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Surface State and Catalytic Activity and Selectivity of Nickel Catalysts in Hydrogenation Reactions

IV. Electronic Effects on the Selectivity in the Hydrogenation of 1,3-Butadiene

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The hydrogenation of 1,3-butadiene was carried out over various unsupported Ni catalysts: nickel-boride, Raney-nickel, decomposed-nickel, nickel-phosphide, and nickel treated with H_2S. It was found that the butene distributions characteristic of the catalysts were explainable in terms of the electron density of Ni metal and the reaction mechanism proposed by Wells and co-workers. It is suggested that there are critical electron densities of Ni metal at which catalytic properties change significantly.

In the previous study (*1*), it has been proposed that the electron density of Ni metal in unsupported Ni catalysts, such as nickel-boride (Ni-B), nickel-phosphide (Ni-P), Raney-nickel (R-Ni), and Urushibara-nickel (U-Ni) catalysts, is modified by the additives (B in Ni-B, P in Ni-P, Al in R-Ni, and Zn in U-Ni) in the catalysts. To represent the extent of change in the electron density of Ni metal induced by charge transfers from or to the additives, a parameter, Δq, has been introduced on the basis of the chemical shifts in the XPS binding energies of the additive elements (*1–3*). Although the definition of Δq is theoretically imperfect and rather tentative as discussed previously (*1*), it has been demonstrated that Δq is a good parameter to predict some catalytic properties of the Ni catalysts: equilibrium adsorption constant of acetophenone, specific hydrogenation activities for styrene, cycloolefins, and acetone, resistivities against sulfur and phosphorus poisonings, and selectivity in the hydrogenation of 1,2-butylene oxide. These results suggest the parameter to be useful in the characterization of modified catalysts in terms of the electronic properties of Ni metal.

It seems intriguing to apply Δq to other hydrogenation reactions in order to examine the electronic effects on the reactions. Establishment of the electronic effects on reactions would help us to understand the support effects as well as the reaction mechanisms. In this study, we carried out the hydrogenation of 1,3-butadiene in the gas phase. Selection of this reaction is based on two major considerations. First, the reaction mechanism of the hydrogenation of 1,3-butadiene is relatively well established. Wells and co-workers (*4–6*) investigated extensively the reaction over various transition metals and proposed a mechanism to explain the butene distributions, selectivity toward partial hydrogenation, and deuterium distributions in the reactant and products. It would be valuable to show how these selectivities correlate with the electron density of Ni metal modified by the additives. The correlation, if present, must be understood on the basis of the reaction mechanism to verify unambiguously the electronic effects on the reaction. Recently, George *et al.* (*7*) explained the high selectivity to *trans*-2-butene over Ni and Co catalysts contaminated with sulfur or halogens in terms of the electronic

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effect of incorporated contaminant. Their suggestion may be clearly examined and extended by using our series of catalysts. Second, there is no report on the 1,3-butadiene hydrogenation, to our knowledge, over Ni-B (*8*) and Ni-P (prepared in the liquid phase) catalysts. Nickel-phosphide catalysts prepared by treating Ni carbonyl supported on Al_2O_3 with PH_3 were shown to be inactive for the reaction (*9*). However, the catalysts obtained by the H_2 reduction of $Ni_3(PO_4)_2$ at high temperatures (>600°C) produced *trans*-2-butene as a major product, whereas at low reduction temperatures (<400°C) they gave 1-butene as a chief product (*10*). Comparison of Ni-P catalysts employed here with these nickel-phosphide catalysts would provide some information on the preparation effect of the catalyst.

It is shown here that the butene distributions characteristic of various unsupported Ni catalysts are explainable in terms of the electronic effects of the additives (boron, phosphorus, aluminum, and sulfur).

EXPERIMENTAL METHODS

Catalysts

Five kinds of Ni catalysts were selected from the catalysts employed in the previous studies (*1–3*). They are listed in Table 1, together with the preparation methods. Detailed procedures were described previously (*2*, *3*). The catalyst was washed with distilled water after preparation, followed by replacing the water with acetone. Then the wet catalyst was charged into a reactor, the acetone being evacuated at 373 K for 1 h. D-Ni catalyst was sulfided *in situ* with H_2S to prepare Ni-S catalysts at 373–573 K and 8–26 Torr (1 Torr = 133 N m^{-2}) of H_2S for various periods up to 1 h. After the H_2S treatment, the catalyst was evacuated at 573 K for 30–45 min. For comparison, Co-B (*2*) and Co-P catalysts were prepared in similar ways to Ni-B and Ni-P-1 catalysts by using the Co salts. See Table 1.

