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Promoting Effect of Oxygen for Hydrogenation of Butadiene over Ni_2P Catalyst

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The influence of oxygen on the rate of hydrogenation of butadiene over Ni_2P catalyst has been investigated in the view of the results reported previously (Nozaki, F., and Adachi, R., *J. Catal.* **40**, 166, 1975).

When a partial pressure of several mm Hg of oxygen was added into the reactant gas mixture, the hydrogenation activity increased remarkably in a complicated manner following an induction period. In addition, the oxygen resulted in a significant increase in the amount of adsorption of hydrogen. The temperature-programmed desorption spectrum of oxygen gives the definitive evidence that there are at least two different surface species of oxygen. Furthermore, with the aid of the information obtained from measurements of adsorption isotherms, infrared spectra of the catalyst, and analysis of the deuterium distribution of the products formed in the reaction of butadiene with D_2, a plausible mechanism for the promoting effect of oxygen on hydrogenation has been proposed.

INTRODUCTION

It is known that hydrogenation activity of metallic catalysts is lowered, in most cases, by addition of oxygen or certain oxygen-containing substances (*1*), although Ref. (*2*), describing the promoting effect of trace oxygen on the hydrogenation activity of Ni catalyst, should be noted. We previously reported (*3*) a structure–activity relationship for a catalyst which was prepared by reduction of $Ni_3(PO_4)_2$ in hydrogen and tentatively pointed out the interesting fact that Ni_2P catalyst prepared at 600°C showed a significant increase in activity for hydrogenation of butadiene by the addition of oxygen to the extent of several mm Hg; in contrast, a metallic Ni catalyst prepared at lower temperatures showed only a steep decrease in activity on the addition of a very small amount of oxygen. In addition, we have reported (*4*) that in the dehydrogenation of methylcyclohexane to toluene, the pretreatment of Ni_2P catalyst with oxygen results in a drastic increase in activity. However, the detailed mechanism of a characteristic promoting effect of oxygen concerning the Ni_2P catalyst has not yet been elucidated.

The first aim of the present investigation was to confirm in detail the promoting effect of oxygen, a preliminary report of which has been published (*3*), and the second was to ascertain the promoting mechanism of oxygen on the basis of information obtained from adsorption measurement, ir absorption spectra, temperature-programmed desorption, and analysis of the deuterium distribution in the products obtained from the reaction between C_4H_6 and D_2.

EXPERIMENTAL METHODS

The catalyst employed in this work was prepared using the same method described in a previous paper (*3*). Ni_2P (20 wt%)–Al_2O_3 catalyst, which was obtained from alumina-supported nickel phosphate by reduction in hydrogen at 600°C, was about 120 m^2/g in surface area, as determined by the BET method using nitrogen as an adsorbate, and its chemical formula of nickel phosphide was identified as Ni_2P by the X-ray diffraction pattern of the catalyst.

The hydrogenation reaction of butadiene

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and the H_2–D_2 exchange reaction were carried out in a conventional closed circulation apparatus using a method similar to that described in (*3*). Butadiene (99.7% purity), hydrogen (99.6%), and deuterium (containing 0.3% HD) were obtained from the Takachiho Company, Ltd., and were used without further purification. The composition of the products in the hydrogenation of butadiene was determined by the use of the gas chromatograph described in (*3*). The conversion of the H_2–D_2 exchange reaction was followed by means of a gas chromatograph connected directly to the reaction system. A column of 1.5 m γ-Al_2O_3–$MnCl_2$, which was reported by Yasumori and Ohno (*5*), was used at the temperature of liquid nitrogen for the separation of H_2, HD, and D_2. In the reaction of butadiene with D_2, the products were analyzed by using gC–ms equipment (Shimazu LKB-9000) for the separation of butadiene, butene isomers, and hydrogens and for the determination of the deuterium distribution in butene isomers.

The adsorption measurements of oxygen or hydrogen on the catalyst were made volumetrically by a conventional closed system. The temperature-programmed desorption spectra were obtained by means of the apparatus reported by Cvetanovic and Amenomiya (*6*), and the temperature of the cell containing the catalyst was raised at the constant rate of 20°C/min by means of an electric furnace. The desorption of surface species from heated catalyst to helium carrier gas was monitored by means of a thermal conductivity cell.

