The Mechanism of the Selective Hydrogenation of 1,3-Butadiene on Copper Surfaces

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The hydrogenation of 1,3-butadiene on copper surfaces was studied in detail. A highly selective formation of 1-butene was observed in the range of temperatures from 27 to 76 °C; the initial rate of the formation was well expressed in terms of the partial pressures of hydrogen, p_h, and butadiene, p_b, as $v=kp_h/(1+Kp_b)^2$ in the pressure range of 5—100 Torr. The reaction with D_2 gave butene-d_0 and -d_1 as the main products, and the butadiene was partly exchanged with D_2 during the hydrogenation. The microwave spectroscopic analysis revealed that the 1-butene produced consisted of $CH_2{=}CHCH_2CH_2D$, $CH_2{=}CHCHDCH_3$, and $CHD{=}CHCH_2CH_3$, without even a trace of $CH_2{=}CDCH_2CH_3$. Therefore, it was concluded that the reaction proceeds *via* the isobutenyl surface intermediate and that the dissociative adsorption of hydrogen is rate-determining. The structural analysis of the surface suggested that the stable lattice planes, such as (111), (100), and (110), are responsible for the reaction. The origin of the high 1-butene selectivity was discussed on the basis of the surface geometry and the proposed mechanism.

The hydrogenation of 1,3-butadiene has frequently been investigated from the viewpoint of selective catalysis, but it has been studied mainly on such d-metals as Ni,[1] Pd, and Pt.[2,3] Though the reaction on these metals produces 1-butene, *trans*-2-butene, *cis*-2-butene, and a smaller amount of *n*-butane from the initial stage of reaction, the isomer distributions of the produced butenes are considerably different from each other. In order to explain this variation, reaction mechanisms including such surface intermediates as π-allylic or σ-π-bonded species have been proposed. The identification of these adsorbed species, however, has not always been successful because of the complication of the simultaneous formation of butene isomers. On the other hand, it has been found that copper, a typical s-metal, is highly selective in the formation of 1-butene. However, only a few works of the hydrogenation on this metal have been reported,[1] and the features of the reaction are not known in detail. The aim of the present study is to ascertain the mechanism of the reaction and to reveal the origin of the high selectivity on the basis of the structure of the copper surface and the mechanism.

In order to ascertain the detailed mechanism of the reaction, the deuterium distribution in the products and the reactants on the reaction with deuterium were examined mass-spectroscopically; further, the deuterated positions of the produced 1-butene-d_1 and their relative abundances were determined by applying microwave spectroscopic analysis. The adsorbed states of hydrogen and butadiene were analyzed by using the thermal-desorption technique.

In the study of butadiene hydrogenation on Ni, it was found that a drastic change in activity and selectivity occurred when Ni was annealed in the temperature range of 350—400 °C.[4] A similar change in the activity was observed in the acetylene hydrogenation on Pd when the catalyst was annealed at temperatures between 250 and 300 °C. These results show that fine structures such as surface vacancies play an important role in the reactions.[5] In the present study, the effect of annealing on these catalytic properties was examined over a wide range of annealing temperatures, from 180 to 500 °C; the corresponding change in surface structure was followed by means of X-ray and electron diffractions.

Experimental

The kinetic measurements were carried out by using conventional closed systems of 360 or 670 ml incorporating a circulation pump. The reaction was examined in the range of temperature from 27 to 76 °C and in the range of total pressure between 5 and 100 Torr. The pressure change during the course of reaction was followed by means of a glass Bourdon gauge, while the composition of the products was determined by the use of a gas chromatograph connected to the reaction system. A 16 m DMS column was used at room temperature for the separation of butadiene, butenes, and butane.

