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Infrared Study of Ethylene Hydrogenation on Alumina-Supported Platinum at Low Temperature

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The chemical species adsorbed during ethylene hydrogenation on Al_2O_3-supported Pt were studied by infrared spectroscopy. The Pt surface was covered by dissociatively adsorbed hydrogen and π-adsorbed ethylene in the steady state of the reaction at 203 K. Dissociatively adsorbed hydrogen covered more than half of the surface Pt atoms and it was revealed that the reaction proceeds between dissociatively adsorbed hydrogen and π-adsorbed ethylene, according to the Langmuir reaction mechanism. However, the rates of migration of both adsorbed species on Pt surface were much slower than the steady-state rate of the reaction at 203 K and consequently only the neighboring adsorbed species were able to participate directly in the steady state of the reaction.

INTRODUCTION

Ethylene hydrogenation on transition metals is one of the fundamental reactions in heterogeneous catalysis and has been the subject of numerous investigations (*1–4*). The reaction intermediate of the overall reaction has been inferred from the D-content distribution of ethylene or ethane in the ethylene–deuterium reaction. The conclusion so far is that the metal surface is covered with ethylene and ethyl radicals but little hydrogen during the reaction (*2, 3*). It is generally considered that the hydrogenation proceeds between adsorbed hydrogen and ethylene, that is, via a Langmuir-type reaction mechanism. However, various species of adsorbed ethylene, such as π-type, σ-type, or dissociative adsorption have been observed and make the reaction mechanism complicated. Direct observation of the surface species present during the reaction is accordingly very important in order to correlate the reaction rate with the amounts of each adsorbed species or gas pressure and thus to elucidate the reaction mechanism.

In a previous paper (*5*), the author showed from ir spectroscopic observations that π-type ethylene was the major adsorbed species of ethylene on Al_2O_3-supported Pt and Pd at 195 K. Absorption bands due to dissociatively adsorbed hydrogen on supported Pt have been observed at 2120 and 2065 cm^{-1} (*6*). An attempt has therefore been made to examine the dynamic behaviour of adsorbed species, both ethylene and hydrogen, during the hydrogenation reaction on Pt at low temperature, where both of the adsorbed species are rather stable and observable by ir spectroscopy. The reaction mechanism has been studied on the basis of the dependence of the reaction rate upon the amounts and behaviour of adsorbed species during the reaction.

EXPERIMENTAL

The preparation of the alumina-supported platinum catalyst, the pretreatment of the catalyst, the infrared cell for the low-temperature measurements, and the purification of gases were the same as described in the previous report (*5*). The platinum content in the catalyst was 9.2 wt%.

The catalyst, about 90 mg, was pressed into a disk and was held in the cell. The reaction rate was followed from the pres-

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sure change and the amounts of adsorbed species during the reaction were determined from the integrated band intensities of the adsorbed species. The initial pressure of ethylene or hydrogen was set above 70 Torr to prevent the gas circulating rate from determining the reaction rate, and the ratio of ethylene and hydrogen pressure was between 0.5 and 2. All of the work was carried out at 203 K.

The amount of hydrogen adsorbed on Pt was estimated from the integrated band intensity of the Pt–H stretching vibration at 2120 cm^{-1} (*6*). Another Pt–H stretching band at 2065 cm^{-1} was not included for the estimation of the adsorbed amount, because the band overlapped with the band of gaseous ethylene at 2040 cm^{-1}. As the intensity ratio of the band at 2120 cm^{-1} and that at 2065 cm^{-1} did not change during the reaction, this procedure of estimation is adequate, and does not lead to serious errors. The amount of ethylene π-adsorbed on Pt was estimated from the integrated intensity of the band at 1205 cm^{-1} due to the C=C stretching vibration (*5*). The full coverages for hydrogen, $\theta_H = 1$, and for ethylene $\theta_E = 1$, were determined from the respective saturated adsorption at the reaction temperature under the gaseous pressure of approximately 100 Torr. The specific intensity of the band at 1205 cm^{-1} due to π-type ethylene changed accordingly with the experimental conditions. The apparent intensity of the 1205-cm^{-1} band observed at 100 Torr ethylene increased to 1.35 times when the gaseous and physically adsorbed ethylene was evacuated. The specific intensity change due to the experimental conditions was not desirable for the quantitative estimation, but there was no other suitable band for π-adsorbed ethylene which does not overlap with the bands of gaseous ethylene.