In order to clarify the adsorption state of oxygen or hydrogen over the catalyst, investigations by ir spectroscopy were made. Infrared spectra were recorded in absorbance using a Nippon-Bunko IRA-1 spectrometer. The catalyst disks (15–25 mg/cm^2) were prepared by compressing small amounts of the catalyst containing Cabosil (in the ratio of about 1:5 by weight), used as a binder for making a catalyst wafer, under a pressure of 300 kg/cm^2. The ir Pyrex cell fitted with an NaCl window could be heated *in vacuo* at any desired temperature and the catalyst could be exposed to the purified adsorbate gas such as oxygen or hydrogen, which were stored in vessels on the conventional adsorption apparatus.

RESULTS AND DISCUSSION

Influence of Oxygen on the Hydrogenation of Butadiene

Hydrogenation activity of the Ni_2P catalyst was affected in a complicated way by changing the oxygen concentration added to the reacting gas. Figure 1 shows the rate of pressure decreases during the course of reaction under various conditions of oxygen pressure.

When oxygen was added into the reacting gas, an induction period having a slow rate of pressure decrease appeared in the initial stage and a rapid hydrogenation occurred after some time. The induction period was prolonged by increasing the oxygen pressure. The maximum rate of pressure decrease was observed after the end of the induction period and depended upon the oxygen pressure. In each run, we define the

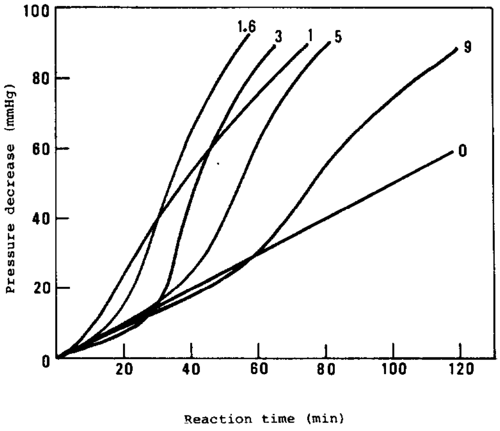

FIG. 1. Pressure decrease–reaction time curves at various oxygen pressure. Reaction temperature, 70°C; catalyst weight, 0.5 g; initial hydrogen pressure, 225 mm Hg; initial butadiene pressure, 75 mm Hg. The number at each curve is the oxygen pressure, in mm Hg, at which oxygen was mixed into the reactant gas.

maximum rate in the pressure decrease as the reaction rate (r_0) of hydrogenation. A correlation between r_0 and the oxygen pressure is shown in Fig. 2; the changes in hydrogenation selectivity are also shown. Figure 2 indicates that r_0 increases with an increase in oxygen pressure, reaches a maximum at about 3 mm Hg, and then decreases. The enhanced reaction rate on addition of 3 mm Hg oxygen was about six times that in the case when hydrogenation was carried out without the addition of oxygen. The variation in hydrogenation selectivity with the addition of oxygen was usually slight; however, increasing the oxygen pressure tended to decrease the selectivity, S_1, for the partial hydrogenation to butene isomers and to increase the selectivity, S_2, for the formation of 1-butene. The promoting effect of oxygen on the reaction rate could also be detected whether oxygen was present in the reacting gas mixture or in the gas used for pretreatments of the catalyst.

The dependence of the reaction rate on the partial pressure of C_4H_6 or H_2 is illustrated in Fig. 3. It can be seen that, both before and after the oxygen addition, the reaction rates are approximately expressed by the equation $r = kP_{C_4H_6}^{0.2}P_{H_2}^{0.8}$, where k is the rate constant (in min^{-1}). Although the dependence of hydrogenation rate on partial pressure would be expected to vary with or without the oxygen addition, the result was approximately of the same order in the power rate formula.

