Effects of Additives on Morphological and Catalytic Properties of Ni–SiO$_2$ Catalysts for Enantioselective Hydrogenation

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Effects of additives such as Pd and Cl in the preparation of precipitated Ni–SiO$_2$ catalysts have been studied by means of X-ray diffraction and thermal gravimetric analysis using various precursors with different compositions. Pd addition stimulates the reduction of NiCO$_3$ species in the precursors but scarcely improves the enantioselectivity of the H$_2$-reduced catalysts. Cl addition causes an increase in the mean crystallite size of Ni and disappearance of small crystallites in the reduced catalysts probably by promoting the reduction of Ni(OH)$_2$ species having strong interaction with support. This explains the increased enantioselectivity and durability of the Cl-promoted catalysts. Mechanism of the crystallite size increase caused by the Cl addition has been discussed. © 1986 Academic Press, Inc.

INTRODUCTION

In the enantioselective hydrogenation of methyl acetoacetate (MAA) to methyl 3-hydroxybutyrate (MHB) on tartaric acid-modified nickel catalysts, Orito *et al.* (*1*) reported that Ni–platinum metal–kieselguhr (1 : 0.01 : 1) catalysts have higher activities and enantioselectivities than the Ni–kieselguhr (1 : 1) catalyst. However, the details of this promoting effect of added platinum metals has not been studied so far. Tartaric acid-modified platinum metals are known to exhibit only low enantioselectivities (*2, 3*).

The enantioselective hydrogenation is known to be highly structure-sensitive. With unsupported nickel catalysts, we have reported that amorphous catalysts such as nickel boride and nickel phosphide have very low enantioselectivities and that the selectivity of modified catalysts increases almost linearly with increasing crystallite size of Ni up to ca. 6 nm and then gradually approaches a certain value which depends on the reaction conditions. The selectivities of the catalysts having larger crystallite sizes than ca. 20 nm were almost constant

and the value (the maximum optical yield of (−)-MHB) was about 60% under our experimental conditions (*4*). These behaviors were explained in terms of the probability to obtain large ensembles of regularly arranged nickel atoms in the catalyst surface for the modifier to adsorb strongly and regularly; the larger crystallites will have the higher probability. The suggestion by Harada *et al.* (*5*) that amorphous part of H$_2$-reduced catalysts obtained from NiO provides nonselective sites is in line with our idea mentioned above. With supported nickel catalysts, we have shown that the enantioselectivity depends primarily on the mean crystallite size of Ni and that the crystallite size distribution (CSD) of Ni plays an important role in determination of the selectivity of the modified catalysts (*6–9*). The presence of small crystallites is undesirable because they have only low selectivity although they have high specific activity and hence large contribution to overall hydrogenation. In other words, catalysts with relatively large and uniform size of Ni metal are expected to have high enantioselectivity. In fact, Hayashi and Nagayama recently reported that "ultrafine parti-

cles" of Ni metal with uniform size of 30 nm exhibited very high enantioselectivity (10).

The conditions of reduction as well as preparation of catalyst precursors were reported to affect the CSD of Ni in supported catalysts (6, 11) and hence affect the activity and enantioselectivity of the catalysts (8, 9). Therefore, the favorable effect of platinum metal on the properties of Ni-kieselguhr catalysts can be attributed to the stimulatory action of platinum metal in the reduction of nickel salt under relatively mild conditions. Roman and Delmon (12) reported that platinum, palladium, and copper promote the reduction of silica-supported nickel oxide to higher rates and a higher degree of transformation. More recently Praliaud et al. (13) showed that, in the CO hydrogenation, the Cr additive results in an increase in the activity and the selectivity for low temperature reduction because of the better reducibility of nickel in the presence of chromium.

On the other hand, the effect of chloride anion, i.e., the counteranion of added platinum metal, in the reduction process should also be taken into consideration. Recently, the effects of electronegative atoms such as chlorine on catalytic and chemisorption properties of Ni catalysts have been investigated and interpreted in terms of changes in the surface electron deficiency (14, 15). In the case of CO hydrogenation on supported Fe or Co catalysts, Barrault (16) observed that the introduction of a chloride greatly modifies the properties of the original metals and suggested that both ensemble and electronic effects must be taken into account to explain activity and selectivity variations. Treatments with halogen compounds are also known to affect the dispersion of noble metal particles (17, 18). With regards to the effects of additives in the modifying solution, Harada et al. reported that the use of alkali halides, especially NaBr, remarkably enhances the enantioselectivity of the modified Raney nickel catalyst (19) and proposed the poisoning effect

of NaBr on nonselective sites (20). Bostelaar and Sachtler suggested that alkali halides in the reaction mixture modify the stereochemistry of the product-determining surface complex (21). Therefore, even in the case that halides are added before reduction process, the effect of halides remaining on the catalyst surface should be taken into account.

In the present study, we examined the effect of Pd or Cl addition on the reducibility of various catalyst precursors and on morphological and catalytic properties of the hydrogen-reduced catalysts. It has been found that Pd addition, although it stimulates the reduction of Ni salt, scarcely improves the enantioselectivity of Ni–SiO₂ catalysts whereas Cl addition significantly increases the mean crystallite sizes of Ni and the enantioselectivity of the hydrogen-reduced catalysts. The role of the added Pd or Cl in the reduction process is assessed in connection with the composition of the precursor.

