Study of Chemisorption and Hydrogenation of 2-Butenes on Platinum by Temperature-programmed Desorption

Shinji Tokitaka,† Hayao Imamura, and Susumu Tsuchiya*
Department of Industrial Chemistry, Faculty of Engineering, Yamaguchi University, Tokiwadai, Ube 755

(Received May 10, 1984)

The temperature-programmed desorption (TPD) chromatograms of *cis*- and *trans*-2-butene from platinum black comprised three peaks (A, B, and C) with peak maxima at about 253, 373, and 573 K, respectively. Peak A was identified to be *cis*- or *trans*-2-butene and butane. Peaks B and C were from mixtures of *cis*- or *trans*-2-butene and butane with a trace amount of propylene. The propylene may have been formed from chemisorbed *cis*- or *trans*-2-butene by decomposition as the temperature was raised during the subsequent TPD. The reactivities of various types of chemisorbed hydrogen previously detected by TPD were also investigated with regard to the hydrogenation of 2-butenes. Two types of chemisorbed hydrogen, presumed to be present on the surface in the form of hydrogen atoms, chemisorbed on top of platinum atoms and in the bridge form of molecular hydrogen, were found to react with 2-butenes.

The existence of four different chemisorbed species of hydrogen (α, β, γ, and δ) on platinum surfaces has previously been detected by a temperature-programmed desorption (TPD) with peak maxima at about 170, 250, 360, and 570 K, respectively.[1] The TPD chromatogram with four peak maxima has been confirmed by Verbeeks and Sachtler.[2] These chemisorbed species were tentatively assumed to correspond to two types of molecularly chemisorbed hydrogen (one in a linear form (α) and the other in a bridge form (β)) and two types of hydrogen atoms (one adsorbed right on top of metal atoms (γ) and the other in the interstices between the metal atoms(δ)). The differences in their reactivities have been investigated for the H_2–D_2 exchange reaction[3] and for the hydrogenation of ethylene,[4] and of propylene.[5] The reactivity, however, was not necessary the same: β-hydrogen not involved in the H_2–D_2 exchange reaction did react with ethylene and propylene to form ethane and propane, respectively.[4,5] It is, therefore, important to investigate this matter more deeply.

In the present study, 2-butenes were employed as the reactants to investigate differences in the reactivity of various forms of chemisorbed hydrogen since it is the lowest olefin that can be hydrogenated and isomerized.

The isotope exchange involving reactant olefins during the hydrogenation in the presence of deuterium has been of interest to many investigators.[6] Information related to this matter can contribute to the understanding of the mechanism regarding the hydrogenation of olefins. If the reactant olefin molecules are more rapidly exchanged than hydrogenated, the deuterated olefin molecules may be stably chemisorbed on the surface. In previous cases (ethylene[4] and propylene[5]) deuterated olefin molecules which were chemisorbed could not be measured. Since the chemisorbed state is an intermediate state, related information on this species is of importance.

In the present study, the chemisorbed species were removed by the TPD technique and collected for further analysis in order to obtain information on the reaction mechanism.

Experimental

Apparatus and Materials. The apparatus used was the same as that used previously[4] and consisted, basically, of two parts. The first part consisted of an adsorption and a reaction system in which adsorption and reaction were measured in conventional manners. The second part consisted of a TPD system, in which adsorbed gas was later desorbed into a carrier-gas stream (N_2 or He) by means of the programmed heating of a catalyst. The concentration of the desorbed gas was measured and recorded by means of a thermal conductivity detector. The catalyst was platinum black from the same lot previously employed.[4] Its surface area was $3.2\times10^3\,cm^2/g$ and the amount used was 2.18 g. The initial reduction and the treatment of the catalyst between experiments have also been described previously.[4]

Cylinder hydrogen (99.975%) supplied by the Osaka hydrogen Co. was stored in a reservoir for use as a reactant after having been passed over platinized silica at 720 K and then through a liquid-nitrogen trap. The same cylinder hydrogen could also be fed through to the reactor for the reduction of the catalyst. Matheson's deuterium (99.5%) passed through a liquid-nitrogen trap was also used as a reactant. *cis*- and *trans*-2-butene obtained from Tokyo Kasei Kogyo Co., Ltd., were purified by repeated distillation *in vacuo*; the purity was confirmed by means of gas chromatography to be more than 99%. High-purity helium (99.995%) and high-purity nitrogen (99.999%), obtained from the Seitetsu Kagaku Co., Ltd., were used as carrier gases for TPD after being passed through a molecular sieve trap.

