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Hydrogenation of Olefins on Alumina

I. Active Sites for Hydrogenation of Ethylene*

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Hydrogenation of ethylene on alumina has been studied at low temperatures (−20° to +90°C). The reaction has been found to occur even at and below room temperature if ethylene is preadsorbed on the catalyst. There are at least two different types of active sites on alumina for ethylene hydrogenation. These are the same sites which were previously found by the authors to be responsible for the chemisorption and polymerization of olefins. However, the hydrogenation occurs much more readily on the active sites on which chemisorption is weaker, while polymerization of ethylene takes place preferentially on the other (stronger) sites. The results of hydrogenation on the stronger sites suggest that these sites are heterogeneous.

INTRODUCTION

Catalytic hydrogenation of ethylene is one of the most extensively investigated catalytic reactions. However, most of the work has been carried out on metal or supported metal catalysts and very little information (*1–4*) is available on the hydrogenation on alumina alone. It is of interest that, on the basis of water-poisoning experiments, Hindin and Weller (*2*) have suggested that a very small fraction of the surface is active for hydrogenation.

Recently the authors have used the temperature-programmed desorption (TPD) technique (in the previous work referred to as the "flash desorption technique") and found that there are two kinds of active sites on alumina for the chemisorption of olefins (*5–7*). In this technique a gas initially preadsorbed on a catalyst is desorbed into a carrier gas stream by raising the catalyst temperature in a programmed manner. In some cases the technique is useful for the study of surface reactions on active sites and in the case of alumina it has been established that the polymerization of ethylene occurs readily at room temperature on the stronger sites (sites II) but not on the weaker sites (sites I) (*8*).

In view of these findings, it was thought of interest to use the temperature-programmed desorption technique to study the hydrogenation of ethylene on the active sites of alumina. The results obtained are presented in this paper. The temperature range (−20° to +90°C) used in the present work is considerably lower than used by the previous authors (120–500°C). The temperature-programmed desorption technique has been recently described and discussed in greater detail (*9*).

EXPERIMENTAL

Apparatus. The design of the apparatus has been in principle the same as described before (*5*). However, several modifications and improvements have been made. The main part of the apparatus is shown schematically in Fig. 1. The two cells of the thermistor-type thermal conductivity detector used are now connected for parallel flow of the carrier gas and not in series as used previously. A rapid equalization of the pressures in the two cells is better achieved in this manner. Also, a capillary inserted

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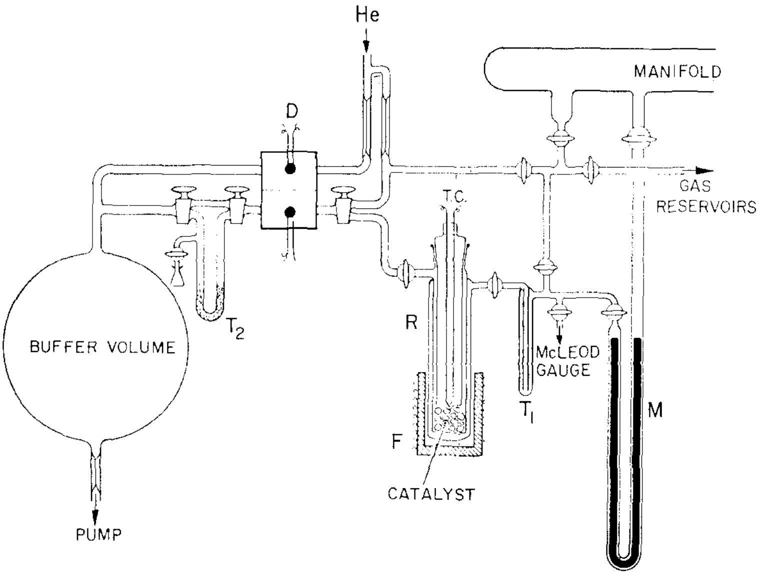

FIG. 1. Apparatus: D, detector; R, reactor; T.C., thermocouple; F, furnace; M, manometer; T_1, T_2, traps.

into the flow stream before the reactor minimizes the effect of a change in the flow resistance in the reactor itself as a result of heating. The reactor is provided with a jacket to eliminate transfer of the sporadic small temperature fluctuations of the heaters. As a result of these modifications, the base line drift is eliminated and smoother desorption peaks are obtained. With a larger ratio of the catalyst volume to the dead volume in the modified reactor, an increased sensitivity for adsorption measurements has also been achieved.