EXPERIMENTAL

Catalyst preparation. Most catalyst precursors (Ni : Support = 1 : 1 by weight) were prepared by a precipitation method with Na₂CO₃ from aqueous Ni(NO₃)₂ solution suspended by silica gel (Nakarai Chemicals, No. 1. 60–200 mesh, 600 m²/g) or kieselguhr (Kg) (Yoneyama Yakuhin Co., 5.7 m²/g) as described previously (6, 7). The molar ratio of Na₂CO₃ to nickel salt, precipitation temperature, aging time, drying temperature, and drying time were varied to prepare Ni–SiO₂ (1 : 1) precursors with different composition (8) as listed in Table 1. Sodium hydroxide was used as a precipitant to prepare a precursor free from carbonate. The palladium-promoted precursors (Ni : Pd : Support = 1 : 0.01 : 1) were prepared by using mixed aqueous solution of Ni(NO₃)₂ and PdCl₂ in precipitation. The halogen-promoted precursors were prepared by adding a certain amount of aqueous solution of a halide to the dried Ni–SiO₂ precursors followed by drying at 110°C

TABLE 1

Preparation Conditions of Ni–SiO$_2$ (1 : 1) Catalyst Precursors

Preparation conditions	A	B	C
Na$_2$CO$_3$/Ni salt (molar ratio)	1	1.2	0.83
Precipitation temperature (°C)	75	85	0
Aging time (min)	15	30	5
Drying temperature (°C)	110	120	50
Drying time (h)	24	45	20
Composition of precursor (NiCO$_3$ content)[a]	Standard (35–40%)	Ni(OH)$_2$-rich (7–10%)	NiCO$_3$-rich (60–65%)

[a] Determined by TG measurements under N$_2$ flow (8).

for 24 h. Two grams of a precursor (containing ca. 0.7 g of Ni) was reduced in a H$_2$ stream of 8 liters/h at 350°C for 1 h unless otherwise stated.

The decomposed nickel (D-Ni) catalyst was obtained by decomposing nickel formate at 300°C for 3 h under a vacuum followed by washing with distilled water (22, 23). The Pd-promoted D-Ni catalysts were prepared by stirring D-Ni in aqueous solution of PdCl$_2$ (5–15 wt% of Ni) at 30°C for 20 min and washed twice with distilled water. The total amount of Pd in the solution was regarded as being replaced by the surface Ni in the D-Ni catalyst.

Hydrogenation. The reduced catalyst was modified with aqueous tartaric acid solution (pH = 5.1 unless otherwise stated) according to the method described previously (4, 24) and was rinsed with distilled water and methanol. Methyl acetoacetate (10 ml) in ethyl acetate (10 ml) was hydrogenated with the modified catalyst at 60°C under a starting H$_2$ pressure of 10 kg/cm^2 as described previously (4). The hydrogenation activity of a catalyst was determined from the pressure decrease during the initial 15 min of the reaction. The optical yield (OY) of MHB determined from the optical rotation (α_D) of distilled product was employed as a measure of the enantioselectivity of the catalyst: OY = (α_D/22.95) × 100 (19).

Analysis. Thermal gravimetric measurements of catalyst precursors were carried

out using a Shimadzu DT-30 thermal analyzer. Freshly prepared samples (40 mg each) were heated either in N$_2$ or in H$_2$ flow to 600°C at a temperature ramp of 10°C/min. In the thermal gravimetric analyses (TGA), both weight loss (TG) and the first derivative of weight loss (DTG) were monitored together with the differential thermal analysis (DTA). Degrees of reduction of some catalysts were evaluated from the weight loss in the range from 200°C to a certain temperature based on the theoretical weight loss for 100% reduction of the precursor.

The X-ray diffraction (XRD) patterns of the catalysts were measured with a Shimadzu VD-1 diffractometer usually after separation from the reaction mixture. The mean crystallite size ($\overline{D_c}$) of Ni was calculated from the half-width of the peak on (111) plane of Ni metal after correction for the effects of instrumental broadening by Warren's method (25). The XRD patterns were also measured for some precursors heated in N$_2$ at 400°C for 2 h.

The amount of tartaric acid adsorbed on the modified D-Ni catalyst was determined colorimetrically according to the method described by Harada *et al.* (20).

The BET and the metal surface areas of some catalysts were measured by N$_2$ adsorption at −196°C and by H$_2$ adsorption at 20°C, respectively.

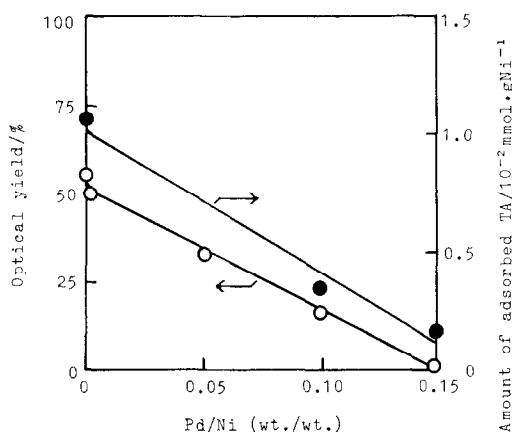TEM measurements of some catalyst samples, suspended in collodion solution

FIG. 1. Effect of Pd added to D-Ni on the enantiose-lectivity and on the amount of adsorbed tartaric acid.

and then placed on a fine mesh copper screen, were conducted using a JEOL JEM-200CX electron microscope.

RESULTS AND DISCUSSION

Effect of Pd Addition

In order to check the net effect of surface Pd in the reaction, avoiding its influence in the reduction process, first we examined the properties of Pd-promoted D-Ni catalysts in enantioselective hydrogenation of MAA. As can be seen from Fig. 1, the enantioselectivity of the Pd-promoted catalyst decreased linearly with increasing amount of surface Pd. The amount of tartaric acid adsorbed on the surface also decreased with increasing surface Pd. Evidently Pd itself has negative effect on the selectivity of modified catalysts. This is probably because of the low ability of Pd to adsorb tartaric acid and, moreover, because added Pd decreases the size of the ensembles of regularly arranged surface Ni atoms on which reactants and modifiers can adsorb strongly and regularly (4).