Procedures

The hydrogenation of 1,3-butadiene was carried out by using a conventional closed-circulation system with a volume of 350 ml including the reactor. The composition of the reactant gas was H_2/butadiene = 6.0 and the total pressure was 60 ± 5 Torr. The reaction temperature was 201–423 K and the amount of catalyst used (< 1 g) depended on the activity for the reaction. Ni-B, R-Ni, and D-Ni catalysts were so active even at the lowest temperature adopted here that the amounts of the catalysts were < 0.01 g and their amounts could not be accurately measured. Therefore, quantitative evaluation of the reaction rate was not made and only the selectivities were noted in this study. The activity of the catalyst per unit surface area was found qualita-

TABLE 1

Nickel and Cobalt Catalysts Employed Here and Their Preparation Methods

Nickel-boride (Ni-B)	Nickel acetate was reduced with $NaBH_4$ at 303 K in water
Raney-nickel (R-Ni)	Al-Ni alloy (42% Ni) was activated with NaOH (20%) at 343 K for 30 min
Decomposed-nickel (D-Ni)	Nickel formate was decomposed at 573 K for 3 h under vacuum
Nickel-phosphide (Ni-P-2)	Nickel hydroxide prepared from nickel chloride was reduced with NaH_2PO_2 at 345 K in 50% ethyl alcohol
(Ni-P-1)	Same as Ni-P-2 but reduced in water
Nickel-sulfide (Ni-S)	D-Ni was treated with H_2S (8–26 Torr) at 375–573 K, followed by evacuation at 573 K
Cobalt-boride (Co-B)	Cobalt chloride was reduced with $NaBH_4$ in water
Cobalt-phosphide (Co-P)	Cobalt hydroxide prepared from cobalt chloride was reduced with NaH_2PO_2 at 345 K in water

tively to decrease as follows:

Ni-B, R-Ni > D-Ni ≫ Ni-P ≫ Ni-S.

1,3-Butadiene was supplied by Tokyo Chemical Ind. Company Ltd. (purity > 99%) and purified further by a repeated freeze–pump technique. Hydrogen was passed through copper granules at an elevated temperature, followed by a zeolite trap at liquid N_2 temperature. The reaction gas was analyzed by gas chromatography (Sebaconitrile/Shimalite at 303 K).

After the hydrogenation reaction at 373 K, the amount of sulfur incorporated into D-Ni catalyst by the H_2S treatment (sulfur level of Ni-S catalyst) was determined by XPS (Hitachi 507 photoelectron spectrometer, Al*Kα* radiation) without exposing the catalyst to air or moisture by immersing it in ethyl alcohol under vacuum. The S/Ni atomic ratio was calculated by using the peak area intensities of the S 2*p* level and the Ni 2*p* level which corresponds to Ni metal (*2*, *3*) or sulfide and the atomic sensitivity factor obtained from $NiSO_4$ (S 2*p*/Ni 2*p* = 0.25 for S/Ni = 1.0). Contrary to the previous papers (*2*, *3*), the binding energies were referenced to the Fermi level of Pd metal (0.0 eV), since the C 1*s* level was substantially broadened, probably, by the adsorption of the reactant and its derivatives and since no significant charging effects were observed (< 0.2 eV) when a stainless-steel sample holder was used (*2*). The reproducibility of the binding energies was estimated within ±0.2 eV for both levels. The Ni $2p_{3/2}$ binding energies for the fresh catalysts were consistent with those in the previous papers (*2*, *3*) which were referenced to the C 1*s* level (285.0 eV). The binding energies for Ni_3S_2 and elemental sulfur were referenced to the C 1*s* level due to contaminants.

RESULTS AND DISCUSSION

General features of the hydrogenation of 1,3-butadiene over the Ni catalysts were: (1) the butadiene pressure decreased linearly with the reaction time at the initial reaction stage (butadiene pressure > ca. 5 Torr) and more slowly after that, (2) butene pressures showed maxima, the pressure of 1-butene showing a maximum at a shorter reaction time than those of 2-butenes, and (3) the butane pressure increased rapidly after the maximum of 1-butene pressure. The reaction behaviors 2 and 3 were obviously observed only at high conversions of butadiene. These observations indicate that the reaction order is zeroth or slightly positive with respect to the butadiene pressure and that the hydrogenation of 1-butene proceeds faster than those of 2-butenes.