Materials. Alumina was prepared by the hydrolysis of purified aluminum isopropoxide in an isopropyl alcohol solution. The precipitate was washed with double-distilled water and dried overnight at 120°C and was then treated with air for 3 hr at 600° before loading into the reactor. The catalyst sample (0.797 g) in the reactor was evacuated for more than 17 hr at 650° before use. During the evacuation water evolved at first; after 17 hr, however, no water evolution could be observed. The surface area of the catalyst after the above treatment was 205 m^2/g, as determined by BET with nitrogen.

Phillips research grade ethylene was thoroughly degassed and stored in a reservoir. Matheson's ultra-pure hydrogen was passed through a Deoxo unit followed by a liquid nitrogen trap.

Procedure. Ethylene was preadsorbed on the catalyst under various conditions and the catalyst was subsequently evacuated so that the pressure in the gas phase became negligible. Hydrogen was then introduced at selected pressures and temperatures. After the reaction, the catalyst was evacuated through a liquid nitrogen trap (T_1) and at the same time the cold bath was removed from the reactor if the reaction temperature was lower than room temperature. The catalyst temperature therefore gradually approached room temperature during the evacuation. When the reaction temperature was 60° or higher, the catalyst was kept at the reaction temperature during its evacuation through the liquid nitrogen trap (T_1). It was found that the gas still remaining on the catalyst after evacuation for 20 min at both temperatures contained only a trace of ethane, as will be mentioned below, indicating that 20 min evacuation was sufficient to remove ethane from the catalyst. In this report the amounts of ethane produced are those collected in the trap T_1 during the 30 to 40 min period of evacuation after the reaction. The gas thus collected in the trap was analyzed by gas chromatography and found to be mainly ethane. Occasionally a small amount of ethylene was present as well, particularly when the amount of preadsorbed ethylene was very large. No other hydrocarbons were found.

Helium carrier gas was next diverted to flow through the reactor, and the programmed heating of the catalyst was started at a constant speed (about 17.5°C/min) as soon as the recorder base line became stabilized. The desorbed gas was trapped in T_2 and gas chromatographic analysis showed it to be ethylene, sometimes with a trace of ethane. No reaction other than hydrogenation therefore occurred. Furthermore, the TPD of ethylene alone (without hydrogenation) showed within the experimental error a good material balance and gave no ethane, so that neither self-hydrogenation nor serious cracking appeared to occur even at the high temperatures (up to about 300°) during TPD. The amounts of ethylene initially adsorbed on the surface were calculated as the sum of C_2 hydrocarbons collected during the evacuation and the temperature-programmed desorption.

The catalyst was usually evacuated at 650° for 2 to 3 hr after each run. This treatment was sufficient to keep the activity of the catalyst constant when the reaction was carried out at room temperature or below it. However, when the reaction temperature was 60° or higher (hydrogenation on the stronger sites), the amount of ethane produced by hydrogenation under the same conditions gradually decreased, unless the catalyst was regenerated after each run by treating it with dry air for 2 hr at 650° followed by evacuation for 2 to 3 hr at the same temperature.

RESULTS

Active Sites on Alumina

It has been reported previously (*5*) that the TPD chromatogram of ethylene on alumina gives two overlapping peaks, indicating that there are two different active sites on alumina for the chemisorption of ethylene. The catalyst used in the previous work was alumina precipitated with ammonia from an aluminum nitrate solution. The alumina used in the present study was prepared from aluminum alcoholate as already described, and again it gave two peaks similar to those obtained before, although the temperatures at which the peak maxima appeared were slightly higher. The sites corresponding to the lower and the higher temperature peak are called sites I and II, respectively.

As in the previous work, the amount of ethylene chemisorbed on the two types of sites could be readily controlled. When a sufficient amount of ethylene is admitted at room temperature or below it, adsorption takes place on both sites; when an amount calculated to be sufficient to cover only sites II is admitted at room temperature or above it, chemisorption takes place only on sites II (and TPD then shows only the higher temperature peak).

