Study of Metal Catalysts by Temperature Programmed Desorption

III. Hydrogen–Deuterium Exchange on Platinum*

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In the preceding paper in this series (Part II) four different chemisorbed species of hydrogen on platinum surface were detected by the temperature programmed desorption technique (TPD). In the present paper, hydrogen–deuterium surface exchange was investigated at low temperatures ($-76°$ to $-195°C$) between D_2 (or H_2) preadsorbed on the platinum surface and H_2 (or D_2) in the gas phase. Various types of chemisorbed hydrogen were prepared by the temperature programmed desorption technique as described in Part II and their participation in the exchange reaction was examined. One of the four types of chemisorbed hydrogen, presumed to be present on the surface in the form of hydrogen atoms chemisorbed on top of platinum atoms, was found to undergo readily surface exchange at $-100°C$ or at higher temperatures with hydrogen molecules in the gas phase. It was found also that isotopic equilibration of gaseous mixtures of H_2 and D_2 occurred much faster than the surface exchange reaction; the former reaction occurred even at $-195°C$ while the latter was immeasurably slow. The results suggest that another type of chemisorbed hydrogen, presumably hydrogen molecules chemisorbed in linear form, may take part in isotopic exchange. Isotopic equilibration at $-195°C$ is believed to involve chemisorbed hydrogen molecules of this type.

INTRODUCTION

Equilibration of gaseous H_2–D_2 mixtures has been studied on a number of metal catalysts and various reaction mechanisms have been postulated. The three traditional types of mechanisms are (I) mixing of hydrogen atoms on the surface (Bonhoeffer–Farkas mechanism), (II) reaction between chemisorbed atoms and physically adsorbed molecules (Rideal–Eley mechanism), and (III) reaction between adsorbed hydrogen molecules (Schwab–Killmann mechanism). These mechanisms have been reviewed and discussed in considerable detail (1–5).

Isotopic exchange between hydrogen preadsorbed on the catalyst and deuterium in the gas phase (and vice versa) has been studied on nickel, tungsten and platinum. The reaction mechanism and surface heterogeneity have been discussed (6–9), mainly on the basis of the rate measurements and the reaction kinetics. However, little information on the state of adsorbed hydrogen has been available.

In the preceding paper in this series (10), Part II, we have reported the existence of four different species of hydrogen chemisorbed on platinum surface, detected as four separate peaks in the temperature programmed desorption (TPD). The peak maxima were at about -100, -20, 90, and $300°C$ and the peaks were tentatively as-

sumed to correspond to two types of hydrogen atoms: one adsorbed right on top of metal atoms and the other in the interstices between the metal atoms, and two types of molecularly chemisorbed hydrogen, one in a bridge form and the other in linear form. It was therefore of interest to determine the difference in the reactivity of these four types of chemisorbed hydrogen for the H_2–D_2 exchange reaction. The results obtained are reported in the present paper.

Isotopic exchange was studied between H_2 (or D_2) preadsorbed in various forms on the platinum surface and D_2 (or H_2) admitted in the gas phase. For comparison, a few experiments were carried out with gaseous mixtures of H_2 and D_2 but without preadsorption. As is customary, the term "surface exchange" will be used for the reaction between a preadsorbed molecule and a molecule in the gas phase, and the term "equilibration" for the reaction of gaseous mixtures of H_2 and D_2. Also, for simplicity, the word "hydrogen" in the present paper will stand for both isotopes, protium and deuterium, and, where necessary, the individual isotopic molecules will be designated as H_2 and D_2.

EXPERIMENTAL METHODS

Apparatus and Materials

The apparatus has been described in Part II (10) and the catalyst used, tabletted platinum black, was the same. Its surface area was 1.25×10^3 cm²/g and the amount used was 2.54 g. The initial reduction and the treatment of the catalyst between the experiments have also been described in Part II.

All gases used were supplied by Matheson of Canada Ltd. Ultrahigh-purity hydrogen (99.999%) and deuterium (99.5%) were passed through two liquid nitrogen traps and used as reactants without further purification. A prepurified grade nitrogen (99.997%) was used as carrier gas in TPD.

