Effect of Preparation Variables on Enantioselectivity of Supported Nickel Catalysts Modified with Tartaric Acid

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Enantioselective hydrogenation of methyl acetoacetate to methyl 3-hydroxybutyrate on various supported nickel catalysts modified with (R,R)-tartaric acid was studied under mild reaction conditions in order to examine the effects of preparation variables on the enantioselectivity and activity of resulting catalysts. The selectivity of the supported nickel catalysts was strongly dependent on the precipitation conditions. The effect of reduction conditions on the selectivity depended on the kind of support. Even Ni–alumina catalysts, when reduced under relatively mild conditions, had high enantioselectivity although their hydrogenation activity was low. Ni–silica catalysts, precipitated under optimum conditions and reduced at 400–500°C for 1–3 h, were much more active than the other catalysts with similar, high enantioselectivity. Various extents of the selectivity of supported nickel catalysts were explained in terms of the effect of preparation conditions on the crystallite size distributions of nickel.

INTRODUCTION

The interaction between the modifier and the substrate during the enantioselective hydrogenation of methyl acetoacetate (MAA) on tartaric acid-modified nickel catalysts (*1*) has been extensively studied. The preparation methods of the enantioselective catalysts have been improved and the optical yield of methyl 3-hydroxybutyrate (MHB) has increased to about 90% (*2, 3*). Although it is well known that the enantioselectivity of modified catalysts is affected strongly by the preparation methods or the conditions of pretreatments of the metal catalysts (*4–7*), only in a few cases a correlation between enantioselectivity and the structure or the state of the catalyst surface itself has been reported.

In the previous paper, we have shown that the enantioselectivity of unsupported nickel catalysts increases with the crystallite size of nickel (*8*). It seemed to be due to the higher probability of obtaining large ensembles of regularly arranged nickel atoms in the catalyst surface for strong and regular adsorption of the modifier. However, unsupported catalysts with larger crystallite sizes (e.g., nickel black prepared by the decomposition of nickel formate or by the reduction of nickel monoxide) have lower hydrogenation activities because of smaller specific surface areas.

In order to prepare a useful catalyst with both high enantioselectivity and high hydrogenation activity, supported nickel catalysts seem to be promising. In addition, supported catalysts will give much useful information concerning the correlation between surface states of the metal and the enantioselectivity, because the surface state or the size distribution of metal particles of supported catalysts can be controlled by the preparation conditions.

Several supported catalysts, such as Ni–silica and Ni–kieselguhr, have been used by other investigators. However, the effect of the support varies widely from one report to another. For example, Hoek and Sachtler (*9*) reported that a silica-supported nickel catalyst displayed an enantioselectivity of nearly the same magnitude as Ra-

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ney Ni, whereas Orito *et al.* (*10*) obtained negative data on Ni–silica catalyst and showed that natural kieselguhr was the best support for enantioselective catalysts. In the case of alumina, Orito *et al.* found that Ni–Pd catalyst supported on alumina had a considerably high enantioselectivity, although it was slightly lower than the selectivity of Ni–Pd on kieselguhr. Hoek and Sachtler reported that alumina lowered the enantioselectivity of modified nickel catalysts in accordance with a result by Vedenyapin *et al.* (*11*) for alumina-supported modified ruthenium catalysts.

The discrepancies between these data seem to be due to the differences in the procedures for preparation of the catalysts. Systematic studies of the effects of preparation conditions upon the enantioselectivity of a resultant catalyst are important for obtaining supported catalyst with high and reproducible enantioselectivity and hydrogenation activity.

This paper presents the results of our studies of the effects of preparation variables (i.e., preparation method, the kind of support, nickel loading, precipitation conditions, and reduction conditions) on the enantioselectivity and activity of resulting catalysts, and describes conditions for the preparation of a highly enantioselective and also highly active Ni–silica catalyst. The correlation between the selectivity of hydrogenation and the surface states of these catalysts is also discussed.

EXPERIMENTAL

Materials

Silica gel No. 1 (Nakarai Chemicals, 60–200 mesh, 600 m^2/g) was used as a silica support. Al_2O_3 (JRC-ALO-5, 253 m^2/g) and TiO_2 (JRC-TID-1, 73 m^2/g) were obtained from the Catalysis Society of Japan. The other supports examined were kieselguhr (Kg) (Yoneyama Yakuhin Co., 5.7 m^2/g), Y-zeolite (Nikka Seiko Co. SK-40, 550 m^2/g), and MgO (42 m^2/g) obtained by calcining the hydroxide at 600°C for 6 h.