Hydrogenation on Sites I

When ethylene is preadsorbed on both sites I and II and hydrogen is then admitted at room temperature or below it, hydrogenation readily occurs. Some typical results are shown in Fig. 2. In these experiments, approximately constant amounts of ethylene were preadsorbed and the ethane produced was removed by evacuation before the temperature-programmed desorption, as already described. The chromatograms shown in Fig. 2 are therefore those of the unreacted ethylene remaining on the surface. It is seen that the first peak (the lower temperature peak) is gradually reduced in size as the conversion increases (using either higher pressures of hydrogen or longer reaction times), but the second peak remains almost unchanged even under severe reaction conditions.

The difference in activity between ethylenes preadsorbed on sites I and II can be seen more clearly in Fig. 3, which shows the course of the reaction as a function of time at a high pressure of hydrogen (146 mm). The reaction is rapid initially but becomes negligible after about 60 min in spite of the fact that as much as about 40% of the initial ethylene still remains on the surface. In the later stages when the reaction becomes negligible, only sites II are covered by ethylene. This is shown, for example, by the peak No. 4 in Fig. 2, which corresponds to the 90-min point in Fig. 3. These results rule out the possibility that the hydrogenation occurs

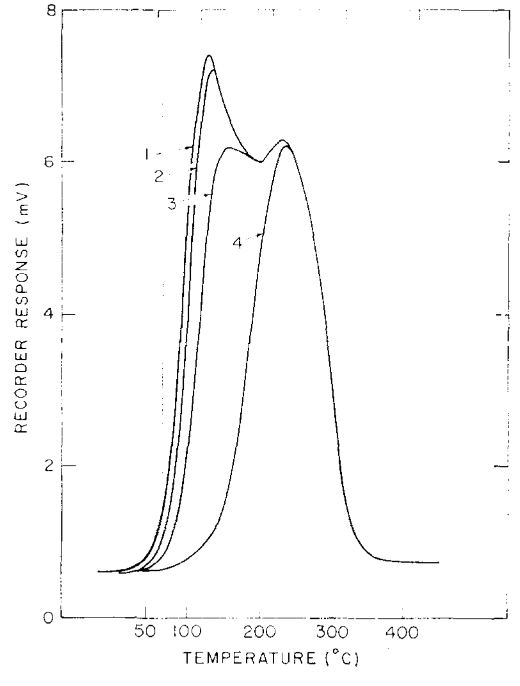

Fig. 2. TPD chromatogram of ethylene after hydrogenation. Temperature increase 17.5°C/min. Hydrogenation was carried out at 25° with approximately constant amount of preadsorbed ethylene (0.2 cc) on 0.797 g of the alumina catalyst. Hydrogen pressures and reaction times are (1) 0.51 mm, 15 min; (2) 1.35 mm, 15 min; (3) 2.80 mm, 30 min; (4) 147.4 mm, 90 min.

preferentially on sites II, but the unreacted ethylene then migrates from sites I to sites II. Sites I (the weaker sites for chemisorption) are therefore much more active for hydrogenation than are sites II, in contrast to the polymerization of ethylene, which occurs preferentially on sites II (*8*).

The two peaks of ethylene on the TPD chromatogram partially overlap and it is difficult to estimate separately the amounts adsorbed on each of the two types of sites. In previous work they were approximately estimated either by drawing a vertical line through the minimum between the peaks (*6*) or by evacuating at higher temperature (100°) to remove ethylene on sites I (*5*). However, the present results suggest a more convenient and more reliable method: the extrapolation of the linear portion of the residual ethylene to zero time, as shown in Fig. 3. A value of 0.123 cc/g is thus obtained and it is regarded to represent more accurately the typical amount of ethylene adsorbed on sites II at complete coverage.

