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

III. Electronic and Catalytic Properties of Nickel Catalysts

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Various nickel catalysts (nickel-boride, nickel-phosphide, Raney-nickel, Urushibara-nickel, and decomposed-nickel) were investigated to examine the relationships between catalytic and electronic properties of nickel catalysts modified by component elements (boron, phosphorus, aluminum, and zinc) in the catalysts. Based on the X-ray photoelectron spectroscopic results, a parameter Δq was tentatively proposed to characterize the electronic properties of the catalysts. The specific activity (activity per surface area of nickel metal) for hydrogenation reaction, the adsorption equilibrium constant of acetophenone, the resistivity against poisoning, and the characteristic selectivities in hydrogenation of 1,2-butylene oxide were found to be summarized in terms of the parameter Δq. It is suggested that Δq is a useful parameter to reflect the electronic properties of the nickel catalysts.

INTRODUCTION

It is well known that nickel catalysts modified by boron (nickel-boride), phosphorus (nickel-phosphide), aluminum (Raney-nickel), and zinc (Urushibara-nickel) show peculiar activity and selectivity for hydrogenation reactions. However, no systematic study has been undertaken to explain the peculiarities of these nickel catalysts in the reactions. In our previous papers (*1, 2*), the X-ray photoelectron spectroscopic studies of nickel-boride (Ni-B), nickel-phosphide (Ni-P), Raney-nickel (R-Ni), Urushibara-nickel (U-Ni), and decomposed-nickel (D-Ni) catalysts have been carried out to characterize the surface states of the catalysts and to explain the differences in the activities of the catalysts in hydrogenation reactions. With Ni-B and Ni-P catalysts, electron transfers between the nickel metal and the component elements were proposed to be as follows (*1*);

$$\text{Ni-B;} \quad \text{Ni} \leftarrow \text{B}$$
$$\text{Ni-P;} \quad \text{Ni} \rightarrow \text{P}$$

Furthermore, it has been suggested (*1*) that the higher specific activities of Ni-B catalysts (activity per surface area of nickel metal) for hydrogenation reactions are ascribable to the higher electron density on the nickel metal, whereas the lower specific activities of Ni-P catalysts are due to the lower electron density on the metal, compared with an unmodified nickel catalyst (D-Ni). As for the relationship between electronic properties and selectivities in hydrogenation reactions, Wells and his coworkers (*3*) have very recently claimed that the selectivity for butadiene hydrogenation over nickel and cobalt metals modified with sulfur can be explained in terms of the electronic effects of sulfur on the catalyst sites. These studies would indicate the importance of electronic properties of metal catalysts in the activity and selectivity for hydrogenation reactions.

In the present paper, it is a main objective to examine correlations between the catalytic and electronic properties of the nickel catalysts modified by the component

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elements in the catalysts. The extent of electron transfer between nickel metal and a component element was estimated based on the previous XPS results (*1*, *2*) and a parameter Δq was tentatively proposed to evaluate the electron density on the nickel metal. The catalytic activities and selectivities of the nickel catalysts for hydrogenation reactions were found to be successfully explained in terms of Δq. The resistivity of the nickel catalysts against poisoning was also discussed based on the parameter Δq.

EXPERIMENTAL

Catalysts. Nickel catalysts studied in the present work were prepared according to the previous papers (*1*, *2*). The catalysts used here are presented in Table 1 together with their preparation methods. The catalyst was washed three times with distilled water and subsequently three times with 99% ethyl alcohol after preparation. With R-Ni catalysts, they were washed five times with water and five times with 99% ethyl alcohol in order to remove sodium ion. Trace amount of sodium ion was detected only for Ni-B(P-2) and Ni-P-1 catalysts by means of XPS (*1*).

The catalysts used for the XPS measurements (*1*, *2*) and for the reactions were prepared by the same procedures and sometimes the XPS spectra of the catalysts were measured after the reactions to examine the changes in the surface concentrations of the component elements and in the oxidation degree of the nickel with the reactions. However, no detectable changes were observed. The oxidized nickel detected by XPS (*1*, *2*) is considered to be produced during the catalyst preparation and not during the XPS measurements or mounting procedures into the spectrometer, since the special care was taken for these procedures (*1*) and since the nickel catalysts previously treated with hydrogen at elevated temperature showed much less oxidized nickel by the same procedures.