In an ethylene deuteration experiment, ethylene and ethane were analyzed by a mass-spectrometer using an electron energy of 15 V, after ethylene and ethane were separated by gas chromatography. The mass pattern of $C_2D_nH_{6-n}$ or $C_2D_mH_{4-m}$ was extrapolated from the mass patterns of C_2H_6, C_2D_6, C_2H_4, or C_2D_4. The content of deuterium in hydrogen was analyzed by gas chromatography using an alumina column at 98 K.

RESULTS

A typical result of the hydrogenation reaction over Pt/Al_2O_3 is shown in Fig. 1. Hydrogen or ethylene was first introduced into the ir cell to equilibrate the catalyst surface with the ambient temperature, prior to the admission of the mixture of hydrogen and ethylene to initiate the reaction. The adsorbed species observed during the reaction were π-adsorbed ethylene and dissociatively adsorbed hydrogen. The amount of another species of adsorbed ethylene observed at low temperature (*5*) was very little in this sample, and could not be observed especially when hydrogen coexisted. The turnover frequency (TOF) of the reaction was around 0.03 sec^{-1} at 203 K and in the pressure range studied, 70 Torr $< P_H$ or $P_E <$ 200 Torr, where the numbers of surface Pt atoms were estimated from hydrogen adsorption at the reaction temperature. In Fig. 1, the change of the adsorbed amounts was so small compared with the reaction rate that the reaction rate observed was considered to be in the steady state.

The rate of the reaction and the adsorbed amounts of hydrogen and ethylene (θ_H, θ_E) were measured during the course of the reaction with different ratios of hydrogen and ethylene pressure (P_H/P_E) in the range between 0.5 and 2. These results are shown in Figs. 2 and 3. The adsorbed amounts of hydrogen and ethylene during the reaction stayed unchanged as far as the pressure ratio (P_H/P_E) was constant in the pressure range studied, namely, 7 Torr $< P_H$ or P_E $<$ 200 Torr. Accordingly the adsorbed amounts of each species may be given as functions of the pressure ratio (P_H/P_E) in Fig. 2. As shown in Fig. 2, the adsorbed amounts of hydrogen or ethylene depended on the gas preadsorbed. When hydrogen