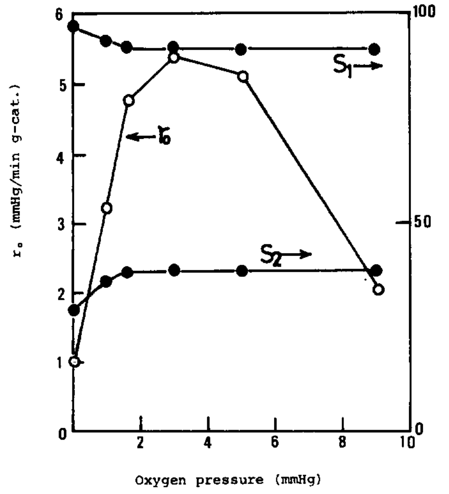

FIG. 2. Reaction rates and selectivities as a function of oxygen pressure. Reaction rate, r_0; selectivity for partial hydrogenation to butene isomers, S_1 = $C_4H_8/C_4H_8 + C_4H_{10}$; selectivity to 1-butene, S_2 = 1 − C_4H_8/1-C_4H_8 + *trans,cis*-2-C_4H_8. The reaction conditions are the same as for Fig. 1.

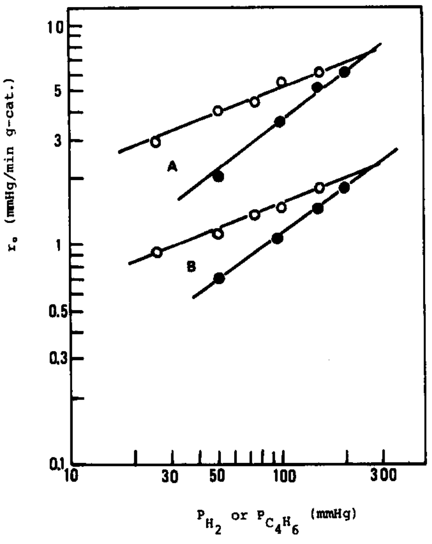

FIG. 3. Reaction rates as a function of partial pressure. Reaction temperature, 70°C; cat. wt, 0.5 g. (A) After 3 mm Hg oxygen was added into the reactant gas; (B) before addition of oxygen. ○, Effect of butadiene partial pressure (P_{H_2} was kept at 100 mm Hg); ●, effect of hydrogen partial pressure ($P_{C_4H_6}$ was kept at 50 mm Hg).

The dependency of the reaction rate on the temperature was examined by varying the temperature from 40 to 100°C. The apparent activation energy for the hydrogenation was found to be about 12 kcal/mol for the reaction without oxygen and about 10 kcal/mol for the reaction with oxygen; thus we concluded that the effect of oxygen on the activation energy was very slight.

In order to clarify the behavior of the promoting effect of oxygen on the activity of Ni_2P catalyst, the influence of evacuation treatment on the succeeding hydrogenation of butadiene was carefully tested. The examination was carried out in the following manner: the rapid hydrogenation with the addition of 3 mm Hg oxygen was run in the first step, and subsequent hydrogenation without oxygen was repeated after the catalyst had been evacuated for 30 min at the desired temperature. The result, shown in Fig. 4, indicates that the enhanced activity resulting from the addition of oxygen remains unaltered until the catalyst is evacuated at temperatures above 50°C. When the catalyst is then evacuated at temperatures above 50°C, the enhanced activity gradually decreases with the increase in evacuation temperature and is lowered to the original activity level prior to addition of oxygen. Thus, it can be speculated that the catalyst contacted with oxygen contains at least two types of surface species of oxygen: one is the oxygen which is readily desorbed by evacuation even at temperatures below 50°C and leads to the appearance of the induction period, but is not responsible for the enhancement of hydrogenation activity. The other oxygen species promotes the hydrogenation and is not desorbed unless the catalyst is evacuated at temperatures above 50°C.

Another characteristic feature to be noted here is the disappearance of the induction period by evacuation treatment. When the catalyst is evacuated below 50°C, the induction periods shown in Fig. 1 can be eliminated without any loss of the oxygen-enhanced activity. This fact is believed to be due to the removal of the excess oxygen which causes the induction period, while the oxygen available for the enhancement of catalyst activity remains over the catalyst surface even after the catalyst has been evacuated.

