

Enantio-differentiating hydrogenation of methyl acetoacetate over tartaric acid-NaBr-modified supported nickel catalyst prepared from nickel acetylacetonate

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Abstract

Supported nickel catalysts were prepared from nickel acetylacetonate, and then modified in a solution containing tartaric acid and sodium bromide. The enantio-differentiating hydrogenation of methyl acetoacetate was carried out over this catalyst. The effects of the preparation variables of the supported nickel catalysts on the optical yield and the effects of the conditions for the nickel surface modification on the optical yield were examined. The catalysts were also characterized by XRD and TEM.

The maximal optical yield of 87% was attained when crystallized α -alumina (sumico rundum) was used as a support. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Nickel acetylacetonate; Modified supported nickel catalyst; Enantio-differentiating; Hydrogenation; Methyl acetoacetate

1. Introduction

The enantio-differentiating hydrogenation over asymmetrically modified heterogeneous metal catalysts has been attracting much attention. There are appropriate catalytic systems for each type of reaction. For example, modified nickel catalysts for the hydrogenation of β -ketoesters and alkanones [1–8], modified platinum catalysts for α -ketoesters [9,10], and modified palladium catalysts for the hydrogenation of

alkenes [11,12] have been intensively studied and have successfully produced optically active products.

For the enantio-differentiating hydrogenation of β -ketoesters and alkanones, TA-NaBr-modified nickel catalysts are the best systems for attaining a high optical yield [8,13]. For the preparation of the modified nickel catalysts, various nickel precursors have already been tested. Raney nickel, nickel powder prepared from nickel oxide or nickel salts, and commercial nickel powder were tested as an unsupported catalyst. Although the modified catalysts prepared from unsupported catalysts show higher

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optical yield than those prepared from supported catalysts, there still remains uncontrollable factors regulating the optical yield. For example, when the Raney nickel alloy was used as the starting material, residual aluminum compounds decreased the optical yield [14]. However, aluminum on Raney catalysts cannot be completely removed. Nickel catalysts prepared from nickel oxide and commercial nickel powder have the problem that the resulting modified catalysts showed a wide range of optical yields based on the manufacturers of the nickel oxide and nickel powder [15–17].

On the other hand, nickel catalysts on various supports were also used for the preparation of asymmetrically modified nickel catalysts, and the studies for attaining a high optical yield have been carried out. However, the resulting optical yields were lower than those obtained using the modified unsupported nickel catalysts [6,18,19].

For preparing a catalyst with a higher hydrogenation activity and a higher enantio-differentiating ability than those of the catalysts reported so far, a breakthrough in the catalyst preparation method is required. From the standpoint that the modified supported nickel catalysts would be promising with the aid of additional effects of the supports, we investigated a new method for the preparation of the modified supported nickel catalysts. In this study, nickel catalysts supported on various supports were prepared from the mixture of nickel acetylacetonate and various supports. The hydrogenation of methyl acetoacetate was then carried out over the resulting modified supported nickel catalysts.

2. Experimental

The GLC measurement of the products was carried out using a Hitachi 263-30 gas chromatograph. The optical rotations were measured with a JASCO DIP-1000 polarimeter. The X-ray diffraction patterns of the catalysts were measured with a Shimadzu XD-3A diffractometer.

The transmission electron microphotographs were obtained with a JEOL JEM-100SX instrument using a beam voltage of 100 kV.

