

Adsorption of Hydrogen and H₂-D₂ Exchange Reaction on Alumina*

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Received October 19, 1970

The chemisorption of hydrogen on alumina was investigated over a wide range of temperatures (−196–450°C). At least five different states of chemisorbed hydrogen on alumina were detected by the temperature-programmed desorption as peaks with the peak maxima at about −40, 25, 100, 200, and 320°C. These peaks (or types) are referred to as H(I), H(II), H(III), H(IV), and H(V), respectively. Except for H(IV), each type of chemisorption was separately investigated in more detail by measuring either the isotherms or the rates of adsorption and desorption. H(I) is the weakest chemisorption which occurs rapidly and reversibly at −75°C and fits the dissociative Langmuir isotherm. At room temperature, H(II) and H(III) are the major chemisorption: The former is a reversible chemisorption which is equilibrated in 30 min, while the latter is a slow irreversible chemisorption which continues up to 70 hr at room temperature. H(V), the strongest chemisorption, is too slow to be detected at temperatures below 250°C, but it is the major adsorption at higher temperatures. The total number of active sites for chemisorption was found to be 1.9×10^{13} sites/cm². The experimental results indicate that at least four types of chemisorption, H(I), H(III), H(IV), and H(V), share all or part of the sites which are the surface defects of alumina.

Isotopic exchange of hydrogen and deuterium was also studied in connection with the above results. Two kinds of reactions were carried out: (1) surface-exchange reaction between various types of preadsorbed H₂ on alumina and D₂ in the gas phase; and (2) equilibration reaction of gaseous mixtures of H₂ and D₂ but without preadsorption. The results showed that at low temperatures the isotopic-exchange reaction occurred only through hydrogen chemisorbed as type H(I) and did not involve the other types of chemisorption.

INTRODUCTION

Since it was demonstrated by Holm and Blue (1) that alumina was an active catalyst for H₂-D₂ equilibration reaction, a number of investigations have been made to clarify the mechanisms of equilibration and ortho-para conversion reactions of hydrogen on alumina (2-5). Recently Yasumori and Ohno (6) studied the kinetics of these reactions on γ -alumina in detail, and showed that their results were explained by the rate equations of Langmuir-Hin-

shelwood type. Van Cauwelaert and Hall (7) also made an extensive study of equilibration and conversion reactions with particular emphasis on active centers of alumina by using CO₂ as a poison. Although much more work is needed to draw a definite conclusion on the mechanisms of the reactions, it seems to be generally accepted that the activity of alumina sharply increases when the catalyst is pretreated at temperatures higher than about 400°C, and that the equilibration and conversion reactions both proceed on a small fraction of the surface. These facts apparently indicate that the reactions take place on defects of alumina surface.

* Contribution No. 11948 from the National Research Council of Canada, Ottawa, Canada.

Investigation of the adsorption of hydrogen on alumina was started much earlier than of the isotopic-equilibration reaction, and several papers have been published (8-15). In these investigations, different experimental conditions were used, and it is, therefore, difficult to draw general conclusions, except that the chemisorption of hydrogen on alumina is generally slow. Gruber (11) suggested two different types of chemisorption. Dolidze, *et al.* (12) found that the order of adsorption rate changed from 1 to 0.5 when the pressure of hydrogen was increased. They explained their results by assuming the existence of two different sites and the migration of hydrogen atoms from one site to the other. Low and Argano (14) measured the rate of adsorption at very low pressures and over a wide range of temperature, and concluded that some dissociative chemisorption occurred over the entire temperature range (-193 to 663°C). The latter two papers suggested very small surface coverages by hydrogen. The preliminary results obtained by Cvetanovic and Amenomiya (16) with the use of temperature-programmed desorption suggested a complex character of the hydrogen-alumina system.

No experimental attempt, however, has been made to obtain correlation between the adsorption and the reaction of hydrogen isotopes. In view of this, it was thought of interest to investigate the adsorption of hydrogen on alumina in more detail with the aid of the temperature-programmed desorption technique and to study the reaction of hydrogen isotopes in connection with the results obtained from the adsorption study. Two kinds of reactions were examined: reaction between H₂ preadsorbed on alumina and D₂ in the gas phase (*surface exchange*), and reaction of gaseous mixtures of H₂ and D₂ without preadsorption (*equilibration*).

EXPERIMENTAL METHODS

Materials

The preparation of alumina has been described in detail previously (17). It was

prepared by the hydrolysis of aluminum isopropoxide, calcined in air for 3 hr at 600°C and finally evacuated in the reactor for several hours at 650°C. X-Ray analysis showed that the alumina thus treated was mainly γ -alumina. The amount of catalyst used for the measurements of adsorption and surface exchange reaction was 0.5-1 g, and that for equilibration reaction was 1.0 mg. The surface area of each catalyst was measured by BET with nitrogen except for the equilibrium reaction. The average was 180 m²/g after the above pretreatment. A Na₂CO₃-poisoned alumina was also used for comparison. Alumina taken from the same batch was dried at 420°C and soaked in an 0.1N solution of Na₂CO₃ for 16 hr. It was dried in an oven without filtering, calcined, and evacuated in the same manner as unpoisoned alumina. Chemical analysis showed that the alkali content was 6.1 wt % as Na₂CO₃, and the surface area was 175 m²/g.

The catalyst was evacuated for 1-2 hr at 600°C after each run, and this treatment usually gave reproducible results for both adsorption and reaction. When a deactivation of catalyst was indicated, the catalyst was treated with dry air for a few hours at 600°C followed by evacuation at 650°C. The catalyst activity was completely recovered by this treatment.