Procedure. In a typical experiment with *cis*-2-butene, for example, a known amount of *cis*-2-butene was adsorbed for 15 min at the experimental temperature. The reactor was then cooled to 238 K with the *cis*-2-butene present in the gas phase, and kept for 90 min. Following this, the carrier gas, helium, was diverted from the bypass into the reactor in order to remove the *cis*-2-butene in its gas phase. After 5 min the catalyst was heated in a programmed manner. The heating was stopped at about 800 K, after which the catalyst was

---

† Present address: Toyo Soda Co., ltd., Tokuyama, 746.

kept in a helium stream for 20 min at the same temperature as before cooling. A more detailed description of the TPD method has been given elsewhere.[7] Reproducible results were usually obtained by this procedure. When the results were not reproducible, however, the catalyst was treated with oxygen to oxidize any organic contamination, and was then reduced by hydrogen. This treatment improved the reproducibility considerably.

In the hydrogenation of *cis*- and *trans*-2-butene, various types of chemisorbed hydrogen were first prepared by the TPD technique described previously,[1,3,8] and then olefin was admitted to the reaction system to start the reaction. Helium was added to dilute the olefin when the circulating pump in the reaction system was operated. After the reaction, all the system except for the reactor was evacuated through a liquid-nitrogen trap to collect any condensable hydrocarbons, which were transferred to a sampler for analysis. The carrier gas was then diverted into the reactor, and any materials adsorbed on the catalyst were removed by TPD.

The reactants, the reaction mixtures, and the desorption products were identified by gas chromatography. The deuterated hydrocarbons obtained after the reaction were analyzed by means of a JEOL JMS D-100 mass spectrometer. Before subjecting the reaction mixtures to mass-spectrometric analysis, if possible, they were separated gas chromatographically to avoid any mutual interference of the mass spectra.

Results and Discussion

Temperature-programmed Desorption. Figure 1 shows some typical TPD chromatograms taken after the *cis*-2-butene had been adsorbed on platium black in the absence, or presence, of hydrogen with helium used as the carrier gas. The pressure of the *cis*-2-butene or hydrogen admitted was *ca.* 5×10^2 Pa, and the reaction temperature was 238 K. These four TPD chromatograms resemble each other, characteristically being composed of three peaks with peak maxima at about 253, 373, and 573 K. These peaks are referred to as A, B, and C in the order of appearance with an increase in the temperature. By gas-chromatographic analysis, peak A was indentified to be *cis*-2-butene and butane. Peaks B and C were identified to be mixtures of *cis*-2-butene and butane with a trace amount of propylene. It is suggested that the butane was formed by the self-hydrogenation of chemisorbed *cis*-2-butene when hydrogen was absent. The propylene may have been formed by decomposition from the chemisorbed *cis*-2-butene heated by TPD.

Similar results were obtained for *trans*-2-butene. The description mentioned above is applicable if the word "*cis*-2-butene" is replaced by "*trans*-2-butene".

Reactivity of Chemisorbed Hydrogen. Table 1 shows the results of the surface-hydrogenation experiments with hydrogen preadsorbed on platinum black in various forms (the surface reactant) and with gaseous *cis*- or *trans*-2-butene subsequently admitted into the reaction system (the gas-phase reactant). No gaseous hydrocarbon other than 2-butenes and *n*-butane was observed under the present experimental conditions. The double-bond migration and the *cis-trans* isomerization of butenes and the skeletal isomerization of butane could not be detected. The amounts of butane formed in Series C-2 and T-2 with δ-hydrogen agreed well with that in Series C-1 and T-1 in which *n*-butane was formed by a self-hydrogenation reaction. Apparently, δ-hydrogen hardly reacts with the gas-phase reactant under the present experimental conditions.