2.1. Materials

All the chemicals except α - Al_2O_3 and SiO_2 were commercially available. α - Al_2O_3 was obtained by the treatment of γ - Al_2O_3 at 1150°C for 6 h. SiO_2 was obtained by drying silica sols (Snowtex 30, Nissan Chemical) at 110°C. The zeolite was the H-type Pentasil powders supplied by Nissan Girdler Catalyst, and Süd Chemie. (Si/Al = 15: EX-122, Si/Al = 46: Y-4480, Si/Al = 123: EX-717, Si/Al = 215: EX-504). Sumico rundum is ultrafine single crystals of α - Al_2O_3 supplied by Sumitomo Chemical (AA-2: mean particle diameter = 2.0 μm , surface area = 0.9 m^2/g , AA-10: mean particle diameter = 9.2 μm , surface area = 0.4 m^2/g). Mordenite was the Na-type powder (HSZ-640NAA) supplied by Toso, Titania (JRC-TIO-3: rutile type, particle diameter = 0.03–0.05 mm, surface area = 40 m^2/g , JRC-TIO-5: rutile type, particle diameter = 0.5–1.0 mm, surface area = 2.7 m^2/g) was supplied by the Catalysis Society of Japan.

2.2. Preparation of supported nickel catalyst

Nickel acetylacetonate (3.3 g) and a support (1 g, 40 wt.%) were well mixed in an agate mortar, and then formed into a pressed pellet at 200 kg/cm^2 . This pellet was treated in an Ar stream at 270°C for 2 h and at 370°C for 1 h. After the decomposition of the nickel acetylacetonate, the sample was ground into a 25–30 mesh powder and then treated in a hydrogen stream typically at 500°C for 3 h.

2.3. Modification of the catalyst

The supported nickel catalyst was immersed in 100 cm^3 of aqueous solution containing (*R,R*)-tartaric acid (1 g) and NaBr (amounts are described in the text) at 0°C or at 100°C for 1 h.

The pH of the modification solution was adjusted in advance with 1 mol dm⁻³ NaOH solution. After the modification, the catalyst was separated from the modification solution by centrifugation. The catalyst was then successively washed once with 45 cm³ of water, twice with 45 cm³ of methanol, and twice with 45 cm³ of tetrahydrofuran (THF).

2.4. Hydrogenation of methyl acetoacetate

The obtained catalyst was used for the hydrogenation of methyl acetoacetate (10 g) in THF (20 cm³) containing acetic acid (0.2 g) in an autoclave. The initial hydrogen pressure was 10 MPa and the temperature was 100°C. The hydrogenation was completed within 12 h using α -Al₂O₃, zeolites, and sumico rundum as a support. The modified catalysts prepared from γ -Al₂O₃ needed 3 days and that from SiO₂ needed 5 days to complete the hydrogenation. A distillation gave the hydrogenation product in a chemical purity of more than 98% (GLC analyses: 90°C, 5% Thermon 1000 on Chromosorb W).

2.5. Measurement of mean crystallite size

The mean crystallite size of the nickel particles on a modified catalyst after the reaction was obtained from the half-width of the Ni (111) peak using Scherrer's method.

2.6. Determination of optical yield

The optical purity of methyl 3-hydroxybutyrate was determined by polarimetry.

Optical purity(%)

$$= \frac{[\alpha]_D^{20} \text{ of hydrogenation product}}{[\alpha]_D^{20} \text{ of optically pure methyl 3-hydroxybutyrate}} \times 100$$

The specific optical rotation of the optically pure (*R*)-methyl 3-hydroxybutyrate is -22.95° (neat) [14].

2.7. Measurement of BET areas of the supports

The BET surface areas of the supports were measured by N₂ adsorption at 77 K after evacuation at 300°C for 2 h. The surface area of the sumico rundum was provided by Sumitomo Chemical.

3. Results and discussion

Fig. 1 shows the procedure for the preparation of the TA-NaBr-modified supported nickel catalysts from nickel acetylacetonate. During the catalyst preparation process, nickel acetylacetonate was decomposed to give nickel particles on a support. This precursor was treated in a hydrogen stream to obtain an active supported nickel catalyst (Ni/Support). In this process, the important parameters affecting the optical yield were the nickel weight percentage of the catalyst, the type of support, the decomposition temperature of the nickel acetylacetonate, and the hydrogen treatment temperature of the precursor. During the following modification step, TA and NaBr were adsorbed onto the nickel surface to produce the modified supported catalyst (TA-NaBr-MNi/Support). The modification pH, the modification temperature, and the concentration of NaBr in the modification solution affected the optical yield.