All gases used in the present study were purchased from Matheson of Canada, Ltd. Ultrahigh-purity grade of hydrogen (99.999%) and C. P. grade deuterium (99.5%) were both passed through a spiral type trap immersed in liquid nitrogen and stored in reservoirs. HD was the only impurity detected by gas chromatography in the deuterium. Prepurified grade nitrogen (99.997%) was used as carrier gas for the temperature-programmed desorption after passing through a molecular sieve trap and a glass bead trap in series, both cooled in liquid nitrogen.

Apparatus and Procedure

The apparatus used for the present study was essentially the same as used for

the study of the deuteration of ethylene on alumina (18). It consisted of three parts: a conventional static system for adsorption measurements; a temperature-programmed desorption system in which the gas adsorbed on the catalyst was later desorbed into a carrier gas stream (N₂) by heating the catalyst in a programmed manner; and a reaction system in which the reactant gas was circulated through a reactor which was common for all the systems. A mercury manometer and a cathetometer were used at first to measure adsorption, but they were later replaced by a capacitance pressure transducer (a Type 523 sensor with a Type 1023 control unit of Datametries Inc., Mass.) so that the pressure change during the adsorption was continuously recorded. Thus the rate of adsorption as well as the adsorbed amount was conveniently measured. The temperature-programmed desorption (TPD) has been described in detail elsewhere (16). In the present experiments, a thermistor type thermal conductivity cell was used as the TPD detector. The volume of reaction system was about 140 ml including a small all-glass circulation pump (single plunger type) operated by an electromagnet.

Adsorption of hydrogen was measured manometrically in a constant volume as already described. After adsorption the catalyst was evacuated under various conditions, and the carrier gas was diverted into the reactor for TPD. TPD was carried out at a speed of $18.5 \pm 1^\circ\text{C}/\text{min}$ regulated by a programmer with a flow rate of nitrogen of about 270 ml/min at the pressure in the reactor (70 Torr). The average residence time of gas in the catalyst bed was about 0.2 sec at this flow rate. When the heating was started from a temperature lower than room temperature, the catalyst was allowed to warm up naturally to room temperature so that the temperature increase in this range was not necessarily linear. However, the heating curve was smooth, and peaks were still clearly separated. The amount of hydrogen desorbed by TPD was calculated from the peak area by comparison with those of known

amounts of hydrogen passed through the detector before and after each TPD experiment.

Surface-exchange reaction was carried out by circulating deuterium gas through the reactor with about 1 g of catalyst on which hydrogen was preadsorbed. The preadsorption and the following evacuation were made at selected temperatures so that desired type(s) of chemisorbed hydrogen remained on the surface. The amount of preadsorbed hydrogen was estimated from a separate TPD experiment carried out under similar conditions. The reaction was stopped by isolating the reactor from the circulation system by closing stopcocks. The volume of reactor was about 10% of that of whole system. The product was collected from the circulation system into a sampler by means of a Toepler pump, and transferred to a gas chromatograph for analysis. The isotopes of hydrogen were analyzed gas chromatographically with a MnCl₂-coated alumina column as described previously (18).

Equilibration reaction was carried out in the same manner as in the surface exchange, except that approximately equimolar mixtures of H₂ and D₂ were circulated over 1.0 mg of catalyst without preadsorption. Before the measurements of the rates, it was found with 1 g of catalyst at room temperature that the reaction product was already equilibrated after 1 min, indicating that the pump was efficient enough to homogenize gas in whole system at least in 1 min. Actual reactions were carried out with the much smaller amount of catalyst (1.0 mg) at longer times (5–30 min), and the products were not equilibrated, assuring that the reaction was not controlled by the pump speed. In both the surface exchange and the equilibration reactions, a few Torr of He was admitted in the reactor and evacuated briefly immediately before reaction in order to cool (or warm) the catalyst quickly to a selected reaction temperature. The catalyst temperature was also watched by a thermocouple inserted at the center of catalyst bed.

RESULTS AND DISCUSSION

I. Adsorption of Hydrogen

(1) Temperature-Programmed Desorption

When hydrogen was admitted at -196°C , hydrogen adsorbed very rapidly, and after evacuation at the same temperature, the subsequent TPD gave a peak at about -110°C as shown by TPD chromatogram (a) in Fig. 1. This peak is referred to as H(P). In the following, the other peaks observed will be similarly referred to as H(*i*) (*i* = I – V) without additional identification since they are clearly indicated in Fig. 1. H(P) peak is believed to be due to a physical adsorption, because hydrogen was easily removed even at -196°C by extended evacuation, and also the surface coverage at high pressures far exceeded the number of chemisorptive sites which will be discussed later.

Hydrogen adsorbed also rapidly at -75°C , and the subsequent TPD gave Chromatogram (b) in Fig. 1, where two peaks, H(I) and H(II), appeared at about -40°C and 25°C , respectively. H(I) adsorption was reversible and easily removed by evacuation at -75°C , while H(II) was not removed at this temperature. During adsorption at -75°C , however, the amount

of H(I) adsorbed was much larger than that of H(II) which occurred very slowly at -75°C .

When hydrogen was adsorbed at temperatures between room temperature and 100°C , a slow adsorption took place, and after evacuation at room temperature, the subsequent TPD gave a peak at about 100°C (H(III)) as shown by Chromatogram (c) in Fig. 1. This adsorption was so slow that it took more than 70 hr at room temperature and at 50 Torr of hydrogen until no appreciable change in pressure was observed. It was found, however, that there was always a difference between the adsorbed amount and the amount desorbed by TPD, suggesting that a part of adsorption was reversible and removed during evacuation at room temperature. Assuming that the above difference roughly represented the amount of the reversible adsorption, it was found that the adsorption was saturated in 30 min when the pressure was higher than 30 Torr. The upper limit of the saturation was estimated as 7×10^{11} molecules/cm². This adsorption is believed to be type H(II), as will be discussed in somewhat more detail in the following section.