Procedure

As mentioned in the Introduction, temperature programmed desorption of hydrogen adsorbed on platinum black between −100 and −170°C and subsequently evacuated at −196°C gives four peaks (10), α, β, γ, and δ, with the peak maxima at about −100, −20, 90, and 300°C, respectively. Evacuation at a suitable temperature, or TPD up to a selected temperature, removes the more weakly chemisorbed forms of hydrogen and leaves on the surface the more strongly chemisorbed forms. For example, with hydrogen adsorbed at −76°C the temperature programmed desorption begun at −76° and interrupted at +20°C, left only γ and δ hydrogen on the surface. Typical temperatures for the adsorption of hydrogen (T_a) and for the subsequent evacuation (or TPD interruption) (T_e) used to isolate different types of chemisorbed hydrogen were: for ($\alpha + \beta + \gamma + \delta$), T_a, −196 to 21°C, T_e, −196°; for ($\beta + \gamma + \delta$), T_a, −76–21°C, T_e, −76°C; for ($\gamma + \delta$), T_a, −76–21°C, T_e, 21°C; for δ, T_a, 21°–300°C, T_e, 200°C. Hydrogen pressure at adsorption was 1.2–1.5 Torr and the adsorption time was 15 min in most cases. Isolation of the different forms of chemisorbed hydrogen on the surface was confirmed by separate TPD experiments up to 500°C on samples prepared in analogous manner. The amounts of preadsorbed hydrogen were estimated from the TPD peak areas in these separate experiments in the manner described in Part II (10).

After the preadsorption of an isotope of hydrogen the catalyst was cooled down to the reaction temperature. A small amount of helium was sometimes admitted to shorten the cooling period. The other isotope of hydrogen (the gas phase reactant) was then admitted to the reaction system to start the reaction. Reaction time was 10 min in most cases. After the reaction, the gas phase molecules were expanded from the reaction system (∼30 ml) to a Toepler-type pump (300 ml) and were later transferred to the gas chromatograph

for analysis. A liquid-nitrogen trap was inserted between the reaction system and the pump to protect the catalyst from contamination by mercury during the sampling.

In some experiments, the gas phase reactant was circulated through the reactor by means of a pump but the results were not different from those obtained in the static system. The static system required a smaller reaction volume and most of the experiments were carried out in it.

Analyses of hydrogen isotopes were carried out by an all-glass gas chromatograph with a 2 m alumina column coated with manganese chloride as suggested by Yasumori and Ohno (11). The column temperature was −195° and the hydrogen eluted from the column was converted into water on copper oxide at 600°C.

RESULTS

The results of the surface exchange experiments with hydrogen preadsorbed on the platinum black in various forms (the surface reactant) and gaseous hydrogen subsequently admitted into the reaction system (the gas phase reactant) are listed

in Table 1. Most reactions were carried out at −76°C. It is apparent from the results of series A in the table that hydrogen chemisorbed in δ form (strongest chemisorption) does not react with the gas phase reactant under the experimental conditions used in spite of the fact that some reactions were carried out at higher temperature or for longer reaction times than in series B and C. In series B, with γ- and δ-forms of hydrogen preadsorbed on the surface, however, HD was produced. The amount formed was in very good agreement with the amount of HD corresponding to complete equilibration of the preadsorbed γ-hydrogen. The latter was calculated from the initial amounts of the hydrogen preadsorbed in γ-form and of the other isotope admitted to the gas phase. The equilibrium constant used in these calculations was obtained from the equation $K = 4.24 \exp (-157/RT)$ (12).