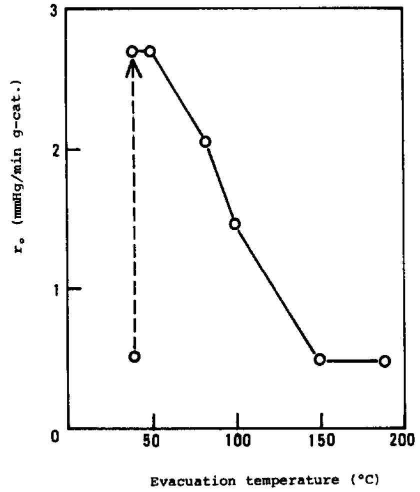

FIG. 4. Change in hydrogenation activity with variation of evacuation temperature after addition of oxygen. Temperature, 40°C; cat. wt, 0.5 g; initial partial pressures of H_2 and C_4H_6 are the same as for Fig. 1. The dashed line indicates the increase in activity on addition of 3 mm Hg oxygen.

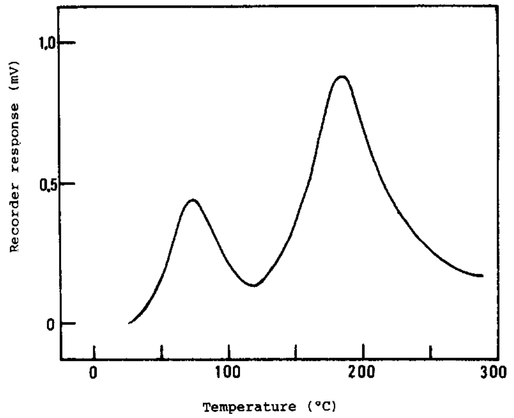

FIG. 5. Temperature-programmed desorption spectrum of oxygen adsorbed on the catalyst. Catalyst wt, 0.7 g; flow rate of helium carrier gas, 30 ml/min; heating rate of the catalyst, 20°C/min.

Adsorption of Oxygen or Hydrogen over Ni_2P Catalyst

In order to offer further corroborating evidence that there are at least two kinds of surface species after the catalyst has been exposed to oxygen, the temperature-programmed desorption spectra were investigated. A typical spectrum is shown in Fig. 5.

Figure 5 shows two broad peaks from 40 to 120°C, with a maximum at about 80°C, and from 120 to 250°C, with a maximum at about 180°C; the latter peak for the strongly adsorbed oxygen is much larger than the peak for the weakly adsorbed oxygen. The evidence that both peaks are caused by desorption of the oxygen surface species has been demonstrated by mass spectrometry. Alumina used alone as a carrier of the catalyst had no detectable peak in the thermal desorption measurement. From a comparison of Figs. 4 and 5, it can be seen that there is a significant difference in the desorption temperature of oxygen. However, this might be due to the difference in the experimental method. In the temperature-programmed desorption technique, the activation energy of oxygen desorption was determined by a method similar to the procedure of Cvetanovic and Amenomiya (*6*). Consequently, the activation energy of desorption was found to be about 7 kcal/mol for the oxygen being desorbed at the low-temperature range (40–120°C) and about 28 kcal/mol for the oxygen being desorbed at the high-temperature range (120–250°C). By reference to the results on the desorption of oxygen reported by many workers (*7–9*), it can be presumed that the oxygen being desorbed at low temperatures with a small activation energy of desorption is the surface species adsorbed in the molecular state, whereas the oxygen being desorbed at high temperatures with a large activation energy of desorption is the surface species adsorbed in the dissociative state. It was difficult to estimate the desorption amount of oxygen because of an imperfection of the separation from peak to peak. However, a rough calculation showed about 2×10^{18} molecules/g-cat. for the weakly held oxygen and about 5×10^{18} molecules/g-cat. for the strongly held oxygen.

The temperature-programmed desorption technique was applied to the hydrogen desorption in a manner similar to that used for the oxygen desorption. In the case in which hydrogen was adsorbed on the catalyst without oxygen, the desorption spectra of hydrogen showed a relatively sharp, small peak with a maximum at about 180°C. In contrast, in the case of the catalyst pretreated with oxygen, the desorption spectra showed a broad, large peak spread over the wide temperature range 70–350°C. This broad peak was complicated because both hydrogen and oxygen desorption were simultaneously encountered. Therefore, it was impossible to determine the desorption amount of hydrogen even roughly. However, it can be said with certainty that the pretreatment with oxygen increases remarkably the amount of hydrogen adsorbed.