3.1. Conditions for the preparation of supported nickel catalyst

Preliminary experiments showed that the decomposition temperature affected the optical yield and that the decomposition at a temperature just above the melting point of the nickel acetylacetonate (270°C) (m.p. of nickel acetylacetonate hydrate: 230–260°C, dec.) for 2 h and followed by a higher temperature treatment (370°C) for 1 h produced a high optical yield.

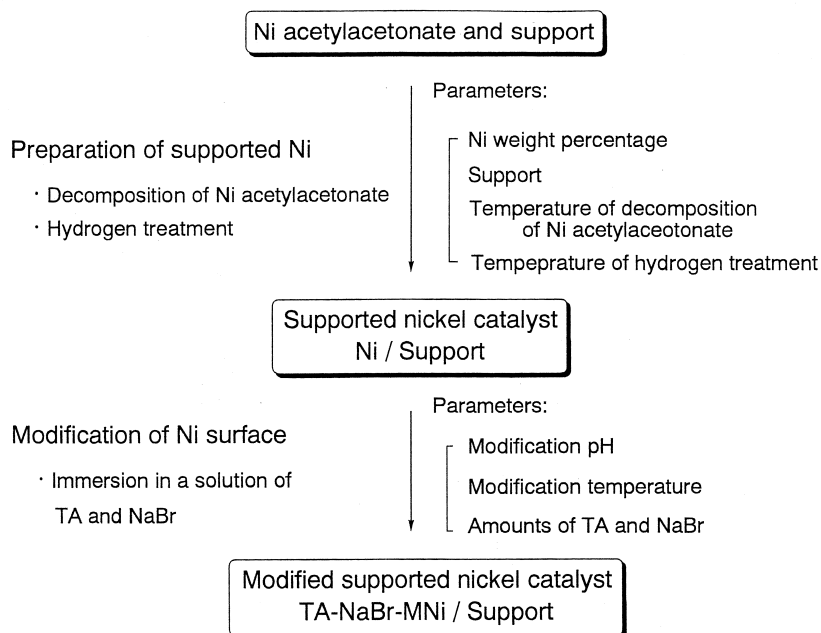


Fig. 1. Preparation of TA-NaBr-modified supported nickel catalysts.

Fig. 2 shows the relation between the initial percentage of the nickel loaded and optical yield. When $\alpha\text{-Al}_2\text{O}_3$ was used as the support, the optical yield increased with an increase in the nickel loading percentage and reached a plateau. More than 40% of the initial nickel loading percentage was necessary to attain greater than an 80% optical yield. In the case of $\gamma\text{-Al}_2\text{O}_3$, more than 60% of the initial nickel loading was needed to attain a high optical yield. On the other hand, when zeolite or sumico rundum (AA-2) was used as the support, 20% was enough to attain a high optical yield, while 60% nickel loading decreased the optical yield. Based on these results, there exists an appropriate initial nickel weight percentage for every support in order to attain a high optical yield. Taking into account the specific surface area of the supports (footnote of Fig. 2), the supports with a large specific surface area would need a large nickel loading percentage to give a high optical yield except for the zeolite. In spite of the zeolite having a large surface area ($463\text{ m}^2/\text{g}$), its pore size would be too small to form nickel

particles inside the pores by the decomposition of nickel acetylacetonate. We consider that the inside of the zeolite pores was not effective for this reaction.

Table 1 shows the effects of the hydrogen treatment temperature on optical yield. The optical yield increased with the elevation of the hydrogen treatment temperature from 300°C to 600°C and the maximum value was attained at $500\text{--}600^\circ\text{C}$. The optical yield decreased above 600°C . Because the hydrogenation activity of the catalyst obtained by the hydrogen treatment at 600°C was lower than that at 500°C , we fixed the hydrogen treatment temperature at 500°C thereafter.

