	4.6
16	8.6	9.3	2.4
15.5	1.5	1.3	1.4
15	5.3	5.0	8.0
14.5	1.8	1.9	1.6
14	2.5	1.3	2.5
13	0.9	0.7	0.6

[a] Mass spectra were taken with an Atlas CH4 mass spectrometer at IV = 70 V.

[b] The mass spectrum of the product was normalized after a small correction for the contribution from trideuteroethane.

[c] Standard spectra reported by Amenomiya and Pottie (*4*).

Deuteroethanes have different mass spectra depending not only on the degree of deuteration but also on the position of deuterium atoms (*4*). The mass spectra of the products were therefore compared with those of 1,1-ethane-d_2 and of 1,2-ethane-d_2, one of such comparisons being shown in Table 1. It is clear from the comparison of the relative ion intensities at *m/e* 30, and 29 and at 17 and 16 in particular that the ethane-d_2 formed by the reaction is mainly 1,2-ethane-d_2. For the evaluation of the spectra of the products, the mass spectrum of 1,1,2-ethane-d_3 was used, but the amount of ethane-d_3 was so small that the use of the spectrum of 1,1,2-ethane-d_3 or 1,1,1-ethane-d_3 did not make a serious difference.

As seen in Fig. 1, hydrogen deuteride also increases in the gas phase as the reaction proceeds. The amount of hydrogen adsorbed on the catalyst during the reaction could be

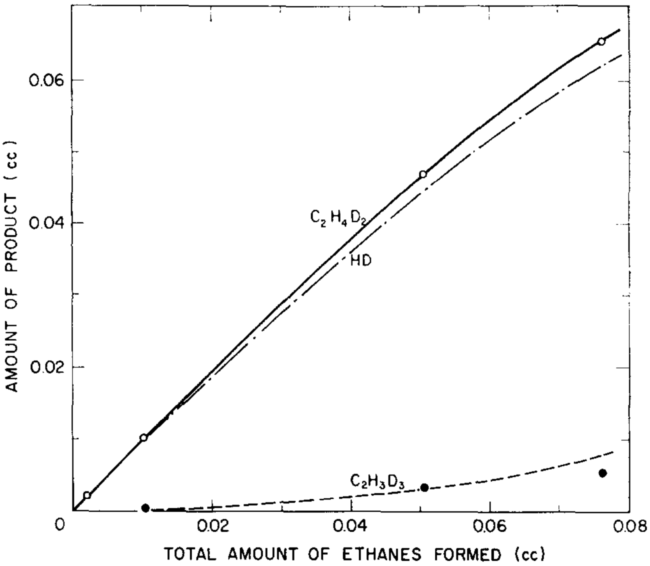


FIG. 1. Products of deuteration of ethylene on sites I at 0°. Catalyst weight 0.976 g, D_2 pressure 10 torr, the initial amount of ethylene on sites I about 0.23 cc. Reaction time was varied from 7 to 60 min. The broken line for $C_2H_3D_3$ was calculated from Fig. 2.

neglected compared with that in the gas phase, so that the amount of HD calculated from the analysis of the gas phase can be regarded as the total amount of HD produced by the reaction. No H_2 was found in the gas phase within the detection limit of the gas chromatograph.

In unreacted ethylene which was collected in the trap with ethane during evacuation after the reaction, monodeuteroethylene was found as well as ethylene. As soon as the evacuation of catalyst was started after the reaction, the ice bath for the reactor was taken off and the temperature of the catalyst was allowed to increase up to room temperature during evacuation for 30 min. No further warming was attempted because of the fear that the exchange reaction might occur at higher temperature between ethylene and a small amount of deuterium remaining on the surface. At higher conversions than 20%, small amounts of more highly deuterated ethylenes were found, but they were so small that these molecules could be neglected. The ratio of ethylene-d_1 to ethylene-d_0 thus found in the unreacted ethylene increased with hydrogenation as shown in Fig. 2, in which the ratio is plotted against the amount of ethane-d_2 produced.