In Series C-3 and T-3 with δ- and γ-hydrogen preadsorbed on the surface, however, relatively larger amounts of butane were produced than for Series C-2 and T-2. In the TPD chromatogram obtained after one of 2-butenes was admitted to the preadsorbed hydrogen, where nitrogen was used as the carrier

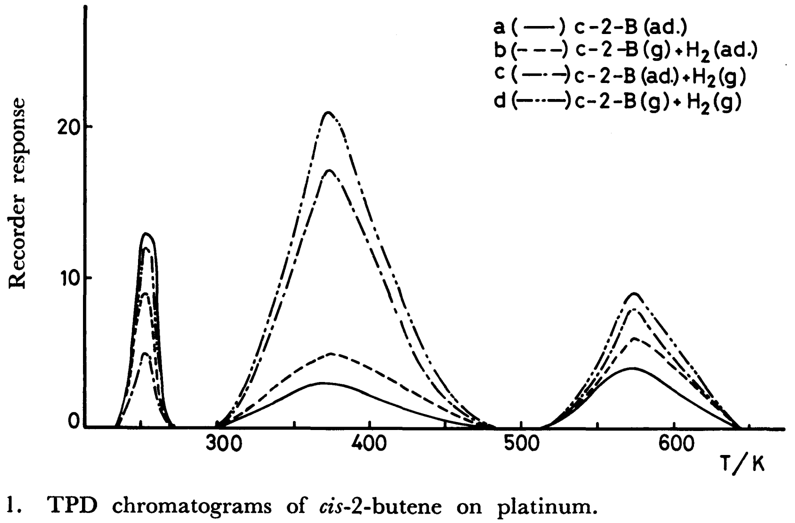

Fig. 1. TPD chromatograms of *cis*-2-butene on platinum.
(a): *cis*-2-Butene only was adsorbed, (b): H_2 was preadsorbed and *cis*-2-butene was subsequently admitted, (c): *cis*-2-Butene was preadsorbed and H_2 was subsequently admitted, (d): *cis*-2-Butene and H_2 were simultaneously admitted.

TABLE 1. HYDROGENATION OF *cis*-2-BUTENE (SERIES C1—C4) AND OF *trans*-2-BUTENE (SERIES T1—T4) ON PLATINUM BLACK[a]

Seriese	Surface reactant Type of chemisorbed hydrogen and estimated amount[b] (n/μmol) β	 γ	 δ	Gas phase Pressure of 2-butene (P/Pa)	 Butane formed (n/μmol)
C-1	—	—	—	893	0.054
C-2	—	—	0.518	786	0.062
C-3	—	0.187	0.540	960	0.183
C-4	0.464	0.223	0.652	920	0.214
T-1	—	—	—	826	0.080
T-2	—	—	0.504	826	0.094
T-3	—	0.178	0.509	986	0.170
T-4	0.357	0.178	0.513	906	0.237

a) Catalyst weight, 2.18 g. Reaction temp 238 K, and reaction time, 90 min. b) Estimated from TPD chromatograms in comparable experiments.

gas, the γ-hydrogen disappeared, while δ-hydrogen was still present in almost the same amount. It is, therefore, clear that γ-hydrogen is involved in the hydrogenation.

In Series C-4 and T-4 in which β-, γ, and α-hydrogen were preadsorbed, the formation of butane was again observed. The contribution of β-hydrogen to the hydrogenation, however, was not clear at this stage, because the amounts of butane formed were not much different from those of γ-hydrogen. Since the amounts of butane formed in C-4 and T-4 were not very much different from those in C-3 and T-3, the results may suggest that β-hydrogen makes a minor contribution, if at all.