Methyl acetoacetate (MAA), ethyl acetate (EA), and methanol were dried and distilled before use. All other reagents were obtained from commercial sources and used without further purification.

Catalyst Preparation

Most catalysts were prepared by a precipitation method with Na_2CO_3 from aqueous $Ni(NO_3)_2$ solution suspended by a support material. The typical procedure was as follows. $Ni(NO_3)_2 \cdot 6H_2O$ (10 g) and a predetermined weight of a support were mixed in 50 ml of distilled water according to the desired percentage of nickel in the catalyst. The mixture was degassed for 1 min under vacuum, and then gently stirred for 15 min at ambient temperature and for 15 min at the precipitation temperature (75°C in most cases). Na_2CO_3 (3.7 g) in 25 ml of distilled water, preheated to the precipitation temperature, was added to the mixture via a syringe during 1 min under vigorous stirring. After 1 min, the precipitate was aged for 15 min at the same temperature with gentle stirring. Thereafter, the precipitate was filtered and washed three times with portions of 50 ml of warm distilled water. The washed samples were dried at 110°C for 24 h. NH_4OH, $NaHCO_3$, and NaOH as the precipitants and $NiSO_4 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, and $Ni(CH_3COO)_2 \cdot 4H_2O$ as the nickel salts were also used for comparison.

An impregnation method with $Ni(NO_3)_2 \cdot 6H_2O$ and a homogeneous precipitation–deposition method with urea (urea method) described by previous investigators (*12, 13*) were also examined for comparison. The total nickel content in the sample prepared by the latter method was determined using atomic absorption spectroscopy. Impregnated samples were calcined in air at 500°C for 5 h before reduction.

A weighed amount (usually 2.5 g, containing 0.88 g of Ni in the case where the Ni loading is 100%) of the resultant sample, after grinding into a powder, was reduced

in a hydrogen stream of 8 liters/h at various temperatures (250–500°C) and times (1–5 h), and then cooled to ambient temperature with the hydrogen gas still flowing.

Modification

The modification of a catalyst was carried out at 83°C by soaking a freshly reduced catalyst in a 1.6% aqueous solution of (R,R)-tartaric acid (TA) (pH = 5.1) for 1.5 h with occasional shaking according to the method described by Izumi et al. (14). After modification, the catalyst was rinsed once with distilled water, twice with methanol, and then once with EA (10-ml portion of each).

Hydrogenation

Ten milliliters of MAA in 10 ml of EA was hydrogenated with the modified catalyst at 60°C in a 50-ml glass autoclave (TEM-U-50, Taiatsu Glass Industry Co., LTD.) equipped with a 200-ml gas cylinder and magnetic stirring system. The starting hydrogen pressure was 10 kg/cm²; it decreased to about 3 kg/cm² at 100% conversion.

Analysis

The reaction product was filtered and distilled under reduced pressure. The conversion and the purity of the distilled product were measured with GLC (Shimadzu model 4APT) with a 2-m column of 20% PEG 20M on Celite 545.

The optical rotation (α_D) of the distilled product was determined with a Union PM-101 automatic digital polarimeter at 20°C in a 0.1-dm cell. The α_D values for the products obtained from the reactions of lower conversions were corrected by using a calibration curve for the concentration of MHB in MAA. The optical yield (OY) of (−)-MHB was calculated from the observed α_D value by the equation OY = (α_D/22.95) × 100 (3).

The X-ray diffraction pattern of the catalysts separated from the reaction mixture was measured with a Shimadzu VD-1 dif-

fractometer after wetting the catalyst with ethylene glycol to avoid the oxidation of nickel metal. Mean crystallite size of nickel ($\bar{D}_c$) was calculated from the half-width of the peak from the (111) plane of nickel metal.

The X-ray photoelectron spectra of the Ni $2p_{3/2}$ level were measured for some Ni–SiO$_2$ and Ni–Kg catalysts by a Hitachi 507 photoelectron spectrometer in order to obtain information concerning the reducibility of nickel oxide in the catalysts. The detailed procedures were reported elsewhere (15).