Table 1 also shows the effect of hydrogen treatment temperature on the mean crystallite size of the nickel measured by XRD. When $\alpha\text{-Al}_2\text{O}_3$ was used as the support, the elevation of hydrogen treatment temperature increased the mean crystallite size. The mean crystallite size of about 50 nm gave over an 80% optical yield (hydrogen treatment temperature: 500°C and 600°C). Although the mean crystallite size was

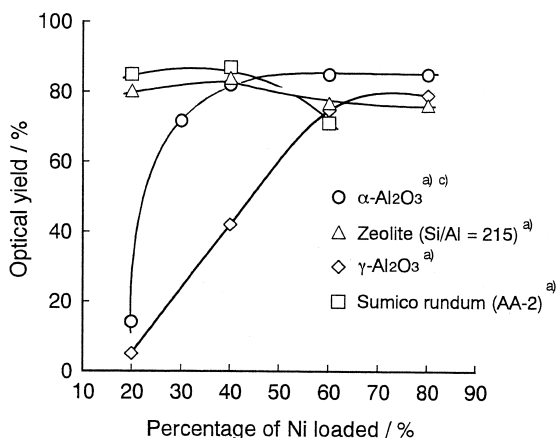


Fig. 2. The relation between nickel weight percentage^{b)} and optical yield.

(a) Specific surface area: α -Al₂O₃ 30 m²/g, γ -Al₂O₃ 54 m²/g, sumico rundum (AA-2) 0.9 m²/g, zeolite (Si/Al = 215) 463 m²/g. (b) This was the initial nickel weight percentage in the preparation of supported nickel catalyst. A small amount of nickel was dissolved in the solution during the modification. (c) Ref. [20].

The catalyst was modified with a 100-ml solution containing TA (1 g) and NaBr (1 g) at pH 3.2, at 100°C.

large, the hydrogenation was completed within 12 h. It has been known that a large nickel crystallite size generally produces a high optical yield [21]. Nitta et al. [22] demonstrated that modified nickel with a 26-nm crystallite size on SiO₂ gave a 62% optical yield. The enantio-differentiating hydrogenation of ethyl acetoacetate over 60% Ni/aerosil with a 120–180 nm mean crystallite size has also been reported. The optical yield of this reaction was 9.3% [23]. The crystallite size of about 50 nm would provide a suitable surface for the effective enantio-differentiation with the aid of TA.

Table 2 shows the results of the enantio-differentiating hydrogenation of methyl acetoacetate over various modified supported nickel catalysts. The results of the hydrogenation over the modified Raney Ni catalyst and the modified supported nickel catalyst prepared from Ni(NO₃)₂ solution by the precipitation method are also listed for comparison. When α -Al₂O₃, zeolite, or sumico rundum was used as the support, an optical yield of over 80% was attained. The maximal optical yield of 86–87%

was achieved over the catalyst with zeolite or sumico rundum (AA-2). This optical yield is high enough compared with the reported values using asymmetrically modified supported nickel catalysts [3,5,6,24] and is comparable to the values obtained by the modified Raney nickel catalysts. The highest optical yield attained by modified supported nickel catalysts has been reported by Orito et al. [25] (83% using Ni–Pd–Kieselgur), but it could not be reproduced by one of the present authors and Nitta et al. [22]. The catalysts prepared from TiO₂ of the rutile type gave a low optical yield. The catalysts prepared from TiO₂ of the anatase type showed a low hydrogen activity (not shown in the table).

When a support was suspended in a THF solution of nickel acetylacetonate and evaporated in vacuo instead of making a pellet without solvent, similar optical yields (81%) were attained. The modified nickel catalyst prepared from Ni(NO₃)₂ by the precipitation method [24], which is the conventional method for preparing supported catalysts, gave only a 71% optical yield. When a nickel catalyst was prepared from nickel acetylacetonate without a support, the resulting modified catalyst had a very low hydrogenation activity.

