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Hydrogenation of 1,3-Butadiene on Pd in Sulfuric Acid Solution

II. Adsorbed Hydrogen Species

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Reactivity of different adsorbed hydrogens on Pd catalysts for the hydrogenation of 1,3-butadiene in 0.5 *M* sulfuric acid solution was examined. Neither the most weakly adsorbed hydrogen (probably molecular) nor the most strongly adsorbed hydrogen, H_{-4} (amount is small) is active, while the others in between, H_{-1}, H_{-2}, and H_{-3}, are active. At higher potential (ca. 160 < ϕ_{oc} < ca. 260 mV), only H_{-3} is active and produces butenes but not butane. On the other hand, at lower potential (ϕ_{oc} < ca. 160 mV) H_{-2} becomes active and causes a further hydrogenation of butenes to butane. At ϕ_{oc} < ca. 60 mV H_{-1} participates in the hydrogenation. H_{-1} is mainly supplied from hydrogen gas but not from the dissolved hydrogen in Pd. The dissolved hydrogen is directly associated with H_{-2} and will take part in the hydrogenation indirectly through H_{-2} at the present conditions.

INTRODUCTION

In Part I (*1*), we have examined the reaction mechanism for the hydrogenation of 1,3-butadiene on Pd catalyst in 0.5 *M* sulfuric acid solution and concluded the reaction intermediates of *syn*- and *anti*-1-methyl-π-allyls which give 1- and *trans*-2-butene, and *cis*-2-butene, respectively. Another entity of the adsorbed hydrogen is also concluded to be a common intermediate among the different hydrogenation methods. Different sources of hydrogen, i.e., H_2, H_{diss} (dissolved hydrogen in Pd), and $H^+ + e^-$ (electroreduction) do not affect reaction rate, distribution of products and the distribution of deuterium (D distribution) in products.

Now, several kinds of adsorbed hydrogens are known to exist on Pd surface (*2–7*). Then, the question arises as to their respective reactivities for the hydrogenation of 1,3-butadiene. In the case of Pt catalyst (*8*), weakly adsorbed hydrogen is active for the hydrogenation but strongly adsorbed one is inactive. Furthermore, Pd metal easily absorbs hydrogen to form α- or β-phase (*9*) and provides another hydrogen state.

The present paper will describe how the adsorbed and dissolved hydrogens take part in the hydrogenation of 1,3-butadiene, based on the time variation of open circuit potential, ϕ_{oc}, upon the contact with 1,3-butadiene and the D distribution in products at the deuterations with hydrogen gas and dissolved hydrogen.

EXPERIMENTAL

Solutions were always subjected to pre-electrolysis overnight. To see the adsorption states of hydrogen, a Au electrode covered with Pd (Pd/Au) was prepared as follows. A Au foil (12 cm^2, 99.98% purity, Tanaka Noble Metals Ind. Co. Ltd.) was first activated at 1.8 V for 30 s and then cathodically polarized for a desired time in 0.5 *M* sulfuric acid solution of 6.5×10^{-5} *M* $PdSO_4$. After the transfer of Pd/Au electrode to a test cell, no further pretreatment was conducted. Other experimental proce-

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dures were the same as those in the previous paper (*1*).

RESULTS

1. *Voltammogram on Pd/Au*

Electrochemical oxidation of the adsorbed hydrogens were carried out on Pd/Au, instead of pure Pd metal because a oxidation peak of the adsorbed hydrogens is veiled with a large peak of dissolved hydrogen. Figure 1a shows a current change when the potential is scanned in the positive and negative directions (voltammogram) on Au covered with a monolayer of Pd in 0.5 *M* H_2SO_4 under He atmosphere. Two main peaks appear in both the positive and negative scans, owing to the oxidation and formation of the adsorbed hydrogens to and from $H^+ + e^-$, respectively. The peak potentials are 175 and 290 mV vs rhe (reversible hydrogen electrode) in the positive scan, and 115 and 255 mV in the negative scan, respectively. A small peak (shoulder) is also observed at ca. 70 mV in the positive scan. These peaks clearly show the presence of three kinds of adsorbed hydrogen. They are named H_{-1}, H_{-2}, and H_{-3} from the negative side.