The effects of the surface coverage of ethylene and of hydrogen pressure on the hydrogenation rate on sites I were examined at lower temperature and shorter reaction time so that the conversion was so small that the amount of ethane produced was proportional to the reaction time. The surface

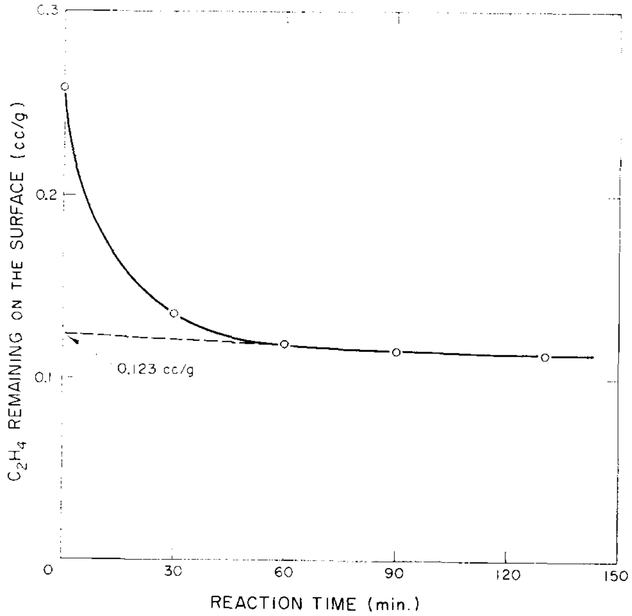

Fig. 3. The course of hydrogenation as a function of time. Hydrogen pressure about 146 mm, temperature 25°, initial amount of ethylene preadsorbed about 0.26 cc/g.

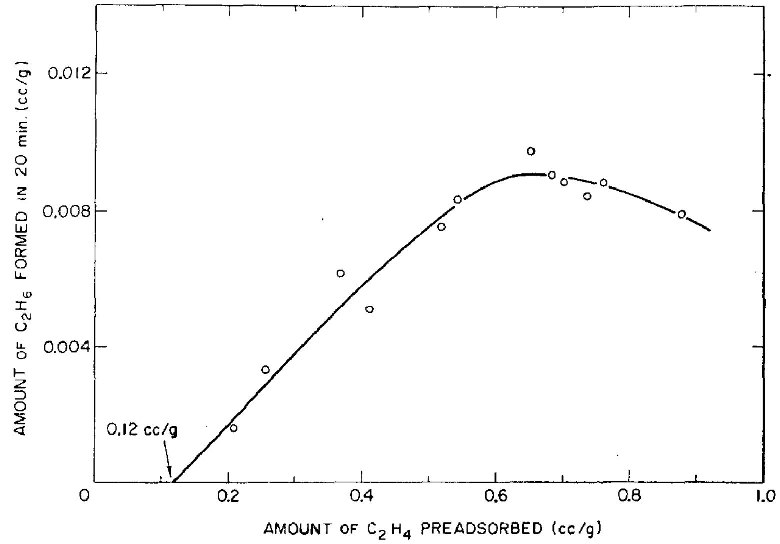

FIG. 4. Surface coverage dependence of the rate of hydrogenation on sites I. Hydrogen pressure 12.5 mm, reaction time 20 min, temperature −20°.

coverage dependence of the rate is shown in Fig. 4, in which the hydrogen pressure is kept constant (12.5 mm) and the amount of preadsorbed ethylene is varied. The extrapolation to zero reaction rate indicates the existence of different active sites, and the extrapolated value of 0.12 cc/g is in good agreement with that estimated for sites II in