It should be pointed out here that after the preadsorption of one isotope of hydrogen in these experiments and the subsequent introduction of the second isotope as the "gas phase reactant," the latter immediately began to adsorb and established,

TABLE 1
SURFACE EXCHANGE REACTION ON PLATINUM BLACK[a]

		Surface reactant			Gas phase reactant			Calculated HD at equilibrium[c] (ml, STP)
		Type of chemisorption and estimated amount[b] (ml, STP)						
Series	Gas	β	γ	δ	Gas	Pressure (Torr)	HD formed (ml, STP)	
A 1	D₂	—	—	0.0011	H₂	4.15	—	
2	H₂	—	—	0.0048	D₂	4.70	—	
3	H₂	—	—	0.0104	D₂	5.00	—	
B 1	H₂	—	0.0056	0.0015	D₂	6.10	0.0106	0.0109
2	H₂	—	0.0090	0.0009	D₂	4.58	0.0170	0.0169
3	D₂	—	0.0090	0.0009	H₂	4.50	0.0170	0.0169
C 1	H₂	0.0076	0.0090	0.0009	D₂	5.64	0.0142	0.0171
2	D₂	0.0076	0.0090	0.0009	H₂	3.90	0.0150	0.0167

[a] Catalyst weight 2.54 g. Reaction temp. −76°C and reaction time 10 min except for A-1 (21°C, 10 min) and A-2 (−76°C, 20 min).

[b] Estimated from TPD chromatograms in comparable experiments.

[c] Calculated from the initial amounts of the chemisorbed γ and the gas phase hydrogen using the equilibrium constant $K = 4.24 \exp (-157/RT)$.

relatively quickly on the platinum surface, the equilibrium amounts of α- and β-chemisorbed forms as well as that of the physically adsorbed hydrogen. The adsorption of γ-hydrogen is not as fast as α or β at this temperature but it too was gradually formed while the exchange reaction proceeded. This behavior was predicted on the basis of the previous results (10), and was indeed confirmed by TPD carried out after the reaction. At the time of reaction, therefore, all four types of chemisorbed hydrogen were present on the platinum surface in each of the series A, B, and C, and the amounts of α- and β-hydrogen formed were roughly constant since the gas phase pressure was approximately the same in all experiments.

In series C, in which three forms of hydrogen were preadsorbed, β, γ, and δ, the amount of HD formed was again in reasonable agreement with the equilibrium amount calculated assuming that only the preadsorbed γ-hydrogen was exchanged. However, since the preadsorbed amounts of β and γ hydrogen were similar, it could be argued that when both β and γ hydrogen are present on platinum surface, as in series

C, only β can exchange but not γ. This possibility can be ruled out because in series B, γ-hydrogen underwent exchange although β-hydrogen also existed on the surface during the reaction as mentioned above. That the exchange occurred between β- and γ-hydrogen can also be ruled out because, if it did occur, the amount of HD formed should have been much greater—approaching the sum of the preadsorbed β- and γ-hydrogen.

It is, therefore, clear that the γ-form of chemisorbed hydrogen is involved in the exchange reaction and that β- and δ-form do not participate in the reaction under these experimental conditions. The results of Table 1 also show that the exchange reaction was almost completed in 10 min at −76°C. It should be noted, however, that the reaction between hydrogen chemisorbed in γ-form and the gas phase hydrogen does not necessarily imply that the reaction mechanism is a direct interaction of the surface species with the molecules from the gas phase. This matter will be discussed later.

Figure 1 shows the results of experiments in which the reaction was carried out at
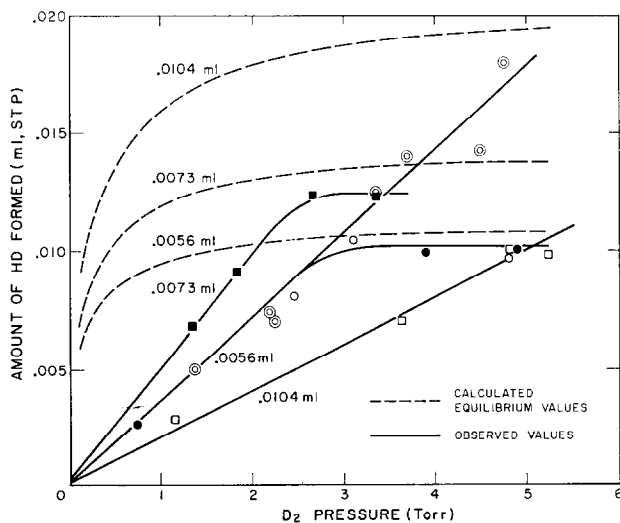