A further deposition of Pd to three layers causes a large growth of H_{-2}'s peak (Fig. 1b) but does not affect practically the other peaks. Therefore, H_{-2} is taken to be directly related to the dissolved hydrogen (H_{diss}).

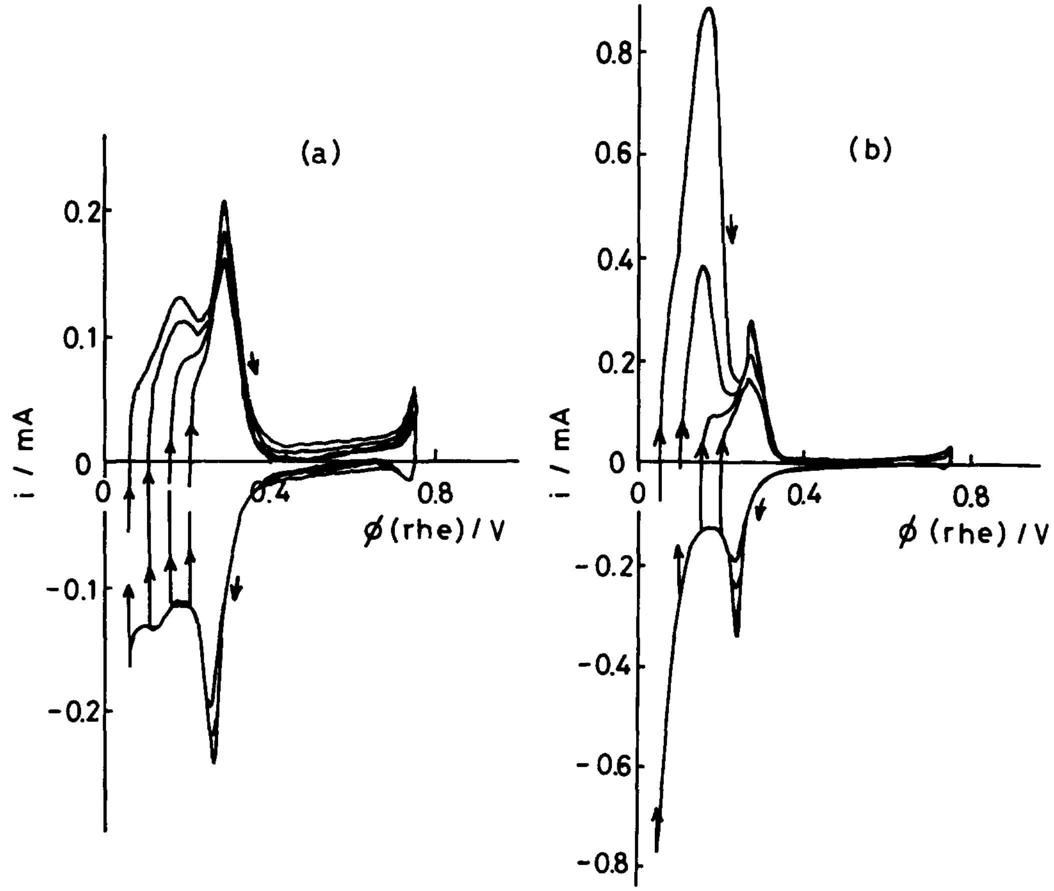

FIG. 1. Voltammograms on (a) a monolayer of Pd deposited on Au and (b) three layers of Pd on Au under He atmosphere. Sweep rate was 25 mV · sec^{-1}.