The positive effect of Pd in Ni–Pd–kieselguhr catalysts reported by Orito et al. (1) is, therefore, expected to be the effect on the reducibility of Ni precursors. Figure 2 shows the DTG profiles measured in H$_2$ flow for various precursors prepared under

different conditions. As we reported previously (9), the proportion of NiCO$_3$ in the Ni–SiO$_2$ precursors, and hence the reducibility of the precursors, decrease in the order of preparation conditions: C → A → B in Table 1. In the case of Pd-added precursors, the reduction starts at a much lower temperature, indicating the stimulatory action of Pd in the reduction of Ni species. In addition, the proportion of the Ni species reduced at the low temperature decreases with decreasing NiCO$_3$ content in the precursor. Thus, the added Pd seems to stimulate the reduction of NiCO$_3$ but scarcely affect the reduction of Ni(OH)$_2$ species which has interaction with the support and is difficult to be reduced (9).

Table 2 shows the effects of Pd addition on the catalytic properties of Ni–SiO$_2$ catalysts prepared or reduced under different
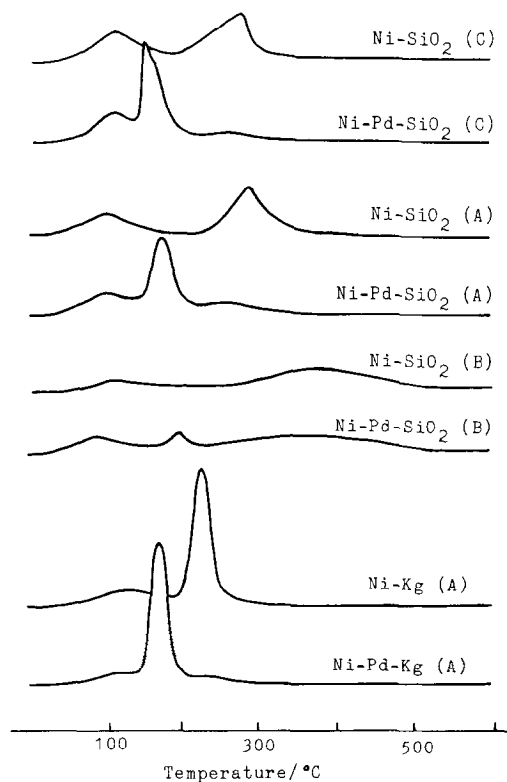

FIG. 2. DTG-in-H$_2$ profiles of various precursors prepared under (A) standard, (B) severe, and (C) mild conditions.

TABLE 2

Catalytic Properties of Modified Ni–SiO₂ (1 : 1) and Ni–Pd–SiO₂ (1 : 0.01 : 1)
Catalysts Prepared under Different Conditions

Catalyst	Preparation conditions[a]	Reduction temp. (°C)[b]	$\overline{D}_c{}^c$ (nm)	$r_0{}^d$ (mmol/min/g Ni)	OY[e] (%)
Ni–SiO₂	A	300	—	0.67	23.9
		350	—	1.03	35.9
		400	9	0.87	50.6
		500	12	0.67	50.5
Ni–Pd–SiO₂	A	300	—	0.43	27.8
		350	—	0.86	36.5
		400	12	0.61	41.6
		500	15	0.79	36.9
Ni–SiO₂	B	300	—	1.10	17.8
		350	3	1.27	19.3
		400	4	2.13	29.8
Ni–Pd–SiO₂	B	300	—	1.03	4.4
		350	3	0.73	16.3
		400	5	0.37	20.1
Ni–SiO₂	C	300	13	0.37	43.4
Ni–Pd–SiO₂	C	300	13	0.37	30.1
Ni–SiO₂[f]	C	300	13	0.37	36.8
Ni–Pd–SiO₂[f]	C	300	13	0.43	34.6

[a] See Table 1.
[b] Reduced for 1 h.
[c] Mean crystallite size of nickel.
[d] Initial hydrogenation rate.
[e] Optical yield of (−)-MHB.
[f] Modified at pH = 4.1 instead of pH = 5.1.

conditions. In almost all cases examined Ni–Pd–SiO₂ catalysts exhibited lower activities and selectivities than Ni–SiO₂ catalysts in accord with the result for the D–Ni catalyst although Ni–Pd–SiO₂(A) catalysts reduced at 300 and 350°C had slightly higher OYs than Ni–SiO₂(A) catalysts. The mean crystallite sizes ($\overline{D}_c$) of Ni obtained from X-ray line broadening were increased slightly by Pd addition. These effects of added Pd on the catalytic properties of Ni–SiO₂ catalysts can be explained by the stimulatory action of Pd in the reduction of Ni species as mentioned above. Relatively large Ni crystallites, reduced from NiCO₃, with high enantioselectivity will slightly grow in the presence of Pd and lose their activity, whereas smaller crystallites, reduced from Ni(OH)₂, with low selectivity will remain unaffected, thus leading to the decrease in the total activity and selectivity of the catalyst. Under mild reduction conditions where Ni(OH)₂ species in the precursor cannot be reduced at all and where the reduction of NiCO₃ produces yet small Ni crystallites, Pd addition can lead to an increase in enantioselectivity of the catalyst according to the slight increase in $\overline{D}_c$ of Ni.