RESULTS

Preliminary experiments showed that lowering of pH (from 5.1 to 3.0) or temperature (from 83 to 0°C) of the modifying solution does not affect the enantioselectivity of the resulting supported catalysts but had negative effect on their hydrogenation activities. Therefore, in this work, modification of supported catalysts was carried out at 83°C and pH = 5.1.

Effects of Support and Preparation Method

Table 1 lists the hydrogenation activity (reaction time and conversion) and the enantioselectivity (optical yield of (−)-MHB) of various supported catalysts prepared by three different methods and reduced at 400°C for 3 h. Both, the enantioselectivity and the activity of the catalysts, were influenced strongly by the kind of support and by the preparation method. It can be seen that SiO$_2$ is the best support for the preparation of highly enantioselective and active nickel catalysts. The selectivity and activity of the catalysts prepared by the precipitation method were reproducible and in most cases were higher than those of the catalysts prepared by the impregnation method; in the latter case the obtained results were not reproducible. In the case of the homogeneous precipitation–deposition method, it was difficult to control the nickel loadings as well as to obtain a

TABLE 1

Effect of Preparation Methods and Supports on Hydrogenation Activity and Enantioselectivity of Modified Ni Catalysts[a]

No.	Method[b]	Support(Ni:support)	Reaction time (h)	Conversion (%)	OY (%)
1	Impr	$SiO_2(1:5)$	26	98.0	27.4
2	Impr	$SiO_2(1:2)$	16	100	30.2
3	Impr	Kg(1:5)	120	23.0	0.0
4	Impr	Kg(1:1)	96	86.5	10.6
5	Impr	Zeolite(1:5)	41	96.8	7.3
6	Impr	MgO(1:1)	117	100	0.0
7	Ppt	$SiO_2(1:1)$	5	100	56.2
8	Ppt	$SiO_2(1:5)$	6	96.7	41.4
9	Ppt	Kg(1:1)	48	93.0	29.1
10	Ppt	$Al_2O_3(1:1)$	94	97.0	43.7
11	Ppt	Zeolite(1:1)	75	98.7	45.6
12	Ppt	MgO(1:1)	14	100	6.1
13[c]	Ppt	$TiO_2(1:1)$	45	63.9	3.1
14	Urea	$SiO_2(1:1.6)$	7	100	46.2
15[d]	—	—	89	96.7	57.0

[a] Catalysts reduced at 400°C for 3 h except Nos. 13 and 15.
[b] Impr: Impregnation method; Ppt: precipitation method; Urea: urea method.
[c] Reduced at 400°C for 1 h.
[d] Prepared by reduction of basic nickel carbonate (4.0 g) without support at 300°C for 3 h.

catalyst with high nickel loading. Therefore, in further experiments we have chosen SiO_2 as the support, and the precipitation method with Na_2CO_3 was used.

Effects of Nickel Salt and Precipitant

A change of nickel salt from nitrate to acetate caused a considerable decrease of the selectivity (from 56 to 42% in OY), accompanied by a decrease of the crystallite size of the resultant catalyst (from 9 to 6 nm in $\bar{D}_c$). The use of nickel sulfate resulted in an almost nonselective catalyst with a very low hydrogenation activity; this result was probably caused by the poisoning effect of the sulfur remaining on the catalyst surface.

The use of Na_2CO_3 as a precipitant gave a selective catalyst, whereas with NaOH a much less selective catalyst (OY = 21%), with much smaller $\bar{D}_c$ (<4 nm), was obtained. The order of the efficiency of some precipitants examined was as follows: $Na_2CO_3 \gtrsim NH_4OH > NaHCO_3 > NaOH$.

Thus, we have chosen nickel nitrate as the starting salt and Na_2CO_3 as the precipitant.