FIG. 1. Pressure dependence of surface exchange reaction. Catalyst weight 2.54 g, reaction temperature −100°C, reaction time 10 min. The amount of γ-H₂ preadsorbed is indicated in the figure. Broken lines show calculated amounts of HD formed at equilibrium from the preadsorbed amounts of γ-H₂ and the amounts of D₂ at the corresponding pressures. With 0.0056 ml of γ-H₂, other types of preadsorbed H₂ were also present: O, γ + δ; ●, β + γ + δ; ◎, α + β + γ + δ.

—100°C between a constant amount of preadsorbed H_2 in γ-form and D_2 introduced to the gas phase at different pressures. Reaction time was 10 min. Included also are the calculated amounts of HD corresponding to complete equilibration of γ-H_2 with the gas phase D_2 (broken lines). Depending on the conditions of preadsorption, other forms of preadsorbed hydrogen besides γ-form were present on the surface in some cases, but only the amount of γ-H_2 has been plotted. The plots show that at low pressures the reaction rate is proportional to the gas phase pressure. At high pressures the reaction is fast and isotopic equilibration is complete in 10 min.

The observed maximum amounts of HD agreed well with the calculated amounts, except for the series with 0.0056 ml of γ-H_2. In this case three different combinations of preadsorption were present initially on the surface depending on the evacuation temperature: $(\gamma + \delta)$ (open circles); $(\beta + \gamma + \delta)$ (filled circles); and $(\alpha + \beta + \gamma + \delta)$ (double circles). For the first two, i.e., in the absence of α, the amount of HD produced reached a constant value which agreed with the calculated amount for complete equilibration of γ-hydrogen, as already pointed out. This agrees with the conclusion based on the results from Table 1, that β- and δ-forms of hydrogen are not involved in the exchange reaction. On the other hand, when α was present the amount of HD produced exceeded the calculated value as shown in Fig. 1, suggesting that α-H_2 was also converted into HD. However, at the reaction temperature, —100°C, a part of α-H_2 was undoubtedly desorbed before D_2 was admitted (10), and mixed with the gaseous reactant during the reaction. The results of Fig. 1, therefore, should not be interpreted to mean that the preadsorbed α-H_2 directly reacts with the gaseous molecules. This matter also will be discussed later in more detail.

It is also of interest that the slopes of the linear portions of the plots in Fig. 1, i.e., the reaction rates, do not increase in the same order as the amounts of preadsorbed γ-hydrogen. In fact the slope for

the largest preadsorbed amount (0.0104 ml) is the smallest. This is shown more clearly in Fig. 2, in which the reaction was carried out for 10 min at —100°C and at constant pressure of D_2 (1.2 and 3.3 Torr) but with different amounts of preadsorbed γ-H_2. Following the treatment of Couper and Eley (13), the first order rate constants k_e (min^{-1}) were obtained from the equation $k_e = (1/t)$ ln $(x_e - x_0)/(x_e - x_t)$, where x_e, x_0 and x_t are the concentrations of an isotope of hydrogen at equilibrium, and at the reaction times $t = 0$ and $t = t$ (min), respectively. The specific initial rate r_m (molecules·sec^{-1}·cm^{-2}), plotted in Fig. 2, were calculated from the equation $r_m = (Nk_e/60A)(x_e - x_0)$, where N is the total number of molecules of the isotope present in the reaction system and A is the surface area of the catalyst.

Figure 2 shows that at 1.2 Torr of D_2 the initial rate r_m goes through a maximum as the preadsorbed amount of H_2 is increased. At the higher D_2 pressure (3.3 Torr), the rate was so fast at smaller amounts of preadsorbed H_2 that the reaction reached equilibrium in 10 min, and the rate could, therefore, not be calculated. Nevertheless, it is still apparent that larger amounts of preadsorbed hydrogen retard the reaction. In these experiments, however, the amount of preadsorbed δ hydrogen also increased as γ hydrogen increased. Therefore, it is not clear at this stage whether the fall off in the reaction rate at high surface coverages was caused by the increase in γ or in δ hydrogen or by both.