It is seen in the Chromatogram (c) in Fig. 1 that a small shoulder appeared at

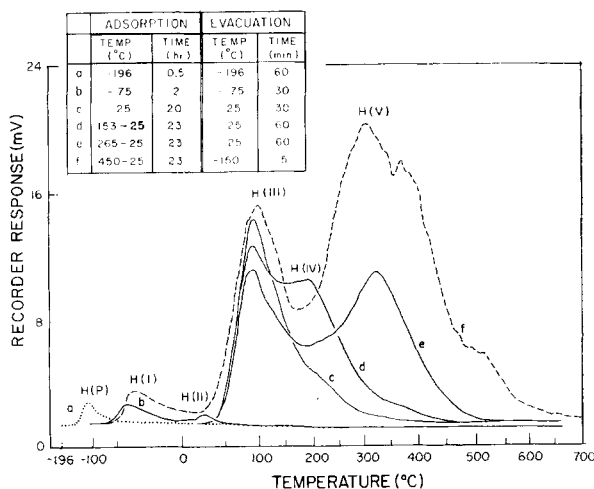


FIG. 1. TPD chromatograms of hydrogen on alumina. Adsorption and evacuation before TPD were carried out as listed in the figure. Hydrogen pressure for adsorption was about 40 Torr except for (f) which was obtained with 150 Torr of hydrogen.

about 200°C following the H(III) peak. This peak, H(IV), became clearer when hydrogen was adsorbed at 150°C, as shown by Chromatogram (d). In this experiment, hydrogen was adsorbed for 1 hr at 150°C and at 40 Torr, and the catalyst was cooled to room temperature and kept at the same temperature for 22 hr with the hydrogen present before evacuation for TPD.

Finally when the adsorption temperature was increased higher than 250°C, the fifth peak, H(V), appeared at about 320°C, as shown by Chromatograms (e) and (f) in Fig. 1. Before the TPD of Chromatogram (f), hydrogen was adsorbed for 2.5 hr at 450°C and at 150 Torr followed by 20 hr adsorption at room temperature. The catalyst was then cooled to -150°C and evacuated briefly before TPD. Therefore, the other peaks, H(I) to H(IV), appeared as well as H(V), and no chemisorbed hydrogen was lost during the evacuation. Other experiments were also carried out in the same manner but at different pressures and adsorption times, and it was found that the amount of hydrogen desorbed by TPD was approximately the same as in (f) in Fig. 1 (9.7×10^{12} molecules/cm²), indicating that the surface was saturated by chemisorbed hydrogen.

Sometimes the TPD experiments were carried out with a liquid nitrogen trap inserted between the reactor and the TPD detector to check if water was formed by hydrogen chemisorption. However, no condensable gas in the trap or change in the

shape of the peaks was found even with the strongest chemisorption, H(V).

Summarizing the results of temperature-programmed desorption, five different types of chemisorption, H(I), to H(V), were found as well as a physical adsorption, H(P). When hydrogen was contacted with alumina at temperatures varying from room temperature to 450°C, however, hydrogen chemisorbed mainly as types H(III) and H(V) in general agreement with the results of Gruber (11), who suggested two different types of chemisorption of hydrogen on alumina from the observed minima in the isobars at about 300°C, as already mentioned.

(2) Adsorption of Hydrogen

a. Type H(I). As already pointed out, adsorption occurring at -75°C was mainly of Type H(I), and it took place very rapidly, while H(II) was so slow at this temperature that its amount was negligibly small compared to that of H(I). It was, therefore, possible to measure the H(I) adsorption manometrically, and an isotherm was measured at -75°C by increasing pressure from 2 to 46 Torr and also by decreasing pressure. All points thus obtained fell on the same curve, indicating that the adsorption was quite reversible. It was also found that the isotherm was well expressed by the Langmuir equation for dissociative adsorption, as shown in Fig. 2. The saturated amount, v_m , was calculated from the intercept of the figure

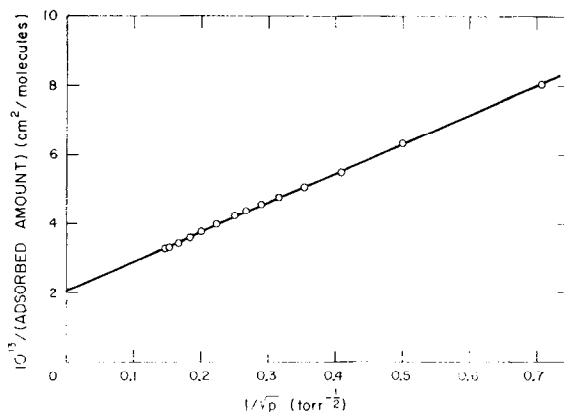


FIG. 2. Linear Langmuir plot of isotherm of H(I) hydrogen at -75°C.

as 9.7×10^{12} atoms/cm². The heat of adsorption calculated from the isotherms at -75 and -123°C was 3.5 ± 0.5 kcal/mole and was almost constant between $\theta = 0.25$ and 0.65 .

b. Types H(II) and H(III). In the preceding section it has been suggested from the difference between the adsorbed amount and the amount desorbed by TPD that two types of chemisorption are occurring simultaneously during the adsorption at room temperature. This was also indicated by an irregularity in adsorption-time curves which usually occurred at 10–30 min after the admission of hydrogen, depending on the pressure.