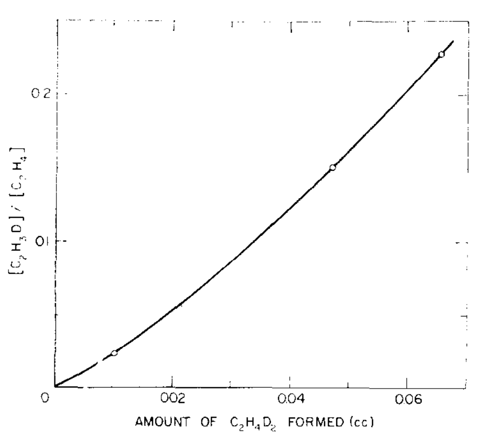


FIG. 2. Composition of ethylene during the course of deuteration on sites I. Reaction conditions are the same as in Fig. 1.

One experiment was carried out under the same reaction conditions but at 25°. It was found that, in the ethane produced, more ethane-d_3 and -d_1 and a not negligible amount of ethane-d_4 were present as well as ethane-d_2. Also in ethylene, the ratio of ethylene-d_1 to ethylene-d_0 became much greater than found at the same conversion at 0°.

The results of an experiment in which C_2H_4 was preadsorbed on sites II and a part

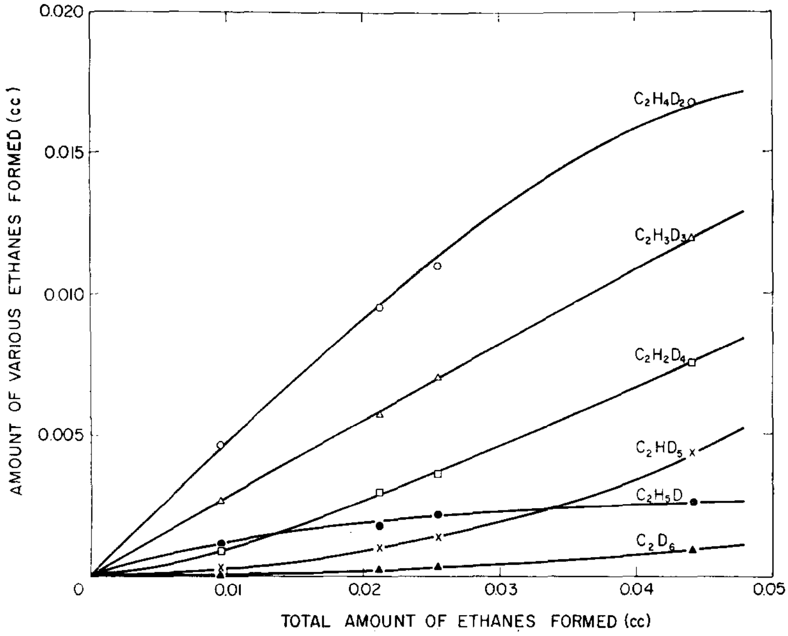


FIG. 3. Formation of ethanes on sites II at 79°. Catalyst weight 0.976 g, D_2 pressure 8 torr, reaction time 5 to 30 min. The initial amount of ethylene on sites II was about 0.12 cc.

of sites I, followed by the additional preadsorption of C_2D_6 on sites I and subsequent introduction of H_2 at 10 torr and 0°, showed that no appreciable exchange occurred between ethylene and ethane or between ethane and hydrogen on sites I, at least under reaction conditions employed in this study.

Reactions on Sites II

Although the activity of sites II (stronger sites) for the hydrogenation is much less than that of sites I, as already reported (*1*), the distribution of deuteroethanes formed on sites II is more complex. The results obtained at 79° and 8 torr of deuterium are shown in Fig. 3, where the amounts of various ethanes produced from about 0.125 cc/g of initial amount of ethylene preadsorbed on sites II ($\theta = 0.85$ on sites II) are plotted against the total amount of ethane formed. It is seen that almost all deuteroethanes were formed on sites II. Although the mass spectrometric analysis for C_2H_6 in these complicated mixtures was not as accurate as for highly deuterated compounds, there was an indication that very small amounts of ethane-d_0 could also exist.