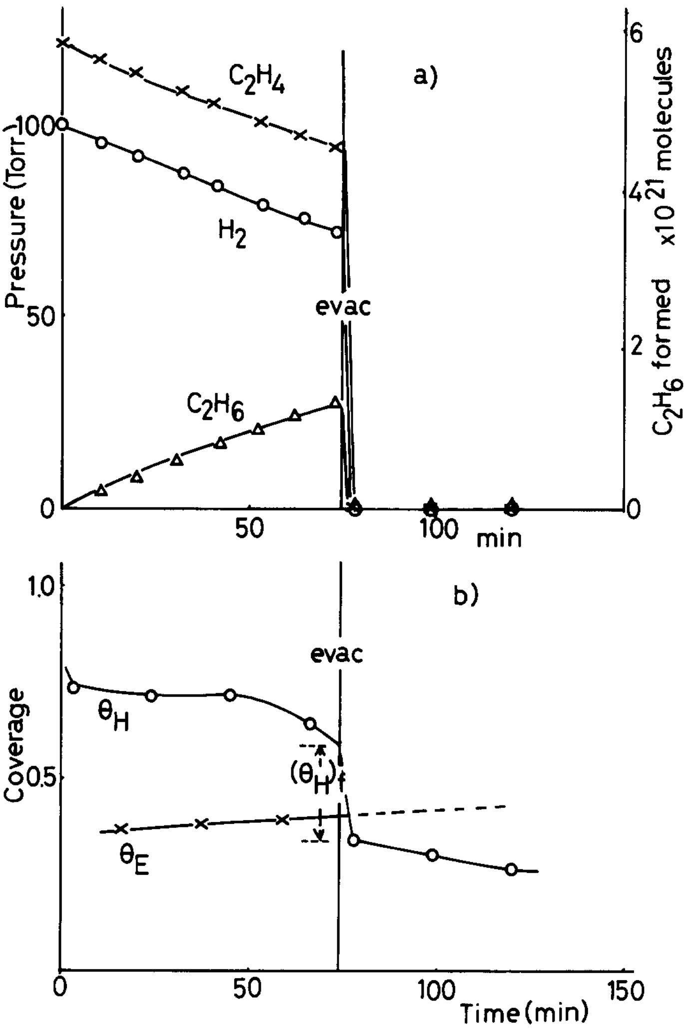

FIG. 1. Hydrogenation of ethylene on Pt/Al_2O_3 at 203 K. (a) Pressure change and (b) amounts of adsorbed species during the reaction. $\theta_H = 1$ corresponds to 1.48×10^{19}H(a) and $\theta_E = 1$ to $9.08 \times 10^{18}C_2H_4$(a).

was first admitted and then ethylene was added to initiate the reaction, the adsorbed amount of hydrogen was more than that when ethylene was preadsorbed. Other adsorbed species such as ethyl radicals or σ-adsorbed ethylene were not detected during the reaction or after evacuation of the gas phase. The sum of θ_H and θ_E became 80–90% of the surface coverage, and sometimes exceeded 100% when hydrogen was first admitted.

The dependences of the reaction rate upon ethylene and hydrogen pressure are shown in Figs. 3a and b, respectively. The plots where the pressure was lower than 50 Torr were estimated from the extrapolation of the first-order reaction rate, because the rate was apparently linear with the hydrogen pressure, and assuming the circulating rates of both gases to be much faster than the reaction rate. The pressure dependence of the reaction rates for both ethylene and hydrogen showed maxima, which suggests that the surface reaction (Langmuir-type reaction) determines the reaction rate.

The pressure dependence of the reaction

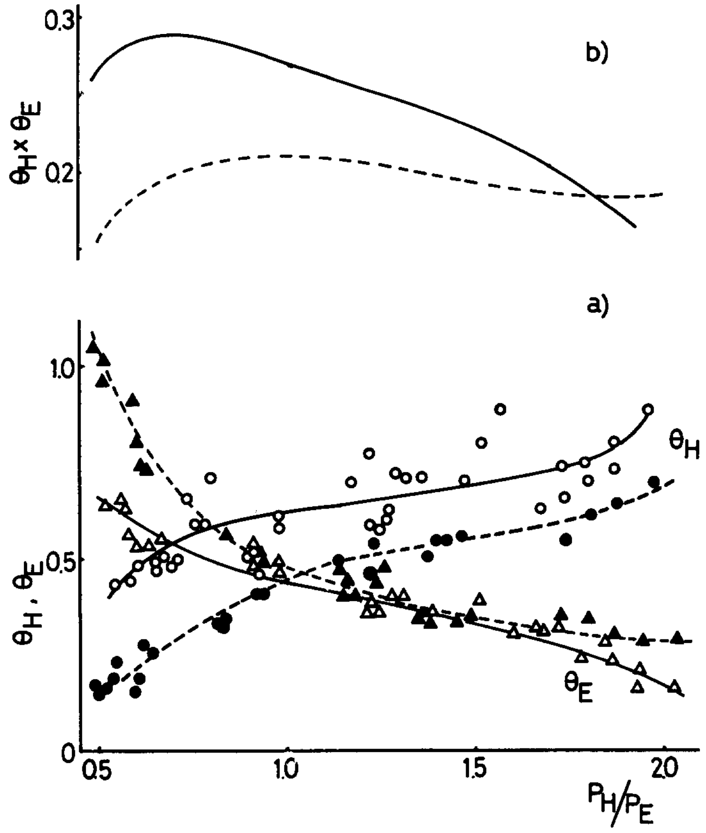

FIG. 2. (a) Surface coverages of π-adsorbed ethylene (θ_E) and dissociatively adsorbed hydrogen (θ_H) during the steady-state reaction as a function of the pressure ratio (P_H/P_E). Reaction temperature: 203 K, 70 Torr < P_H, P_E < 200 Torr. (b) The product of θ_H and θ_E. ○△—; H_2 was admitted first, then C_2H_4 was added to initiate the reaction. ●▲--; C_2H_4 was admitted first, then H_2 was added to initiate the reaction.

rate was also dependent upon the order of the admission of gases, as is shown in Fig. 3. The observed rate was faster when hydrogen was preadsorbed on the catalyst.