Effect of Nickel Loading

The data in Table 1, obtained for the catalysts supported on Kg and on SiO_2, suggest a dependence of the enantioselectivity on nickel loading. The results reported by Orito et al. (2, 10) also showed that supported nickel catalysts with high enantioselectivity should have relatively high nickel loadings. Figure 1 shows the effect of nickel loading on the enantioselectivity of Ni–SiO_2 catalysts reduced at 400°C for 3 h. The optical yield of (−)-MHB increased with an increase in the nickel loading and approached the maximum value (about 60%) which had been previously reported for an unsupported nickel catalyst prepared by the reduction of nickel monoxide (8). Since the reaction was carried out at relatively low temperature, unfavorable hydrogen pressure (16), and without additives such
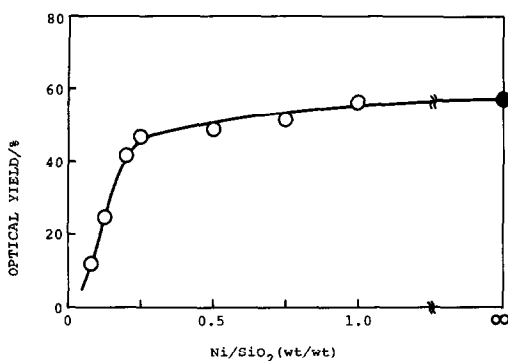
FIG. 1. Effect of nickel loading on the enantioselectivity of Ni–SiO$_2$ catalysts (●: no support used).

as acetic acid (2) or sodium bromide (3), this value of OY seems to be rather high.

The mean crystallite sizes of nickel ($\bar{D}_c$) in these catalysts increased with increase in the nickel loading: the values of $\bar{D}_c$ were 6.0, 7.5, 8.0, 9.0, and 9.0 nm for the catalysts with nickel loadings of 20, 25, 50, 75, and 100%, respectively. The values of $\bar{D}_c$

for the catalysts with lower nickel loadings than 20% were too small to be exactly measured by the XRD method. The hydrogenation activity of these catalysts increased rapidly with increase in the nickel loading up to 50% nickel and then remained almost constant.

Effect of Precipitation Conditions

Table 2 shows some results for Ni–SiO$_2$ (1:1) catalysts reduced at 400°C for 3 h. For preparation of a highly enantioselective catalyst, the concentrations of the solutions of nickel salt and precipitant, precipitation temperature, and the pouring time had optimum values around 0.69 mol/liter 1.38 mol/liter, 75°C, and 1 min, respectively. As illustrated in Fig. 2, the temperature only 5°C higher or lower than 75°C resulted in about 10% decrease in OY. Increase of the precipitation temperature above 75°C was accompanied by a decrease of the mean crystallite size of Ni. The stirring speed of

TABLE 2

Effect of Precipitation Conditions on the Properties of Modified Ni–SiO$_2$(1 : 1) Catalysts[a]

No.	Concn of Ni solution[b] (mol/liter)	Ppt temp. (°C)	Pouring time (min)	Aging time (min)	$\bar{D}_c$[c] (nm)	Reaction time (h)	Conv. (%)	OY (%)
1	1.38	75	1.0	15	11	8	98.5	42.7
2	0.69	75	1.0	15	9	5	100	56.2
3	0.46	75	1.0	15	12	5	96.2	42.7
4	0.69	85	1.0	15	4	3	100	38.1
5	0.69	79	1.0	15	6	3	100	47.3
6	0.69	77	1.0	15	7	5	100	53.3
7	0.69	70	1.0	15	10	4	100	45.3
8	0.69	65	1.0	15	7	4	100	43.9
9	0.69	55	1.0	15	7	4	100	43.3
10	0.69	0	1.0	15	11	7	100	42.1
11	0.69	75	0.75	15	10	5	100	40.1
12	0.69	75	1.5	15	5	4	100	48.7
13	0.69	75	1.0	0	13	7	100	44.2
14	0.69	75	1.0	5	9	6	100	57.2
15	0.69	75	1.0	30	7	4	100	55.0
16	0.69	75	1.0	60	5	3	100	41.7
17	0.69	75	1.0	180	—	25	98.5	12.3

[a] Catalysts reduced at 400°C for 3 h.
[b] Concentration of Na$_2$CO$_3$ solution was 1.38 mol/liter.
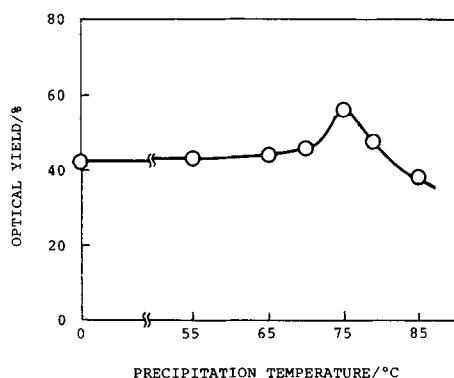[c] Mean crystallite size of Ni measured by XRD method.