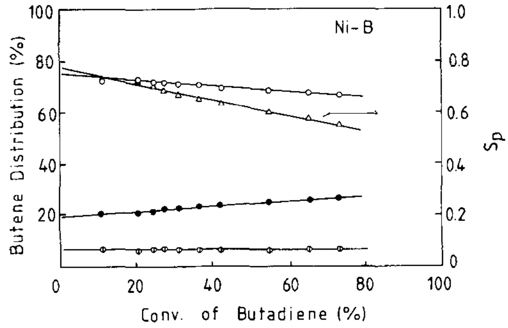

FIG. 1. Butene distribution and selectivity S_p (butene/butene + butane) in the 1,3-butadiene hydrogenation over Ni-B catalyst as a function of the butadiene conversion (H_2/butadiene = 6.0; reaction temperature, 201 K). ○, 1-butene; ●, *trans*-2-butene; ⦶, *cis*-2-butene; and △, S_p.

Shown in Figs. 1 and 2 are typical prod-

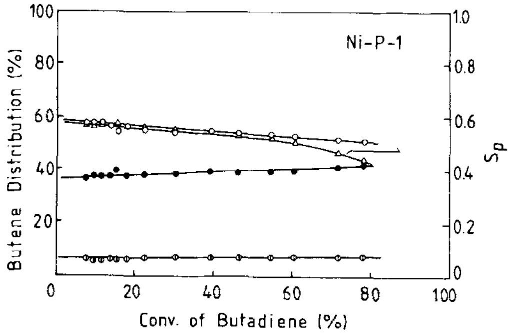

FIG. 2. Butene distribution and selectivity S_p (butene/butene + butane) in the 1,3-butadiene hydrogenation over Ni-P-1 catalyst as a function of the butadiene conversion (H_2/butadiene = 6.0; reaction temperature, 201 K). ○, 1-butene; ●, *trans*-2-butene; ⦶, *cis*-2-butene; and △, S_p.

uct distributions during the hydrogenation of butadiene over the Ni catalysts (Ni-B and Ni-P-1) as a function of the conversion of butadiene. As shown in Figs. 1 and 2, the product distributions depend on the butadiene conversion; the fraction of 1-butene decreases and that of *trans*-2-butene increases as the reaction progresses, while the fraction of *cis*-2-butene seems almost invariant until a very high conversion of butadiene is reached. The selectivity for the partial hydrogenation, S_p = butene/butene + butane, decreases as butadiene is consumed. In order to evaluate the product distributions of the catalysts, the initial distributions were obtained by extrapolating the distribution curves to 0% conversion of butadiene. The selectivities, S_1 = 1-butene/butenes, S_c = *cis*-2-butene/*trans*-2-butene, and S_p thus obtained at various reaction temperatures are summarized in Table 2.

The selectivities S_1 and S_c are nearly independent of the reaction temperature between 201 and 293 K and characteristic of the catalysts. However, S_p seems to show a tendency to increase with the reaction temperature. These findings are essentially consistent with those of Wells and coworkers (*4–6*) for supported transition metal catalysts. These results imply that the activation energy of the hydrogenation

TABLE 2

Hydrogenation of 1,3-Butadiene over Ni and Co Catalysts at Various Temperatures[a]

Catalyst	Reaction temperature (K)	Butene Distribution (%)[b] 1-b	t-2-b	c-2-b	S_c[c]	S_p[d]	Δq[e]
Ni-B	201	74	19	7	0.37	0.77	−0.11
	253	71	20	9	0.45	0.80	
	293	72	20	8	0.40	0.82	
R-Ni	201	64	29	7	0.24	0.79	−0.07
	253	67	28	5	0.18	0.78	
	293	65	28	7	0.25	0.76	
D-Ni	201	60	34	6	0.18	0.55	0.00
	253	64	30	6	0.20	0.78	
	293	65	28	7	0.25	0.97	
Ni-P-2	201	58	36	6	0.17	0.72	+0.22
	253	60	36	4	0.11	0.75	
	293	63	30	7	0.23	0.90	
Ni-P-1	201	58	36	6	0.17	0.58	+0.36
	253	59	35	6	0.17	0.75	
	293	56	37	7	0.19	0.97	
Co-B	273	71	20	9	0.45	0.91	
	292	71	21	8	0.38	0.87	
Co-P	293	69	23	8	0.35	0.96	
	373	68	21	11	0.52	0.95	
	423	62	24	14	0.58	0.93	

[a] Reaction conditions: H_2/1,3-butadiene = 6.0; total pressure = 60 ± 5 Torr; initial product composition was measured.