It was also found that HD increased in the gas phase as the reaction proceeded much more rapidly than it did in the reaction on sites I. The amount of HD was, on a mole basis, about four times larger than that of total ethane produced, and this ratio decreased with temperature.

On sites II, ethylene adsorbed so strongly that no ethylene was collected with ethane in the trap. Therefore ethylene desorbed by the temperature-programmed desorption after the reaction was analyzed mass spectrometrically, and it was found that all deuteroethylenes were produced on the surface, as shown in Fig. 4. Of course, some exchange reaction might have occurred at higher temperatures during the temperature-programmed desorption between ethylene and a small amount of deuterium still remaining on the surface. The loss of hydrogen from both ethane and ethylene calculated from the mass spectrometric analyses agreed within 10%, however, with the amount of HD found in the gas phase during the reaction. Therefore the distribution of ethylenes shown in Fig. 4 seems to represent the distribution on the surface during the reaction.

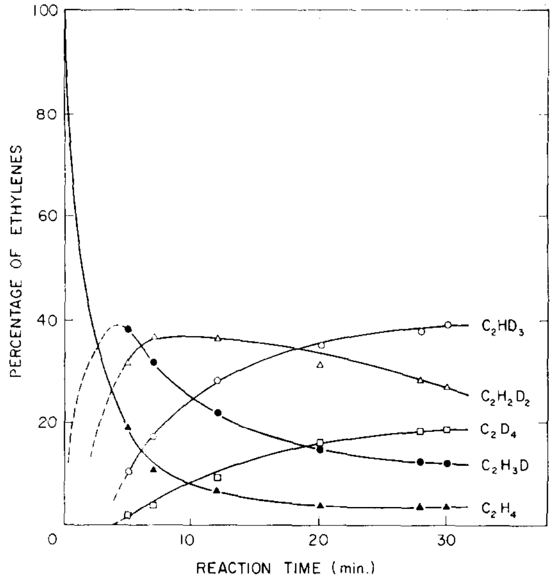


FIG. 4. Composition of ethylenes during the course of deuteration on sites II. Reaction conditions are the same as in Fig. 3.

The curves of Fig. 4 are of a typical consecutive first order reaction with respect to ethylene. Similar results were also obtained on alumina by Trokhimets and Markevich (*5*). It was found from the descending curve of C_2H_4 at different pressures of deuterium (4–23 torr) and different temperatures (60–90°) that the order of the exchange reaction with respect to deuterium pressure was about 0.2 and the activation energy varied from 6 to 10 kcal/mole depending on the surface coverage of ethylene. However it was difficult to obtain these values exactly because the rate seriously depended on the surface coverage, as already reported (*1*).

The reaction order with respect to hydrogen pressure and the activation energy of hydrogenation on sites II were reported in Part I of this series (*1*) to be, respectively, 0.5 and 10 to 15 kcal/mole, both being larger than for the exchange reaction, as described above. This difference in the activation energy agrees with the observation that the ratio of HD to ethane decreases with temperature. Also the ratio decreased slightly (from 4.9 to 3.6) when the deuterium pressure was increased from 4 to 23 torr at 80°, indicating that the order with respect to hydrogen pressure in the hydrogenation reaction was a little larger than in the exchange reaction.

DISCUSSION

Reactions on Sites I

A great deal of experimental information has been obtained by many authors on the metal-catalyzed reactions between olefins and deuterium (*6*). Although the reaction conditions in the present study were somewhat different from most of those on metal catalysts, since ethylene was not present in the gas phase, the results obtained on sites I of alumina are in marked contrast to those obtained on metal catalysts. Dideuteroethane is the major product on sites I without accompanying C_2H_6 and highly deuterated ethanes except for a small amount of ethane-d_3, while on metals, all deuteroethanes are usually found and C_2H_6 is sometimes the largest component in the initial stage of the reaction.