In the case of Kg-supported catalysts, Pd addition increased activities of all catalysts examined and, in conformity with this, decreased the selectivities and $\overline{D}_c$ of the catalysts except the one modified at pH = 4.1 as shown in Table 3. These results are also explained by the stimulatory action of Pd in the reduction of Ni precursor similarly to the case of Ni–SiO₂(A) catalysts. The Ni precursors supported on Kg are highly reducible compared to the SiO₂-supported precursors (6). In such a case, Pd may pro-

TABLE 3

Catalytic Properties of Modified Ni–Kg (1 : 1) and
Ni–Pd–Kg (1 : 0.01 : 1) Catalysts Prepared under
Standard Conditions

Catalyst	Reduction temp.[a] (°C)	$\overline{D}_c$[b] (nm)	r_0[c] (mmol/ min/g Ni)	OY[d] (%)
Ni–Kg	225	35	0.37	31.0
	250	31	0.30	32.5
	300	31	0.24	22.0
Ni–Pd–Kg	225	15	1.03	22.6
	250	16	0.97	26.3
	300	19	0.97	16.0
Ni–Kg[e]	300	31	0.13	12.1
Ni–Pd–Kg[e]	300	12	0.43	27.7

[a] Reduced for 1 h.
[b] Mean crystallite size of nickel.
[c] Initial hydrogenation rate.
[d] Optical yield of (−)-MHB.
[e] Modified at pH = 4.1 instead of pH = 5.1.

mote the reduction of Ni precursors so deeply that the Ni crystallite sizes become smaller because of redispersion or of the presence of hetero atoms. The exceptional increase in the selectivity of Ni–Pd–Kg catalyst modified at pH = 4.1 could be attributed to the impurity such as Na in kieselguhr, because in the case of Ni–SiO₂ catalysts modified at pH = 4.1 such increase in selectivity was not observed. The positive effects of platinum metals reported by Orito *et al.* (*1*) can also be due to the difference in the pH value of the modifying solution; they modified their catalysts with a solution of pH = 4.1. In order to make clear the effect of impurity, further studies will be required. The impurities in kieselguhr, however, vary depending on the source of the material. This makes it difficult to study the effect of added Pd on the catalytic properties of Ni–Kg catalysts.

Effect of Cl Addition

Preliminary experiments carried out to check the effect of chloride ion, introduced in the preparation of Ni–Pd–SiO₂, showed

that addition of HCl to the catalyst precursor significantly increases $\overline{D}_c$ of Ni and the enantioselectivity of the H₂-reduced catalyst, especially when the catalyst without additives has low selectivity. This suggested a change in the CSD of Ni in the catalyst. Therefore, we examined further the effect of various halides and acids added to the precursors on the morphological and catalytic properties of the reduced catalysts.

As listed in Table 4, addition of metal chlorides as well as bromides and iodides to the standard precursor increased $\overline{D}_c$ of Ni and the selectivity of the catalyst, and caused considerable decrease in the initial hydrogenation rate. The order of effectiveness of the additives was as follows: HBr ~ NaBr > HCl ~ NiCl₂ > FeCl₂ ~ CuCl₂ > NaCl ~ KCl. Iodides induced almost complete inactivation of the catalyst. On the

TABLE 4

Effect of Halide Addition to Ni–SiO₂ (1 : 1)
Precursor on Properties of the H₂-Reduced
Catalysts[a]

No.	Additives	X/Ni[b]	$\overline{D}_c$[c] (nm)	r_0[d] (mmol/ min/g Ni)	OY[e] (%)
1	—	0	13	1.17	36.1
2	HCl	0.125	16	0.49	52.3
3	HCl	0.250	22	0.37	52.7
4	NaCl	0.183	15	0.80	40.8
5	NaCl	0.549	22	0.37	54.0
6	KCl	0.167	16	0.56	44.0
7	NiCl₂	0.145	24	0.30	54.0
8	CuCl₂	0.124	20	0.43	48.8
9	FeCl₂	0.186	20	0.24	49.7
10	HBr	0.125	24	0.30	51.9
11	NaBr	0.183	31	0.30	57.5
12[f]	NiI₂	0.041	20	0.06	44.0
13[f]	CuI	0.097	19	—[g]	—

[a] Reduced at 400°C for 1 h.
[b] Atomic ratio of halogen to Ni.
[c] Mean crystallite size of Ni.
[d] Initial hydrogenation rate.
[e] Optical yield of (−)-MHB.
[f] Reduced at 350°C for 1 h.
[g] The reaction was very slow.

other hand, addition of nitric acid or acetic
acid increased neither $\overline{D}_c$ nor OY. These
findings indicate that the effect of HCl ad-
dition is not attributed to the action of acid
but caused by the presence of halogen dur-
ing the reduction process. As we reported
previously (9), the reducibility of Ni–SiO$_2$
precursors, and hence the crystallinity of
Ni in the H$_2$-reduced catalysts, depend on
the composition of the precursors. There-
fore, the effect of halide (NiCl$_2$) addition on
the crystallinity of Ni was examined using
three kinds of precursors with different
NiCO$_3$ contents. In the case of the
Ni(OH)$_2$-rich precursor the crystallinity re-
markably changed with halide addition
from nearly amorphous to crystalline as il-
lustrated in Fig. 3. As for the catalyst ob-
tained from the NiCO$_3$-rich precursor, a de-
crease in the wings as well as in the
half-width of the profile with the halide ad-
dition was observed. Therefore, the pres-
ence of a halide during the reduction of Ni–
SiO$_2$ precursors seems to cause the
disappearance or the growth of relatively
small crystallites originating from Ni(OH)$_2$
species in the precursor, and hence result
not only in large $\overline{D}_c$ but also in narrow CSD
of Ni in the catalyst. This can explain the
increased enantioselectivity of the halide-
promoted catalysts.