The copper powder catalyst was prepared in a way similar to the method reported by Hirota *et al.*[6] Copper nitrate, $Cu(NO_3)_2 \cdot 3H_2O$ of a guaranteed-reagent grade, was dissolved into distilled water at 80 °C, and then a 20% solution of NaOH was added steadily. The copper oxide thus precipitated was washed several times, calcinated in air at 110 °C for 1 hr, and then evacuated for 1 hr. Prior to the reaction, the oxide was reduced *in situ* with hydrogen of 100 Torr at 180 °C for 3 days and then evacuated for 2 hr at the same temperature. Though a step-by-step decrease in the activity occurred in a repeated run, contact with H_2 at 180 °C prior to each kinetic run could recover the initial activity within a 10% decrease. The catalytic activity was also examined on copper catalysts annealed at 300, 400, and 500 °C *in vacuo* for 1 hr. The surface area was evaluated by means of the BET method, using Kr at 77 K, while the change in surface structure was investigated by means of the X-ray and electron diffractions.

In the reaction of butadiene with D_2, the products were separated gas chromatographically, and the deuterium distributions in respective components were determined by using a mass spectrometer, Hitachi RMU-5B. The relative abundance of 1-butene-d_1 and -d_2 with different deuterium positions was determined by means of microwave spectroscopy.[7] Hydrogen, hydrogen deuteride and deuterium were analyzed gas chromatographically.[8]

The thermal desorption spectra were obtained by using an apparatus which could be pumped out at a constant rate during the desorption of surface species from the heated catalyst. Copper (1.06 g) was exposed to hydrogen or butadiene of 10 Torr at room temperature for 10 min; then it was cooled and evacuated at −78 °C for several minutes. The temperature of the cell containing copper was raised at a constant rate of 0.14 °C/s by means of an electric furnace. The pressure of the desorbed gases was monitored by means of a Pirani gauge, and the composition of the desorbed gas was determined by using a quadrupole mass spectrometer.

Butadiene (99.6% purity), hydrogen (99.9%), and deuterium (containing 0.3% HD) were obtained from the Takachiho Co., Ltd., and were used without further purification.

Results

A typical time-course of the hydrogenation, when the copper catalyst was reduced at 180 °C, is shown in Fig. 1. The only products at the initial stage were butenes; the absence of butane was evident. The butenes consisted of 1-butene (92%), *t*-2-butene (3%), and *c*-2-butene (5%); this composition was almost unchanged until more than 95% of the butadiene had been consumed. This finding predicts that, in the initial stage of the reaction, each butene is formed directly by the hydrogenation of adsorbed butadiene and that the butenes, once desorbed into the gas phase, hardly participate in the further process of the reaction. After the butadiene in the gas phase had disappeared, however, the isomerization of 1-butene and the slow hydrogenation of butenes took place concurrently, producing 2-butenes and *n*-butane respectively. This selective formation of 1-butene was observed also on the Cu annealed at 500 °C under similar conditions. In the absence of hydrogen, neither the isomerization nor hydrogenation occurred, not even at 76 °C, the highest reaction temperature in the present study.

Kinetics of Hydrogenation. The kinetic measurements were carried out in the temperature range of 27—76 °C, using Cu annealed at 180 and 500 °C. By changing the partial pressure of hydrogen from 13 to 97 Torr, and that of butadiene from 7 to 36 Torr, the initial rate of 1-butene formation, v, was measured. It was found that the rate was proportional to the hydrogen pressure, p_h, and that a linear relationship held between the square root of the reciprocal of v and the butadiene pressure, p_b, as is shown in Fig. 2. Accordingly, the rate was well expressed in this form;

$$v = kp_h/(1+Kp_b)^2 \qquad (1)$$

where k and K are constants. From the temperature dependence of the rate, the apparent energy of activation was estimated; it is listed in Table 1, together with that for the reaction with D_2.