It has been found in Part I (*1*) that the rate of hydrogenation on sites I, r_h, can be expressed by the empirical equation $r_h = kp_H\,(1-\theta_I)\theta_I$, where p_H and θ_I are, respectively, the pressure of hydrogen and the surface coverage of ethylene on sites I. This rate equation and the present results with deuterium can be explained by a Twigg-Rideal mechanism (*7*), that is, ethylene adsorbed on sites I as a π-complex reacts with hydrogen either from van der Waals' adsorption as suggested by Twigg or from the gas phase to produce σ-bonded ethyl radical and hydrogen atom on the site, and finally ethane is produced from the ethyl radical and the hydrogen atom. The exchange reaction of ethylene in which HD and deuteroethylene are formed occurs via the backward reaction of the first step.

These reactions are illustrated in Fig. 5, where θ_{1-3} are the surface coverages of ethylene, ethyl radicals, and deuterium atoms, respectively, x_i and y_i are the fractions of various ethylene and ethyl radical species on the surface ($\Sigma x_i = 1$, $\Sigma y_i = 1$), and k_i is the rate constant of each elementary reaction. Solid arrows show that the reactions involve deuterium and the broken arrow that it involves hydrogen. The back-

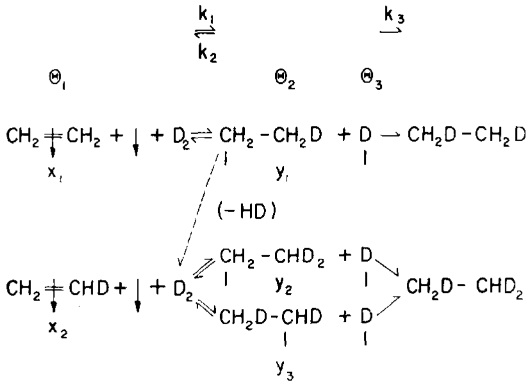


FIG. 5. Reaction scheme of hydrogenation on sites I.

ward reaction of ethane was omitted because the equilibrium is far on the side of ethane, and moreover ethane was trapped in the present study as soon as it was formed. Neglected also are the reverse reactions of dideuteroethyl radicals to form HD, since they are not involved in the steady state treatment, as will be seen below. Furthermore, ethane-d_4 was not found in the product at low temperature and only a negligible amount of ethylene-d_2 was present on the surface. It should also be noted that the amount of deuterium used in the present study was so large compared to the amount of HD produced that the hydrogen reacting with ethylene was almost exclusively deuterium.

Ignoring isotope effects in all steps in Fig. 5, we have the following steady state equations:

$$k_1 p_D x_1 \theta_1(1 - \theta_1) - k_2 y_1 \theta_2 \theta_3 = k_3 y_1 \theta_2 \theta_3 \quad (1)$$

$$\tfrac{1}{2} k_1 p_D x_2 \theta_1(1 - \theta_1) - k_2 y_2 \theta_2 \theta_3 = k_3 y_2 \theta_2 \theta_3 \quad (2)$$

$$\tfrac{1}{2} k_1 p_D x_2 \theta_1(1 - \theta_1) - k_2 y_3 \theta_2 \theta_3 = k_3 y_3 \theta_2 \theta_3 \quad (3)$$

It is also obvious that the corresponding steady state equation for the overall hydrogenation reaction gives the following expression for the rate of hydrogenation:

$$r_h = \frac{k_1 k_3}{k_2 + k_3} p_D \theta_1 (1 - \theta_1)$$

which agrees with the empirical rate equation obtained with hydrogen, as already mentioned.