Table 5 shows the effects of NiCl$_2$ addi-
tion to three kinds of precursors on the sur-
face areas and metal particle sizes for the
H$_2$-reduced catalysts. The nickel surface
areas drastically decreased with the halide
addition, indicating not only the increase in
the particle diameters but also the presence
of remaining chlorine which may inhibit the
hydrogen adsorption on nickel (15). With
the catalysts obtained from unpromoted
precursors, the average particle diameter
determined from metal surface area ($\overline{D}_s$)
(26) is smaller than the mean crystallite size
of Ni determined from X-ray line broaden-
ing ($\overline{D}_c$). This supports the presence of
small Ni crystallites in these unpromoted
catalysts. Figure 4 compares TEM micro-
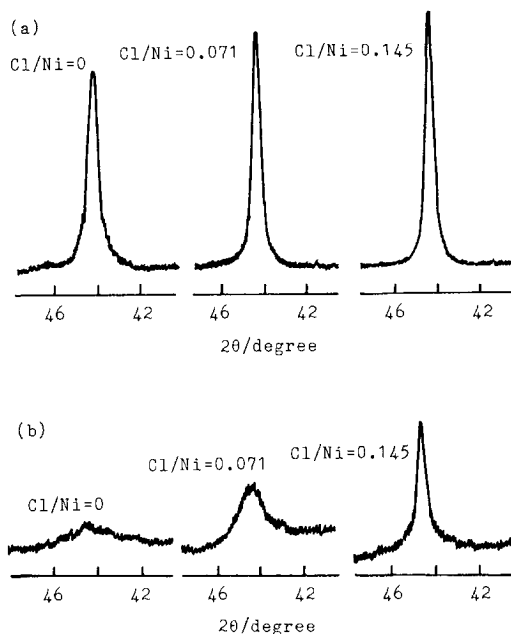graphs for two kinds of catalysts; one ob-

FIG. 3. The Ni(111) lines of XRD profiles for Cl-
promoted Ni–SiO$_2$ catalysts obtained from (a) NiCO$_3$-
rich and (b) Ni(OH)$_2$-rich precursors.

tained from the NiCO$_3$-rich precursor ap-
parently has broader distribution of Ni
crystallite size than another obtained from
the NiCl$_2$-promoted Ni(OH)$_2$-rich precur-
sor. This explains the lower enantioselec-
tivity of the former catalyst in spite of the
larger $\overline{D}_c$ value (Table 5).

On the other hand, halides remaining on
the catalysts surface after H$_2$-reduction of
halide-promoted precursors can act as addi-
tives in the modifying solution just as those
reported by Harada and Izumi (19). In or-
der to check if this is the main reason of the
improved enantioselectivity of halide-pro-
moted catalysts, we examined the durabili-
ties of these catalysts for repeating uses
(Table 6). The catalyst used for the hydro-
genation was separated from the reaction
product by decantation, rinsed with 5 ml of
ethyl acetate, and then successively used
for the next hydrogenation under the same
conditions as before. The catalyst modified
with aq. solution (pH = 3.2) of tartaric acid
and NaBr (NaBr–TA-modified), according
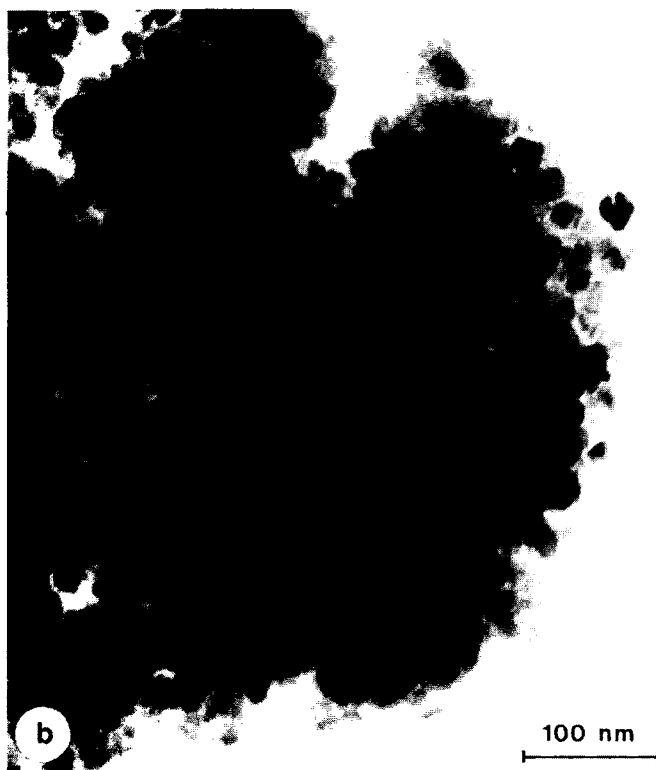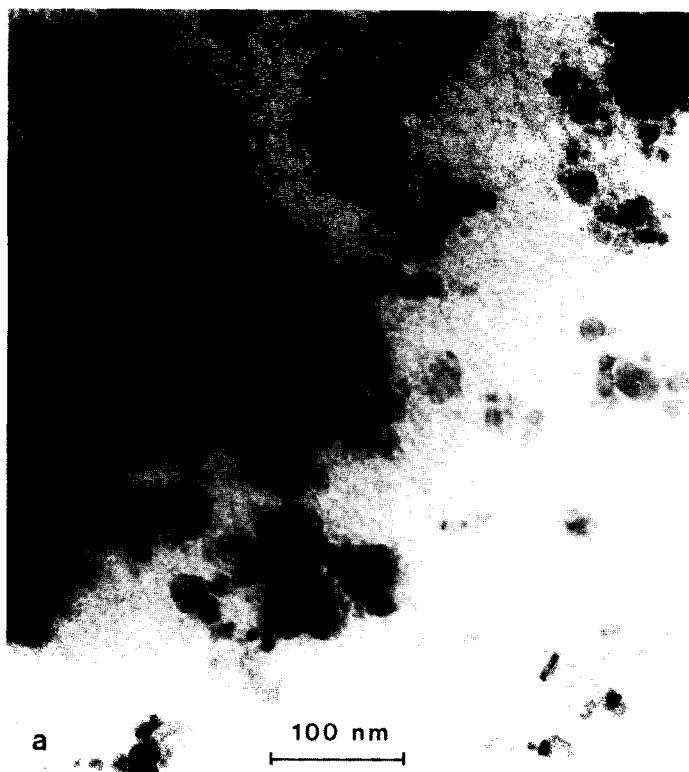to the method described by Harada and