Measurements of the activity and selectivity of nickel catalyst in hydrogenation reactions. Hydrogenation reactions of styrene, cyclohexene, cyclooctene, acetophenone, and 1,2-butylene oxide were carried out under vigorous stirring over the nickel catalysts in 99% ethyl alcohol at 30°C and the atmospheric pressure of hydrogen using an apparatus similar to that described previously (*4*). The rate measurement was performed under conditions where the rate was independent of stirring and the amount of the catalyst. An initial hydrogenation rate, which was calculated from the hydrogen consumption with an open-end manometer, was regarded as the activity of the catalyst. These procedures

TABLE 1

Nickel Catalysts and Their Preparation Methods

Number	Catalyst	Preparation method
1	Ni-B(P-1)-Ac	Nickel acetate was reduced with $NaBH_4$ at 30°C in water
2	Ni-B(P-1)-Cl	Ni-B(P-1) prepared from nickel chloride
3	Ni-B(P-1)-SO_4	Ni-B(P-1) prepared from nickel sulfate
4	Ni-B(P-2)-Ac	Nickel acetate was reduced with $NaBH_4$ at 30°C in 95% ethyl alcohol
5	Ni-B(P-2)-Cl	Ni-B(P-2) prepared from nickel chloride
6	N-P-1	Nickel hydroxide prepared from nickel chloride was reduced with NaH_2PO_2 at 72°C in water
7	Ni-P-2	Ni-P reduced in 50% ethyl alcohol
8	R-Ni	Al-Ni alloy (42 wt% Ni) was activated at 70°C for 30 min
9	U-Ni(A)	ppt-Ni prepared by reduction of nickel chloride with zinc dust was activated at 50°C for 7.5 min with a 20% acetic acid aqueous solution
10	D-Ni	Nickel formate was decomposed at 300°C for 3 hr in a vacuum

were described in detail elsewhere (*4*). The concentration of the reactant was ca. 0.2 *M*. In the case of the hydrogenation of acetophenone, the concentration of the ketone was varied in the range of 0.2 to 2 *M* to obtain kinetic parameters. With the 1,2-butylene oxide hydrogenation, the products were predominantly *n*- and *sec*-butyl alcohols up to several percent conversion of the epoxide. The selectivity of the epoxide hydrogenation was measured at ca. 1–6% conversion, since the hydrogenation rate was relatively slow over the nickel catalysts under the experimental conditions.

The resistivities of the nickel catalysts against poisons, carbon disulfide and triphenylphosphine, were measured for the styrene hydrogenation at 30°C by adding an appropriate amount of the poison into the solvent as described in detail previously (*5*).

In order to estimate the intrinsic activity of nickel metal for the hydrogenation reaction, the specificity activity is defined as the activity per unit surface area of nickel metal (H_2 ml STP/min · m^2 of nickel metal), where the surface area of nickel metal is estimated from the fraction of nickel metal in the surface nickel (oxide + metal) and BET surface area (*1*). In this definition, the BET surface area measured by N_2 adsorption at 77 K was adopted as the "nickel surface." However, some contribution of the second component to the BET surface area of the catalyst would not be neglected. With R-Ni catalysts, Anderson and his coworkers (*6, 7*) measured the surface area of nickel metal by CO adsorption technique and reported that 50–90% of the BET surface area was due to the nickel, depending on the activation conditions. It is estimated from their results that 70–80% of the BET surface area is due to the nickel in our preparation method. With the U-Ni catalyst, the BET surface area is considered to be comprised of larger nickel surface area than the R-Ni catalyst, since it has been revealed that nickel covers the zinc surface in the U-Ni catalyst (*2*). As for the Ni-B and Ni-P catalysts, the nickel surface areas are considered to be very close to the BET surface area. Consequently, the specific activity obtained from the BET surface area and the fraction of nickel metal in total surface nickel was adopted here to compare the activity of the nickel. Slight modifications by the approximations would not change the results so much.

RESULTS AND DISCUSSIONS

Definition of a Parameter Δq for Ni-B and Ni-P Catalysts

In our previous paper (*1*), it has been suggested from the XPS characterization of the Ni-B and Ni-P catalysts that electron transfers occur between the nickel metals and the component elements (B in Ni-B, P in Ni-P) in the catalysts, modifying the electron densities on the nickel metals. The extent of the electron transfer must be evaluated in order to characterize the electronic properties of the catalysts and to explain the catalytic features in terms of the electronic properties.