[b] 1-b, 1-butene; *t*-2-b, *trans*-2-butene; *c*-2-b, *cis*-2-butene.

[c] S_c = *c*-2-b/*t*-2-b.

[d] S_p = butene/butene + butane.

[e] Electron density of Ni metal (charge/Ni atom) taken from Ref. (*1*).

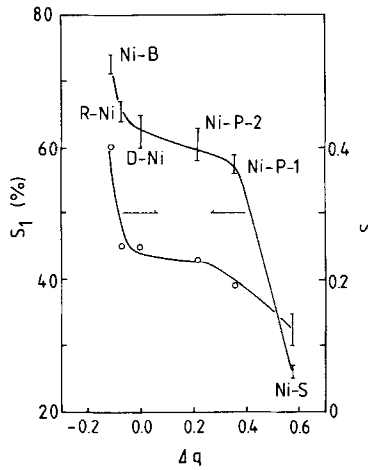

FIG. 3. Dependencies of the selectivities S_1 (1-butene/butenes) and S_c (*cis*-2-butene/*trans*-2-butene) in the 1,3-butadiene hydrogenation over the unsupported Ni catalysts on Δq (charge/Ni atom). The bars for S_1 show the highest and lowest values at the reaction temperatures between 201 and 293 K. For S_c, only the values at 293 K are shown. The reaction temperature for Ni-S catalyst was 373 K.

of butadiene is higher than that of butene and that the activation energies for the formations of 1-butene and *trans*- and *cis*-2-butene are nearly identical.

The electron densities of Ni metal (Δq; charge/Ni atom) in the catalysts are quoted in Table 2 from the previous paper (*1*); the negative Δq for Ni-B and R-Ni catalysts mean that the electron densities of Ni metal are increased by the electron transfer from B or Al to Ni metal compared to that for D-Ni catalyst ($\Delta q = 0.00$) and the positive Δq for Ni-P catalysts indicate a decrease in the electron density by the electron transfer from Ni metal to P. The dependencies of S_1 and S_c on Δq are shown in Fig. 3. It is noteworthy that both selectivities decrease with decreasing electron density of Ni metal. As for S_p, however, no systematic sequence was observed. In the case of the Co catalysts, Co-B catalyst (*2*) shows negative Δq and Co-P catalyst would show a positive one as deduced from Ni-P catalysts (*2*). Analogous tendencies in the selectivities were observed with the Co catalysts, although they were not so significant as those for the Ni catalysts. It is concluded that Δq is a reasonable parameter to describe the sequence of the selectivities, S_1 and S_c, in the hydrogenation of butadiene and, accordingly, to characterize the Ni catalysts employed in the series of the present study (*1*–*3*).

The decreasing tendency of 1-butene production with decreasing electron density of Ni metal is not due to the increasing activity of the Ni metal for the isomerization of 1-butene to 2-butenes during the reaction. The hydrogenation of 1-butene (H_2/1-butene = 2) over the Ni catalysts showed that about 90% of 1-butene consumed was hydrogenated to butane and that only about 10% of 1-butene reacted was isomerized to 2-butenes irrespective of the catalyst (e.g., butane, 92%, *trans*-2-butene, 5%, and *cis*-2-butene, 3%, for R-Ni catalyst at 253 K; 87, 8, and 5% for Ni-B catalyst at 373 K; and 91, 5, and 4% for Ni-P-1 catalyst at 253 K, respectively, at 10% conversion of 1-butene). Consequently, it is concluded that S_1 and S_c are closely associated with the electron density of the Ni metal.