From Fig. 5, we have

$$\frac{d[C_2H_4D_2]/dt}{d[C_2H_3D_3]/dt} = \frac{k_3 y_1 \theta_2 \theta_3}{k_3(y_2 + y_3)\theta_2 \theta_3} = \frac{y_1}{y_2 + y_3}$$

Combining Eqs. (2) and (3) and comparing it with Eq. (1), we have the relation $y_1/(y_2+y_3) = x_1/x_2$, therefore

$$[C_2H_3D_3] = \int_0^{-[C_2H_4D_2]} \frac{x_2}{x_1} \, d[C_2H_4D_2]$$

The ratio x_2/x_1 has been obtained experimentally and is shown in Fig. 2 as a function of $[C_2H_4D_2]$. Therefore the amount of ethane-d_3 can be calculated from the area under the curve of Fig. 2 and the results are shown in Fig. 1 by a broken line which is in reasonable agreement with the observed amounts.

For the exchange reaction,

$$d[HD]/dt = \tfrac{2}{3} k_2 y_1 \theta_2 \theta_3$$
$$d[C_2H_4D_2]/dt = k_3 y_1 \theta_2 \theta_3$$

so that $[HD]/[C_2H_4D_2] = \frac{2}{3}\ k_2/k_3 = \text{const.}$ The results obtained at 12 and 30 min of the reaction time gave 1.03 and 1.01 as the ratio of HD to ethane-d_2, showing a good constancy. From the average of the ratios, k_2/k_3 was obtained as 1.53.

As was already described, the exchange reaction between deuterium and ethylene adsorbed on sites II occurs at higher temperatures. However, the temperature dependence of this reaction shows that the reaction becomes negligible at room temperature, so that the exchange reaction on sites II is not contributing to the formation of HD on sites I at the low temperatures. Also the exchange reaction between deuterium and the alumina could be neglected at low temperatures, although it became more important at 80°.

The activation energy of the exchange reaction was found to be 11 kcal/mole from the rates of increase of HD at 0° and 25° and about 3 kcal higher than the activation energy of hydrogenation (7.7 kcal/mole) obtained previously (*1*). This difference in activation energy explains the fact that more highly deuterated ethane and ethylene as well as higher ratio of ethane-d_3/ethane-d_2 were found at 25° than at 0°.

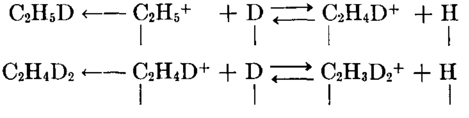
A molecular addition of deuterium to ethylene could explain at least the fact that the major product is 1,2-ethane-d_2. It was also found that the H_2–D_2 equilibration reaction took place on the alumina catalyst used in this study, and its rate was so fast that the equilibrium was established within a few minutes at 0° even when the present amounts of ethylene covered the surface, although the equilibration reaction was retarded at $-75°$ if the amount of preadsorbed ethylene became larger. Therefore the fact that only HD was found in the gas phase does not necessarily exclude formation of H_2, because most H_2 becomes HD at equilibrium when the concentration of D_2 is very high. However, if molecular addition took place, the same amount of ethane-d_4 as ethane-d_3 would have to be formed unless a serious isotope effect existed, because the chance of removal of HD from ethane is equal to that of H_2. It is therefore unlikely that a molecular addition of hydrogen is the mechanism on sites I.

As discussed above, the present results can be explained well by the simple Twigg-Rideal mechanism (*7*). It should be noted, however, that the present results on alumina do not require postulation of the additional and faster reaction proposed by Twigg (*8*) since little isotopic exchange takes place.

Reactions on Sites II

The rate of hydrogenation on sites II was found to be of 0.5 order with respect to hydrogen pressure, as reported in Part I (*1*). It has also been suggested from the results of adsorption of C_2D_4 that ethylene is adsorbed as an ethyl carbonium ion on sites II, which are probably Brönsted acid sites (*9*).