The ir spectra of the catalyst and the sample after oxygen treatment are illustrated in Fig. 6. In the range 910–970 cm^{-1}, a catalyst disk, after oxygen had been preadsorbed, showed a new, single, sharp peak with a minimum at 940 cm^{-1}, (spectrum 1). This absorption band centered at 940 cm^{-1}, was completely missing both in spectrum (2) of the catalyst itself and in spectrum (3) of Cabosil, which was used as a binder for the sake of convenience in the preparation of the catalyst disk. This new absorption band reversibly developed or disappeared with oxygen addition or evacuation at temperatures above 150°C. By reference to (*10*), this band was assigned to P–O stretching vibration. Thus, oxygen is probably being dissociatively adsorbed on the P atom of the Ni_2P catalyst.

An attempt using ir spectroscopy was also made to characterize the adsorption of

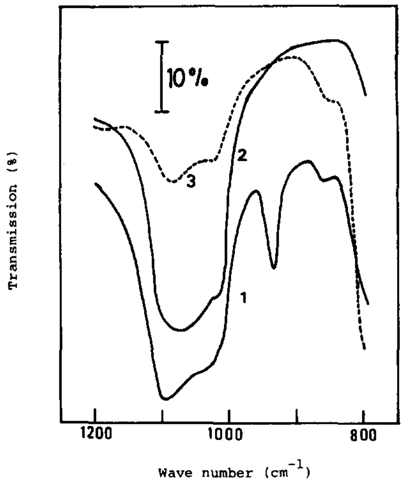

FIG. 6. Infrared spectra of the Ni_2P catalyst. (*1*) After addition of oxygen; (2) before addition of oxygen; (3) spectrum of Cabosil used as a binder for preparation of catalyst disk.

hydrogen; however, no special change in the spectrum could be detected before or after the adsorption of hydrogen regardless of whether or not the catalyst had been pretreated with oxygen.

In a preliminary investigation, it had been found that the preadsorption of oxygen on the Ni_2P catalyst induced a considerable increase in the adsorption of hydrogen. Thereupon, further details were studied on the adsorption of hydrogen before and after the catalyst was pretreated with oxygen. The adsorption isotherms, shown in Fig. 7, indicate that the adsorption amount of hydrogen is increased several times by the preadsorption of oxygen. By applying the conventional treatment of the Langmuir-type expression to the adsorption data, we obtained the results shown in Fig. 8. A plot of $1/P_{H_2}^{1/2}$ vs $1/N_{ads}$ for the catalyst without oxygen pretreatment and a plot of $1/P_{H_2}$ vs $1/N_{ads}$ for the catalyst with oxygen pretreatment yielded good linear correlation.

Information Obtained from the Experiments Using Deuterium

The H_2–D_2 exchange reaction over Ni_2P catalyst proceeded in the temperature range 0–100°C, although the reaction rate depended to some degree on whether or not the catalyst was pretreated with oxygen. The rate of HD formation was followed by first-order kinetics: $\ln X_e/(X_e - X_t) = k't$, where X_e and X_t are HD mole fractions at equilibrium and at time t (min), respectively, and k' is the rate constant (min^{-1}). As an example, the result obtained at 90°C is shown in Fig. 9. From the slopes of the straight lines, k' was evaluated to be about 7.5×10^{-2} for the catalyst without oxygen pretreatment and about 5.3×10^{-2} for the catalyst with oxygen pretreatment. The fact that oxygen pretreatment tends to somewhat decrease the rate of HD formation is particularly interesting because of the pronounced contrast with the finding that oxygen results in a considerable increase in the rate of butadiene hydrogenation. No precise explanation for the opposite effects of oxygen treatment observed in the hydrogenation of butadiene and in the H_2–D_2 exchange reaction can be offered at the present time.