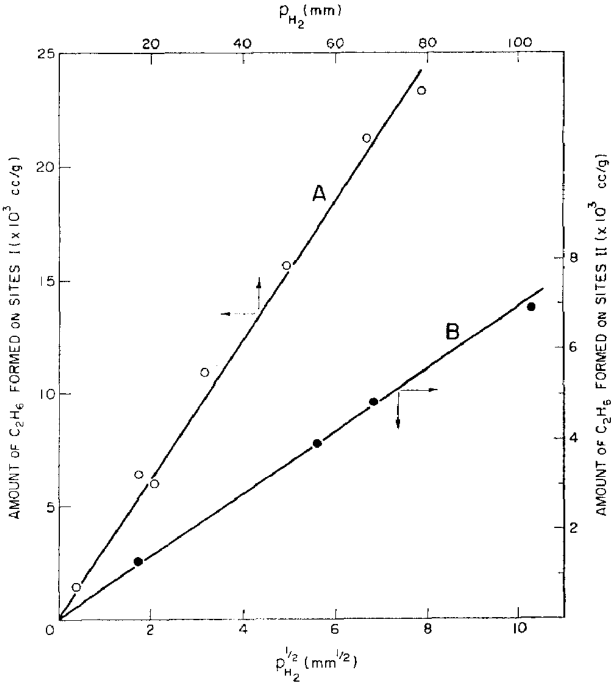

FIG. 5. Hydrogen pressure dependence of the rate of hydrogenation. A, Sites I, initial ethylene preadsorbed about 0.37 cc/g, reaction time 20 min, temperature −23°. B, Sites II, initial ethylene preadsorbed about 0.057 cc/g, reaction time 15 min, temperature 76°.

Fig. 3 (0.123 cc/g). It is seen in Fig. 4 that the rate increases at first with the surface coverage but finally reaches a maximum.

The hydrogen pressure dependence of the hydrogenation rate was studied at a constant amount of preadsorbed ethylene (0.37 cc/g) at which the curve of Fig. 4 is almost linear. The results are shown by line A in Fig. 5, which indicates that the hydrogenation rate on sites I is proportional to the hydrogen pressure.

The results obtained in Figs. 4 and 5 can be expressed by the rate equation

$$r = kp_{\mathrm{H_2}}(1 - \theta_{\mathrm{I}})\,\theta_{\mathrm{I}} \qquad (1)$$

where r is the rate of hydrogenation on sites I, $p_{\mathrm{H_2}}$ is the pressure of hydrogen, θ_{I} is the surface coverage of ethylene on sites I, and k the rate constant. The rate is proportional to $p_{\mathrm{H_2}}$ at constant surface coverage, and at constant $p_{\mathrm{H_2}}$ the rate has a maximum at $dr/d\theta_{\mathrm{I}} = kp_{\mathrm{H_2}}(1 - 2\theta_{\mathrm{I}}) = 0$. Applying Eq. (1) to the results of reactions at temperatures between −20° and 25°, the rate constant was obtained as $k = 7.2 \times 10^1 \exp(-7700/RT)$ molecules/mm sec site.

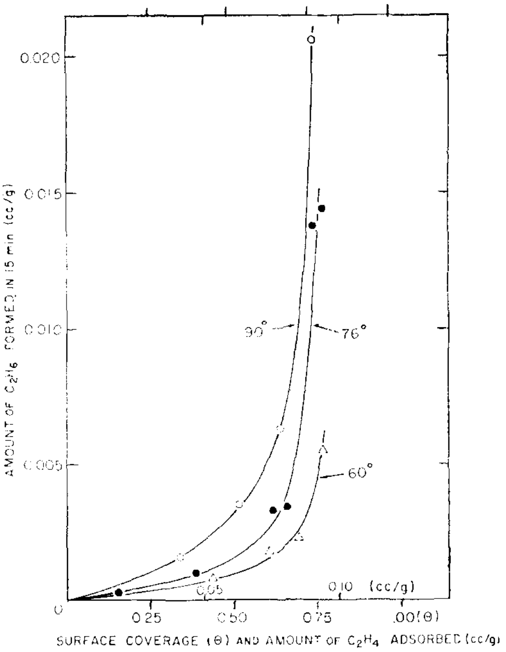

FIG. 6. Surface coverage dependence of the rate of hydrogenation on sites II. Hydrogen pressure 3.5 mm, reaction time 15 min. Ethylene was preadsorbed at 90° and partially removed by TPD up to temperatures between 90° and 240° to achieve different surface coverages.