According to the extended Hückel calculations and XPS studies for boron and phosphorus compounds (*8, 9*), the XPS chemical shifts (ΔE_0) of B 1s and P 2p levels correlate linearly with the calculated charges (q_0) on boron and phosphorus, that is,

$$\Delta E_0 \propto kq_0. \tag{1}$$

The values of k were calculated from the published results (*8, 9*) to be 2.92 and 1.00 for B 1s and P 2p, respectively. It was found from the Ni $2p_{3/2}$ and Ni 3p XPS intensities (*2*) that the distributions of B and P in the Ni-B and Ni-P catalysts were homogeneous in the direction of depth. Therefore, assuming that the catalyst surface retains an electric neutrality and that the electron density on the nickel metal depends linearly upon the amount of the component element, a parameter, which would reflect the extent of change in the electron density on the nickel metal induced by B or P, is tentatively defined by the following equation;

$$\Delta q = \frac{-\Delta E}{k}\left(\frac{\mathrm{A}}{\mathrm{Ni}}\right) \qquad (2)$$

where Δq is a parameter to represent the extent of change in the electron density on the nickel metal as a result of an electron transfer between the nickel metal and the component element A (B or P), in comparison with D-Ni catalyst ($\Delta q = 0$) which contains no modifier. ΔE is the XPS chemical shift for the component element A in the nickel catalyst compared to pure element A. The ΔE values were +0.7 eV for B 1s level on Ni-B catalysts and −0.7 eV for P 2p level in Ni-P catalysts (*1*). The (A/Ni) ratio represents the concentration of A responsible for the electron transfer expressed by the atomic ratio of A to the nickel metal in the catalyst surface. The (A/Ni) values have been reported in the previous paper (*1*) and are cited in Table 2. The second assumption would be verified by the facts that the number of 3d electrons per cobalt and iron in cobalt- and iron-boride compounds increased with increasing boron content (8.2 for Fe_2B and 8.9 for FeB, 9.2 for Co_2B, and 9.7 for CoB) (*10*).

However, the definition of Δq by Eq. (2) is apparently oversimplified to describe the true electron density on the nickel metal. It is generally required to evaluate carefully the matrix effects, such as a lattice potential and an extra atomic relaxation, on the binding energies for B, P, and Ni in the catalyst in order to obtain meaningful electron density on the nickel metal (*11*). No significant change in the binding energy of the Ni $2p_{3/2}$ level for these catalysts was observed by the addition of P or B within the accuracy of the spectrometer (±0.3 eV) (*1*), being probably due to the extra atomic relaxation effects (*11*). Although Eq. (2) is theoretically imperfect and tentative, it is probable that the parameter Δq correlates to the change in the electron density on the nickel metal by the addition of B or P ($\Delta q < 0$, increase in electron density; $\Delta q > 0$, decrease in electron density). The Δq values thus obtained are tabulated in Table 2 for Ni-B and Ni-P catalysts prepared under various conditions. The absolute value of the parameter Δq is itself meaningless as discussed above. However, Δq was found to be a useful parameter to summarize the peculiarities of the nickel catalysts as shown below.

TABLE 2

Δq Values for the Nickel Catalysts

Catalyst	A/Ni[a]	Δq[b]
Ni-B(P-1)-Ac	0.45	−0.11
Ni-B(P-1)-Cl	0.32	−0.08
Ni-B(P-1)-SO_4	0.37	−0.09
Ni-B(P-2)-Ac	0.21	−0.05
Ni-B(P-2)-Cl	0.21	−0.05
D-Ni	0	0
Ni-P-1	0.52	+0.36
Ni-P-2	0.31	+0.22
R-Ni	0.4 ± 0.1	−0.07[c]
U-Ni(A)	0.5 ± 0.1	−0.06[c]

[a] Atomic ratio of a component element (B, P, Al, Zn) to nickel metal in the catalyst surface (*1, 2*).

[b] Defined by Eq. (2).

[c] Estimated from the correlation between r_c/r_m and Δq in Fig. 1.