From the experiments such as those shown in Fig. 1, the relation between the reaction rates and the coverage of π-adsorbed ethylene or that of dissociatively adsorbed hydrogen was obtained. The data in Fig. 3b were replotted against the product of the coverage ($\theta_H \times \theta_E$) in Fig. 4. The reaction rate increases with the increase of $\theta_H \times \theta_E$, which shows that the surface reaction between dissociatively adsorbed hydrogen and π-adsorbed ethylene determines the reaction rate.

To examine the role of π-adsorbed ethylene in the reaction, the following experiments were performed. C_2H_4 was hydrogenated on a C_2D_4 preadsorbed surface, and the decrease of π-adsorbed C_2D_4 was measured from the intensity change of $\nu_{C=C}(C_2D_4)$ at 1320 cm^{-1}. Figure 5 shows the decrease of the adsorbed amount of C_2D_4 in the course of the reaction between C_2H_4 and H_2. The decreasing rate of C_2D_4(a) was divided into two parts, an initial fast decrease and a following slow decrease, and the rates were linear with the amount of C_2D_4(a). The frequency of $\nu_{C=C}$ did not change with the decreasing amount of adsorbed species and all the π-C_2D_4(a) reacted continuously. The rate of the initial fast decrease in Fig. 5 and that of

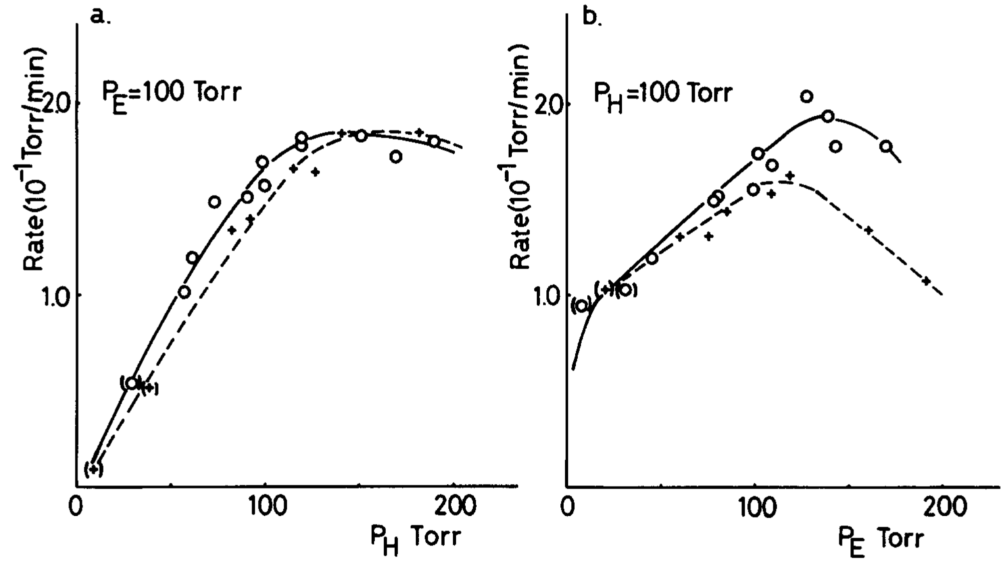

FIG. 3. Pressure dependence of the hydrogenation rate of ethylene on Pt/Al_2O_3 at 203 K. (a) The dependence on H_2 pressure, P_E = 100 Torr, (b) the dependence on C_2H_4 pressure, P_H = 100 Torr. -o-: H_2 was admitted first, then C_2H_4 was added. -+-: C_2H_4 was admitted first, then H_2 was added. Points in parentheses were estimated from extrapolation of the first-order reaction rate.

ethane formation was compared. The amount of ethane formed during the initial fast decrease of π-C_2D_4(a) in Fig. 5 was about three times of the disappeared amount of π-C_2D_4(a). Thus a large part of π-adsorbed ethylene (75%) is considered to take part directly in the steady-state reaction.