The results of the butadiene hydrogenation, when C_4H_6 was reacted with an equimolar mixture of H_2 and D_2, are summa-

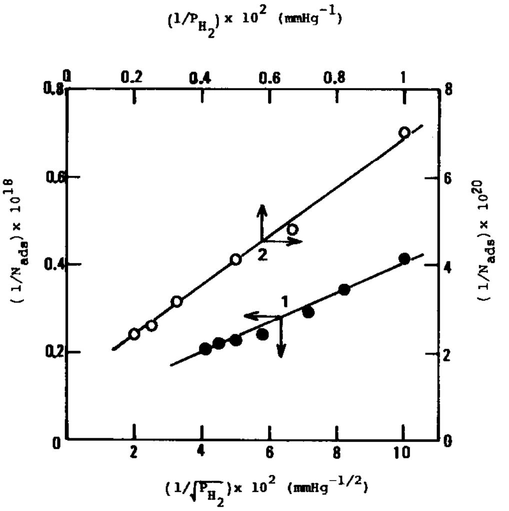

FIG. 8. $1/N_{ads}$ vs $1/P_{H_2}^{1/2}$ plot and $1/N_{ads}$ vs $1/P_{H_2}$ plots. (1) For the adsorption data shown by curve 1 in Fig. 7; (2) for the adsorption data shown by curve 2 in Fig. 7.

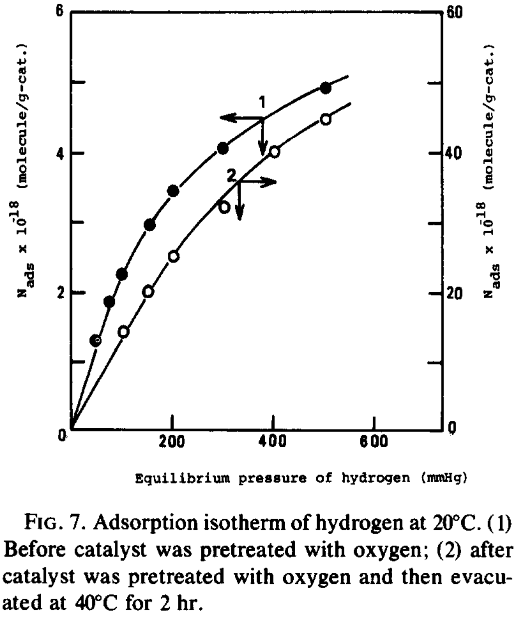

FIG. 7. Adsorption isotherm of hydrogen at 20°C. (1) Before catalyst was pretreated with oxygen; (2) after catalyst was pretreated with oxygen and then evacuated at 40°C for 2 hr.

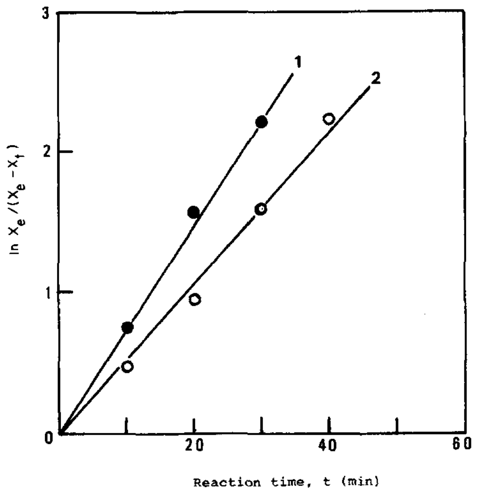

FIG. 9. ln $X_e/(X_e - X_t)$ vs t plots for H_2–D_2 exchange reaction at 90°C. (1) Before addition of oxygen; (2) after catalyst was pretreated with oxygen and then evacuated at 40°C for 2 hr.

rized in Table 1. The amounts of butane formed were negligibly small. The hydrogenation to butene isomers and the H_2–D_2 exchange reaction proceeded simultaneously, although the rate of the H_2–D_2 exchange reaction was considerably lowered by the coexistence of butadiene. The distribution of deuterium in the butene isomers was restricted to the narrow range butene-d_0 ~ -d_2, that is, the deuterobutene containing more than three deuterium atoms was rarely found in the product. In Table 1, it is worth noting that there is a characteristic difference in the distribution of deuterobutenes between the non-pretreated and pretreated catalysts. For the non-pretreated catalyst, the fraction of formation of butenes decreases in the order of butene-d_0 > -d_1 > -d_2, and especially in the initial stage of low conversion butene-d_0 and -d_1 are the main products. In contrast, in the catalyst pretreated with oxygen, the fraction of formation of butene-d_0 ~ -d_2 is quite irregular as butene-d_0 > -d_2 ≫ -d_1, and in the initial stage of the reaction the formation of butene-d_1 is very slight. Such behavior in the distribution of deuterium suggests that the hydrogenation of butadiene to butene isomers proceeds via the different route depending on whether or not the catalyst has been pretreated with oxygen. That is to say, the hydrogenation over the non-pretreated catalyst occurs successively through a stepwise addition of H atoms, whereas the pretreated catalyst promotes the hydrogenation in which the addition of two atoms of hydrogen occurs at once by the capture of a hydrogen molecule. This speculation of the reaction path is consistent with the other information obtained in this work.