The reaction mechanism of the 1,3-butadiene hydrogenation was extensively studied by Wells and co-workers (*4*–*6*). According to them, Ni catalysts can be classified into two distinct groups on the basis of the butene distribution; type A Ni catalysts with S_1 = ca. 0.6 (preferential 1,2-addition) and type B catalysts with S_1 = ca. 0.3 (preferential 1.4-addition). They proposed different mechanisms for the two types of catalyst (*6*, *11*); a majority of the half-hydrogenated species are π-allylic intermediates for type B catalysts (mechanism B) and σ-bonded and π-olefin-bonded intermediates for type A catalysts (mechanism A). According to their classification, the Ni catalysts in Table 2 belong to type A. It is noteworthy that Ni-B catalyst shows an extremely high selectivity for the 1-butene production compared with other Ni catalysts employed here and by Wells and co-workers (*6*, *7*). The dependency of S_1 on Δq can be well interpreted on the basis of the reaction scheme proposed by Wells and co-workers (*6*, *11*), that is, the extent of the contribution of π-olefin-bonded intermediates to the reaction through σ-bonded intermediates increases as the electron density of Ni metal decreases, since π-olefin-bonded intermediates are considered to favor electron-deficient Ni metal rather than an electron-rich one due to their electron-donating properties. The decrease in S_c with decreasing electron density of the Ni metal is also understandable on the basis of the increasing importance of the π-olefin-bonded intermediates in the reaction, since conformational interconversions of the π-olefin-bonded intermediates derived from the two conformations of 1,3-butadiene may be partly inhibited. The remarkably high 1-butene selectivity of Ni-B catalyst is considered to be due to a preferential formation of σ-bonded intermediates because of the high electron density of the Ni metal.

In order to extend the relationship between the selectivities and electron density of Ni metal, Ni-S catalysts which were prepared by sulfiding D-Ni with H_2S under various conditions were examined. Table 3 shows the selectivities of the butadiene hydrogenation over Ni-S catalysts, together with the XPS binding energies of the S $2p$ and Ni $2p_{3/2}$ bands and the sulfur content obtained from the XPS measurements. The XPS data for Ni_3S_2 and elemental sulfur are also given in Table 3.

The binding energy of the Ni $2p_{3/2}$ level remained unaffected (852.1 ± 0.2 eV) when the S/Ni atomic ratio was lower than 0.25. With a further increase in the sulfur content (S/Ni $>$ 0.35), the Ni $2p_{3/2}$ binding energy increased by ca. 0.3 eV. As for the S $2p$ level, the binding energy was 161.7 ± 0.2 eV below S/Ni = 0.25 and consistent with that for Ni_3S_2. It increased, however, by 0.7 eV (162.4 ± 0.2 eV) above S/Ni = 0.35. It is concluded from Table 3 that sulfur species observed below S/Ni = 0.25 is analogous to the sulfide sulfur and that a new sulfur species appears at S/Ni $\geq$ 0.35 which

TABLE 3

XPS Binding Energies of the Ni $2p_{3/2}$ and S $2p$ Levels for Ni-S Catalysts and Selectivities in the Hydrogenation of 1,3-Butadiene over the Catalysts at 373 K[a]

Sulfur level[b] (S/Ni)	Binding energy (eV)		Butene Distribution (%)[c]			S_c[d]	S_p[e]
	Ni $2p_{3/2}$	S $2p$	1-b	*t*-2-b	*c*-2-b		
0.00[f]	852.2	—	65	28	7	0.25	0.97
0.20	852.1	161.7	41	51	8	0.16	0.98
0.22	851.9	161.5	39	52	9	0.17	1.00
0.25	852.0	162.0	33	57	10	0.18	1.00
0.35	852.5	162.4	30	61	9	0.15	0.99
0.38	852.4	162.5	25	68	7	0.10	1.00
0.51	852.4	162.5	27	62	11	0.18	1.00
0.62	852.5	162.2	27	64	9	0.14	1.00
Ni_3S_2	853.3	161.7					
S	—	164.3					

[a] Reaction conditions: H_2/butadiene = 6.0; total pressure = 60 Torr; initial product distributions were measured.

[b] Atomic ratio obtained from XPS.

[c] 1-b, 1-butene; *t*-2-b, *trans*-2-butene; *c*-2-b, *cis*-2-butene.

[d] S_c = *c*-2-b/*t*-2-b.

[e] Butene/butene + butane.