The adsorbed species of both hydrogen and π-adsorbed ethylene coexisted for a considerable time on the surface after the gas phase was evacuated during the steady state reaction. An example is shown in Fig. 1b. The decrease of the adsorbed hydrogen on evacuation of gas phase in Fig. 1b was divided into two parts, that is, a first rapid drop and a following slow decrease. Although the decrease of π-adsorbed ethylene

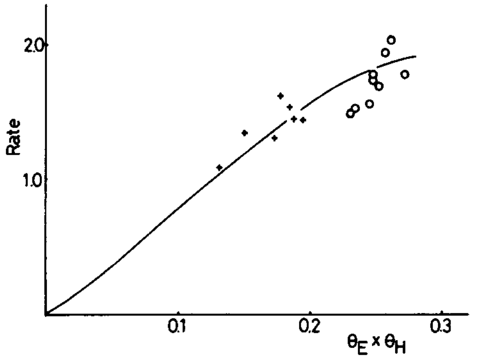

FIG. 4. The dependence of the rate of ethylene hydrogenation (P_H = 100 Torr) on Pt/Al_2O_3 at 203 K upon the product of coverages ($\theta_H \times \theta_E$). Plots were from the same experiments as those in Fig. 3b. O: H_2 was admitted first, then C_2H_4 was added. +: C_2H_4 was admitted first, then H_2 was added.

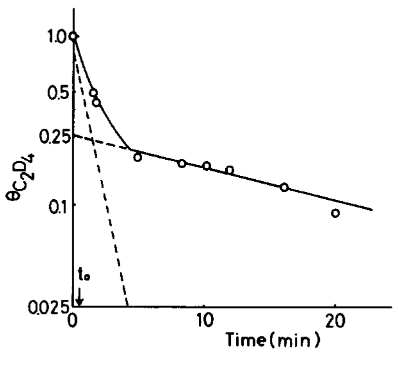

FIG. 5. The decrease of preadsorbed π-C_2D_4 in the steady-state reaction of C_2H_4 and H_2 at 203 K. P_H(initial) = 74.2 Torr, P_E(initial) = 98.6 Torr. t_0 shows the time that the amount of ethane produced exceeded that of ethylene preadsorbed on the catalyst.

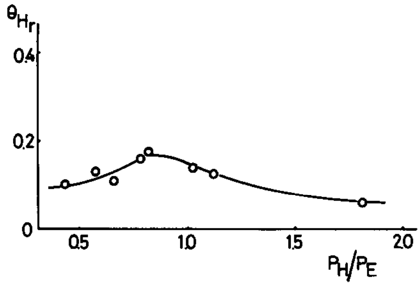

FIG. 6. Estimate of the coverage of dissociatively adsorbed hydrogen which participated in the steady state reaction at 203 K. 70 Torr < P_H, P_E < 200 Torr. $(\theta_H)_r = (\theta_H)_f - (\theta_H)_g$.

could not be estimated quantitatively because of the change in the specific intensity after evacuation, the decrease of the adsorbed hydrogen in the latter stage was very slow compared to the steady-state reaction rate.

The portion of dissociatively adsorbed hydrogen $(\theta_H)_r$ which disappeared rapidly from the surface through the reaction with ethylene was estimated from the amount of the first rapid decrease $(\theta_H)_f$ in Fig. 1. The amount desorbed as hydrogen gas through evacuation, $(\theta_H)_g$, was estimated independently from the decreasing rate of the amount of adsorbed hydrogen after hydrogen alone was adsorbed.

$$(\theta_H)_r = (\theta_H)_f - (\theta_H)_g,$$

$(\theta_H)_r$ was measured, changing the ratio of hydrogen and ethylene pressure before evacuation, and this is shown in Fig. 6. About 10% of the surface hydrogen was estimated to participate in the steady-state reaction directly. The adsorbed hydrogen which was more strongly adsorbed and not observed in ir spectra, for example, the bridged hydrogen species, would possibly exist on the Pt surface. The surface preadsorbed with hydrogen was evacuated until the ir active adsorbed hydrogen disappeared, while the strongly adsorbed hydrogen remained. Negligible ethane was observed when ethylene was introduced on this surface. Therefore the amount of ir-inactive adsorbed hydrogen which participates in ethylene hydrogenation was considered to be small.