The temperature dependence of the first order rate constants k_e of the surface exchange reaction (circles) is shown in Fig. 3, together with the corresponding results for the isotopic equilibration reaction (triangles) carried out with gaseous mixtures of H_2 and D_2 but without preadsorption. The exchange reaction was carried out at 1.4 Torr D_2 and with 0.0056 ml preadsorbed γ-H_2, at which surface coverage the reaction was not retarded by preadsorbed hydrogen, as shown in Fig. 2. The equilibration reaction was carried out with approximately equimolar mixtures of H_2
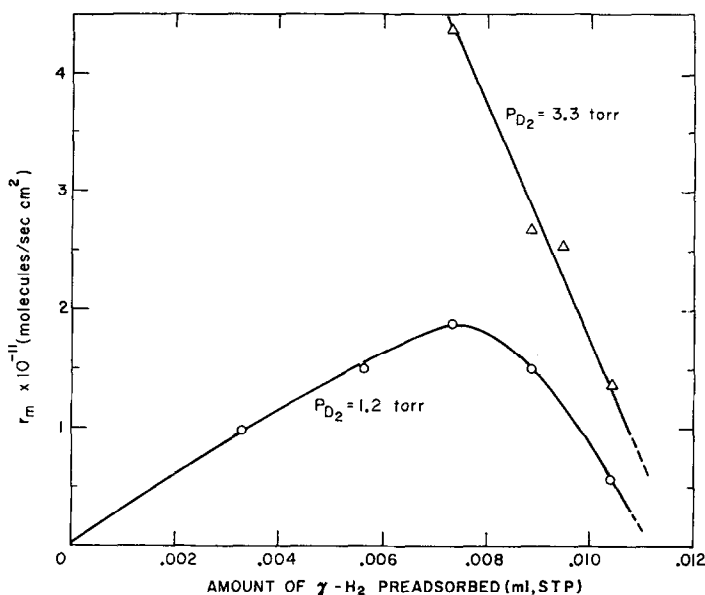
FIG. 2. Effect of preadsorbed γ-H_2 on the reaction rate. Catalyst weight 2.54g, reaction temperature $-100°C$.

and D_2, and the total pressure was again about 1.4 Torr. Reaction time was 10 min in both cases.

It can be seen from Fig. 3 that, at low temperatures the equilibration is much

FIG. 3. Arrehenius plot of k_e.

faster than surface exchange. In fact no HD was detected within 1 hr in the surface exchange reaction at $-195°C$. Much faster reaction rates for the gaseous mixtures (equilibration reaction) were also frequently reported by other workers (7–9). The apparent activation energy calculated from Fig. 3 is 3.9 kcal/mole for the surface exchange and has an average value of about 0.4 kcal/mole for the equilibration reaction. In the latter case there is perhaps a decrease in the activation energy at lower temperatures.
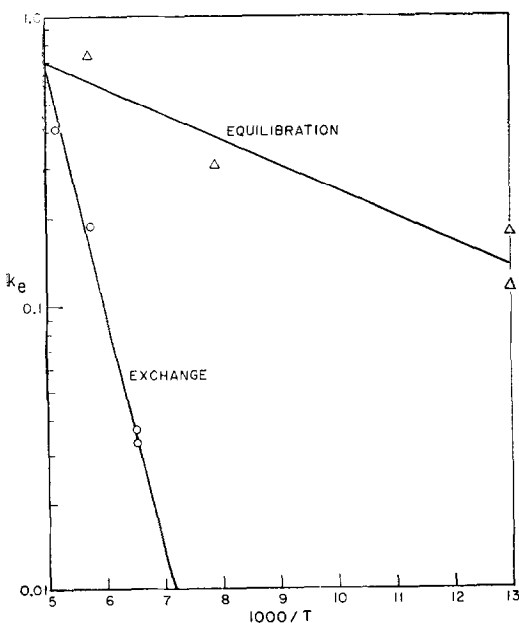
DISCUSSION