The Estimation of Δq for R-Ni and U-Ni Catalysts

With R-Ni and U-Ni catalysts, our previous XPS study (*2*) has shown that Al and Zn metals are present in the surface of R-Ni and U-Ni catalysts, respectively. These findings would indicate partial alloy formation in the activated phases between Ni and Al or Zn, as indicated by the Mössbauer spectroscopy study (*12*) for U-Fe catalysts and as shown by the magnetic (*13*) and XPS (*14*) techniques for Raney-nickel catalysts. In the cases of Ni-Al and Ni-Zn alloys, it is well established experimentally (*15–17*) and theoretically (*18*) that the electron transfers from Al and Zn to Ni metal occur in the alloys, leading to the increases in the electron densities on the nickel metals. However, the direct estimation of Δq based on Eq. (2) is not possible, since no significant chemical shift of the Al 2s, Zn $2p_{3/2}$, and Zn LMM Auger levels for Al and Zn metals was detected, partly due to the superposition of Al 2s and Ni 3s levels, within the accuracy of the spectrometer (±0.3 eV) (*2*). Nevertheless, there is a possible clue to estimate Δq for these catalysts using the adsorption equilibrium constant of a reactant, since the adsorption strength of a reactant is considered to reflect directly the effect of electronic properties of the nickel catalysts (*1*). The accurate measurements of adsorption constants are, however, rather difficult in our catalyst systems as shown below in Fig. 2. Therefore, a more convenient and reliable method was employed here.

In the competitive hydrogenation of reactants R_1 and R_2, the product ratios (r_c) of R_1H_2 to R_2H_2 were obtained for the nickel catalysts. The rate ratios (r_m) in the individual hydrogenations of R_1 and R_2 were also measured over the catalysts. When R_1 and R_2 adsorb much more strongly than hydrogen ($1 + K_HP_H \ll K_iC_i$) and the concentrations of R_1 and R_2 are identical ($C_1 = C_2$), the ratio of r_c to r_m reduces to Eq. (3).

$$\frac{r_c}{r_m} = \left(\frac{K_1}{K_2}\right)^2 \qquad (3)$$

where K_1 and K_2 are the adsorption equilibrium constants for the reactants R_1 and R_2, respectively, in the following Langmuir equations:

for individual hydrogenation

$$r_i = \frac{k_iK_HP_HK_iC_i}{(1 + K_HP_H + K_iC_i)^2} \qquad (4)$$

for competitive hydrogenation

$$r_i' = \frac{k_iK_HP_HK_iC_i}{(1 + K_HP_H + K_1C_1 + K_2C_2)^2} \qquad i = 1 \text{ or } 2 \quad (5)$$

where k_i is the rate constant for reactant R_i (i = 1 or 2), K_H is the adsorption equilibrium constant of hydrogen, P_H is the hydrogen pressure, and C_i is the concentration of reactant R_i.

In the present paper, cyclohexene and cyclooctene were chosen as reactants R_1 and R_2, respectively, because these reactants satisfy the above requirements and r_c/r_m ratio varies considerably with the catalysts (*19, 20*) in spite of the comparable size and structure. The r_c/r_m values are summarized in Table 3 and plotted in Fig. 1 as a function of Δq for the various Ni-B and Ni-P catalysts, for which Δq are already evaluated based on the XPS results. Figure 1 confirms that r_c/r_m ratios can be well summarized in terms of Δq. Therefore, it would be reasonable to apply the results in Fig. 1 to R-Ni and U-Ni catalysts. From the relationship in Fig. 1, Δq values for R-Ni and U-Ni catalysts were estimated as indicated in Fig. 1 using the r_c/r_m values for these catalysts, taking into account the fact that the electron densities on the nickel metals in R-Ni and U-Ni catalysts are increased by electron transfers from Al and Zn metals to the nickel metals ($\Delta q < 0$) as discussed above. The Δq values thus obtained are listed up in Table 2. It seems that Al metal influences more strongly the electron density on the nickel metal than Zn

TABLE 3

Hydrogenation of Cyclohexene and Cyclooctene over Nickel Catalysts at 30°C under the Atmospheric Pressure of Hydrogen

Catalyst	r_c[a]	r_m[b]	r_c/r_m
Ni-B(P-1)-Ac	0.23	0.85	0.27
Ni-B(P-1)-Cl	0.26	0.92	0.29
Ni-B(P-1)-SO_4	0.27	0.90	0.30
Ni-B(P-2)-Ac	0.35	0.81	0.44
Ni-B(P-2)-Cl	0.43	1.03	0.43
D-Ni	2.96	4.81	0.62
Ni-P-1	0.23	0.60	0.38
Ni-P-2	0.40	0.83	0.48
R-Ni	0.55	1.54	0.36
U-Ni(A)			0.41[c]

[a] Yield of cyclohexane/yield of cyclooctane in the competitive hydrogenation of cyclohexene and cyclooctene.