Hydrogenation on Sites II

Although the rate of hydrogenation on sites II at room temperature or lower is negligibly small, it becomes measurable at temperatures higher than about 60°. However, the surface coverage dependence on sites II deviates upwards from a straight line, as seen in Fig. 6 where the hydrogen pressure was kept constant. In these experiments, an amount of ethylene which was slightly less than required to cover sites II was preadsorbed at 90° and partially desorbed in a stream of helium by heating up to various temperatures between 90° and 240° (TPD) to control the surface coverage on sites II. The catalyst was then cooled down to the reaction temperature. The subsequent TPD showed that all ethylene was adsorbed, as expected, on sites II and not on sites I. It is therefore unlikely that a small amount of ethylene still remaining on sites I was responsible for the sharp rise of the curves at higher surface coverages in Fig. 6. Indeed even when ethylene was preadsorbed and hydrogenated at lower temperature, the hydrogenation rate became zero when the amount of preadsorbed ethylene was less than 0.12 cc/g, as already seen in Fig. 4. The nonlinear plots of Fig. 6, therefore, seem to indicate that sites II are heterogeneous, i.e., that the activation energy of the reaction is strongly dependent on the coverage of sites II.

It was in general difficult to determine the pressure dependence of the rate because of the nonlinear dependence on the surface coverage. In a series of experiments the surface coverage of sites II was therefore kept as constant as possible (approximately 0.057 cc/g) and the pressure of hydrogen was varied from 3 to 106 mm at 76°C. The results, shown by line B in Fig. 5, indicate that the rate is proportional to the square root of hydrogen pressure at this particular surface coverage.

Although it was not possible to obtain exact values of the activation energy for ethylene hydrogenation on sites II, the data plotted in Fig. 6 indicate a decrease in the activation energy from about 15 to 10 kcal/mole as the surface coverage increases from 10% to 75%.

Adsorption of Hydrogen and Its Effect on Hydrogenation on Sites I

It has been found by the temperature-programmed desorption method with nitrogen as carrier gas that there are at least two kinds of adsorption of hydrogen on alumina. Typical results are shown in Fig. 7. When hydrogen is preadsorbed at temperatures below 100° only one TPD peak is obtained, at about 130°. This is shown by chromatogram A in Fig. 7, obtained by programmed heating from −195°. The small peak at about −90° is thought to be due to physical adsorption because it is removed easily if the evacuation before TPD is carried out at −60°. When the preadsorption temperature is higher than 250° a second peak also appears, with the maximum at about 320° (chromatogram B). These results are consistent with those of Gruber (*10*), who suggested two kinds of hydrogen chemisorption on alumina (below and above 300°) from the observed minima in the isobars.

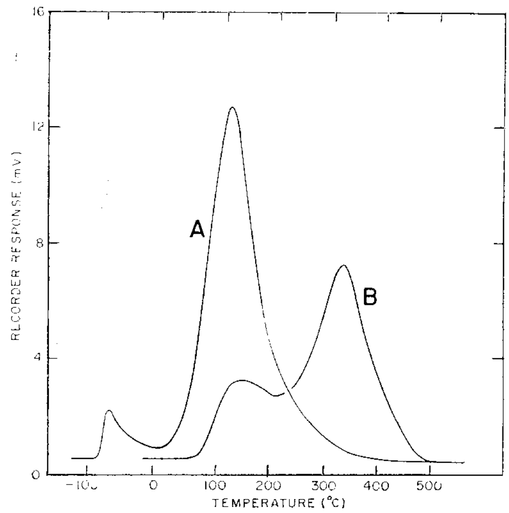

FIG. 7. TPD chromatogram of hydrogen on alumina. Temperature increase 18.4°C/min. A, hydrogen was preadsorbed for 114 hr at 25° and 298 mm, and evacuated for 1 hr between −195° and −90° before TPD. B, hydrogen adsorption 2.5 hr at 250° and 56 mm, evacuation before TPD 1 hr at 25°.

In view of the above results with hydrogen alone, two series of experiments were carried out to see whether chemisorbed hydrogen participates in the hydrogenation of ethylene on sites I of alumina: (1) hydrogen was preadsorbed and evacuated at room temperature and ethylene was then admitted at room temperature; (2) hydrogen was preadsorbed at 250°C and evacuated at 150° before admitting ethylene at room temperature. The TPD chromatograms showed, as expected, that in (1) only one hydrogen peak appeared, with the maximum at about 130°, and in (2) again only one peak but this time with the maximum at 320°.