FIG. 4. TEM micrographs of Ni–SiO$_2$ catalysts obtained from (a) NiCO$_3$-rich and (b) NiCl$_2$-promoted (Cl/Ni = 0.298) Ni(OH)$_2$-rich precursors.

TABLE 5

Surface Areas, Nickel Particle Sizes, and Enantioselectivities for $NiCl_2$-Promoted
$Ni-SiO_2$ (1 : 1) Catalysts[a]

Precursor (NiCO₃ content)	Amount of added Cl[b]	Surface areas		Average particle diameters (nm)		OY[e] (%)
		BET (m²/g)	Metal (m²/g Ni)	$\overline{D_c}^c$	$\overline{D_s}^d$	
Ni(OH)₂-rich (7.3%)	0	295	66.1	—	—	19.3
	0.145	292	16.6	11	—	29.8
	0.298	255	12.3	13	—	51.0
Standard (37.5%)	0	309	70.6	10	6	36.1
	0.145	301	11.0	17	—	52.7
	0.298	250	3.7	20	—	54.9
NiCO₃-rich (60%)	0	296	28.5	17	15	39.4
	0.145	268	5.0	26	—	62.3
	0.298	281	3.6	33	—	53.2

[a] Reduced at 350°C for 1 h.
[b] Atomic ratios of added Cl to Ni.
[c] Determined from X-ray line broadening.
[d] Determined from metal surface area: $\overline{D_s} = 4310/S_{Ni}$ (26).
[e] Optical yield of (−)-MHB.

Izumi (19), showed higher selectivity than that modified as usual (TA-modified) for the first run. However, both selectivity and activity of the NaBr–TA-modified catalyst decreased significantly for the second run. These decreases were observed even in the course of the first run; the higher the conversion, the lower the activity and selectivity. This is ascribed to the desorption of adsorbed modifier from the catalyst surface probably because of the high stirring speed employed here (27), and also to the partial dissolution of nickel metal under the relatively acidic conditions; the reaction mixture turned green in the course of hydrogenation. In the case of the catalyst obtained from the $NiCl_2$-promoted precursor ($NiCl_2$-promoted TA-modified), both activity and selectivity did not vary so much for the repeated runs. Thus, the increased enantioselectivity of $NiCl_2$-promoted catalysts cannot be explained only by the action of remaining halide in the modification (20, 21) but rather should be explained by the intrinsic property of the catalyst, i.e., the more favorable CSD of Ni in these catalysts. The highest selectivity of NaBr-promoted catalyst shown in Table 4 is considered to be due to both effects mentioned above.

TABLE 6

Comparison of Durabilities for Modified $Ni-SiO_2$
(1 : 1) Catalysts

Catalyst	Repeated run	Reaction time (h)	Conversion (%)	OY[d] (%)
TA-modified[a]	1st	20	100	36.1
NaBr-TA- modified[b]	1st	19	50	46.0
	2nd	70	32	11.0
NiCl₂-promoted TA-modified[c]	1st	19	90	52.7
	2nd	20	79	55.0
	3rd	24	81	54.9

[a] The standard precursor reduced at 350°C for 1 h was modified with aq. tartaric acid solution (pH = 5.1) as usual.
[b] The standard precursor reduced at 350°C for 1 h was modified with aq. solution (pH = 3.2) containing tartaric acid (1 g) and NaBr (10 g) (19).
[c] $NiCl_2$-promoted standard precursor (Cl/Ni = 0.145) was reduced at 350°C for 1 h and modified with aq. tartaric acid solution (pH = 5.1) as usual.
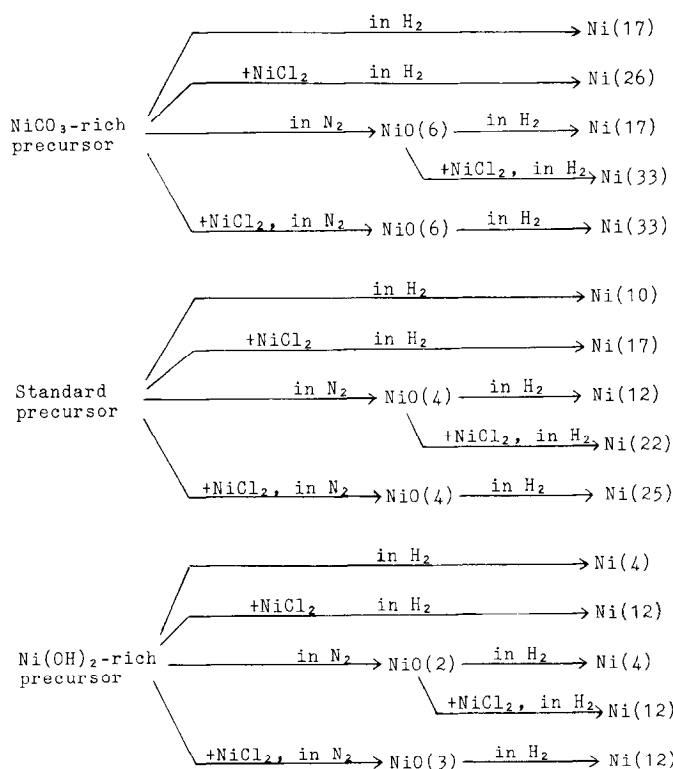[d] Optical yield of (−)-MHB.