In order to see this matter more clearly, the rates of adsorption and desorption were respectively evaluated from the adsorption-time ($a-t$) curves obtained at various pressures by a method published previously (19). In this method, da/dt is first obtained from $a-t$ curves measured at various pressures (p), and then da/dt at the same a is plotted against a function of p (usually p), so that the plot is a straight line. The slope of the straight line then gives the rate of adsorption (r_a) at 1 Torr and the negative intercept the rate of desorption (r_d) at this adsorbed amount. Some of the

results thus obtained with the present H₂-alumina system are shown in Fig. 3 of the previous paper (19). In the present study, however, the method was extended over wider range of surface coverage by using the capacitance pressure transducer connected with a recorder which was useful particularly for fast adsorption in the initial stage. da/dt was calculated by approximating a portion of $a-t$ curve (the period of 1–10 min depending on the rate of adsorption) to a cubic equation $a = Bt + Ct^2 + Dt^3$ and by setting a program with a Monroe Epic 3000 calculator to obtain da/dt as the first derivative of the equation.

A good linearity was found for the plot of da/dt against p , and the net rates of adsorption and desorption thus obtained at room temperature are shown in Fig. 3 as a function of the adsorbed amount. It is now clearly shown that the different types of adsorption are occurring simultaneously, a fast and a slow adsorption whose rates differ by about two orders of magnitude. The fast adsorption is equilibrated in 10–30 min at room temperature, while the slow adsorption continues up to more than 70 hr, as already described. The former is easily removed by evacuation

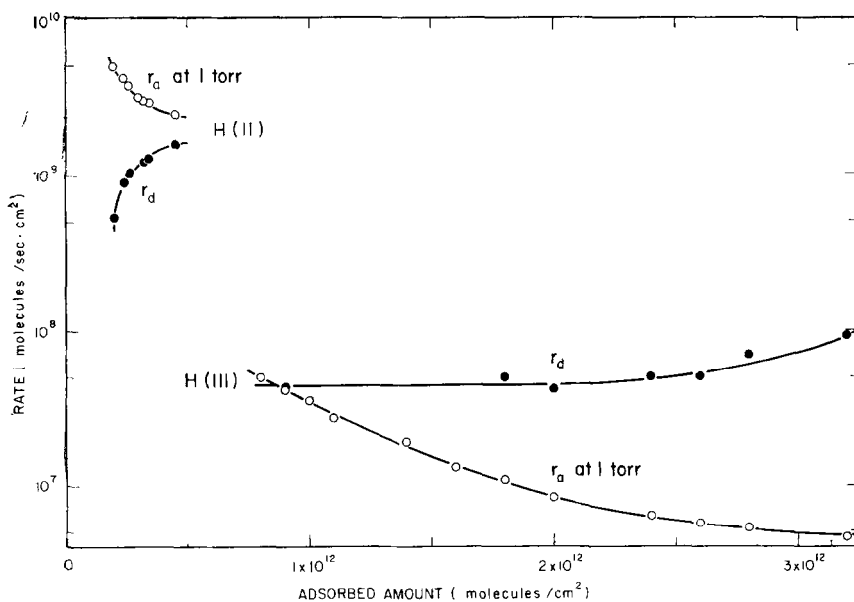


FIG. 3. Rates of adsorption and desorption of hydrogen on alumina at room temperature.

at room temperature, because it has an appreciable rate of desorption at this temperature, as shown in Fig. 3.

An advantage of this analytical method is that da/dt is compared at different pressures but at the same surface coverage, so that the method can be applied whether or not the surface is homogeneous, and also the isotherm is constructed by calculating the equilibrium pressures by equalizing r_a and r_d at each surface coverage. The isotherm of the fast adsorption thus constructed showed that the adsorbed amounts were all reasonably within the saturated amount (7×10^{11} molecules/cm²) estimated in the preceding section, but at least one order of magnitude larger than the amounts of H(I) extrapolated to room temperature. It was therefore concluded that the fast (reversible) adsorption observed at room temperature was not type H(I) but H(II) chemisorption which was detected by TPD at about 25°C.

c. Type H(V). Unfortunately the adsorption of H(IV) did not take place without accompanying simultaneous adsorption of either H(III) or H(V) as was understandable from the extensive overlapping of the corresponding peaks shown in Fig. 1. Therefore this type of chemisorption could not be studied separately.

However, only type (V) chemisorption was expected to occur at temperatures higher than 300°C where other chemisorption would either be negligibly small or be quickly equilibrated and, therefore, would not affect the evaluation of da/dt . It was found from the results obtained at 300°C that da/dt showed the best linearity against $p^{1.5}$ over a pressure range between 0.3 and 10 Torr for the surface coverage

from 0.02 to 0.13. The average activation energy of adsorption was estimated as about 13 kcal/mole from the rates at 300 and 350°C. Unfortunately the evaluation of the desorption rate was not accurate enough to obtain the activation energy. It was reported by Dolidge *et al.* (12) that the rate of adsorption of hydrogen on γ -alumina was proportional to $p^{0.5}$ with an activation energy of 19.5 kcal/mole. Low and Argano (14) also reported the same pressure dependence with 1.25–4.27 kcal/mole of activation energy. Both results were explained by a lateral diffusion of hydrogen atoms on the surface. However, the pressure dependence was obtained in a small pressure range by the former authors and only at 27°C by the latter. Mechanism which explains the present kinetics is not yet known.

(3) Sites for Chemisorption

The experimental results described above provide the saturated amounts of monolayer adsorption for various types of chemisorption. Although it is not clear, except perhaps for H(I), whether hydrogen is adsorbed as atoms or molecules, the site densities summarized in Table I have been calculated by tentatively assuming that all adsorption is atomic. In view of the method of assessment used, it is likely that the number of sites for H(II) is not as accurate as for the other types of chemisorption. The total number of sites (1.9×10^{13}) includes all types of chemisorption but are occupied mainly by hydrogen chemisorbed as types H(III) and H(V). A comparison of the Chromatograms (c) and (e) in Fig. 1 shows that the peak H(III) in (e) is larger than in

TABLE I
SITE DENSITY

Type	Site density ^a (sites/cm ²)	Method of assessment
H(I)	9.7×10^{12}	Isotherm observed at -75°C .
H(II)	1.4×10^{12}	The amount of H ₂ removed by evacuation at room temperature.
Total ^b	1.9×10^{13}	TPD by saturation at high pressures over a wide temperature range.