2. *Open Circuit Potential of Pd/Au*

Under helium. After a polarization of Pd (monolayer)/Au at 0 V, a potential on open circuit, ϕ_{oc}, was followed under He atmosphere. Typical results are shown in Fig. 2 (curves a and b). Potential change in the positive direction is caused by desorption of the adsorbed hydrogens by

$$2H(a) \rightarrow H_2$$

where the potential of catalyst is determined by $H(a) \rightleftarrows H^+ + e^-$. Though ϕ_{oc} in curve a changes more rapidly than that in curve b obtained in the solution purified by prolonged preelectrolysis, both curves exhibit a stepwise shift of ϕ_{oc} with halts at ca. 110, 210, and 360 mV, indicating the presence of the corresponding adsorbed hydrogens.

Under 1,3-butadiene. The open circuit potential is now followed by introducing 1,3-butadiene (22 mm Hg, 1 mm Hg = 133.3 $N \cdot m^{-2}$) after the polarization at 0 V. Curve c in Fig. 2 shows an abrupt shift of ϕ_{oc} to a value above 300 mV within 3 min and then a gradual decrease to a constant value of ca. 280 mV. ϕ_{oc} is further followed after the intermission by the polarization at 0.75 V for 5 min, which ensure the complete removal of the adsorbed hydrogens. Subsequent, monotonous shift of ϕ_{oc} from 0.75 V to the above constant value indicates a dissociative adsorption of 1,3-butadiene releasing a potential-determining H(a). A removal of 1,3-butadiene by helium causes a deviation of ϕ_{oc} from the constant value in the positive direction.

3. *Deuteration by Both Hydrogen Gas and Dissolved Hydrogen*

In order to examine how the respective adsorbed hydrogens are reactive, deuteration of 1,3-butadiene was carried out by circulating an atmospheric mixture of 1,3-butadiene (12 mm Hg), D_2 or H_2 (300 mm Hg) and He on a Pd metal catalyst which preabsorbed the hydrogen. Now, four possible combinations, D_2–D_{diss}, H_2–D_{diss}, D_2–H_{diss}, and H_2–H_{diss}, as a source of hydrogen, were all examined. In these runs, a potential of

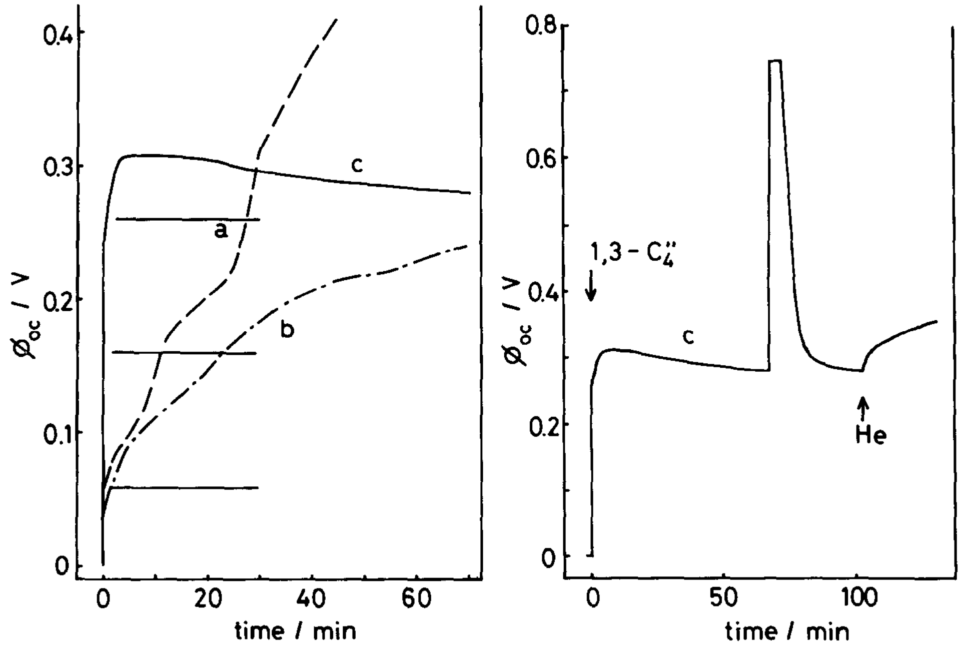

FIG. 2. Time variation of open circuit potential of Pd/Au under He atmosphere (a, b) and under 1,3-butadiene (P_R = 22 mm Hg, c).