FIG. 2. Effect of precipitation temperature on the enantioselectivity of Ni–SiO$_2$(1 : 1) catalysts.

the mixture of nickel solution and support during precipitation was also very important for obtaining a precipitate as homogeneous as possible. The increase of the molar ratio of Na$_2$CO$_3$ to nickel salt from 0.9 to 1.1 did not essentially affect enantioselectivity of the resultant catalyst, but with further increase of the amount of added

Na$_2$CO$_3$ considerable decrease of the selectivity was observed. The aging of the precipitate from 5 to 30 min only slightly affected selectivity of the catalyst while longer aging caused considerable decrease of both, activity and selectivity.

The OYs of (−)-MHB were reproducible to ±2% for the catalysts prepared by paying careful attention to the precipitation conditions.

Effect of Reduction Conditions

The effects of reduction temperature and time on catalytic properties of some precipitated catalysts (Ni : support = 1 : 1) are shown in Table 3 and in Fig. 3. Nickel–alumina catalysts reduced at around 300°C had considerably high enantioselectivity in contrast to those previously reported (5, 8) claiming the detrimental effect of alumina on the selectivity. In the case of Ni–SiO$_2$ catalysts, reduction temperature and time in the range of 400–500°C and 1–3 h, re-

TABLE 3

Effect of Reduction Conditions on the Properties of Modified Ni Catalysts

No.	Catalyst[a]	Reduction		$\bar{D}_c$ (nm)	Reaction time (h)	Conv. (%)	OY (%)
		Temp. (°C)	Time (h)				
1	Ni–SiO$_2$	300	1	—	6	89.0	23.9
2	Ni–SiO$_2$	300	3	(8)[b]	4	99.0	40.4
3	Ni–SiO$_2$	400	1	9	5	100	50.6
4	Ni–SiO$_2$	400	3	9	5	100	56.2
5	Ni–SiO$_2$	500	1	10	5	100	50.5
6	Ni–SiO$_2$	500	3	11	4	100	49.1
7	Ni–SiO$_2$	500	5	10	5	100	46.1
8	Ni–Kg	300	1	14	92	100	47.5
9	Ni–Kg	300	3	17	115	99.0	41.0
10	Ni–Kg	400	3	25	48	93.0	29.1
11	Ni–Al$_2$O$_3$	250	1	18	28	100	44.9
12	Ni–Al$_2$O$_3$	300	1	16	64	96.0	49.9
13	Ni–Al$_2$O$_3$	300	3	19	115	100	44.8
14	Ni–Al$_2$O$_3$	400	3	22	94	97.0	43.7
15	Ni–Al$_2$O$_3$	500	3	19	41	98.3	11.9
16	Ni–TiO$_2$	250	1	22	64	83.8	38.2
17	Ni–TiO$_2$	300	1	23	12	100	14.8
18	Ni–TiO$_2$	400	1	28	44	95.0	3.3
19	Ni–TiO$_2$	500	1	27	45	63.9	0.4

[a] Ni: support = 1 : 1.
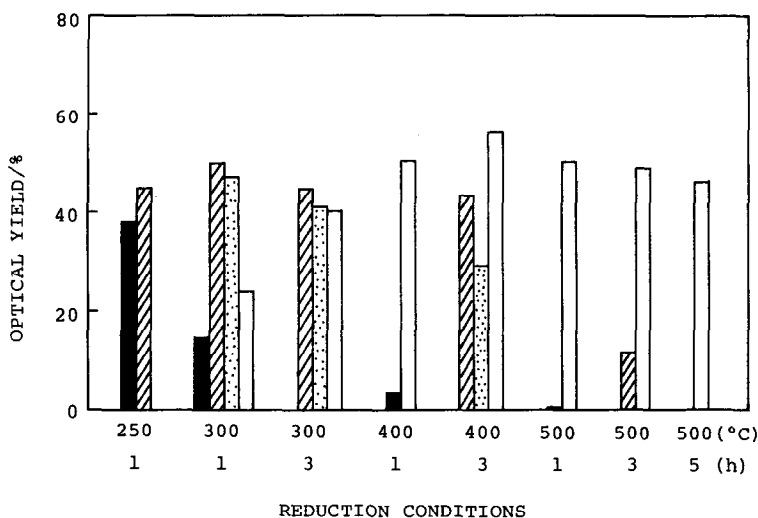[b] The (111) peak of Ni was very weak.