Fig. 3 shows the effects of supports on the nickel crystallite size and optical yield. When the nickel crystallite size is larger than about 50 nm, more than an 80% optical yield was attained. However, catalysts prepared from TiO₂ (JRC-TIO-3) showed low optical yield although

Table 1
Effect of the hydrogen treatment temperature on optical yield^{a,b}

Support	Hydrogen treatment temp. [°C]	Optical yield [%]	Mean crystallite size [nm]
α -Al ₂ O ₃	300	32	8
α -Al ₂ O ₃	400	56	12
α -Al ₂ O ₃	500	83	53
α -Al ₂ O ₃	600	85	51
α -Al ₂ O ₃	700	76	68

^aInitial Ni percentage loaded: 40 wt.%. Modification was carried out in the 100 cm³ aqueous solution containing 1 g tartaric acid and 6 g NaBr at pH 3.2 and 100°C for 1 h.

^bRef. [20].

Table 2
Effects of Ni sources and supports on optical yield

Ni source	Support	Initial Ni percentage loaded [wt.%]	Optical yield [%]
Ni acetylacetonate	without support	–	– ^{a,b,c}
Ni acetylacetonate	α -Al ₂ O ₃	40 ^d	81 ^{a,c}
Ni acetylacetonate	α -Al ₂ O ₃	40 ^d	83 ^{c,e}
Ni acetylacetonate	γ -Al ₂ O ₃	80 ^d	78 ^{c,e}
Ni acetylacetonate	zeolite (Si/Al = 15)	40 ^d	86 ^{a,c}
Ni acetylacetonate	zeolite (Si/Al = 46)	40 ^d	83 ^{a,c}
Ni acetylacetonate	zeolite (Si/Al = 123)	40 ^d	84 ^{a,c}
Ni acetylacetonate	zeolite (Si/Al = 215)	40 ^d	84 ^{a,c}
Ni acetylacetonate	SiO ₂	40 ^d	73 ^{a,c}
Ni acetylacetonate	sumico rundum (AA-2)	40 ^d	87 ^a
Ni acetylacetonate	sumico rundum (AA-10)	40 ^d	83 ^a
Ni acetylacetonate	TiO ₂ (JRC-TIO-3)	40	50 ^a
Ni acetylacetonate	TiO ₂ (JRC-TIO-5)	40	73 ^a
Ni acetylacetonate	Na Mordenite	40	82 ^a
Ni acetylacetonate ^f	α -Al ₂ O ₃	40	81 ^{a,c}
Ni(NO ₃) ₂ ^g	α -Al ₂ O ₃	40	71 ^{a,c}
Raney Ni	without support	–	86 ^{c,e}

^a Modification was carried out in the 100-cm³ aqueous solution containing 1 g tartaric acid and 1 g NaBr at pH 3.2 and 100°C for 1 h.

^b Hydrogenation reaction did not take place.

^c Ref. [20].

^d Initial Ni percentage loaded giving maximal optical yield.

^e Modification was carried out in the 100-cm³ aqueous solution containing 1 g tartaric acid and 6 g NaBr at pH 3.2 and 100°C for 1 h.

^f Ni acetylacetonate and a support were suspended in THF and then evaporated. (decomposition condition was the same as in the case of making a tablet without solvent).

^g The catalyst was prepared by a precipitation method [24].

it had a 68-nm crystallite size. Therefore, there is some support effects other than the nickel crystallite size.

The effects of the supports on the optical yield are not clear, but it seems that supports with high crystallinity (zeolite, sumico rundum,