TABLE 1

D Distributions in Products Formed by the Hydrogenation of 1,3-Butadiene with Hydrogen Gas or Dissolved Hydrogen

Run	Hydrogen source	Conv. (%)	S	Product	x_i (%)											D.N.
					0	1	2	3	4	5	6	7	8	9	10	
8	D_2–D_{diss}	8.9	0.09	Butane	0.5	1.6	3.6	5.4	6.9	8.8	11.5	15.3	18.4	17.3	10.7	6.8
				1-Butene	29.2	24.6	18.5	9.0	5.9	4.3	4.1	3.5	0.9			1.9
				trans-2-Butene	4.6	11.2	11.4	9.2	10.1	11.9	14.8	15.6	11.1			4.5
				cis-2-Butene	3.4	5.8	8.2	8.8	9.6	12.0	16.1	19.8	16.4			5.1
9	H_2–D_{diss}	6.0	0.22	Butane	16.2	17.4	14.7	11.6	9.3	7.4	6.4	5.5	4.9	4.0	2.6	3.3
				1-Butene	41.6	25.1	14.1	8.1	4.9	2.8	1.8	0.9	0.8			1.3
				trans-2-Butene	33.9	22.0	14.2	9.3	6.6	4.9	3.8	3.0	2.3			1.9
				cis-2-Butene	28.7	22.4	15.6	10.7	7.5	5.6	4.2	3.2	2.1			2.1
10	D_2–H_{diss}	7.0	0.15	Butane	2.1	5.0	7.1	9.3	12.5	15.6	17.8	15.8	10.2	3.9	0.7	5.2
				1-Butene	44.8	18.7	16.0	7.2	4.9	3.7	2.8	1.4	0.6			1.4
				trans-2-Butene	7.9	10.6	10.4	10.7	13.4	16.1	16.1	11.1	3.7			4.0
				cis-2-Butene	6.0	8.8	10.4	11.9	14.2	16.7	16.6	11.4	3.9			4.2
11	H_2–H_{diss}	7.6	0.24	Butane	32.5	30.3	19.1	9.4	4.4	2.2	1.2	0.6	0.2	0.0	0.0	1.4
				1-Butene	72.3	15.1	7.3	3.4	1.4	0.4	0.0	0.0	0.0			0.5
				trans-2-Butene	42.4	28.0	15.4	7.4	3.7	1.9	0.9	0.3	0.0			1.1
				cis-2-Butene	35.8	32.2	17.5	8.2	3.7	1.7	0.7	0.2	0.0			1.2

Pd settled around a constant value of 30 ± 2 mV which is known as an equilibrium potential for the coexistence of α- and β-phases in 0.5 *M* D_2SO_4 solution (*10*). Low ϕ_{oc} and low selectivity of butene ($S = 0.09 \sim 0.24$, S is defined as the ratio of butenes to total products, Table 1) show that the reaction proceeds in region R where the diffusion of 1,3-butadiene controls the reaction rate (*1*).