To elucidate the point, the preadsorbed hydrogen was partially displaced by deuterium before *cis*- or *trans*-2-butene was introduced, and the deuteriobutanes formed by hydrogenation were then analyzed. The participation of the different types of chemisorbed hydrogen was consequently elucidated. For the sake of simplicity, the word "hydrogen" in the present paper will hereafter stand for both isotopes, protium and deuterium, and, where necessary, the individual isotopes will be designated as H and D. The types of surfaces used were as follows: 1) δ-Hydrogen was displaced by deuterium, and γ- and β-hydrogen were displaced by protium (βH–γH–δD); 2) δ- and β-hydrogen were displaced by deuterium, and γ-hydrogen was displaced by protium (βD–γH–δD); 3) δ-Hydrogen was displaced by protium, and β- and γ-hydrogen were displaced by deuterium (βD–γD–δH). The method of preparation was described previously;[8] the isolation of different types of chemisorbed hydrogen was confirmed by separate TPD experiments.

Table 2 shows the results of hydrogenation: The type of surface employed, the amounts of hydrogen preadsorbed and those of the individual deuteriobutanes formed by the hydrogenation are shown. The reactions were carried out at 238 K for 90 min. In the mass spectra of *cis*- or *trans*-2-butene, the reactant, the $m/e>56$ could not be observed, the ^{13}C contribution having been corrected; the H–D exchange between surface deuterium and gaseous *cis*- or *trans*-2-butene could not be detected.

Obviously, *cis*- and *trans*-2-butene were deuterated to deuteriobutanes over the βD–γH–δD, βD–γH–δH, and βH–γD–δH surfaces, but not over the βH–γH–δD surface. These results agree quite well with the above suggestions that δ-hydrogen does not, and γ-hydrogen does, participate in the hydrogenation. The results also suggest the participation of β-hydrogen, which was not clearly detected before.

It is natural that two possibilities for the participation of β-hydrogen be considered: 1) β-Hydrogen directly reacts with 2-butenes. 2) β-Hydrogen first converts to the γ-form and then reacts with 2-butenes. The very slow conversion of β-hydrogen to γ- and/or δ-hydrogen has previously been reported.[1] In this case, olefin was absent and only hydrogen was present in the system. Therefore, if such conversion takes place during the hydrogenation, the conversion must proceed very fast and the 2-butenes also act as accelerators for the conversion. Since the conversion is actually the dissociation of a hydrogen molecule and the accelerator compound generally contacts with a reactant, 2-butenes must come into contact with β-hydrogen. The step is, namely, a direct reaction. Accordingly, these two types are essentially the same.

After the reaction, the reactant, *cis*- or *trans*-2-butene adsorbed and the product, butane, adsorbed on the surface were removed by TPD technique, and then analyzed by means of the mass spectrometer. The mass spectrometric analysis of reactant olefins chemisorbed and removed by TPD could not be succeeded in the previous cases with ethylene and propylene,[4,5] because

TABLE 2. HYDROGENATION OF *cis*- AND *trans*-2-BUTENE WITH LABELED HYDROGEN CHEMISORBED ON PLATINUM BLACK[a)]

Type of surface employed	Surface reactant			Gas phase		Deuteriobutanes formed					
	Type of preadsorbed hydrogen and estimated amount[b)] (n/μmol)			Reactant type	Olefin pressure (P/Pa)	(n/μmol)					
	β	γ	δ			d_0	d_1	d_2	d_3	d_4	Total
βH-γH-δD	0.357	0.178	0.509	*cis*-2	920	0.054	—	—	—	—	0.054
βD-γH-δD	0.464	0.223	0.638	*cis*-2	986	0.098	0.013	0.045	—	—	0.156
βD-γH-δH	0.366	0.183	0.527	*cis*-2	880	0.201	0.013	0.040	—	—	0.254
βH-γD-δH	0.460	0.219	0.629	*cis*-2	973	0.156	0.018	0.076	0.009	0.004	0.263
βH-γH-δD	0.339	0.174	0.495	*trans*-2	840	0.250	—	—	—	—	0.250
βD-γH-δD	0.357	0.178	0.513	*trans*-2	906	0.116	0.045	0.076	—	—	0.237
βD-γH-δH	0.375	0.187	0.536	*trans*-2	826	0.228	0.027	0.067	—	—	0.322
βH-γD-δH	0.335	0.170	0.491	*trans*-2	813	0.223	0.001	0.022	0.007	0.003	0.256

a) Catalyst weight, 2.18 g. Reaction temp 238 K, and reaction time 90 min. b) Estimated from TPD chromatograms in comparable experiments.