[f] Reaction temperature, 293 K.

could be elemental sulfur or sulfur species interacting weakly with Ni. The small increase in the Ni $2p_{3/2}$ binding energy in the region of S/Ni $\geq$ 0.35 implies that superficial sulfide formation over Ni metal is completed at S/Ni = ca. 0.3 and that a further increase in the sulfur content produces a few sulfide layers, accompanying the new sulfur species mentioned above. A superficial sulfidation of Ni metal contacted with H_2S was reported by Takeuchi *et al.* (*12*) on the basis of the AES combined with an Ar sputtering technique. The higher binding energy of the Ni $2p_{3/2}$ level and lower binding energy of the S $2p$ band for Ni-S catalysts compared with those for pure Ni metal and elemental sulfur indicate obviously the decrease in the electron density of Ni metal in Ni-S catalysts due to the electron transfer from Ni to sulfur. With the other Ni catalysts in Table 2, no appreciable chemical shift of the Ni $2p_{3/2}$ level was observed within an accuracy of ± 0.3 eV (*2, 3*). This indicates a considerably larger change in the electron density of Ni metal in Ni-S catalysts, compared with the other Ni catalysts. At a low sulfur level, no detectable chemical shift of the Ni $2p_{3/2}$ band for Ni-S catalysts was observed. This is due to the fact that the XPS technique provides the information on the surface layer (ca. 2 nm) but not on the topmost surface of the catalyst.

The typical isomer distribution in butene produced in the hydrogenation of butadiene over Ni-S catalyst is illustrated in Fig. 4 against the conversion of butadiene. Contrary to the other Ni catalysts, the product distribution was invariant up to a very high conversion of butadiene. This is due to the fact that no hydrogenation of butene occurs over Ni-S catalysts. In Fig. 5, the butene distributions at 0% conversion of butadiene are shown as a function of the S/Ni atomic ratio. The fraction of *trans*-2-butene increased and reached a constant value (63%) at the expense of 1-butene, whereas the fraction of *cis*-2-butene was not affected by the incorporation of sulfur. Thus sulfur-contaminated Ni catalysts show a typical behavior of type B catalyst. These results are in good agreement with other workers (*7*). The selectivity is constant above S/Ni = 0.3 as can be seen in Fig. 5. This is consistent with the XPS results in Table 3, which indicate that superficial sulfidation of the Ni metal is completed above there. The additional sulfur species do not affect the selectivity of the catalysts, indicating weak interactions between Ni and the new sulfur species.

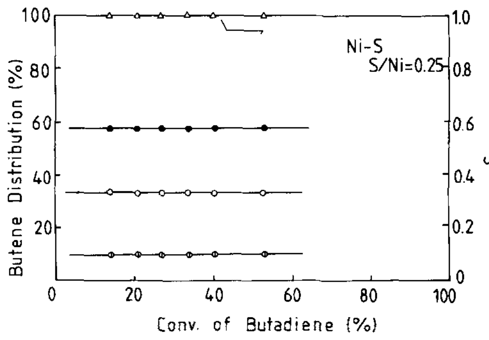

FIG. 4. Butene distribution and selectivity S_p (butene/butene + butane) in the hydrogenation of 1,3-butadiene over Ni-S catalyst (S/Ni = 0.25) as a function of the butadiene conversion (H_2/butadiene = 6.0; reaction temperature, 373 K). ○, 1-butene; ●, *trans*-2-butene; ⦶, *cis*-2-butene; and △, S_p.

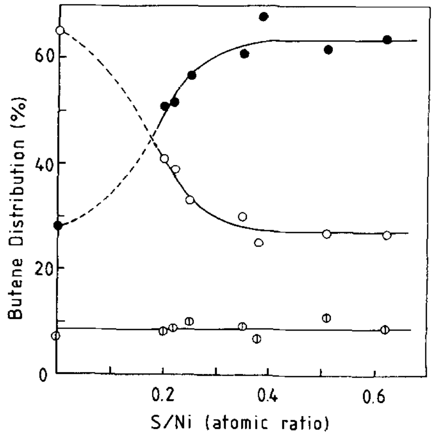

FIG. 5. Dependencies of butene distribution in the 1,3-butadiene hydrogenation over Ni-S catalyst at 373 K (H_2/butadiene = 6.0) on the S/Ni atomic ratio obtained from XPS. ○, 1-butene; ●, *trans*-2-butene; and ⦶, *cis*-2-butene.