FIG. 5. Effect of chloride addition (Cl/Ni = 0.145) on the growth of Ni crystallite. Catalyst precursors were heated in N$_2$ at 400°C for 2 h and/or reduced in H$_2$ at 350°C for 1 h. Numbers in parentheses refer to the mean crystallite sizes ($\overline{D_c}$ in nm).

Mechanism of $\overline{D_c}$ Increase Caused by Cl Addition

The crystallinity of Ni in the catalysts obtained from different precursors usually reflects the difference in the crystallinity of nickel oxide which exists as an intermediate product in the course of the reduction process (8). In order to see if the added halide affects the crystallinity of nickel oxide, we examined the XRD patterns of heated precursors with or without NiCl$_2$ addition. As shown in Fig. 5, the addition of NiCl$_2$ to any kinds of precursors did not increase the $\overline{D_c}$ of nickel oxide, whereas the Ni metal reduced from the oxide had always increased $\overline{D_c}$ regardless of the stage of the NiCl$_2$ addition and similar to the case of direct reduction. Thus, it is obvious that the effect of added halides arises not in the

course of the decomposition of Ni precursors to nickel oxide but in the reduction process of nickel oxide to nickel metal. Figure 6 shows the DTG profiles measured in N$_2$ flow for the standard precursors promoted by different amounts of NiCl$_2$. There were no significant differences between these profiles. This supports the idea that the effect of halide addition is not present in the decomposition process.

On the other hand, the DTG profiles measured in H$_2$ flow had striking difference between NiCl$_2$-promoted and unpromoted precursors as shown in Fig. 7. The peak around 300°C (peak I) and the small shoulder peak around 350°C (peak II) correspond to the weight losses due to the reduction of NiCO$_3$ and of Ni(OH)$_2$ having weak support interaction, respectively. The sharp peaks (peak III) at higher temperatures which ap-

FIG. 6. DTG-in-N_2 profiles of Cl-promoted precursors. Atomic ratios of added Cl to Ni are (a) 0, (b) 0.059, (c) 0.120, and (d) 0.182.
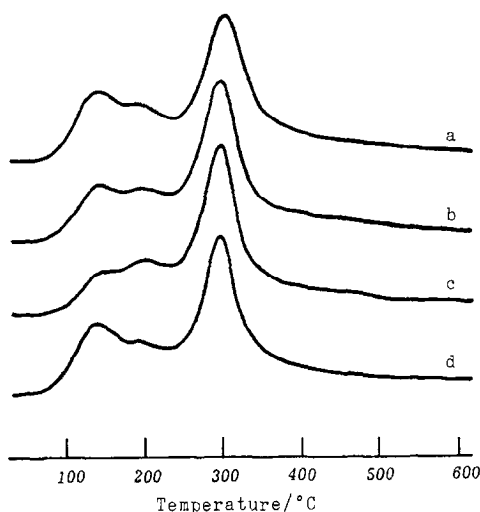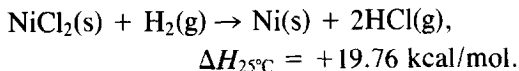

FIG. 7. DTG-in-H_2 profiles of Cl-promoted precursors. Atomic ratios of added Cl to Ni are (a) 0, (b) 0.059, (c) 0.120, and (d) 0.182.

pear in the profiles of Cl-promoted precursors may be attributed to the reduction of added $NiCl_2$.

The reduction of $NiCl_2$ is an endothermic reaction as follows (28):

$$NiCl_2(s) + H_2(g) \rightarrow Ni(s) + 2HCl(g),$$
$$\Delta H_{25°C} = +19.76 \text{ kcal/mol.}$$

The DTA-in-H_2 profiles of Cl-promoted precursors, shown in Fig. 8, also exhibited sharp endothermic peaks at the temperatures corresponding to the peak III in the DTG profiles, supporting the peak assignment to the reduction of $NiCl_2$. The peak III was shifted to a lower temperature with increasing amount of added chloride and superposed on the peak II when the atomic ratio of added Cl to Ni increased up to 0.182 (curve d in Fig. 7). Figure 9 shows the DTG-in-H_2 profiles of various precursors with different $NiCO_3$ contents promoted by a constant amount of $NiCl_2$. The reduction peak of $NiCl_2$ again shifted to a lower temperature with increasing proportion of $NiCO_3$ in the precursor and superposed on the peak II when the $NiCO_3$ content reached 65% (curve d in Fig. 9).
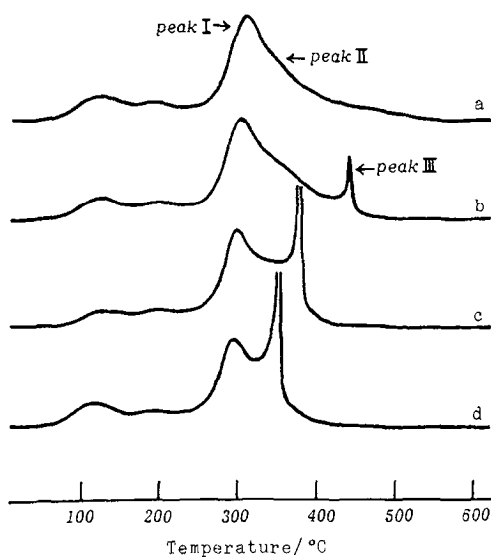
These findings suggest that the added