TABLE 3. TPD PRODUCTS AFTER HYDROGENATION OF *cis*- AND *trans*-2-BUTENES

Type of surface employed	Reactant 2-butene	TPD peaks	Deuterio-2-butenes (n/μmol)					Deuteriobutanes (n/μmol)			
			Type	d_0	d_1	d_2	Total	d_0	d_1	d_2	Total
		A		0.06	—	—	0.06	0.03	—	—	0.03
βH-γH-δD	*cis*	B	*cis*	0.24	—	—	0.24	0.04	—	—	0.04
		C		0.10	0.01	—	0.11	0.02	—	0.01	0.03
		A		0.11	—	—	0.11	0.11	—	—	0.11
βH-γH-δD	*trans*	B	*trans*	0.13	—	—	0.13	0.15	—	—	0.15
		C		0.29	0.01	0.01	0.31	0.08	—	—	0.08
		A		0.06	0.01	—	0.07	0.04	0.01	0.01	0.06
βH-γD-δH	*cis*	B	*cis*	0.20	0.05	0.02	0.27	0.01	0.01	0.02	0.04
		C		0.11	0.01	—	0.12	0.03	0.01	0.02	0.06
		A		0.39	—	0.01	0.40	0.10	0.01	0.01	0.12
βH-γD-δH	*trans*	B	*trans*	0.27	0.01	0.02	0.30	0.09	—	0.01	0.10
		C		0.20	0.01	0.02	0.23	0.11	—	0.01	0.12
		A		0.14	0.01	—	0.15	0.06	0.01	0.03	0.10
βD-γH-δH	*cis*	B	*cis*	0.12	0.01	—	0.13	0.05	0.01	0.02	0.08
		C		0.16	0.02	0.01	0.19	0.06	0.02	—	0.08
		A		0.08	0.02	0.01	0.11	0.18	0.05	0.05	0.28
βD-γH-δH	*trans*	B	*trans*	0.03	0.01	0.01	0.05	0.17	—	0.01	0.18
		C		0.07	—	—	0.07	0.12	0.02	0.04	0.18

the amounts of olefins desorbed were too small to be transferred to the sampler for analysis. The results of *cis*- and *trans*-2-butene are shown in Table 3; deuterio-2-butenes and deuteriobutanes were observed. Since any deuteriobutene was not observed in the gase phase, the results suggest that the hydrogenation of chemisorbed *cis*- or *trans*-2-butene is easier than the desorption.

In peak A, any deuterio-2-butene was not observed in the case with βH-γH-δD surface. The result suggests that δ-deuterium does not react with *cis*- and *trans*-2-butene to form deuterio-2-butenes below 273 K. The formation of deuterio-2-butenes observed in the case of the βD-γH-δD and of the βD-γH-δH surfaces was therefore due to the participation of β-deuterium. In the case of the βH-γD-δH surface, the deuterio-2-butenes observed may have been formed by a reaction with γ-deuterium at 238 K.

In peak B, no deuterio-2-butenes was observed in the case of the βH-γH-δD surface. Since peak B appeared between 290—490 K, and since δ-hydrogen, peak δ, appeared between 470—670 K, δ-deuterium does not suggestively participate in the H–D exchange reaction with 2-butenes. The result with βH–γD–δH surface is reasonably explained by the participation of γ-deuterium.

Small amounts of deuterio-2-butenes were observed in the case of the βD–γH–δD and of the βD–γH–δH surfaces, where the γ-hydrogen was protium. The results can be explained in such a way that the deuterio-2-butenes were formed from β-deuterium and 2-butenes at a lower temperature and, subsequently, desorbed by the rise of temperature.

Peak C appeared between 510—650 K, where δ-hydrogen mostly desorbed. In the case of the βH–γH–δD surface, therefore, the deuterium atoms in deuterio-2-butenes observed obviously came from δ-deuterium, which is only deuterium source.