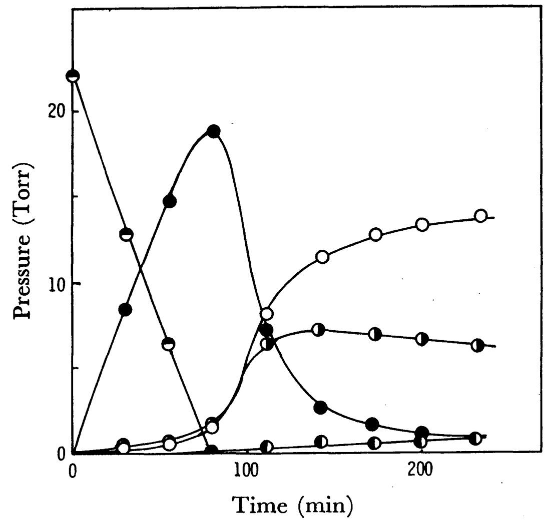


Fig. 1. Hydrogenation of 1,3-butadiene on Cu at 64.5 °C. $p_h=24$ Torr, $p_b=12$ Torr.
◓: 1,3-butadiene, ○: *t*-2-butene, ◑: *c*-2-butene, ●: 1-butene, ◐: *n*-butane.

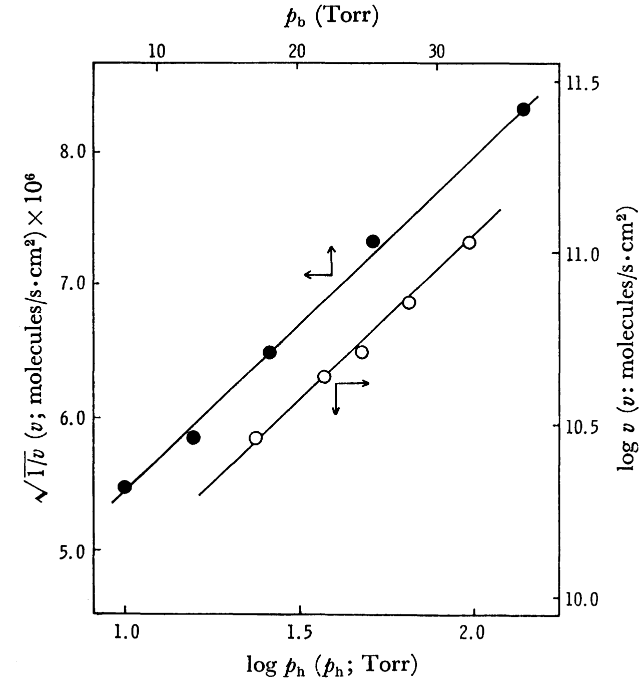


Fig. 2. Dependence of rate on partial pressures at 50 °C.
○: hydrogen ($p_b=12$ Torr), ●: 1,3-butadiene ($p_h=24$ Torr).

Table 1. Activation energies of 1,3-butadiene hydrogenation on Cu
($p_D=24$ Torr, $p_h=24$ Torr, $p_b=12$ Torr)

Annealing temperature	Reaction	Activation energy (kcal/mol)
180 °C	$C_4H_6+H_2$	13.5±0.2
180 °C	$C_4H_6+D_2$	13.8±0.1
500 °C	$C_4H_6+H_2$	13.4±0.2

Deuterium Distributions. The distributions of deuterium in butenes and butadiene were investigated on the reaction with deuterium at 50 °C. Figure 3 shows the changes in the fractions of 1-butene-d_0∼-d_3 with the degree of conversion. In the stage of low conversion, the main products were 1-butene-d_0 and -d_1. The decrease in 1-butene-d_0 with an increase in the conversion was counterbalanced by the formation of d_1∼d_3 compounds. It should be noted that a considerable amount of butadiene-d_1 appeared as the reaction proceeded; at 40% conversion, the d_1 fraction

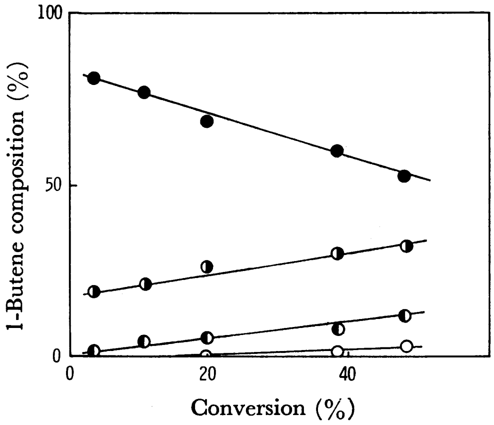


Fig. 3. Deuterium distribution in product from the reaction of butadiene with deuterium at 50 °C.
p_D=24 Torr, p_b=12 Torr
●: 1-butene-d_0, ◑: -d_1, ◐: -d_2, ○: -d_3.