chloride may have some connection with the $Ni(OH)_2$ species having strong interaction with support and that the reducibility of $NiCl_2$ increases with increasing ratio of $NiCl_2$ to $Ni(OH)_2$ species. It can be presumed that hydrogen chloride produced by the abrupt reduction of $NiCl_2$ reacts with the $Ni(OH)_2$ species and facilitates the reduction of the species, resulting not only in
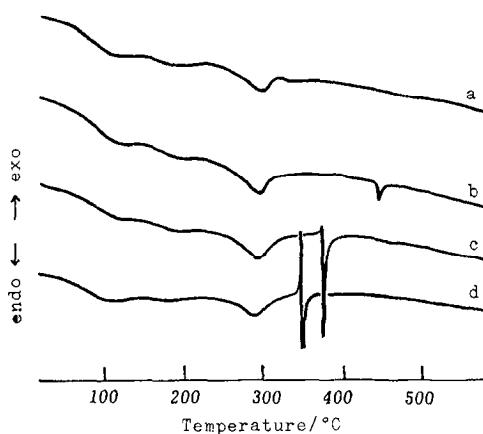

FIG. 8. DTA-in-H_2 profiles of Cl-promoted precursors. Atomic ratios of added Cl to Ni are (a) 0, (b) 0.059, (c) 0.120, and (d) 0.182.
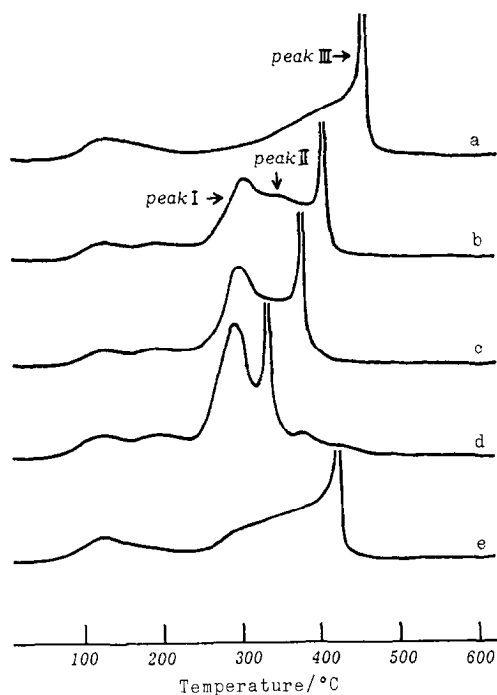
FIG. 9. DTG-in-H₂ profiles of Cl-promoted (Cl/Ni = 0.120) precursors with different NiCO₃ contents: the NiCO₃ contents of original precursors are (a) 8%, (b) 27%, (c) 46%, (d) 65%, and (e) 0% (precipitated by NaOH).

FIG. 10. Reducibility of Cl-promoted precursors. Atomic ratios of added Cl to Ni are (a) 0, (b) 0.059, (c) 0.120, and (d) 0.182.

large $\overline{D_c}$ but also in narrow CSD of Ni in the catalyst. The reducibility of various Cl-promoted precursors is illustrated in Fig. 10. The degrees of reduction are in fact larger for Cl-promoted precursors than for the unpromoted one especially at a temperature above 350°C. This again supports the promoting effect of added chloride on the reduction of Ni(OH)₂ species which is originally difficult to reduce because of the strong interaction with support. Such a promotion of reduction by chlorides is exemplified by the chloride volatilization used in industry for the separation of heavy metals contained in sludge (28, 29).

In enantioselective hydrogenation with tartaric acid-modified Ni catalysts, Cl addition was found to be preferable because larger $\overline{D_c}$ of Ni is favored in this reaction. However, in most reactions in which higher metal dispersion is favored, it is important
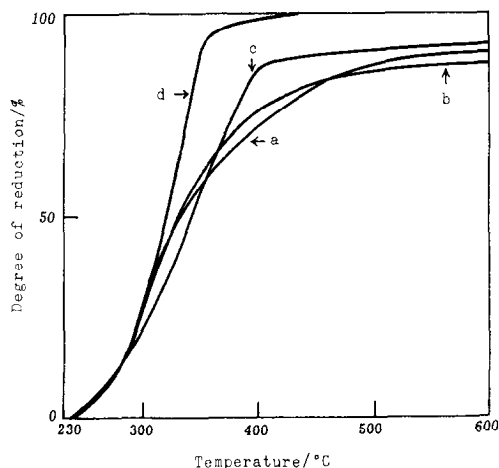
to remove halides in the precursors in order to avoid $\overline{D_c}$ increase during reduction process.

The crystallite size effects on enantioselectivity appear to reflect the influence of surface morphologies on the stereochemistry of asymmetric surface complex (21) or on the strength and regularity of the adsorption of reactants and modifiers. Not only the smoothness but also the crystallography of the metal surface might be the explanation. It is known that the fraction of (111) plane in the fcc cubooctahedron crystallites increases with increasing crystallite size (30). Further studies concerning the detailed explanation for the crystallite size effects are now in progress.

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