It is required first to discuss the origin of the type B behavior on Ni-S catalysts. The surface structures of Ni metal treated with H_2S have been studied by many workers (*13*). According to the recent LEED studies with a Ni(111) surface by Erley and Wagner (*14*), specific surface structures are formed by H_2S treatments; the $p(2 \times 2)$, $(3^{1/2} \times 3^{1/2})R30°$, and $c(20 \times 2)$ structures form with increasing S coverage. Perdereau and Oudar (*15*) observed a somewhat different behavior of the surface structure. Upon high-temperature annealing, the $p(2 \times 2)$ and $(3^{1/2} \times 3^{1/2})R30°$ LEED patterns were irreversibly changed to complex patterns, which were assigned to two-dimensional Ni-S surface compounds and one of which was observed by Erley and Wagner (*14*). It might be possible to explain the type B behavior of Ni-S catalysts in terms of such ordered surface structures. However, as shown by George *et al.* (*7*), type B behavior is a general phenomenon, since it is not confined to S but also is caused by halogens, P, Se, and As. In addition, type B behavior can be produced even when the treatment conditions are not strictly controlled. As shown in Fig. 5, the butene distributions are independent of the treatment conditions (8–26 Torr of H_2S at 373–573 K for various periods) and dependent only on the sulfur level in the surface.

Ni-P-1 catalyst contains enough phosphorus (P/Ni = 0.52 (*2*)) to show type B behavior on the basis of the reaction mechanism proposed by Nozaki and Adachi (*10*). However, it belongs to type A as shown in Table 2. Even when reduced at 573 K with H_2 (100 Torr) for 30 min, Ni-P-1 catalyst did not show any appreciable changes in the selectivities ($S_1 = 0.58$ and $S_c = 0.18$ at 201 K), although some crystallization of Ni_2P took place. Furthermore, the Ni–Ni atomic distance in Ni-B catalyst is enlarged by the presence of B (*16*). However, Ni-B catalyst does not show a type B behavior (Table 2) but does belong to the type A group. On the basis of these considerations, we are inclined to regard the electronic effects of S on Ni metal as a major origin of the change of type A to type B behaviors, although we recognize that the structural effects may, to some extent, contribute to the transformations in catalyst behavior. Much more comprehensive studies including, at least, LEED, UPS, and XPS combined with sputtering techniques, and catalytic tests are required to obtain further information on this subject.

As described above, the electron density of the Ni metal in Ni-S catalysts is lowered. With sulfur-segregated Pd metal, Matsumoto *et al.* (*17*) demonstrated the decrease in the electron density of Pd by using UPS techniques. It is necessary to evaluate the parameter Δq in order to examine the relationship between the electron density of Ni metal and S_1 or S_c. Since the sulfur incorporated onto or into Ni metal distributes inhomogeneously in the direction of the depth, Δq cannot directly be obtained from the chemical shift of the S $2p$ level and the sulfur content in Table 3 on the basis of the following equation defined for uniform catalysts in the previous paper (*1*):

$$\Delta q = -\frac{\Delta E}{k}\left(\frac{\mathrm{S}}{\mathrm{Ni}}\right), \tag{1}$$

$$\Delta E_0 \propto k q_0, \tag{2}$$

where ΔE_0 (eV) is the chemical shift of the S $2p$ level for a sulfur compound with respect to elemental sulfur and q_0 is the charge density of sulfur atom in the compound calculated by extended Hückel methods. k is a slope in the linear correlation between q_0 and ΔE_0. ΔE is the XPS chemical shift of the S $2p$ level observed for S in Ni-S catalysts. (S/Ni) denotes the atomic ratio in the catalysts. Nevertheless, with the Ni catalysts sulfided with H_2S under conditions similar to those employed here, Takeuchi *et al.* (*12*) showed a surface stoichiometry corresponding to Ni_3S_2 by AES combined with Ar sputtering techniques. Therefore, it would be natural to assume that in the range of S/Ni > 0.3, the surface state of Ni-S catalysts is analogous to that of Ni_3S_2 (S/Ni = 0.67). This is adequate from the viewpoint of thermodynamics (*18*) and from the XPS results in Table 3. Assuming the Ni_3S_2 formation in the Ni-S catalyst surface, Δq is estimated to be 0.58 by using the chemical shift of the S $2p$ level ($\Delta E = -2.6$ eV) and k (3.0) which is calculated from the extended Hückel calculation of the charges on sulfur atoms in various sulfur-containing compounds and the S $2p$ binding energy values for these compounds reported by Kramer and Klein (*19*). Small modifications in Δq do not affect the discussions below. In Fig. 3, S_1 and S_c for Ni-S catalysts are also plotted.