^a All adsorptions are assumed to be atomic.

^b Includes all types from H(I) to H(V) but mainly H(III) and H(V).

(e) where type H(V) was first formed on the surface at higher adsorption temperatures. This fact suggests that the chemisorption of H(III) and H(V) takes place on the same sites but in different forms. The same argument can probably be made also for H(III) and H(IV) from a comparison of Chromatograms (c) and (d) in the same figure. Chromatograms (c), (d), and (e) were all obtained with about the same pressure and time for adsorption, while (f) was obtained with exceptionally high pressure of hydrogen.

The above view was further confirmed by a more quantitative comparison of two experiments in which (1) hydrogen was adsorbed at room temperature and at 45 Torr on a fresh surface of alumina, and (2) hydrogen was adsorbed at the same temperature and pressure but on the alumina on which 9.2×10^{12} atoms/cm² hydrogen had been preadsorbed as type H(V). In the latter experiment hydrogen was preadsorbed at 250°C and evacuated at 150°C so that only type H(V) was left on the surface, as was confirmed in a TPD experiment carried out separately but under similar conditions. After the same adsorption time (between 2 and 60 min) the adsorbed amount of hydrogen at room temperature (H(III)) in (1) was constantly larger than in (2) by a factor of 2.0 ± 0.1 . Taking 1.9×10^{13} atoms/cm² from Table 1 as the total number of sites, the preadsorbed H(V) (9.2×10^{12}) shows a 52% availability of the sites for H(III) chemisorption in Expt. 2, which is in reasonable agreement with the above factor of 2.

The mutual interference of H(I) and H(III), or H(V) was also studied by determining v_m 's from the isotherms measured at -75°C on alumina on which hydrogen had been preadsorbed as types H(III) and H(V), respectively. It was found that one atom of preadsorbed H(III) or H(V) blocked about 0.5 sites for H(I) chemisorption, although H(III) was slightly more effective for blocking than was H(V). This ratio is close to that of the site densities found in Table 1 for the total and H(I) chemisorption. The for-

malistically simplest way to explain this ratio would be to assume that types H(III) and H(V) are molecular adsorption. It was also found in the TPD experiments carried out at a constant speed of 18.5°/min that the peak temperature of H(III) remained constant at $97 \pm 3^\circ\text{C}$ over a wide range of surface coverage between $\theta = 0.04$ and 0.52, suggesting that the desorption process was first order (16). It is unlikely, however, that such strong chemisorptions take place in a simple molecular form. Instead it seems more likely that the sites for H(III) and H(V) consist of a pair of defects only on one of which hydrogen can chemisorb as type H(I). For example, H(III) hydrogen chemisorbs in a quasi-atomic state, one on top of the aluminum ion and the other on top of the oxide ion, but there is still interaction between the atoms. In this case, desorption would take place as a first-order process. Similar type of chemisorption of hydrogen on alumina was postulated by Pines and Ravoire (4). However, the ratio of 2 found here may be fortuitous, and certainly more experimental information is needed to draw a definite conclusion on the nature of these sites.

The total number of active sites for the chemisorption of hydrogen (2×10^{13} sites/cm²) is still only a small fraction of the total surface, indicating that these sites are the defects of alumina surface. When the alumina was evacuated at increasing temperatures from 520 to 650°C, the total number of active sites was increased by about 3.5 times. It is also of interest that the number of total sites for hydrogen chemisorption found in the present study is in range of total acidity ($1-5 \times 10^{13}$ sites/cm²) found on alumina by other authors (20-23).

II. Exchange Reaction

(1) Surface-Exchange Reaction

Surface-exchange reaction was carried out between deuterium in the gas phase and hydrogen preadsorbed on the alumina in various forms, as explained in the Experimental section. The alternative combination, gaseous H₂ and preadsorbed D₂,

has, in principle, an advantage over the above combination, if an appreciable exchange takes place between hydrogen in the gas phase and that of the catalyst. However, the results with D₂ gas and the catalyst showed that such exchange was negligibly small at and below room temperature. Hall *et al.* (24) also found that the exchange rate of the catalyst hydrogen in alumina with deuterium gas was negligible at temperatures below about 140°C. Moreover, hydrogen isotopes eluted from the gas chromatographic column in the order H₂, HD, D₂, so that an accurate analysis of a small peak of HD following a large peak of H₂ was difficult. Therefore, the preadsorbed D₂ was used only in a few cases where the reaction temperature was very high.