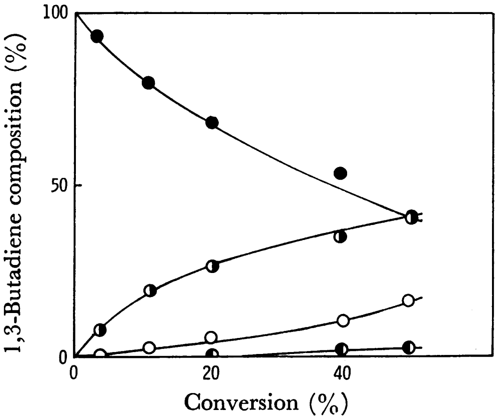


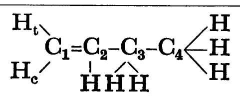
Fig. 4. Deuterium distribution in reactant from the reaction of butadiene with deuterium at 50 °C.
p_D=24 Torr, p_b=12 Torr
●: butadiene-d_0, ◑: -d_1, ○: -d_2, ◐: -d_3.

reached 35% of all the butadienes, as is shown in Fig. 4. It is apparent that the formation of 1-butene-d_2 and -d_3 in the region of high conversion is due to the hydrogenation of deuterobutadiene. On the other hand, a negligibly small amount of HD was found in the gas phase. In the reaction of butadiene with an equi-molar mixture of H_2 and D_2, the amount of HD produced was also negligibly small. These results clearly indicate that the recombination of surface hydrogen into the molecule is very slow.

The microwave spectroscopic analysis was applied to the products at conversions of 15.5 and 48%. The results for butene-d_1 are summarized in Table 2. The deuterium positions of products other than 1-butene-d_1 could not be determined because of their small yields (below the limits of analysis). As may be seen from Table 2, about 54% of the $CH_2{=}CHCH_2CH_2D$ (4-d_1) and 31% of the $CH_2{=}CHCHDCH_3$ (3-d_1) were formed at the stage of low conversion. A small fraction, 15%, of $CHD{=}CHCH_2CH_3$ (1-d_1) was also produced, but $CH_2{=}CDCH_2CH_3$ (2-d_1) was not detected. The increase in the fraction of the 1-d_1 component was compensated for the decrease in that of the 3-d_1 compound.

TABLE 2. THE RELATIVE ABUNDANCE OF 1-BUTENE-d_1 WITH DIFFERENT DEUTERIUM POSITIONS
(p_b=12 Torr, p_D=24 Torr, reaction temperature=50°C)

Conversion		15.5%	48.1%	
		%deuterium	% deuterium	
Position[a)]	1c	7.5	12.7	
	1t	7.5	17.5	1-d_1
	2	0	0	2-d_1
	3	30.7(15.4)[b)]	16.3 (8.2)	3-d_1
	4	54.3 (18.1)	53.5 (17.8)	4-d_1

a)


b) Values in parentheses represent deuterium fraction per hydrogen atom.

The rate of the reaction with H_2 was approximately five times as fast as that of the reaction with D_2 at 50 °C. This isotope effect is mainly attributable to the mass ratio, $(m_D/m_H)^{5/2}$, in the frequency factors of the hydrogen and deuterium adsorption rates, though the difference in activation energy contributes to some extent.