The results of the reactions are listed in Table 1 along with the typical results of hydrogenation with preadsorbed ethylene, for comparison. In the table, the preadsorbed amount of hydrogen in part A is the amount of hydrogen remaining on the surface after the evacuation following the preadsorption as described above. The adsorption of ethylene during the reaction was rapid and almost completed in a minute, in contrast to the slow adsorption of hydrogen on the clean surface or the slow decrease in the gas-phase pressure during the reaction with preadsorbed ethylene. In spite of the fact that the hydrogen preadsorbed was much larger than the amount of hydrogen consumed during the reaction with preadsorbed ethylene (0.007 + 0.044 in Expt. No. 189), as seen in Table 1, the amounts of ethane produced in these reactions were negligible, although small amounts of ethane were found in the gas desorbed by TPD when hydrogen was preadsorbed. As already mentioned, almost all ethane can be removed by evacuation; the ethane found by TPD must therefore be assumed to be formed during the heating process when the preadsorbed hydrogen is released into the gas phase. It is seen in Figs. 2 and 7 that the temperature range of the ethylene peaks lies within that of two hydrogen peaks. Therefore it is clear that in (1) hydrogen desorbs into the gas phase while ethylene still remains on the surface, while in (2) hydrogen desorbs only after most of the ethylene has gone. Indeed

TABLE 1
HYDROGENATION OF ETHYLENE ON SITES I WITH PREADSORBED HYDROGEN (A) AND ETHYLENE (B)[a]

	Preadsorption		Reaction			
Expt. No.	Temp (°C)	Adsorbed amount (cc NTP)	Reaction time (min)	Pressure of gas admitted (mm)	Adsorbed amount (cc NTP)	C_2H_6 produced[b] (cc NTP)
		A. Hydrogen is preadsorbed and ethylene is admitted later				
		(H_2)		(C_2H_4)	(C_2H_4)	
168	25°	0.163	20	0.12	0.256	0.001
166	25°	0.230	20	0.16	0.254	0.001
167	25°	0.234	20	0.24	0.244	0.002
171	250°	0.125	20	0.01	0.253	0.000
172	250°	0.263	20	0.03	0.254	0.000
		B. Ethylene is preadsorbed and hydrogen is admitted later				
		(C_2H_4)		(H_2)	(H_2)	
189	25°	0.248	15	3.8	0.007[c]	0.044

[a] Catalyst weight 0.797 g, reaction temperature 25°.
[b] Collected in the trap during 30 min evacuation after the reaction.
[c] Obtained by TPD with nitrogen carrier gas after the reaction.

the amount of ethane found by TPD in (1) was about twice as large as found in (2).

It can be concluded, therefore, that neither of the two types of chemisorbed hydrogen contributes to the hydrogenation of ethylene on sites I.

DISCUSSION

Active Sites for Hydrogenation

The present results show clearly that there are two different active sites on alumina for the hydrogenation of ethylene. It is particularly of interest that sites I are much more active than sites II for hydrogenation, while the polymerization of ethylene occurs preferentially on sites II (8). A tentative estimate of sites I from Eq. (1) and Fig. 4, in which the maximum of the curve corresponds to $\theta_I = 0.5$, gives 1.1 cc/g or 1.4×10^{13} sites/cm^2 as the number of sites I. The spectrographic analysis of the alumina used in this study showed less than 0.05% of iron as the major metallic impurity, and this is too small to explain the number of sites I even if all metal ions were exposed on the surface.

Another sample of alumina, stated to have total metallic impurity of less than 50 ppm (*11*) and kindly supplied by Dr. W. K. Hall of Mellon Institute, Pittsburgh, Pa., was also examined, for comparison. The temperature-programmed desorption of ethylene with this alumina gave also two peaks (the temperatures of the peak maxima were almost the same as those obtained with our alumina) when the alumina was evacuated for 6 hr at 450°, although the peak sizes (number of sites) were much smaller. When the catalyst was evacuated for a longer period and at higher temperatures, however, the peak sizes and the activity for hydrogenation became greater, and after evacuation for 24 hr at 650°, the catalyst showed about the same order of activity for hydrogenation as that of the alumina used in the present work. Again the reaction did not occur practically at all on sites II at room temperature. The above results, as well as the already mentioned observation of two similar peaks of ethylene with alumina precipitated from aluminum nitrate, support the conclusion that the two different active sites on alumina are not due to metallic impurities but are an intrinsic property of alumina catalysts prepared by the techniques currently available.