D distributions in products are listed in Table 1. Values of d_0-1-butene appear extremely large owing to the residual 1-butene (d_0) left unremoved in the reactant after the rigorous purification process. Such a trace of impurity apparently amplifies d_0 value since the amount of 1-butene formed is very small (ca. 0.1% of the total hydrocarbon pressure). From Table 1, one can see that the D distribution in *trans*-2-butene is clearly different from that in 1-butene and very similar to that in *cis*-2-butene (run 10 exhibits this situation most clearly) in contrast with the results in regions H and I (*1*). Among the four combinations, D_2–D_{diss} (run 8) accelerates H/D exchange to a great extent, e.g., average number of deuterium atoms, D.N., of *cis*-2-butene in run 8 is 5.1, much larger than 2.6 at $P_D = 55$ mm Hg in region H. Successive replacements of D_2 and D_{diss} with protium (light hydrogen) cause a decrease in D.N. by the following sequence:

$$D_2\text{–}D_{diss} > D_2\text{–}H_{diss} \gg H_2 - D_{diss} > H_2 - H_{diss}$$

A large decrease in D.N. at the replacement of D_2 with H_2 clearly shows that the hydrogenation associated with the H/D exchange predominantly proceeds by the adsorbed hydrogen from hydrogen gas, and to a much less extent by that from the dissolved hydrogen.

The origin of deuterium atom in run 11 (H_2–H_{diss}) must be D^+ in solution which exchanges with the adsorbed protium on Pd. However, small D.N.'s in run 11 indicate that the rate of exchange reaction, $X(a) \rightleftarrows X^+ + e^-$ (X = D or H), is much slower than that of hydrogenation.

DISCUSSION

1. *Adsorption State of Hydrogen*

Before discussing how adsorbed and dissolved hydrogens take part in the surface reaction, we must first examine the adsorbed hydrogens and their relation with the dissolved one. The latter hydrogen is usually assumed to reach interstitial positions via a adsorption state (*11*). However, this does not always mean that all the kinds of adsorbed hydrogen can be directly dissolved into Pd and hence can be a precursor of the dissolved hydrogen.

This problem is examined on Pd/Au instead of pure Pd metal. Here, a question arises as to an alloy formation between Pd and Au since they produce a solid solution over a whole range of the composition. However, this possibility is excluded from the voltammogram on Pd/Au which exhibits the same peak potential for the reduction of surface oxide as in the case of a pure Pd metal; the alloy formation shifts the peak potential to a more positive value (*12*). Furthermore, a deposition of Pd to three layers does not affect the peak potential. Even though some Au is assumed to expose on the surface, little influence will be expected since Au neither adsorbs nor absorbs hydrogen because of its filled *d* band (*13*). In addition, the catalytic properties of Pd and Pd/Au electrodes are much the same as shown in Table 2. Thus, Pd/Au is taken to provide the information concerning the adsorption states of hydrogen on pure Pd.

From the voltammograms on Pd/Au (Fig. 1), three kinds of adsorbed hydrogen become clear. Analysis of ϕ_{oc}–time curve under helium confirms this observation and even reveals another state of adsorbed hydrogen, as follows. A potential-determining reaction on Pd,

$$H(a) \rightleftarrows H^+ + e^- \qquad (1)$$

TABLE 2

Electroreduction of 1,3-Butadiene on Pd and Pd/Au Electrodes in 0.5 M H_2SO_4

Electrode potential (mV)	Electrode	Current (t = 5 min)/mA · cm^{-2}	Products (%)			
			Butane	1-Butene	*trans*-2-Butene	*cis*-2-Butene
50	Pd foil	0.28	69	3	20	8
	Pd/Au	0.18	68	3	18	10
180	Pd foil	0.046	0	55	33	12
	Pd/Au	0.033	0	53	32	15

gives the following equation for ϕ_{oc},

$$\phi_{oc} = \text{const} - \frac{RT}{F} \ln \frac{\theta_H}{1 - \theta_H} \qquad (2)$$

where θ_H is the coverage of hydrogen and a mutual interaction between H(a)'s is neglected. Thus, ϕ_{oc} is expected to change in S shape with the change of θ_H for each kind of the adsorbed hydrogens. Curve a in Fig. 2 consists of three S-shaped curves as divided conventionally by horizontal lines. From each section and the corresponding peak in the voltammogram (Fig. 1) four kinds of adsorbed hydrogen are derived (Table 3).