[b] Reaction rate of cyclohexene/reaction rate of cyclooctene in the individual hydrogenations.

[c] Reported by Kajitani *et al.* (*20*).

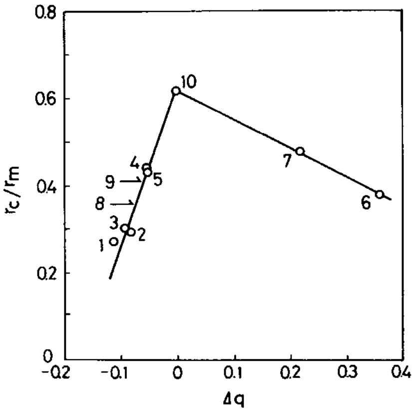

FIG. 1. Correlation between Δq and r_c/r_m for nickel catalysts. Numbers in the figure correspond to the catalyst entry number in Table 1.

metal does. This is consistent with the theoretical (*18*) and experimental (*5*) estimations for Ni-Al and Ni-Zn alloys, suggesting the reasonableness of the evaluation of Δq for R-Ni and U-Ni catalysts from Fig. 1.

In order to examine the validity of Δq for representing the electronic properties of the nickel catalyst, the adsorption equilibrium constants of acetophenone were measured with some nickel catalysts using Eq. (4). They are shown in Fig. 2 as a function of Δq. It is apparent that the adsorption equilibrium constant increases with increasing Δq. This is easily understood, if one adopts that Δq reflects the electron density on the nickel metal. Namely, the adsorption equilibrium constant increases with decreasing the electron density on the nickel metal, indicating that acetophenone adsorbs more strongly on electron deficient metal than on electron rich one as expected. Consequently, it is very probable that Δq thus obtained is a parameter to describe the electronic properties of the nickel catalysts.

Catalytic Properties of the Nickel Catalysts and Δq

In our previous paper (*1*), we have discussed the specific activities of Ni-B and Ni-P catalysts for the hydrogenation of styrene in terms of the electron density on the nickel metal and concluded that the specific activity increases with increasing the electron density on the nickel metal by decreasing the self-poisoning effect of styrene. In Fig. 3, the specific activity of the nickel catalyst for styrene hydrogenation is plotted against Δq. The correlation in Fig. 3 would confirm the above conclusions, that is, the specific activity of nickel metal increases with increases in the electron density on the nickel metal. The identical conclusions can be drawn from the hydrogenations of cyclohexene, cyclooctene, methylcyclohexene, and norbornadiene over the nickel catalysts (*19*).

Another important feature of catalysts which would reflect the electronic properties of the catalysts is the resistivity of the catalyst against poisoning. Accordingly, the correlation between Δq and the resistivity was examined. The poisoning coefficients α(m²/mmol) were determined from Maxted equation (*21*);

$$r = r_0(1 - \alpha C_p) \qquad (6)$$

where r_0(H_2 ml STP/min · m² of nickel metal) represents the specific activity of a fresh catalyst and r, the specific activity when a catalyst is poisoned by an inhibitor of the concentration C_p (mmol/m²). The

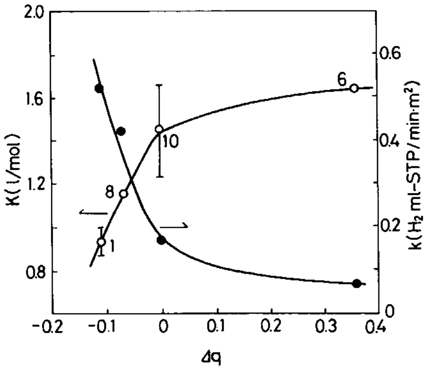

FIG. 2. Adsorption equilibrium constant (K) and rate constant (k) of acetophenone for nickel catalyst calculated from Eq. (4) as a function of Δq. ○, K(1/mol); ●, k(H_2 ml STP/min · m²). Numbers in the figure correspond to the catalyst entry number in Table 1.