Adsorbed States of Hydrogen and Butadiene. By the use of copper annealed at 180 °C, the adsorption measurement of butadiene was carried out at 50 °C under pressures up to 30 Torr. The adsorption was saturated at equilibrium pressures higher than 7 Torr, and the surface was occupied by 1.9×10^{14} molecules/cm^2, corresponding to about 20% of all the surface Cu atoms. After the evacuation at 50 °C, a considerable amount of the butadiene, 1.3×10^{14} molecules/cm^2, still remained on the surface. The reaction with hydrogen at the same temperature decreased this strongly bound butadiene to 0.47×10^{14} molecules/cm^2, with a slower rate compared to the stationary rate of the hydrogenation.

The thermal desorption spectra of butadiene showed a broad peak which spread over −40~100 °C, with a maximum at 53 °C, indicating that even the most strongly adsorbed butadiene is almost desorbed at temperatures higher than 100 °C. On the other hand, the desorption spectra of hydrogen showed a sharp peak with a maximum at 58 °C; this peak has the characteristic shape of the second-order desorption, indicating a drastic fall on the high-temperature side. This result suggests that the hydrogen is adsorbed dissociatively and exists in a single state on the surface.

Carbon monoxide was added to the reactant up to 22 Torr, but no decay in the activity was observed. However, a preliminary study of ethylene hydrogenation at 50 °C using an equi-molar mixture of ethylene and hydrogen (24 Torr in total pressure) showed that the activity of the copper catalyst decreased proportionally with the pressure of the introduced CO up to about 3 Torr. These results provide evidence of the stronger bond between butadiene and the copper surface than that between ethylene and Cu.

Effect of Annealing on the Activity and the Surface Structure. The effect of annealing on the catalytic activity and the surface area is shown in Fig. 5. It is evident that the decreases in the activity and the surface area are parallel with each other, keeping the specific

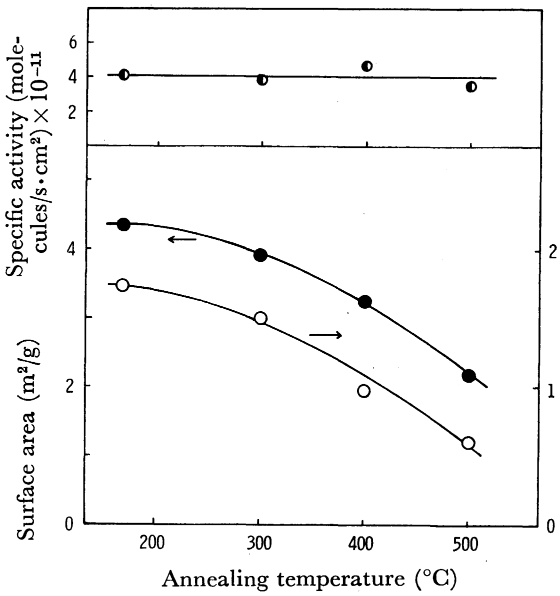


Fig. 5. The changes in activity and surface area with annealing temperature.

activity, the rate per unit area, constant. In the case of the 500 °C-annealed Cu, the selectivity of 1-butene formation was higher than 90% and the activation energy was estimated as 13.4 kcal/mol, as is shown in Table 1. These values coincide with those in the case of the 180 °C-annealed Cu.

X-Ray and electron diffractions of the 180 °C-annealed Cu showed the characteristic patterns due to the (111), (220), and (200) planes. When the copper was annealed at 500 °C, the pattern remained almost unchanged, except that the intensity of the (200) plane became slightly weaker. These findings were in close agreement with those observed by Yamaguchi[9] and by Young *et al.*[10] and showed that the exposed surface was mainly composed of the stable (111), (100), and (110).