In the case of the βD–γH–δH surface, some amounts of deuterio-2-butenes were observed. The result suggests that the deuterium atoms in the deuterio-2-butenes came from β-deuterium, and that deuterio-2-butenes formed at a lower temperature subsequently desorbed by the rise of temperature during TPD. In the case of the βH–γD–δH surface, deuterio-2-butenes observed may also be formed during TPD. The results with βD–γH–δD surface are qualitatively consistent with the explanation mentioned above.

The results of the mass spectrometric analysis of deuteriobutanes in peak A, B, and C shown in Table 3 agree quite well with the above suggestions that β- and γ-hydrogen do, and δ-hydrogen does not, participate in the hydrogenation.

In peak B, small amounts of deuteriobutanes were observed in the case of the βD–γH–δD and of the βD–γH–δH surface, where the γ-hydrogen was protium, but the β-hydrogen was deuterium. The results can be explained in such a way that the deuteriobutanes were formed from β-deuterium and 2-butene at a lower temperature and subsequently desorbed by the rise of temperature.

Peak C appeared between 510—650 K, where δ-hydrogen was mostly desorbed. In the case of the βH–γH–δD surface, therefore, the deuterium atoms in deuteriobutanes observed obviously came from δ-deuterium, which was the only deuterium source.

For the βD–γH–δH surface, some amounts of deuteriobutanes were observed. The result suggests that the deuterium atoms in the deuteriobutanes may have come from β-deuterium, and that deuteriobutanes formed at a lower temperature was subsequently desorbed by the rise of temperature during TPD. In the case of the βH–γD–δH surface, deuteriobutanes observed may also be formed during TPD. The results regarding the βD–γH–δD surface are qualitatively consistent with the explanation mentioned above.

A mass spectrometric analysis of propylene with regard to peaks B and C, was not carried out since the amount of propylene was too small to be separated from other components and from the carrier gas by condensation in the gas chromatograph stream. If any deuteriopropylene is observed, they are reasonably considered to have been formed from the chemisorbed deuteriobutenes by decomposition during TPD. The deuteriobutenes, however, do not necessary give the deuteriopropylenes which may depend on the degree of deuteration and the mechanism of decomposition of the chemisorbed deuteriobutanes.

Regarding the mechanism of the hydrogenation of olefins, extensive studies have been reported.6,9,10) In the hydrogenation of ethylene over platinum catalyst, Bond-Wells mechanism may be accepted. According to the IR study by Soma (Soma-Noto),10) π-adsorbed ethylene was easily hydrogenated at such low temperature as 195 K, and no hydrogenated species remained on the surface. The obsevation is consistent with the present result that the hydrogenation of *cis*- or *trans*-2-butene was more rapid than the desorption. Accordingly, the following scheme of the hydrogenation of *cis*- or *trans*-2-butene may be suggested. *cis*- or *trans*-2-butene is first chemisorbed on the surface and rapidly exchanged with the surface deuterium, without desorbing from the surface. The deuterio-2-butenes formed are stably chemisorbed on the surface with π-bond. Then, the deuterio-2-butenes are hydrogenated to deuteriobutanes and desorbed from the surface.

The four types of chemisorbed hydrogen were tentatively assigned on the basis of the previous results1) and the postulates of other workers.11–16) The γ- and δ-hydrogen were assigned to the weakly and strongly chemisorbed hydrogen atoms so far proposed. The α-hydrogen was assigned to the linearly chemisorbed hydrogen molecules. The β-hydrogen was the intermediate between α- and γ-hydrogen. Later, Primet *et al.*17) and Dixon *et al.*18,19) independently proposed their assignment on the basis of the IR studies. Dixon *et al.* deduced the existence of five kinds of hydrogen adsorption. Type I is physisorption, and the other four types, II—V, were corresponded to α—δ hydrogen.

It has previously been presumed that γ-hydrogen is present on the surface in the form of hydrogen atoms chemisorbed on top of platinum atoms, and that β-hydrogen is molecular hydrogen chemisorbed in a bridge form.1) The difference in the reactivity may, accordingly, be due to the chemisorbed state, whether or not the H–H bond has been split. In the H_2–D_2 exchange reaction, β-hydrogen is not reactive, but it is reactive in the hydrogenation of olefins, and in the H–D exchange between the surface deuterium and 2-butenes. It is, accordingly, probable that a different tendency would be shown depending upon the sort of reaction; the explication of the other reactions awaits further investigations.