The results obtained are summarized in Table 2, which also includes the result of an equilibration reaction with a mixture of H₂ and D₂ for comparison. As seen in the table, the equilibration reaction, Expt. 23 proceeded rapidly at -75°C, and the product was equilibrated at least in 5 min: The value of $[HD]^2/[H_2][D_2]$ calculated from the composition of the product was 2.99, which agreed well with the theoretical equilibrium constant (2.85) at -75°C calculated from the equation $K = 4.24 \exp(-157/RT)$ (25). On the other hand, no HD was formed within experimental error

by the surface exchange reaction with hydrogen chemisorbed as types H(III) and H(V) even at higher temperatures and longer times. The data listed in Table 2 were all corrected for HD contained as impurity in the reactant D₂. In Expt. 55, hydrogen was preadsorbed at room temperature and the reactor was closed with some 4.4 Torr of hydrogen remaining in the gas phase while the rest of the reaction system was evacuated and filled with D₂. Therefore, the total amount preadsorbed and the amount of gaseous H₂ were accurately measured although the distribution of H(II) and H(III) was estimated from the results of adsorption experiments described in the preceding sections. The hydrogen left in the gas phase in the reactor was, of course, mixed with deuterium in the gas phase as soon as the reaction was started. The result showed that only this amount of H₂ (the amount left in the gas phase) was converted into HD, indicating that H(II) hydrogen was also not eligible for the surface exchange at least at -75°C. It might be feared that in these reactions the preadsorbed hydrogen blocked the active sites and thus retarded reaction. However, the maximum coverage by the preadsorbed hydrogen (0.30 ml/0.976 g) was 44% of the total active sites, and the reaction rate would have, therefore, been still reasonably fast if it was

TABLE 2
SURFACE-EXCHANGE REACTION BETWEEN PREADSORBED H₂ AND D₂ IN THE GAS PHASE, CATALYST WEIGHT, 0.976 g

Expt No.	H ₂ preadsorbed		Gas phase		Reaction conditions			Product		
	Type	Amount ^a (ml)	H ₂ (ml)	D ₂ (ml)	Temp (°C)	Pressure (Torr)	Time (min)	H ₂ (ml)	HD (ml)	D ₂ (ml)
23	—	—	1.00	0.92	-75	10.3	5	0.54	0.89	0.49
66	H(V)	0.30	—	3.22	-75	18.0	30	—	—	3.18
67	H(V)	0.30	—	3.46	24	20.1	30	—	—	3.41
54	H(III)	0.25	—	2.34	-75	13.1	30	—	—	2.31
51	H(III)	0.25	—	2.35	-47	13.4	30	—	—	2.31
52	H(III)	0.25	—	2.43	18	14.1	31	—	—	2.39
55	{ H(III) H(II)	0.092	0.078 ^b	1.43	-75	8.3	20	—	0.15	1.36
		0.057								
53	H(I)	0.073	0.097 ^b	1.16	-75	7.2	20	0.015	0.25	0.98

^a Estimated from separate TPD experiments except for Expts (55) and (53).

^b Left in the gas phase in the reactor during preadsorption and mixed with the D₂ subsequently admitted.

proportional to the available sites. It should also be noted that a small amount of H(IV) was preadsorbed as well as H(III) listed in Table 2, as was predicted from the Chromatogram (c) in Fig. 1. Therefore type H(IV) is also inactive for the exchange reaction.

A similar procedure for preadsorption was used in Expt. (53) as was used in Expt. 55 except for the temperature of preadsorption (-75°C). At this temperature, only H(I) hydrogen was present on the surface, although a very small amount of H(II) might have been present as well in view of the TPD Chromatogram (b) in Fig. 1. Table 2 shows that the total amount of H atoms found in the product corresponded to 0.140 ml of H_2 , which exceeded the hydrogen left in the gas phase (0.097) and was close to the total of H_2 present initially. This fact suggests that hydrogen chemisorbed as type H(I) is involved in the surface-exchange reaction. Since H(I) chemisorption is reversible at -75°C , as already pointed out, consideration must be given to the possibility that hydrogen desorbs from the sites and re-adsorbs as another type of chemisorption for the reaction. However, H(I) was found to be the sole chemisorption occurring at -75°C , and the results of Table 2 showed that other types of chemisorption were not involved in the exchange reaction at this low temperature. It is, therefore, concluded that the exchange reaction takes place by hydrogen chemisorbed as type H(I), at least at low temperatures.

Although the stronger adsorptions were not involved in the exchange reaction at low temperatures, D_2 chemisorbed in the forms of H(III), H(IV), and H(V) was almost quantitatively recovered as HD when an excess of H_2 was circulated over it and temperature was raised from room temperature to 600°C .

(2) Equilibration Reaction

Equilibration reaction was carried out on a small amount of catalyst (1.0 mg) with approximately equimolar mixtures of H_2 and D_2 , as already explained. It was found that the time course of the reaction well

fitted the first order-rate equation $dx/dt = k_e(x_e - x)$ where x and x_e were the fraction of an isotope at time t (min) and at equilibrium, respectively. A specific rate, k_m , was calculated from $k_m = Nk_e/60 A$ molecules $\cdot\text{sec}^{-1}\cdot\text{cm}^{-2}$ according to the treatment of Couper and Eley (26). Here N is the total number of molecules in the reaction system, and A is the surface area (cm^2) of the catalyst.

The pressure dependence of k_m at -75°C is shown in Fig. 4 which also includes the results obtained with an alkali-poisoned alumina (Na_2CO_3 6.1 wt %). The curves showed a similar trend as was observed by Yasumori and Ohno (6), and the values of k_m obtained at -75°C were of the same order of magnitude as those obtained by them at the same temperature.