The exchange reaction between adsorbed deuterium and adsorbed ethylene or between hydrogen and deuterium was examined by mass spectrometry or by gas chromatography. When the mixture of H_2 and D_2 reacted with about an equal amount of C_2H_4, the exchange reaction between H_2 and D_2 rapidly reached equilibrium while only about 10% of ethylene hydrogenated. However, H_2 or HD did not appear in the gas phase when D_2 reacted with C_2H_4. Also little D-exchanged ethylene appeared in the gas phase, but multiexchanged ethane $C_2D_xH_{6-x}$ was found in the reaction product. The observed distribution is shown in Table 1. There was no significant effect of increasing conversion on the product distribution in the range 5–23%. When a higher ratio $P_{D_2}/P_{C_2H_4}$ was employed at the beginning, the amount of $C_2D_2H_4$ was slightly increased.

DISCUSSION

The above experiments using H_2, D_2, and C_2H_4 revealed that the rate of the exchange reaction between gaseous hydrogen and adsorbed hydrogen was rapid compared with the hydrogenation rate, but no exchange was observed between deuterium and π-adsorbed ethylene or between gaseous ethylene and π-adsorbed ethylene, whereas multiexchanged ethane appeared in the

TABLE 1

Product Distribution from the Reaction of C_2H_4 with D_2 at 200 K

	Run 1	Run 2	Run 3	Run 4
$(P_{D_2}/P_{C_2H_4})_{\text{initial}}$	1.01	1.01	5.17	0.55
Conversion (%)	5.6	23.1	22.5	7.99
Ethane-d_6 (%)	1.4	1.4	—	1.6
-d_5	2.5	2.5	2.3	2.3
-d_4	3.9	4.0	3.9	3.7
-d_3	9.6	10.0	8.2	9.2
-d_2	60.9	62.8	67.8	60.2
-d_1	19.0	17.3	16.3	21.4
-d_0	2.8	2.1	1.6	1.7

case of $C_2H_4 + D_2$ reaction. All of these observations are consistent with the results obtained formerly by Bond and others (*2–4*), although the percentage of $C_2D_2H_4$ in the product ethanes was rather high in our case compared with the results obtained by Bond *et al.* under similar experimental conditions but at higher reaction temperature. The former investigators did not observe the surface directly during the reaction, but extracted the composition of the adsorbed species from the results of C_2H_4 and D_2 reactions by a steady-state treatment of the reaction.

$$C_2X_4(g) \rightleftharpoons C_2X_4(a) \rightleftharpoons C_2X_5(a) \rightarrow C_2X_6.$$

The D-distribution of ethanes thus observed was compared with the computed distribution, which gave the relative rates of each process. It was thus concluded that almost the whole surface was covered with ethyl radicals and ethylene but that almost no hydrogen stayed on the surface. However, ir spectra observed during the reaction showed that more than 80% of the Pt surface was covered with a comparable amount of dissociatively adsorbed hydrogen and π-adsorbed ethylene at the low temperature of 203 K, as shown in Fig. 2. Although the exchange reaction between deuterium and ethylene was not observed, the adsorbed amount of hydrogen on Pt exceeded that of π-ethylene in the reaction when P_H/P_E was higher than 0.8. Furthermore, the ir bands due to ethyl radicals could be hardly observed on the surface during the reaction.

The amounts of dissociatively adsorbed hydrogen and π-adsorbed ethylene did not reach adsorption equilibrium during the reaction and the adsorbed amounts differed according to the preadsorbed species (ethylene or hydrogen), as shown in Fig. 2. However, the surface during the reaction was in the stationary state as was seen in Fig. 1. The total coverage of hydrogen and ethylene ($\theta_H + \theta_E$) became more than unity when hydrogen was preadsorbed, when saturated coverage of each component was measured independently. From volumetric measurements, the amount of H(a) on Pt was estimated to be about twice that of π-adsorbed ethylene; the adsorption of one ethylene molecule accordingly uses 2 Pt atoms from geometric requirement (*5*). However, the bonding between Pt and C_2H_4 would require only one Pt atom, and since the size of the H atom is so small that it will not disturb the adsorption of C_2H_4 molecules at the neighboring Pt atom. This could be the reason why the total coverage of H(a) and π-C_2H_4 in the case of H_2 preadsorption can be unity.