Discussion

In the present study using the Cu metal, the high selectivity of 1-butene formation was observed under all the conditions used. The kinetics of the reaction on Cu is not markedly different from those on Pd, Pt, and Ni metals of lower selectivities. However, there were some differences in the activation energy; the value for Cu is considerably higher than those for the other metals. The dissociative adsorption of hydrogen on Cu was also confirmed from a study of the H_2–D_2 equilibration reaction.[11] The adsorption and the thermal-desorption measurements showed that the Cu surface was covered, to a large extent, with butadiene, which is in the reversibly adsorbed and the strongly bound states. The mass analyses showed a considerable formation of butadiene-d_1 and -d_2 during the hydrogenation with deuterium. However, it is clear that the dissociatively adsorbed butadiene scarcely contributes at all to the hydrogenation, since 1-butene-2-d_1 was completely absent in the products, whereas 1-butene-3-d_1 were present in large amounts. Hence, the reversibly adsorbed butadiene and butenyl radicals can be suggested as the intermediates. The following reaction scheme is proposed:

$$C_4H_6 \underset{\overleftarrow{\text{Ia}}}{\overset{\overrightarrow{\text{Ia}}}{\rightleftarrows}} C_4H_6(a) \tag{Ia}$$

$$H_2 \underset{\overleftarrow{\text{Ib}}}{\overset{\overrightarrow{\text{Ib}}}{\rightleftarrows}} 2H(a) \tag{Ib}$$

$$H(a) + C_4H_6(a) \underset{\overleftarrow{\text{II}}}{\overset{\overrightarrow{\text{II}}}{\rightleftarrows}} C_4H_7(a) \tag{II}$$

$$H(a) + C_4H_7(a) \xrightarrow{\overrightarrow{\text{III}}} C_4H_8 \tag{III}$$

where the symbol (a) denotes the adsorbed state which participates in the reaction. The first-order dependence of the rate with respect to the hydrogen pressure leads to the conclusion that either step, $\overrightarrow{\text{Ib}}$ or $\overrightarrow{\text{III}}$, is rate-determining. In both reactions, with D_2 and with an equimolar mixture of H_2 and D_2, the amount of HD formed was found to be negligibly small. This suggests that the adsorption of hydrogen is irreversible during the hydrogenation. Accordingly, the $\overrightarrow{\text{Ib}}$ step is considered to be rate-determining and the rate of hydrogenation is given by:

$$v = k_1 p_h (1-\theta_b)^2 \tag{2}$$

where θ_b is the fraction of surface coverage of the reversibly adsorbed butadiene and where k_1 is the rate constant of the $\overrightarrow{\text{Ib}}$ step. When the pseudo-equilibrium between gaseous and adsorbed butadiene is established, θ_b is expressed as:

$$\theta_b = Kp_b/(1+Kp_b) \tag{3}$$

where K is the adsorption constant. Then, by substituting Eq. (3) to Eq. (2), the final expression:

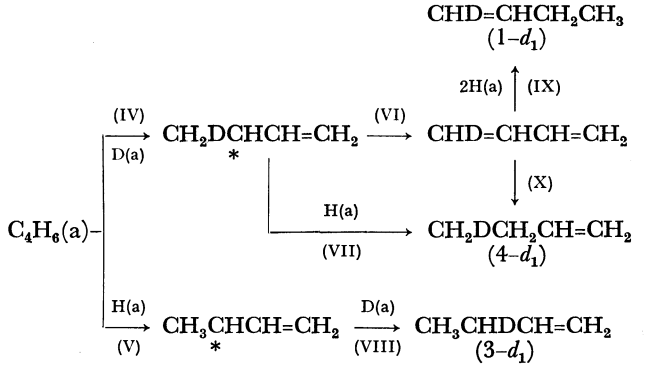
$$v = k_1 p_h/(1+Kp_b)^2 \tag{4}$$

is obtained. The pressure dependence shown by this equation is in accord with the empirical one given by Eq. (1). It should be noted that the same rate-determining step was concluded in the hydrogenation of ethylene on evaporated copper film at low temperatures.[12] No other mechanism which includes the disproportionation between two adsorbed butenyls as the rate-determining step can interpret the observed dependence of the rate on the butadiene pressure.