The temperature-dependence measurements at a total pressure of 9.5 Torr produced unexpected results, as shown in Fig. 5. A marked decrease in the activation energy was observed in the higher temperature region with both catalysts. The transient temperatures were about -10 and -50°C , respectively on alumina and alkali-poisoned alumina. The activation energy on alumina was found to be 2.1 and 0.26 kcal/mole in the low and the high temperature regions, respectively, and 2.9 and -1.4 kcal/mole on Na_2CO_3 -alumina. Although the activation energy of 2.1 kcal found on the alumina at low temperatures is in a reasonable range (1.5–2.5 kcal) observed by other authors (2, 5–7) as the apparent activation energy of equilibration on alumina, the decrease in energy at high temperatures such as shown in Fig. 5 has not been observed previously. Acres *et al.* (5) found a maximum at about 110°C in the Arrhenius plot of the ortho-para hydrogen-conversion reaction on an α -alumina, but the rate of H_2 - D_2 equilibration steadily increased from -80 to 550°C . The speed of the circulation pump used in the present reaction system was sufficiently fast, as already pointed out, and the order of experiments was so chosen that the sequential effect due to catalyst fatigue, if any, was eliminated. As mentioned already, the catalyst

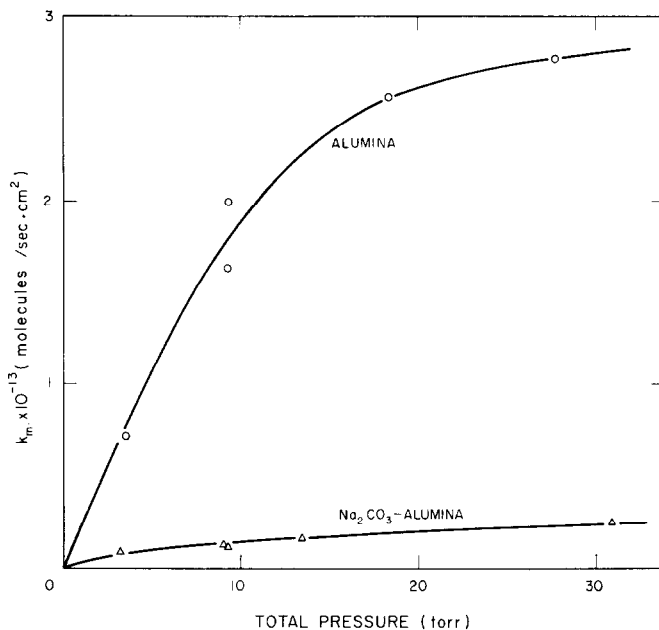


Fig. 4. Pressure dependence of equilibration reaction at -75°C .

was precooled (or prewarmed) by helium, and the temperature of the catalyst bed was followed by means of a thermocouple and was found not to undergo any serious

change during the reaction. Actually, the true curves in the low temperature regions would have been steeper if Fig. 5 resulted from a temperature change caused by the

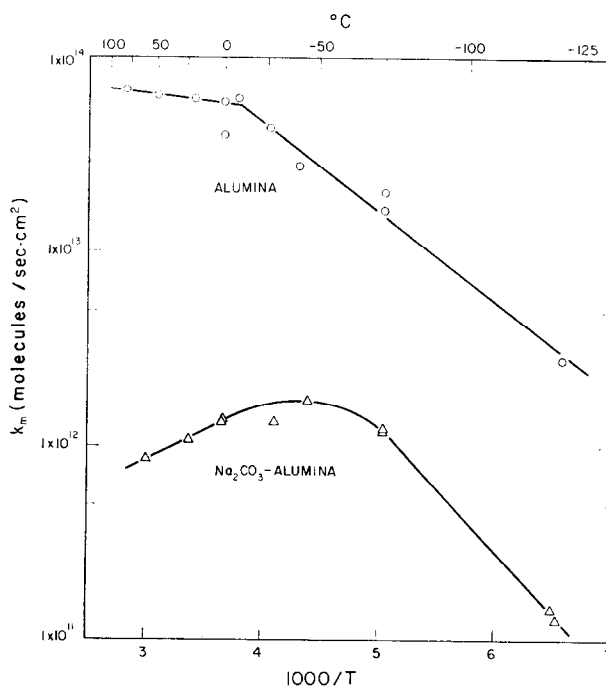
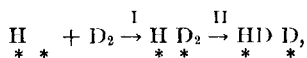


Fig. 5. Temperature dependence of equilibration reaction.

admittance or circulation of the gas. Moreover, the negative activation energy cannot be explained by such a temperature effect. It is, therefore, unlikely that the break in the Arrhenius plots observed here is due to spurious effects of temperature or apparatus.

Eley and Norton (27) found an increase in the activation energy of H_2 - D_2 equilibration on a nickel catalyst from 2.4 kcal (200–300°K) to 7.5 kcal (300–400°K), and explained it by the change of mechanism from the Eley-Rideal (28) to the Bonhoeffer-Farkas (29) type. Similar mechanistic change was also assumed by Acres *et al.* (5) for equilibration reaction on α -alumina. Although the present results are not sufficient to determine the mechanism, the fact that the Arrhenius plots fall off at higher temperatures seems to suggest other possibilities such as (1) change of rate-controlling step with temperature, (2) change of the apparent activation energy due to the temperature dependence of the Langmuir-Hinshelwood rate equation, or (3) self-poisoning of the catalyst by hydrogen at higher temperatures. For example, if the reaction occurs by Rideal mechanism (30),



and the exchange of atoms (Step II) is the slowest step at low temperatures, the rate-controlling step could shift at higher temperatures to the Step I, in which molecular D_2 is brought to an adjacent site to a chemisorbed H either by adsorption or by surface migration. The change of apparent activation energy can also be explained by the temperature dependence of Langmuir-Hinshelwood rate equation, and a maximum in the rate may be observed when the heat of adsorption of reactant is larger than the activation energy of the elementary reaction which controls the overall reaction. Finally, a stronger chemisorption of hydrogen would tend to become faster at higher temperatures and result in a blocking of the sites for H(I) chemisorption (self-poisoning). Although the observed rate of H(III) chemisorption at room temperature seems to be too slow to retard the equilibration reaction appreciably, this effect will have to be considered at higher temperatures. In any case, more experimental evidence is needed to clarify this matter.