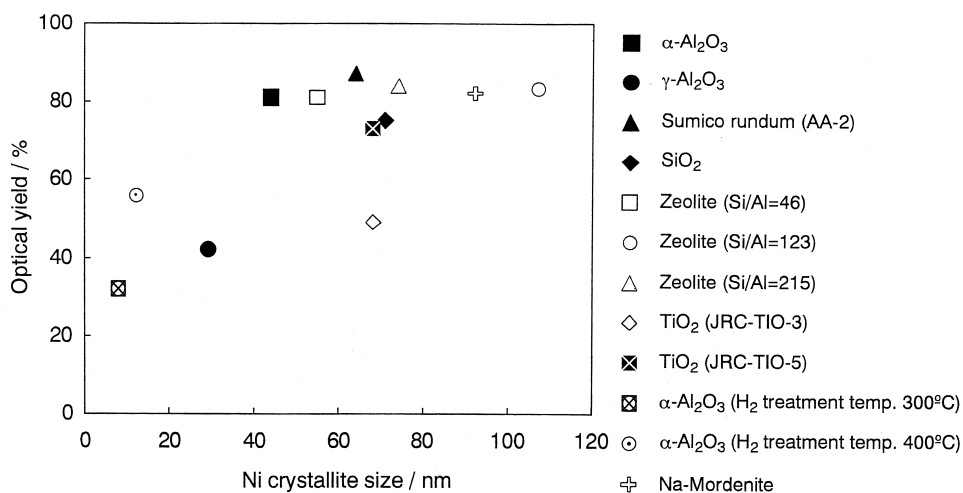


Fig. 3. Effects of supports on nickel crystallite size and optical yield. The catalyst was modified with a 100-ml solution containing TA (1 g) and NaBr (1 g) at pH 3.2, at 100°C.

and $\alpha\text{-Al}_2\text{O}_3$) gave the modified nickel catalysts a high optical yield effect. It could suggest that when nickel particles grow on the supports, the high crystallinity of the supports could be favorable to the growth of nickel crystals, which would provide a suitable surface for the high enantio-differentiating ability.

3.2. TEM analyses of supported nickel catalysts

Fig. 4 shows the TEM photographs of Ni/ $\alpha\text{-Al}_2\text{O}_3$ and Ni/sumico rundum (AA-2) prepared by a hydrogen treatment temperature at 300°C and 500°C. When the hydrogen treatment was carried out at 300°C, the diameter of almost all the nickel particles was less than 10 nm. On the other hand, at 500°C, around 50-nm diameter crystallized nickel particles were observed al-

though part of the particles still remained at about 10 nm. These results support the findings obtained by the XRD measurement, that is, the catalysts that gave the highest optical yield have about a 50-nm nickel crystallite size.

3.3. Conditions for the modification of nickel surface

It has been demonstrated that a modification pH, a modification temperature, and a modification time are the key parameters for attaining a high optical yield with the already reported modified Raney nickel catalysts [26,27] and modified supported nickel catalysts [6].

Fig. 5 indicates the relation between the modification pH and optical yield when $\alpha\text{-Al}_2\text{O}_3$ was used as the support. When the pH was not