Reactivity of Different Forms of Chemisorbed Hydrogen

The results obtained in the present work show pronounced differences in reactivity of the four forms of hydrogen chemisorbed on platinum which have been previously (10) detected by the TPD technique. The γ-form and possibly also the α-form are readily exchangeable with the gaseous isotope while the β- and δ-forms do not participate in the reaction at temperatures below $-76°C$. The difference in reactivity

of the individual forms of chemisorbed hydrogen probably provides an explanation for the differences in catalytic activity observed by earlier workers (8, 9, 14–16).

The results plotted in Fig. 1 show that preadsorbed α-hydrogen was converted to HD but, as already pointed out, do not necessarily prove its direct interaction with the gaseous isotope. There are three possible explanations of the conversion of α-H₂ to HD: (I) preadsorbed α-H₂ reacted with γ-D₂ produced by reaction between γ-H₂ and the gas phase D₂; (II) α-H₂ desorbed into the gas phase and reacted with γ-D₂ produced in the same manner as in (I); (III) α-H₂ reacted directly with the gas phase D₂ or with α-D₂ formed by adsorption of the gas phase reactant D₂. To discriminate between these alternatives, reference is made to the plots in Fig. 3, which show that equilibration is much faster than surface exchange at low temperatures and suggest that the two reactions occur by different mechanisms. At $-195°$C, for example, equilibration is measurable while no HD is formed in 1 hr by surface exchange. The equilibration at low temperatures would seem therefore not to involve γ-hydrogen and leaves α-hydrogen as the only likely participant since β- and δ-hydrogens are nonreactive even at appreciably higher temperatures. Thus, if the above alternative (I) (reaction between α- and γ-hydrogen) is the mechanism of equilibration, the surface exchange should have occurred equally fast or faster since in the exchange experiments of Fig. 3 γ-hydrogen was initially already present on the surface. An analogous argument can be applied to the alternative (II), leaving as the probable mechanism of equilibration the alternative (III), i.e., a reaction either between α-hydrogen and the gas phase isotope or between the isotopic molecules chemisorbed in α-form. On the other hand, in view of the appreciable rate of desorption of α-H₂ at $-100°$C, it is likely that in the conversion of α-H₂ to HD shown by the plot in Fig. 1 both alternatives (II) and (III) were involved to some extent.

At first glance, it may appear that the present conclusions are in conflict with the results of Hall and Lutinski (15). They used the method of differential hydrogen analysis and found on an alumina supported platinum catalyst that about 45% of the hydrogen held by platinum was readily exchanged with the gas phase isotope at $-195°$C and the remainder was exchanged at $-80°$C. In our surface exchange experiments plotted in Fig. 3, γ- and small amounts of δ-hydrogen were preadsorbed but any α- and β-hydrogen were removed by evacuation at $21°$C before the reaction. The lack of exchange at $-195°$C then simply means that at this low temperature the rate of exchange between γ-hydrogen and the gas phase isotope is immeasurably small. In the work of Hall and Lutinski, the catalyst was cooled in hydrogen to $-195°$C and was then outgassed for 1 hr prior to the exchange experiment. Under such conditions, a considerable amount of α-hydrogen (as well as γ-hydrogen) was probably left on platinum, as demonstrated in our previous paper (10). If this is true, then it is possible that α-hydrogen underwent exchange at $-195°$C and γ-hydrogen at $-80°$C, which is in agreement with our conclusions. Their report that all hydrogen held on platinum was exchanged at $-80°$C is also not in conflict with our observations since they measured the "total" hydrogen held on platinum by exchange at room temperature. Any forms of unexchangeable hydrogen, such as β- and particularly δ-hydrogen, would not have been detected in this manner. Our previous results (Fig. 5 of Ref. 10) show that when platinum is contacted with hydrogen for long time at room temperature the amounts of γ- and δ-hydrogen increase while that of β-hydrogen becomes negligible.