FIG. 3. Effect of reduction conditions on the enantioselectivity of some Ni–support(1 : 1) catalysts.
■: Ni–TiO$_2$; ▨: Ni–Al$_2$O$_3$; ⊡: Ni–Kg; □: Ni–SiO$_2$.

spectively, had slight effect on the activity and enantioselectivity. For other catalysts, especially for Ni–TiO$_2$ catalysts, higher temperature or longer time of the reduction resulted in rapid decreases in the activity and selectivity accompanied by very rapid growth of nickel crystallite.

The X-ray photoelectron spectra of the Ni $2p_{3/2}$ level for some Ni–SiO$_2$ (1 : 1) and Ni–Kg (1 : 1) catalysts are shown in Fig. 4. The reducibility of nickel oxide on SiO$_2$ is much lower than that on Kg under the same reduction conditions; the nickel metal peak (852.2 eV) is very weak compared to the oxide peaks (856.2 and 862.1 eV) for the Ni–SiO$_2$ catalyst reduced at 300°C for 3 h, whereas the oxide peaks are negligible for the Ni–Kg catalyst curve (b) on the right-hand side of Fig. 4).

Varying the hydrogen flow rate from 8 to 16 liters/h had only a slight effect on the enantioselectivity of resulting Ni–SiO$_2$ catalysts.

DISCUSSION

Catalyst Preparation Variables

The data in Tables 2 and 3 show that all Ni–SiO$_2$ catalysts with small $\bar{D}_c$, unmeasurable by the XRD method, give only low

OYs of (−)-MHB and that the catalysts with $\bar{D}_c$ larger than about 6 nm have relatively high enantioselectivity similarly to unsupported catalysts (8). Figure 1 also provides evidence of the crystallite size effect on the enantioselectivity of supported catalysts, because increasing nickel loading resulted in larger crystallite size consistent with the previous report (13). The increase of nickel loading in the catalysts obtained from the constant weight of the precursors increases not only the mean crystallite size of Ni but also the net weight of Ni metal used in the reaction. This, however, cannot be the reason for the increase of OY of (−)-MHB; the result of a separate experiment showed that the OY was almost independent of the ratio of nickel metal to the substrate. We suppose that the favorable effect of wide-pore support reported by Hoek et al. (17) is attributable to the large crystallite size of Ni in the catalyst, where the support has rather low surface area and the nickel loading is rather low. The effect of supports with different properties or pretreated in different ways will be studied later in detail.

The data in Table 3 show that the nickel metal in SiO$_2$-supported catalysts has relatively high dispersion which is unfavorable
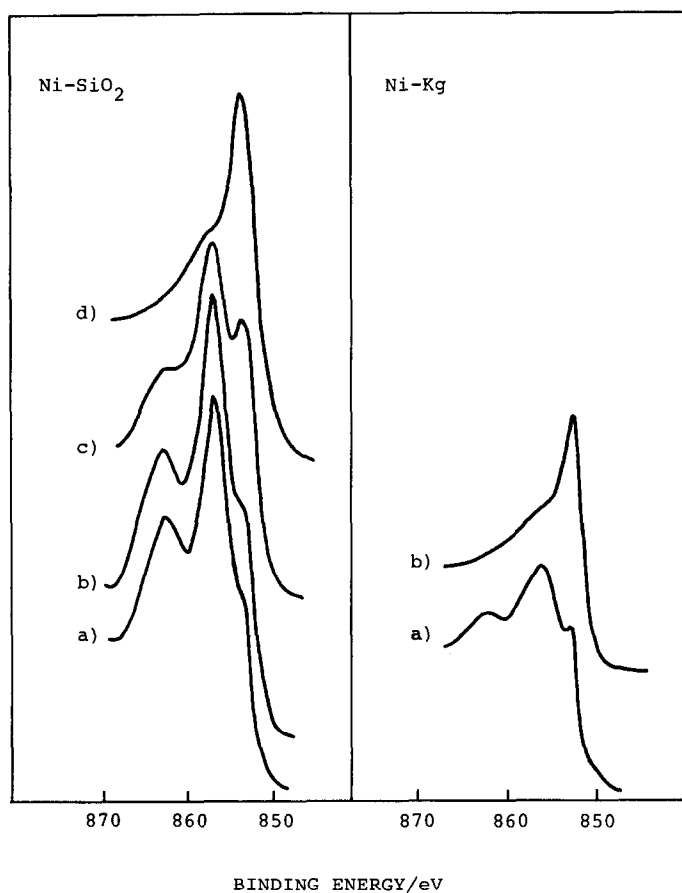
BINDING ENERGY/eV