Figure 6 shows the effect of preadsorbed ethylene on the rate of equilibration. In these experiments, known amounts of ethylene were admitted at room temperature, and the reactor was then cooled to

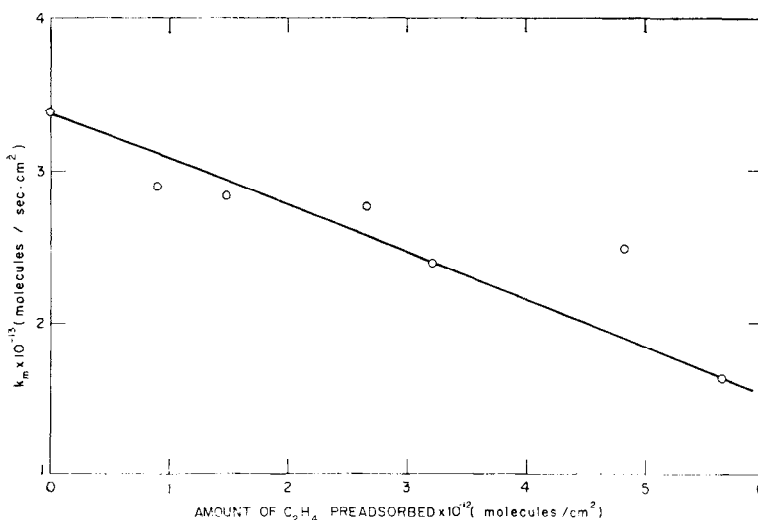


FIG. 6. Effect of preadsorbed ethylene on the rate of equilibration. The specific rate, k_m , was measured at -26°C and at a total pressure of 9.5 Torr.

-26°C to assure chemisorption of ethylene on stronger sites first. The final pressure of ethylene at -26°C was so small (less than 10⁻³ Torr) that the reactant gas (H₂ + D₂) was subsequently admitted without evacuation. The reaction was carried out for 5 min at -26°C and at a total pressure of 9.5 Torr. The previous results of hydrogenation of ethylene pre-adsorbed on alumina (17, 18) showed that the hydrogenation and the exchange of hydrogen atoms between ethylene and D₂ were negligibly small under these reaction conditions compared to the amount of HD produced by the equilibration reaction.

Two different groups of active sites for the chemisorption of ethylene were previously found on alumina by Amenomiya and Cvetanovic (31) as sites I (weaker sites) and II (stronger sites). Yasumori and Ohno (6) recently reported that three different peaks were observed in the thermal desorption of ethylene on γ -alumina and concluded that ethylene adsorbed most strongly (sites II) retarded both the equilibration and the conversion reactions via a chemical mechanism. It was confirmed in Fig. 6 that the equilibration reaction was retarded by the preadsorbed ethylene. However, the number of stronger sites (sites II) was about 1.6×10^{12} sites/cm², as estimated from the hydrogenation of ethylene (17), but, as shown in Fig. 6, much larger amount of ethylene was needed to stop completely the equilibration reaction. The extrapolation of the straight line in Fig. 6 to $k_m = 0$ gives 11×10^{12} molecules of C₂H₄/cm². Bearing in mind that this is a rough estimate, particularly in view of the extremely small amount of catalyst (1 mg) used in the present experiments, the number of sites thus found is thought to be in rather good agreement with the total number of sites for ethylene chemisorption (sites I + II) found on alumina by Amenomiya and Cvetanovic (8.7×10^{12} sites/cm²) (32). It is of interest that the above site densities approximately coincide with the site density of H(I) (9.7×10^{12}). Van Cauwelaert and Hall (7) also found, by using CO₂ as poison, that the number of active sites on alumina

for H₂-D₂ equilibration reaction was $8-16 \times 10^{12}$ sites/cm². These facts suggest that the equilibration reaction also requires hydrogen chemisorbed in type H(I).

(3) Alkali-Poisoned Alumina

As shown in Figs. 4 and 5, the rate of equilibration on the Na₂CO₃-alumina is about ten times smaller than on alumina. Although the adsorption of hydrogen on the poisoned alumina at -75°C was so small that v_m for H(I) chemisorption could not be obtained from the isotherm, it seems apparent that sodium ions block the sites for H(I). The activation energies obtained on this catalyst differed, however, from those on alumina, as already described, suggesting that the strength of the sites is probably also influenced by poisoning to some extent. The adsorbed amounts of hydrogen measured manometrically at 250°C and room temperature were also much smaller than those obtained on the unpoisoned catalyst at corresponding temperatures. Consequently, the temperature-programmed desorption on the poisoned alumina showed much smaller peaks in the desorption chromatograms. The peak shapes and temperatures were almost the same as shown in Fig. 1 except for H(IV), which appeared at the same temperature (200°C), but was not decreased by poisoning as much as the other peaks. The peak height of H(IV) was comparable to that of H(III), even for room temperature adsorption, so that the two peak maxima were clearly separated, while in the Chromatogram (c) in Fig. 1 H(IV) was only a shoulder of H(III). The reason for this, however, is not yet known.

CONCLUSIONS

The present study revealed a complex character of the chemisorption of hydrogen on alumina. At least five different types of chemisorbed hydrogen were detected by the temperature-programmed desorption as different peaks which appeared respectively at about -40, 25, 100, 200, and 320°C. These peaks (or types) are referred to as H(I), H(II), H(III), H(IV), and H(V), respectively. The experimental

results indicated that at least four types of chemisorption, H(I), H(III), H(IV), and H(V), shared all or part of the same sites which were defects of alumina surface. It was found that H(I) was the weakest chemisorption, and it fitted the dissociative Langmuir isotherm, and that this was the only type of chemisorption which was involved in the H₂-D₂ exchange reaction at low temperatures.

ACKNOWLEDGMENT

The author is grateful to Mr. G. Pleizier, who carried out most of the experimental work of the present study.

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