In view of these comments, it is clear that the surface exchange reaction observed by Hall and Lutinski at $-195°$C can be explained in a manner consistent with present results by assuming involvement of α-hydrogen in the exchange. At the same time, we wish to call attention to our experience in some experiments at $-195°$C,

although it may not be relevant to this particular case. With the reactor immersed in a Dewar flask with liquid nitrogen, a thermocouple inserted in the center of the reactor showed a temperature increase during catalyst evacuation, beginning after about 15 min. After one hr, the temperature reached $-130°C$ but returned immediately to $-195°C$ when deuterium was admitted. In this case, some exchange of γ-H_2 was observed after a 10 min contact with D_2, while no exchange occurred for contact times up to one hr if the catalyst was evacuated only for 5 min and D_2 was then admitted.

Reaction Mechanisms

The results of the present study indicate that the surface exchange of hydrogen on platinum takes place by a reaction between γ-hydrogen and the gas phase isotope. They also suggest that α-hydrogen can undergo exchange as well and is responsible for the isotopic equilibration at very low temperatures. In our previous paper (*10*) we have tentatively identified γ-hydrogen with the chemisorbed hydrogen atoms on top of platinum atoms and assumed that α-hydrogen are hydrogen molecules chemisorbed in linear form. The question then naturally arises whether it is possible to formulate detailed reaction mechanisms. Unfortunately, as is frequently the case in the mechanistic studies of the catalytic isotopic exchange processes, this cannot be done in a definitive manner, particularly in view of the possible intrinsic or induced surface heterogeneity of the catalyst. A brief discussion of the results obtained in the light of the H_2–D_2 exchange mechanisms on metal catalysts usually invoked, may nevertheless be worthwhile. These are (with the metal atom of the catalyst denoted by M):

(I) Bonhoeffer–Farkas mechanism (*17*),

$$MH + MD \rightarrow MHDM \rightarrow M + M + HD;$$

(IIa) Rideal mechanism (*18*),

$$MH + MD_2 \rightarrow MHDDM \rightarrow M + MD + HD;$$

(IIb) Eley mechanism (*19*),

$$MH \cdot D_2 \rightarrow MHD_2 \rightarrow MD + HD;$$

(IIc) Boreskov–Vassilevitch mechanism (*9*),

$$MH + MD_2 \rightarrow MHD + MD \rightarrow M + MD + HD;$$

(III) Schwab–Killmann mechanism (*1, 20*),

$$MH_2 + MD_2 \rightarrow MH_2D_2M \rightarrow M + M + 2HD.$$

The surface exchange involving γ-hydrogen, as indicated by present results, can be explained either by the mechanism (I) or (IIa). The Eley mechanism (IIb), which is related to (IIa), does not explain the maximum in the rate shown in Fig. 2. The presence of a maximum suggests that the second reactant, the gas phase isotope, requires vacant sites for adsorption and competes for them either with γ-hydrogen itself or with other types of adsorption. Mechanism (IIc) assumes migration of a D atom over the adjacent preadsorbed H atoms until HD is formed on a site of sufficiently low energy so that it can desorb. Surface heterogeneity is therefore implied. If the heterogeneity is intrinsic, for example in the sense of Keier and Roginsky (*21*), the procedure used in this work to obtain preadsorbed γ-H_2 would be expected to leave on the metal surface, hydrogen atoms preferentially on high energy sites. The isotopic exchange would have then to be extremely slow or not to occur at all. On the other hand, if the heterogeneity is induced, i.e., the bond strength of all Pt–H becomes weaker as soon as the surface coverage is increased as a result of the admission (and adsorption) of D_2, the exchange will take place between a Pt–H and an adjacent adsorbed D_2. This situation then becomes equivalent to the Rideal mechanism (IIa).

The isotopic exchange involving α-hydrogen can be explained by the Schwab–Killmann mechanism (III). In the equilibration at higher temperatures, shown in Fig. 3, both α-hydrogen and γ-hydrogen would be expected to be involved simultaneously, in two concurrent reactions.

ACKNOWLEDGMENT

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