FIG. 4. X-Ray photoelectron spectra of the Ni $2p_{3/2}$ level for Ni–SiO$_2$(1 : 1) and Ni–Kg(1 : 1) catalysts reduced at (a) 300°C for 1 h, (b) 300°C for 3 h, (c) 400°C for 3 h, and (d) 500°C for 3 h.

for the sintering of nickel and which leads to the high hydrogenation activity of the catalysts even under relatively severe reduction conditions (e.g., 500°C for 5 h): the $\bar{D}_c$ of nickel on SiO$_2$ remains unchanged at about 10 nm. The high dispersion of nickel on SiO$_2$ will be partially attributable to the large surface area of the SiO$_2$ used in this work; the nickel loadings per unit surface area of SiO$_2$ are relatively low. On the other hand, nickel metals supported on Kg and on TiO$_2$, which have much smaller surface areas than SiO$_2$, are easily reduced and liable to sinter even under relatively mild reduction conditions. This difference between the reducibility of nickel oxides on SiO$_2$ and on the other supports, listed in

Table 3, is also evident from the result shown in Fig. 4.

The enantioselectivity of the catalysts other than Ni–SiO$_2$ decreased at high reduction temperatures in spite of the increase in $\bar{D}_c$ of nickel. This fact can be explained on the basis of the crystallite size distribution (CSD) of nickel in these catalysts. Since the crystallite size measured by the XRD method tends to give predominantly information concerning larger crystallites, the $\bar{D}_c$ values do not necessarily reflect the selectivity of the catalysts, especially when they have different CSDs. With Ni–SiO$_2$ catalysts prepared by the homogeneous precipitation–deposition method, Richardson and Dubus (*13*) reported that the

reduction at temperatures higher than 400°C resulted in broader CSDs or bimodal distributions. Bartholomew *et al.* (*18*) showed that for catalysts with low nickel loading the extent of interaction of nickel with supports increased in the order Ni–SiO$_2$ < Ni–Al$_2$O$_3$ < Ni–TiO$_2$. In the case of our catalysts, the reduction at high temperatures probably deactivates larger crystallites with high enantioselectivity by sintering, increasing the contribution of smaller crystallites with low selectivity to overall hydrogenation and leading to a low optical activity of the product. The extent of this phenomenon seems to increase in the order: Ni–SiO$_2$ < Ni–Al$_2$O$_3$ < Ni–TiO$_2$, in good agreement with the results shown in Table 3; the strong interaction of small crystallites of nickel with support, mentioned above, retards the growth of crystallite size during the reduction at high temperatures.

This idea is supported by the fact that a part of a Ni–Al$_2$O$_3$ catalyst with larger crystallites, magnetically separated from the other part with smaller crystallites, gives much higher OY of (−)-MHB (36.8%) than the original catalyst (11.9%; No. 15 in Table 3). The fact that catalysts with larger $\bar{D}_c$ do not always have lower hydrogenation activity (e.g., Nos. 10, 15, and 17 in Table 3) also supports the possibility of the presence of active small crystallites in these catalysts.

On the basis of the above discussion, the discrepancy of the data reported by the above-mentioned investigators (*9–11*) appears to arise mainly from the differences in the reduction conditions. For example, the reduction made by Orito *et al.* (*10*) (300°C, 1 h) was too mild to provide high enantioselectivity to the Ni–SiO$_2$ catalyst, and the reduction made by Hoek and Sachtler (*9*) (400°C, 15 h) was too severe for the Ni–Al$_2$O$_3$ catalyst.

Thus, the CSD seems to have a very important role in determining the enantioselectivity of supported catalysts. In other words, catalysts which have larger $\bar{D}_c$ and

narrower CSD will have higher enanselectivity. However, catalysts with too large crystallites have only low hydrogenation activity. Therefore, a support such as SiO$_2$ which gives moderate crystallites of nickel around 6 to 10 nm after the reduction at around 400°C seems to be suitable for the preparation of supported nickel catalysts with high activity and selectivity.