Mechanism of Hydrogenation

It is of course premature to attempt at this time to discuss in detail the mechanism of the reaction or the nature of the two types of active sites. However the rate equation (1) for sites I can be derived from two different mechanisms: (1) the rate-determining step is the molecular combination of an adsorbed ethylene molecule on sites I and an adsorbed hydrogen molecule on the remainder of sites I; (2) the rate-determining step is the reaction of a hydrogen molecule from either the gas phase or the physically adsorbed hydrogen with an ethylene molecule on sites I, producing an ethyl radical and an adsorbed hydrogen atom (Twigg-Rideal mechanism, that is,

$$H_2 + \underset{*\ *}{C_2H_4} \rightarrow \underset{*}{C_2H_5} + \underset{*}{H}$$

In both cases, hydrogen molecules or atoms share the adsorptive sites (sites I) with ethylene molecules so that a maximum appears on the curve of Fig. 4. Neither the simple molecular addition of hydrogen from the gas phase nor the hydrogen adsorption itself is the rate-determining step for this reaction, because the former leads to the rate equation $r = kp_{H_2}\theta_I$ and the latter to $r = kp_{H_2}(1 - \theta_I)$, and neither gives a maximum with the surface coverage of ethylene.

In the mechanism (1), the adsorption of hydrogen must be equilibrated or close to being equilibrated, and it has also to be weak in order to satisfy Eq. (1). This mechanism seems to be less likely, since preadsorbed hydrogen could not hydrogenate ethylene, as already described. However, one cannot exclude the possibility that weakly adsorbed hydrogen, which is easily removed by evacuation, is the hydrogen used in the reaction. In this case, a weak and fast equilibrated adsorption of hydrogen has to be invoked, in addition to the two types of adsorption shown in Fig. 7. The present results can be also well explained by mechanism (2). Additional experimental information is, therefore, needed to decide in a definite manner the mechansim of ethylene hydrogenation.

The observed order of the rate of hydrogenation on sites II of about 0.5 with respect to hydrogen pressure suggests that the rate-determining step on these sites is the combination of adsorbed ethyl radicals and of hydrogen atoms adsorbed dissociatively on the surface. The adsorbed state of ethylene on sites II has been suggested to be an ethyl carbonium ion or an ethyl radical (*8*).

Hydrogenation of Ethylene at Higher Temperatures

Although the present results show that at lower temperatures sites I are much more active than sites II, it is possible that sites II are exclusively responsible for the reaction at higher temperatures such as used in previous work (1–4), since the adsorption of ethylene on sites I will then become very small. The activation energy obtained in this paper for sites I (7.7 kcal/mole) is for ethylene adsorbed on the catalyst surface (sites I). At higher temperatures, however, the adsorption of ethylene would be so small (weak) that the rate equation might become $r = kp_{H_2}\theta_I$ and $\theta_I = Kp_e$ (p_e is the ethylene pressure), and therefore $r = kKp_{H_2}p_e$. In this case, the overall rate constant includes the heat of adsorption and the apparent activation energy could be very small or even negative. Indeed the heat of adsorption of ethylene on sites I is about 27 kcal (*5*) which gives −19 kcal for the apparent activation energy of hydrogenation on sites I.

As mentioned in the introduction, Hindin and Weller (*2*) have reported that a small amount of water, corresponding to less than 2% of the total surface area of alumina, completely inhibits ethylene hydrogenation if the water is added back to the catalyst at a sufficiently high temperature. Sites II on the alumina used in the present work are 0.123 cc/g or 1.6×10^{12} sites/cm^2, which corresponds only to 0.3% of the total surface area if the cross-sectional area of ethylene molecule is assumed to be 20 Å^2. It should also be mentioned that the present authors have reported previously that a sufficiently high temperature was necessary in order to block effectively by ammonia sites II of alumina for the chemisorption of ethylene (*12*).

In conclusion, the present results show that the two different active sites found on alumina by the authors are an intrinsic property of alumina catalysts, and exhibit, at room temperature, vastly different abilities to induce different catalytic reactions, such as hydrogenation and polymerization.

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