The remarkable formation of butene-d_0 at the early stage of reaction was quite similar to the formation of ethane-d_0 in the C_2H_4–D_2 reaction on the Ni surface.[13] The present situation of the reaction predicts the following order of the rates of elementary processes: $v(\overrightarrow{\text{Ib}}) < v(\overrightarrow{\text{III}}) < v(\overrightarrow{\text{Ia}}) \simeq v(\overleftarrow{\text{Ia}}) \simeq v(\overrightarrow{\text{II}}) \simeq v(\overleftarrow{\text{II}})$. Thus, it can be understood why the concentration of surface hydrogen becomes reasonably high, because the adsorbed deuterium is quickly consumed through the Ia and II steps by exchanging with hydrogen atoms in the hydrocarbon species. The observed isotope effect on the hydrogenation can be related to the straightforward isotope effect, as is seen in the adsorption of hydrogen and deuterium on copper.[11]

Transition metals of Group VIII, such as Ni,[1] Pd, and Pt,[2,3] provide a considerable amount of *trans*-2-

and *cis*-2-butenes in the products of the hydrogenation. These results can be explained by assuming π-allylic or σ-π bonded intermediates formed by the simultaneous interaction of two double bonds in butadiene with the surface atoms. In the case of copper, however, the absence of 2-butenes predicts that only one double bond of the molecule associates with the surface. The formation of 1-butene-1-d_1, 3-d_1 and 4-d_1 can be well expressed by making use of this adsorbed state:



where the asterisk indicates the active site. The attack of the terminal and second carbon atoms of the adsorbed butadiene with D and then H atoms produces butene-4-d_1 (IV and VII). The formation of 3-d_1 is attributed to the hydrogen addition in the reversed order (V and VIII). In the case of 1-d_1 formation, however, deuteriobutadiene-1-d_1 is hydrogenated with two hydrogen atoms (VI and IX). It is clear that no *n*-butenyl such as $\underset{*}{\mathrm{C}}\mathrm{H_2CH_2CH{=}CH_2}$ is produced on the surface, since such a formation would result in the formation of butadiene-d_1, $\mathrm{CH_2{=}CDCH{=}CH_2}$, the subsequent hydrogenation of which would produce both butene-2-d_1 and -3-d_1 in similar amounts. Therefore, it may safely be concluded that the reaction intermediate is isobutenyl, $\mathrm{CH_3\underset{*}{C}HCH{=}CH_2}$. At a high conversion of 48%, the fraction of deuterium at the 1t and 1c positions increases and that of 3-d_1 decreases. As the partial pressure of mono-deuteriobutadiene became higher with an increase in the conversion, the chance of a reaction proceeding *via* Steps (IX) and (X) increases as compared to the chance *via* Step (VIII).

The importance of surface defects in catalysis has been pointed out; Uhara *et al.*[14] reported that the activity of Cu on the decomposition of benzene diazonium chloride was markedly depressed by heat treatment around 350 °C and correlated this depression with the disappearance of dislocations. However, in the present study the decrease in the catalytic activity due to annealing was parallel to that of the surface area. This suggests that the activity of the hydrogenation is not due to the characteristic surface structure of defects, but depends only on the number of exposed metal atoms.[15] The fact that annealing at 500 and 180 °C makes no difference in the activation energy provides other evidence for this conclusion. The present result also supports the previous conclusion that the structural defects in the s-metals are less important in catalysis.[11]

X-Ray and electron diffraction studies indicated that the surfaces of Cu annealed at 180 and 500 °C were mainly composed of low index planes, such as (111), (100), and (110). The valence state of copper is characterized by a half-filled s-band which makes no directed bond. Therefore, the atomic distance in the lattice plane becomes a dominant factor in the interaction with adsorbed molecules. These lattice planes have the closest atomic distance of 2.56 Å; this configuration is not suited to the simultaneous use of two double bonds of butadiene upon adsorption, because the carbon-to-carbon bond length, 1.48 Å, is too short to make a bridge between two copper atoms. As for the isobutenyl radical on the surface, the length of the carbon chain containing a double bond is 1.54 Å. The intermediate can hardly find the copper atom located at a suitable position where the remaining double bond may interact so as to give adsorbed 2-butenes. Accordingly, it seems reasonable that this surface geometry is responsible for the high selectivity of 1-butene formation.

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