On the basis of the Results and Discussion, the adsorption model of oxygen and hydrogen over the Ni_2P catalyst is depicted in Fig. 10. According to this model, the reason the induction period appears in the initial stage when small amounts of oxygen coexist with reacting gas is presumed as follows: the oxygen molecules adsorbed over Ni atoms of the Ni_2P catalyst are

TABLE 1

Deuterium Distribution of Products Obtained from the Reaction of C_4H_6 with a Mixture of H_2 + D_2[a]

	Reaction temp. (°C)	Conversion of C_4H_6	Hydrogen (mol%)			Butene (mol%)			
			H_2	HD	D_2	d_0	d_1	d_2	d_3–d_8
Without oxygen preadsorption	60	62	34	29	37	41	34	25	0
With oxygen preadsorption	50	60	40	18	42	52	8	40	0

[a] An equimolar mixture of H_2 and D_2 was used for the reaction; Initial pressures of C_4H_6 and H_2 + D_2 were 75 and 225 mm Hg, respectively. The deuterium distribution in the butene is the average value of the butene isomers.

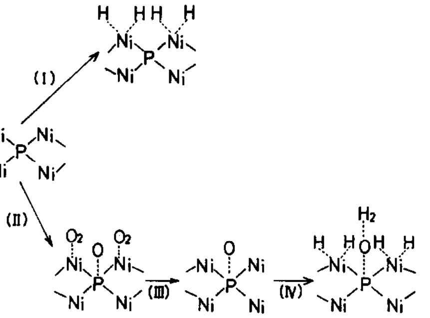

FIG. 10. Plausible model for the adsorption of hydrogen over Ni_2P catalyst before and after addition of oxygen. (I) When exposed to hydrogen before addition of oxygen; (II) when exposed to oxygen; (III) when evacuated below 50°C after step (II); (IV) when exposed to hydrogen after step (III).

allowed to reversibly desorb by butadiene which is able to adsorb more strongly than the oxygen, and this process of oxygen desorption by butadiene will result in the appearance of an induction period. In conformity with this view one may readily explain the fact that a rapid hydrogenation without an induction period can proceed immediately at the beginning of the reaction if the catalyst is evacuated below 50°C even when excess oxygen has been introduced into the catalyst surface. This reaction model of the hydrogenation of butadiene has also been described in (*3*) by reference to the reaction model proposed by Siegel (*11*). However, it should be emphasized here that the oxygen molecules, which were newly brought into the catalyst surface by the addition of oxygen, play an important role in the increase in the rate of hydrogenation. Now, it remains an anxious problem whether or not the model (Fig. 10) is able to explain the suppressing effect of oxygen on the H_2–D_2 exchange reaction. As mentioned previously, oxygen pretreatment tends to somewhat decrease the rate of HD formation. The explanation for this fact is given as follows: even after the evacuation of the oxygen-pretreated catalyst below 50°C or after the end of the induction period, a slight portion of the excess oxygen adsorbed on Ni atoms of the Ni_2P catalyst remains undesorbed. This oxygen serves to block the Ni sites participating in the H_2–D_2 exchange reaction and suppresses the HD formation. Even in this situation, the remarkable increase in the adsorption amount of hydrogen owing to the oxygen addition may enable the Ni_2P catalysts to increase the activity of hydrogenation.

Finally, as an additional remark concerning the characteristic features of the Ni_2P catalyst, it has also been noted that the addition of oxygen to the Ni_2P catalyst greatly accelerates the hydrogenation of butene to butane which can barely be observed without the addition of oxygen.

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