Conclusion

While some of the information could perhaps be obtained otherwise, the TPD technique in many cases can be used with unique advantage. Although the information that 2-butenes are more strongly chemisorbed than hydrogen on a catalyst had already been suggested on the basis of kinetic data,[9] it was more clearly shown by TPD, and in addition, the amounts of chemisorbed species could be estimated. Using isotopes, the individual chemisorbed species can be differently labeled, and the reactivity of each is separately measurable. The participation of various types of chemisorbed hydrogen in the 2-butenes hydrogenation were similar to that in the hydrogenation of ethylene and of propylene. γ-Hydrogen, presumed to be present on the surface in the form of hydrogen atoms chemisorbed on top of platinum atoms and β-hydrogen, presumed to be molecular hydrogen chemisorbed in a bridge form, were found to be involved in the 2-butenes hydrogenation. The information on the chemisorbed deuterio-2-butenes during the reaction revealed by the labeled TPD technique, suggests the following scheme of hydrogenation: *cis*- or *trans*-2-butene chemisorbed was first exchanged with deuterium to form deuterio-2-butenes, and before desorbing from the surface, the deuterio-2-butenes were hydrogenated to form deuteriobutanes.

The authors are grateful to Dr. Shizuo Fujisaki of this faculty for obtaining the mass spectra. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, and by Watanabe foundation for which the authors' thanks are due.

References

1) S. Tsuchiya, Y. Amenomiya, and K. J. Cvetanović, *J. Catal.,* **19**, 245 (1970).

2) H. Verbeek and W. E. H. Sachtler, *J. Catal.,* **42**, 257 (1976).

3) S. Tsuchiya, Y. Amenomiya, and K. J. Cvetanović, *J. Catal.,* **20**, 1 (1971).

4) S. Tsuchiva and M. Nakamura, *J. Catal.,* **50**, 1 (1977).

5) S. Tsuchiya, M. Nakamura, and N. Yoshioka, *Bull. Chem. Soc. Jpn.,* **51**, 981 (1978).

6) G. C. Bond, "Catalysis by Metals," Academic Press, *New York, 1962, p. 229.*

7) K. J. Cvetanović and Y. Amenomiya, "Advances in Catalysis," ed by D. D. Eley, H. Pines, and P. B. Weisz, Vol. 17, p. 103, Academic Press, New York, 1967.

8) N. Yoshioka, M. Nakamura, and S. Tsuchiya, *Chem. Lett.,* **1977**, 445; S. Tsuchiya, *Hyomen,* 16 (2), 65 (1978).

9) G. C. Bond, and P. H. Wells, "Advances in Catalysis," ed by D. D. Eley, H. Pines, and P. B. Weisz, Vol. 15, p. 91, Academic Press, New York, 1964.

10) Y. Soma, *J. Catal.,* **59**, 239 (1979).

11) W. A. Pliskin and R. P. Eischens, *Z. Phys. Chem.,* **24**, 11 (1962).

12) T. Toya, *J. Res. Inst. Catal., Hokkaido Univ.,* **10**, 236 (1962).

13) R. Suhrmann, "Advances in Catalysis and Related Subject," ed by W. G. Frankenburg, V. I. Komarevsky, and E. K. Rideal, Vol. 7, (1955) p. 303.

14) J. C. P. Mignolet, *J. Chim. Phys.,* **54**, 19 (1957).

15) R. Suhrmann, G. Wedler, and H. Gentsch, *Z. Phys. Chem.,* **17**, 350 (1958).

16) W. H. Smith, H. C. Eckstrom, and F. Bär, *J. Phys. Chem.,* **72**, 369 (1968).

17) M. Primet, J. M. Basset., and M. V. Mathieu, *J. Catal.,* **28**, 368 (1973).

18) L. T. Dixon, R. Barth, and J. W. Gryder, *J. Catal.,* **37**, 368 (1975).

19) L. T. Dixon, R. Barth, R. J. Kokes, and J. W. Gryder, *J. Catal.,* **37**, 376, (1975).