The existence of H_{-1} is expected from the results of voltammogram but not clearly noticed in Fig. 2 because of the rapid change of ϕ_{oc}. On the other hand, H_{-4} exists clearly in ϕ_{oc}–time curve. The potential region of H_{-3} is situated more negative than the peak potential of H_{-3} in the voltammogram. The potential regions determined from ϕ_{oc}–time curve seem to be more reliable than those from voltammograms since the former is obtained under the equilibrium conditions of Eq. (1) but the latters are under the dynamical conditions. Here, we must remind that the potential region of H_{-3}, for example, allows the presence of not only H_{-3} but also H_{-4} whereas does not allow more weakly adsorbed hydrogens such as H_{-1} and H_{-2}. The observation on Pd (three monolayers)/Au (Fig. 1) clearly tells us that H_{-2} is associated with the dissolved hydrogen (H_{diss}), and H_{-1}, H_{-3}, and H_{-4} are not.

TABLE 3

Potential Regions and Adsorbed Hydrogens

Potential region (mV)	Type	Data source		Region
		ϕ_{oc}[a] (mV)	Voltammogram[b]	
~ ca. 60	H_{-1}		70	B
ca. 60 ~ ca. 160	H_{-2}	110	175, 115	I
ca. 160 ~ ca. 260	H_{-3}	210	290, 255	H
ca. 260 ~	H_{-4}	360		

[a] The potential at which potential halt is observed in ϕ_{oc}–time curve.

[b] Peak potentials in the positive and negative scans (mV).

In addition, one more, most weakly adsorbed hydrogen will be introduced as reported in both electrochemical and gas–solid systems as a species associated with the formation of β-phase (*3–5, 7*). One of the possible forms of this species will be a molecular species (*5, 7*). On Pt, weakly adsorbed molecular hydrogen has been suggested by ESR study (*14*).

In the electrochemical system, a few works dealed with the adsorption state of hydrogen on Pd. Furuya and Motoo (*2*) have shown two adsorption states on atomically dispersed Pd on Au. A strongly adsorbed hydrogen attains its maximum coverage at 150 mV while weakly adsorbed one at 50 mV. The latter species is associated with the dissolved hydrogen (α-phase). Voltammogram on Pd-plated Au electrode has been reported by Chevillot *et al.* (*3*), where two oxidation peaks and a shoulder appear at 60, 270, and ca. 190 mV at pH $\simeq$ 0, respectively. According to their interpretation, the former two are due to the oxidation of adsorbed hydrogens and the latter due to the dissolved hydrogen (α-phase).

Furuya and Motoo's observations are in good agreement with ours if their strongly and weakly adsorbed hydrogens are regarded as H_{-3} and H_{-2}, respectively. The strongly adsorbed hydrogen of Chevillot *et al.* is clearly the same species as H_{-3}. However, the interpretation for the shoulder at ca. 190 mV is different from present one for the corresponding hydrogen at 175 mV. Namely, they assigned the dissolved hydrogen itself but we assume the adsorbed hydrogen associated with H_{diss}, H_{-2}, by the following reasons. (i) H_{-2} appears in the voltammogram on Au with a monolayer of Pd. (ii) It is most plausible to assume that H_{diss} is oxidized via the adsorption state.