The selectivity S_1 decreases steeply when Δq exceeds a certain critical value, ca. 0.4 (shift from type A to type B). This is ascribable to a sudden change in the reaction mechanism of the hydrogenation; half-hydrogenated intermediates shift from σ-bonded and π-bonded species to π-allylic species. As for S_c, analogous discussions are applicable. Consequently, the selectivities S_1 and S_c in the hydrogenation of 1,3-butadiene can be interpreted in terms of the electron density of Ni metal and the reaction mechanism proposed by Wells and coworkers (*4–6*).

It is interesting to note here the critical electron density of Ni metal at which catalytic properties change remarkably. As shown in Fig. 3, a critical Δq is found at Δq = ca. 0.0 and ca. 0.4 for the hydrogenation of butadiene. It is considered that the main reaction intermediates shift as follows with decreasing electron density of Ni metal: σ-bonded ($\Delta q < 0.0$), σ-bonded and π-olefin-bonded ($0.0 < \Delta q < 0.4$), and π-allylic ($\Delta q > 0.4$) intermediates. In the other hydrogenation reactions over the Ni catalysts (*1*), an analogous critical electron density of Ni metal can be seen at $\Delta q = 0.0$ where the specific activity for the hydrogenation shows a deflection, the selectivity to n-butyl alcohol in the hydrogenation of 1,2-butylene oxide shows a minimum, and the ratio of the equilibrium adsorption constants for cyclohexene and cyclooctene has a maximum. Therefore, the appearance of the critical electron density seems a general phenomenon rather than an artifact caused by improper evaluation of Δq.

Finally, the preparation effects of nickel-phosphide catalysts are to be discussed. Contrary to Ni-P catalysts prepared by reducing nickel hydroxide with NaH_2PO_2 in an aqueous or alcoholic solution, nickel-phosphide catalysts (*10*) prepared by H_2 reduction of $Ni_3(PO_4)_2$ produce type B catalysts when reduction temperatures are higher than 600°C, whereas they produce type A catalysts when reduced at lower than 400°C. These phenomena would be understandable on the basis of the P/Ni ratio in the catalyst surface of the electron density of Ni metal. At the low reduction temperatures, the P/Ni ratio may be lower than about 0.5 (0.31 for Ni-P-2 and 0.52 for Ni-P-1 (*2*)). Actually, Nozaki and Adachi (*10*) detected Ni metal by ESR and attributed the remaining to $Ni_2P_2O_7$. However, at the high reduction temperatures, they observed Ni_2P by X-ray diffraction analyses and estimated the concomitant formation of free phosphorus from the consideration of the stoichiometry of $Ni_3(PO_4)_2$ (P/Ni = 0.67). In our opinion, if some of the free phosphorus is incorporated into the Ni_2P surface (when P/Ni > 0.7 in the surface, $\Delta q > 0.5$), type A catalysts shift to type B. Such segregation is considered to occur easily as does the sulfur segregation in Pd metal containing sulfur as an impurity (*17*). On the basis of the above considerations, we are inclined to consider that the shift in the product distributions from type A to type B as the reduction temperature increases is due to the decrease in the electron density of Ni metal through the critical value by the surface segregation of phosphorus.

In nickel-phosphide catalysts prepared by Mutterties and Sauer (*9*) by treating Ni carbonyl/Al_2O_3 with PH_3, the surface concentration of P must be much higher than that estimated from X-ray diffraction analyses as suggested by them. Such catalysts are expected to show less activity and type

B behavior, in agreement with the fact that their nickel-phosphide catalysts showed no activity for the hydrogenation of butadiene (*9*). Thus catalytic behavior of various nickel-phosphide catalysts seems to be understandable in terms of the surface concentration of phosphorus and, in turn, the electronic effects of phosphorus on Ni metal.

In summary, the selectivities of the 1,3-butadiene hydrogenation are correlated with the electron density of the Ni metal and with the change in the reaction mechanism induced by the alteration in the electron density. Furthermore, it is suggested that there are critical electron densities of Ni metal where catalytic properties change remarkably.

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