When the hydrogenation rates in Fig. 3 are compared, it is recognized that plots have maxima with change of pressure. That is, the reaction rate decreased in the high P_E or P_H region where π-adsorbed ethylene or dissociatively adsorbed hydrogen occupied a major part of the surface. Thus the reaction rate could be written as

$$\text{Rate} = k\theta_H \times \theta_E. \qquad (1)$$

Certainly Fig. 4 shows that the rate increases with the increase of ($\theta_H \times \theta_E$). This observation leads to the conclusion that the ethylene hydrogenation reaction has occurred by the Langmuir-type mechanism, that is, the reaction has proceeded between dissociatively adsorbed hydrogen and π-adsorbed ethylene.

Thus the hydrogenation reaction of ethylene is considered to proceed in the following steps:

$$H_2 \rightleftharpoons 2H(a), \qquad (2)$$

$$C_2H_4 \rightarrow \pi\text{-}C_2H_4(a), \qquad (3)$$

$$\pi\text{-}C_2H_4(a) + H(a) \rightleftharpoons C_2H_5(a) \xrightarrow{H(a)} C_2H_6. \qquad (4)$$

The occurrence of the reactions in the reverse directions in Reaction (4) was confirmed from the ($C_2H_4 + D_2$) reaction. Gaseous C_2D_4 did not desorb during the ($C_2H_4 + H_2$) reaction on the C_2D_4 preadsorbed surface, and the irreversibility of Reaction (3) was confirmed. The exchange reaction between gaseous hydrogen and adsorbed hydrogen, Reaction (2), was much more rapid compared with the rate of hydrogenation. The existence of ethyl radicals on the surface during the reaction could not be confirmed by ir measurements, so the reaction of the ethyl radical with H(a) was considered to proceed fast. However, multideuterated ethane was produced in the C_2H_4 and D_2 reaction to some extent. This would presume that the rate-determining step turns to another step at higher temperatures. The overall reaction rate showed the Langmuir-type behaviour as written in Eq. (1).

However, all the adsorbed hydrogen or ethylene did not uniformly take part in the steady-state reaction as was seen in Figs. 1, 5, and 6. The turnover frequency in this reaction condition was observed to be about 0.03 sec^{-1}. Consequently if the adsorbed ethylene or hydrogen reacts uniformly, all of these species would disappear from the surface in a minute, but hydrogen and ethylene coexisted rather stably after evacuation of the gas phase, as was seen in Fig. 1. Thus it is indicated that the migration of both adsorbed species on Pt at 203 K was very slow compared with the reaction rate and that only the neighboring adsorbed species were able to react in the steady state of the reaction.

As described in the previous report (5), π-adsorbed ethylene disappeared instantly when excess hydrogen gas was introduced in the cell at 203 K and only the dissociatively adsorbed hydrogen remained on the surface. Similarly dissociatively adsorbed hydrogen disappeared completely with the admission of gaseous ethylene.

$$H(a) + C_2H_4 \rightharpoonup C_2H_6 + C_2H_4 + C_2H_4(a),$$

$$C_2H_4(a) + H_2 \rightharpoonup H_2 + C_2H_6 + H(a).$$

Thus all of the π-adsorbed ethylene can react with adsorbed hydrogen if the neighboring site of adsorbed ethylene is occupied by hydrogen.

In conclusion, the platinum surface during the ethylene hydrogenation is mainly covered with π-adsorbed ethylene and dissociatively adsorbed hydrogen at 203 K, where both adsorbed species react to produce ethane. Furthermore, as both adsorbed species have very small migration rates on the surface compared with the hydrogenation rate, the adsorbed species which have the reaction partner in the neighboring sites, about 10% of H(a) and 75% of π-C_2H_4(a), take part in the steady-state reaction at this temperature.

At higher reaction temperature, the migration of adsorbed hydrogen increases and the greater part of the adsorbed species become able to participate in the steady-state reaction.

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