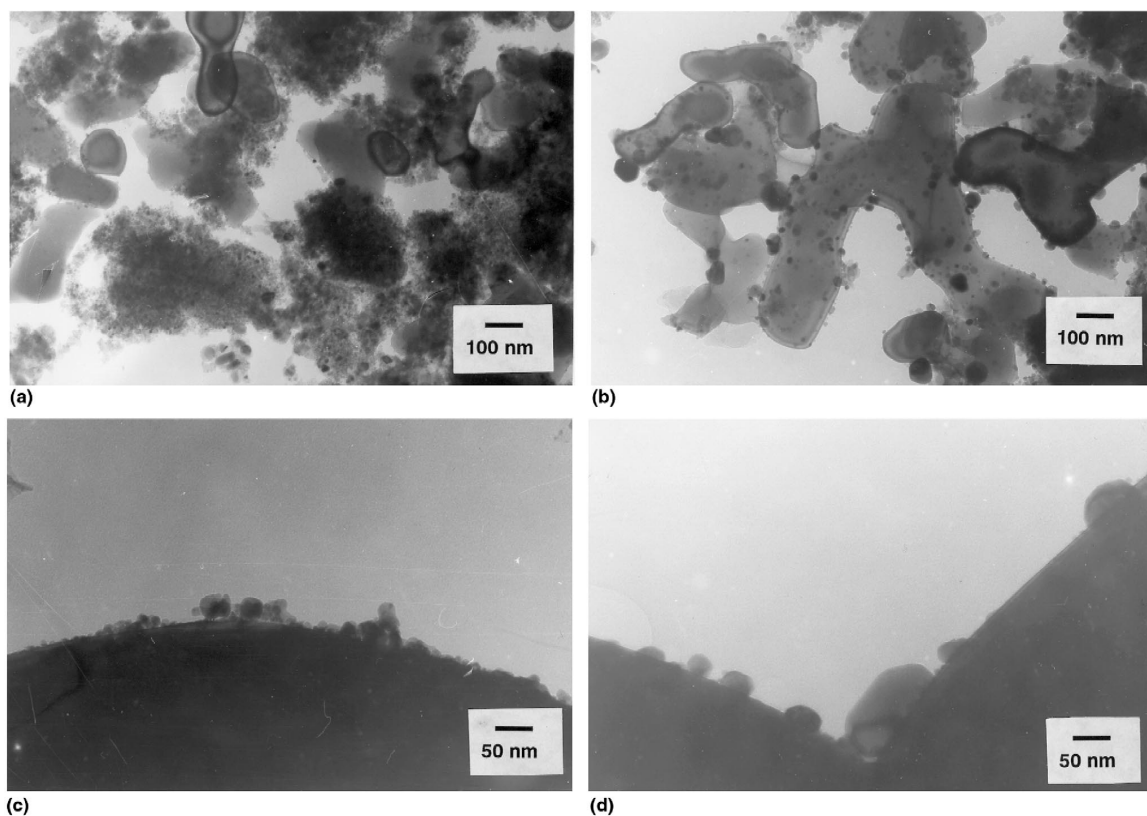


Fig. 4. TEM analyses of supported nickel catalysts. (a) Ni/ $\alpha\text{-Al}_2\text{O}_3$ (Ni: 40 wt%, H_2 treatment temperature: 300°C); (b) Ni/ $\alpha\text{-Al}_2\text{O}_3$ (Ni: 40 wt%, H_2 treatment temperature: 500°C); (c) Ni/Sumico rundum (AA-2) (Ni: 40 wt%, H_2 treatment temperature: 300°C); (d) Ni/Sumico rundum (AA-2) (Ni: 40 wt%, H_2 treatment temperature: 500°C).

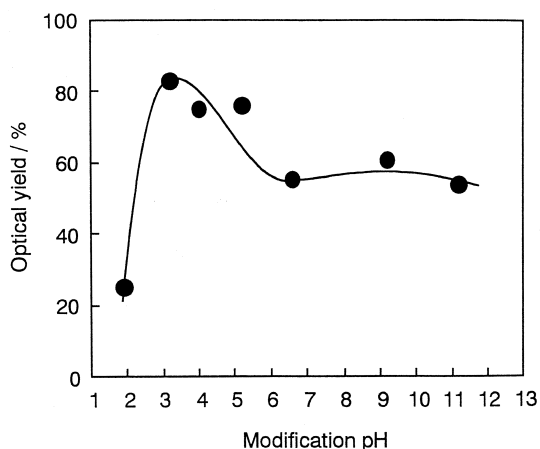


Fig. 5. The relation between the modification pH and optical yield. The catalyst was modified with a 100-ml solution containing TA (1 g) and NaBr (6 g) at 100°C.

adjusted with NaOH solution (pH 1.9), a low optical yield was obtained. The pH of 3.2 gave the maximal optical yield, while the optical yield decreased above pH 3.2. These phenomena were similar to the case of the Raney nickel catalyst modified at 100°C [14]. However, the pH dependence on optical yield using a supported nickel catalyst or Cu–Ni catalyst reported in the literature are different from that of the Raney nickel catalyst. Bennett et al., demonstrated that there were two maximums in the modification pH–optical yield curve (pH 3.2 and 9) with the Ni/SiO₂ catalyst [28]. Klabinovskii et al. [29,30] reported that about 5.5 and 11 were the maximum pHs with the Cu–Ni catalyst. Our results showed that there was no distinct maximum in the optical yield at