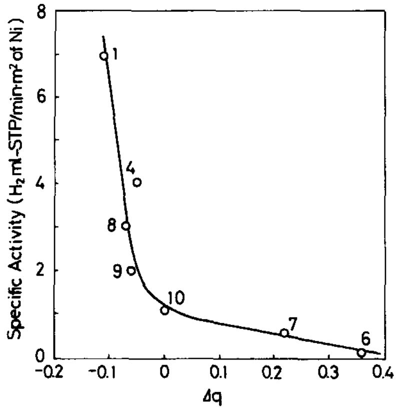

FIG. 3. Dependence of the specific activity (H_2 ml STP/min · m^2 of Ni) of the nickel catalyst upon Δq for the hydrogenation of styrene at 30°C under the atmospheric pressure of hydrogen. Numbers in the figure correspond to the catalyst number in Table 1.

values of α for carbon disulfide and triphenylphosphine in the styrene hydrogenation are shown in Fig. 4 as a function of Δq. It is evident that the electron-rich nickel metal shows high resistivity against catalyst poisons as a result of the weak adsorption strength of a poison on the catalyst surface. This observation is in good agreement with that obtained previously by the calorimetric measurements of the heat of adsorption for several poisons on D-Ni and Ni-B catalysts (*22*).

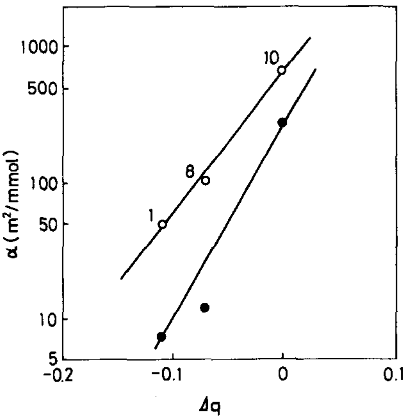

FIG. 4. Poisoning coefficient α calculated from Maxted equation vs Δq in the hydrogenation of styrene. ○, Carbon disulfide; ●, triphenylphosphine. Numbers in the figure correspond to the catalyst number in Table 1.

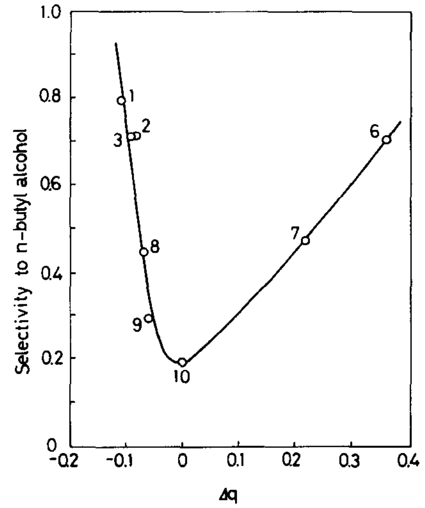

FIG. 5. Correlation between the selectivity of the nickel catalyst to the formation of *n*-butyl alcohol and Δq in the hydrogenation of 1,2-butylene oxide at 30°C under the atmospheric pressure of hydrogen. Selectivity is represented by *n*-butyl alcohol/*n*-butyl alcohol + *sec*-butyl alcohol. Numbers in the figure show the catalyst entry number in Table 1.

To correlate between Δq and the selectivity of the nickel metal for hydrogenation reactions, the hydrogenation of 1,2-butylene oxide was studied over the nickel catalysts. As shown in Fig. 5, the selectivity of the reaction was found to be successfully represented in terms of Δq. It is beyond the scope of the present paper to reveal the reasons why the selectivity depends on Δq as in Fig. 5, since this may be connected with the reaction intermediates (such as radical and π allylic species) formed on the nickel catalysts and no reasonable reaction mechanism has been presented. The correlation in Fig. 5, though, would provide an important insight for the reaction mechanism. We would like to stress the usefulness of Δq as a parameter characterizing the catalytic properties, such as the activity, selectivity, and resistivity against poisoning in hydrogenation reactions. It is very probable that Δq reflects the electronic properties of the catalysts.

SUMMARY

A parameter Δq was tentatively proposed to define the electronic properties of the nickel catalysts. The specific activity of the nickel catalyst for hydrogenation reactions was successfully explained in terms of Δq. The resistivity of the nickel catalyst against poisoning was also well understood by using Δq. The selectivity of the hydrogenation of 1,2-butylene oxide was simply represented as a function of Δq. It seems that Δq is a good parameter to characterize the electronic properties of the catalysts.

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