The reactions on sites II can therefore be described by the following scheme:



$$\begin{array}{l} C_2H_5D \xleftarrow{\text{slow}} \underset{|}{C_2H_5^+} + \underset{|}{D} \overset{\text{fast}}{\rightleftarrows} \underset{|}{C_2H_4D^+} + \underset{|}{H} \\ C_2H_4D_2 \longleftarrow \underset{|}{C_2H_4D^+} + \underset{|}{D} \rightleftarrows \underset{|}{C_2H_3D_2^+} + \underset{|}{H} \end{array}$$

The reactions take place between ethyl carbonium ions on sites II and hydrogen atoms which are formed by a dissociative adsorption of hydrogen, probably on sites I, and migrate to sites II. When the dissociative adsorption of hydrogen is weak, the surface concentration of hydrogen atoms is proportional to the square root of hydrogen pressure, so that the hydrogenation rate has the order of 0.5. In spite of the fast exchange reaction, the hydrogen atoms on the surface are almost entirely deuterium because of still faster equilibration with gaseous deuterium, leaving very small amounts of C_2H_6 in the product, as observed.

The exchange reaction between deuterium and ethylene adsorbed on sites II occurs very quickly at temperatures employed in this study. Although the loss of hydrogen from hydrocarbons agreed within 10% with the amount of HD formed in the gas phase, as mentioned in the previous section, exchange between deuterium and the catalyst occurred at 80°, at least when no ethylene was preadsorbed. Therefore the rate of exchange of ethylene was calculated from the descending curve of C_2H_4 in Fig. 4 rather than from the increase in HD, and it was found that the rate of exchange was about 35 times faster than that of hydrogenation at 8 torr of deuterium and 80°. It should also be mentioned that the composition of exchanged ethylene was determined in the ethylene desorbed from the surface by temperature-programmed desorption and, for example, $C_2H_4D^+$ would give some C_2H_4 as well as C_2H_3D. This means that the exchange reaction could be still faster than observed. Indeed H–D exchange reaction of olefins on alumina without serious hydrogenation was also reported by Larson, Hightower, and Hall (*10*).

The hydrogenation occurs, therefore, between deuterium atoms and the highly exchanged ethyl carbonium ions, so that various deuteroethanes can be produced. There should also be a chance for an ethyl carbonium ion to react with a hydrogen atom formed in the exchange processes to give C_2H_6, although the probability of this happening is very small because of the fast equilibration reaction as already pointed out.

ACKNOWLEDGMENTS

The author is grateful to Dr. R. J. Cvetanovic for very helpful discussion and encouragement. Thanks are also due to Dr. R. F. Pottie and Mr. R. Sander of this Division for obtaining the mass spectra.

REFERENCES

1. AMENOMIYA, Y., CHENIER, J. H. B., AND CVETANOVIC, R J., *J. Catalysis* **9,** 28 (1967).
2. AMENOMIYA, Y., AND CVETANOVIC, R. J., *J. Phys. Chem.* **67,** 144 (1963); *ibid.* **67,** 2046 (1963); *ibid.* **67,** 2705 (1963).
3. YASUMORI, I., AND OHNO, S., *Bull. Chem. Soc. (Japan)* **39,** 1302 (1966).
4. AMENOMIYA, Y., AND POTTIE, R. F., *Can. J. Chem.* **46,** 1735, 1741 (1968).
5. TROKHIMETS, A. I., AND MARKEVICH, S. V., *Zh. Fiz. Khim.* **38,** 1293 (1964).
6. See, e.g., BOND, G. C., "Catalysis by Metals," p. 252, Academic Press, New York, 1962; BOND, G. C., AND WELLS, P. B., *Advan. Catalysis* **15,** 91 (1964).
7. TWIGG, G. H., AND RIDEAL, E. K., *Proc. Roy. Soc. (London)* **A171,** 55 (1939).
8. TWIGG, G. H., *Discussions Faraday Soc.* **8,** 152 (1950).
9. AMENOMIYA, Y., CHENIER, J. H. B., AND CVETANOVIC, R. J., *Intern. Congr. Catalysis, 3rd, Amsterdam, 1964* **2,** 1135. (North-Holland Publ. Co., Amsterdam, 1965).
10. LARSON, J. G., HIGHTOWER, J. W., AND HALL, W. K., *J. Org. Chem.* **31,** 1225 (1966).