Adsorption state of hydrogen on Pd catalyst in gas–solid system has also been studied. Aldag and Schmidt (*4*) have found four peaks in the hydrogen desorption spectra from Pd wires. Duś (*5*) has clarified electric nature of three kinds of adsorbed hydrogen; one of two atomically adsorbed hydrogens is a electronegatively charged species (β_1^-) appearing at low hydrogen coverage and the other is electropositive one (β_2^+) at high coverage, the third species is an electropositive molecular one (α) observed at higher coverage. According to Duś (*5*), β_2^+ is converted to H_{diss} much more easily than β_1^- because the latter requires a change in electrical character in the process. Eley and Pearson (*7*) have proposed that β_1^- is chemisorbed on the top of Pd atom, β_2^+, and α at interstices of (100) plane in an atomic and molecular form, respectively, and that α is the precursor of the dissolved hydrogen. Their assignment is based on the fact that the dissolved hydrogen atoms are located at octahedral interstices (*15, 16*) and that surface octahedral interstices are only possible on the (100) plane.

The above results in gas–solid system lead us to assign, though tentative, our two main adsorbed hydrogen of H_{-2} and H_{-3} as follows. H_{-2}: atomically adsorbed at interstitial site. H_{-3}: atomically adsorbed just above the surface Pd atom. Thus, H_{diss} can be associated with H_{-2}, but not H_{-3}.

2. *Reactivity of the Respective Adsorbed Hydrogens*

When 1,3-butadiene was introduced after the polarization at 0 V, ϕ_{oc} shifted rapidly in the positive direction and approached the potential region of H_{-4}. The fast removal of H_{-1}, H_{-2}, and H_{-3} at the initial stage implies their high reactivity for the hydrogenation of 1,3-butadiene. A constant ϕ_{oc} in an intermediate region between H_{-3} and H_{-4} shows a lack of reactivity of H_{-4}; if active, ϕ_{oc} may shift to a positive potential out of the hydrogen region (>0.5 V) because of its consumption. A halt of ϕ_{oc} at the potential of the border between H_{-3} and H_{-4} suggests a conversion of H_{-4} and H_{-3} during the reaction as confirmed on Pt in the hydrogenation of 1,3-butadiene (*8*).

The potential regions of H_{-3} and H_{-2} correspond to regions H and I where only butenes and in addition butane are formed, respectively (*1*). Our separate experiments show that butenes are electrochemically reduced to butane only at $\phi \leq 150$ mV (*17*), that is, in the region of H_{-2}. Therefore, the high selective butene formation in region H will be attributed to a critical nature of H_{-3} being active for the hydrogenation of 1,3-butadiene and inactive for butenes. A high selective formation of butenes on Pd in the gas–solid system has been explained by a strong adsorbability of 1,3-butadiene which replaces the weakly adsorbed butenes. However, little attention has been paid on the function of the adsorbed hydrogens. The present electrochemical system makes it possible to clarify the reactivity of the adsorbed hydrogen, H_{-3}, which exhibits different activity for 1,3-butadiene and butenes.

Next, we discuss the reactivity of H_{-1} and how H_{diss} participates in the hydrogenation from the data on the deuteration under the presence of the dissolved hydrogen and hydrogen gas. Under such conditions ($\phi_{oc} = 30 \pm 2$ mV) H_{-1}, H_{-2}, H_{-3}, and H_{-4} exist on Pd surface. The results in Table 1 show the following. (i) Rate of the discharge process of D^+ is slower than that of the hydrogenation because the replacement of D_2 with H_2 causes a large decrease in D.N. (ii) Nevertheless, the rapid H/D exchange observed during the deuteration leads us to assume a rapid surface exchange among the reactive adsorbed hydrogens, i.e., between the hydrogen atom formed by the cleavage of C—H bond and the adsorbed deuterium atom. (iii) The absence of a sharp maximum at d_2-butene excludes a direct addition of molecular D_2 to 1,3-butadiene. From (i)–(iii), we can rule out the molecularly adsorbed hydrogen, if present as expected from many literatures, as an active species for the hydrogenation reaction. Under the conditions of the present deuteration, the most active adsorbed hydrogen is concluded to be H_{-1}. H_{-1} is mainly supplied from hydrogen gas but not from the dissolved hydrogen since H_{-1} cannot be converted to H_{diss} as stated above. H_{diss} will take part in the hydrogenation through H_{-2}.

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