Among the three preparation methods listed in Table 1, the homogeneous precipitation with urea seems to be the most suitable method for the preparation of highly enantioselective catalysts; however, we did not study this method further because it was difficult to control the nickel loadings.

Almost all preparation variables may affect the CSDs and hence vary the enantioselectivity of resulting catalysts. For example, variation of the precipitation temperature will cause directly a change in the particle size distribution of the precipitate or alter the composition of the basic nickel carbonate, leading to a change of the CSD in the catalyst after the reduction. In order to obtain a highly enantioselective catalyst with good reproducibility, it was necessary to control the preparation variables, especially the precipitation conditions, very precisely. We observed that even small alterations in the washing procedure of the precipitate provide a striking effect on the selectivity of the resultant catalysts. Both too heavy and too light washings, decreased the selectivity. These facts again mean that the enantioselective hydrogenation of MAA on modified nickel catalysts is one of the highly structure sensitive reactions and that it gives information concerning the CSD of a supported catalyst used.

Hydrogenation Activity

As shown in Table 3, the Ni–SiO$_2$ (1 : 1) catalysts reduced at temperatures higher than 400°C have high hydrogenation activity as well as high enantioselectivity. Table 4 compares hydrogenation activities under initial hydrogen pressure of 10 kg/cm^2 for

TABLE 4

Hydrogenation Activity of Enantioselective Ni Catalysts

Catalyst	Amount of Ni (g)	$\bar{D}_c$ (nm)	OY (%)	Reaction time (h)	Conversion (%)
H–Ni[a]	3.0	29	56.2	147	94.5
D–Ni[b]	3.0	22	54.8	70	95.8
R–Ni[c]	0.6	8	36.8	66	100
Ni–SiO₂	0.88	9	56.2	5	100
Ni–Kg	0.88	14	47.5	92	100
Ni–Al₂O₃	0.88	16	49.9	64	96.0
Ni–TiO₂	0.88	22	38.2	64	83.8

[a] Ni black prepared by reduction of NiO at 350°C for 1.5 h.
[b] Ni black prepared by decomposing Ni(HCOO)₂ · 2H₂O at 300°C for 6 h.
[c] Raney-Ni catalyst refluxed in 20% NaOH for 5 h (7).

some supported and unsupported catalysts which have similar enantioselectivity (8). The Ni–SiO₂ catalysts are highly active for this hydrogenation reaction. The hydrogenation of 10 ml of MAA in 10 ml of EA was completed within 12 h on this Ni–SiO₂ catalyst even under atmospheric hydrogen pressure (16). Because of these properties, Ni–SiO₂ catalysts can be convenient material for the mechanistic investigation of this reaction (16). Further studies concerning this problem are now in progress.

CONCLUSION

1. The enantioselectivity of supported Ni catalysts depends primarily on the crystallite sizes of Ni similarly to the case of unsupported catalysts (3), i.e., the larger the mean crystallite size ($\bar{D}_c$) of nickel, the higher the enantioselectivity. The selectivity of a Ni–SiO₂ catalyst increased with an increase in the nickel loading.

2. For supported catalysts, not only the mean crystallite size but also the CSD of nickel plays an important role in determining the enantioselectivity: a smaller crystallite with high specific activity and low selectivity has a larger contribution on the overall enantioselectivity. Narrow CSD, containing around 10-nm crystallites, seems to be suitable for obtaining catalysts with high enantioselectivity.

3. Almost all preparation variables affect the CSDs after reduction and hence affect the enantioselectivity of resulting catalysts. A reproducible enantioselectivity of a supported catalyst was obtained by paying careful attention especially to the precipitation conditions.

4. Enantioselectivity of supported catalysts also depends on the reduction conditions. Selectivity of Ni–SiO₂ (1 : 1) catalyst increases with increase in the reduction temperature and time up to 400°C and 3 h, and is accompanied by a rather small increase in $\bar{D}_c$ up to 10 nm. Even the Ni–Al₂O₃ catalyst can exhibit considerably high enantioselectivity when reduced under relatively mild conditions.

5. In particular, the Ni–SiO₂ (1 : 1) catalyst has not only high enantioselectivity but also very high hydrogenation activity.

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