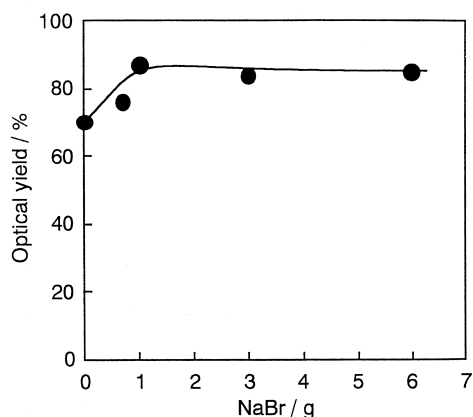


Fig. 6. Effects of the amount of NaBr in the modification solution on optical yield. The catalyst was modified with a 100-ml solution containing TA (1 g) and NaBr at pH 3.2, at 100°C.

around pH 10. The nickel surface of the catalysts presented in this study would be similar to that of the Raney nickel catalysts.

Table 3 shows the effect of a modification temperature on the optical yield. The modification at 100°C gave a higher optical yield than the 0°C modification. According to the studies of the modified Raney Ni catalyst, the following two factors are important for attaining a high optical yield: (1) sodium tartrate or disodium tartrate adsorbs on the catalyst surface [31,32], and (2) the surface is composed of pure nickel or regularly arranged nickel [33]. These two factors would be achieved by a pH 3.2 modification at high temperature (100°C). In the case of the modified supported nickel catalyst prepared in this study, the conditioning of the

Table 3
Effect of the modification temperature on optical yield

Support	Modification temp. [°C]	Modification time [h]	NaBr [g]	Optical yield [%]
α-Al ₂ O ₃	0	1	1	63
α-Al ₂ O ₃	100	1	1	81
α-Al ₂ O ₃	0	1	6	65
α-Al ₂ O ₃	100	1	6	83
Sumico rundum (AA-2)	0	1	1	75
Sumico rundum (AA-2)	100	1	1	87

Initial Ni percentage loaded: 40 wt.%, modification pH: 3.2.

Table 4
The effect of the amount of NaBr on optical yield

Support	Optical yield [%]		
	NaBr 0 g	NaBr 1 g	NaBr 6 g
Zeolite (Si/Al = 15)	80	86	–
Zeolite (Si/Al = 46)	66	83	48
Zeolite (Si/Al = 123)	63	84	83
Zeolite (Si/Al = 215)	69	84	50

Initial Ni percentage loaded: 40 wt.%, modification pH: 3.2.

nickel surface is necessary for attaining a high optical yield and the same adsorbed species as that of the modified Raney Ni would provide an effective enantio-differentiation.

Inorganic salts in the modification solution increase the optical yield for the hydrogenation over the modified Raney nickel [34] or modified supported nickel catalysts [35,36]. The consensus for the role of NaBr has not yet been achieved [35–37]. We proposed that inorganic salts are selectively adsorbed and deactivate the non-enantio-differentiating site (site where racemic products are produced) [37]. NaBr is known to be the most effective inorganic salt for improving the optical yield. Fig. 6 shows the relation between the amount of NaBr in the modification solution and optical yield when sumico rundum (AA-2) was used as a support. The addition of NaBr increased the optical yield, which reached a plateau when using more than 1 g of NaBr. Table 4 shows the effects of the amount of NaBr in the case of the zeolite supports. In spite of the differences on the Si/Al ratio, 1 g of NaBr was enough for attain a high optical yield. When zeolites were used as supports, the addition of 6 g of NaBr decreased the optical yield. The difference in the optical yield between the conditions without NaBr and of a plateau is smaller than that of Raney nickel catalysts. From these results, the number of non-enantio-differentiating sites of the modified Ni/sumico rundum or Ni/zeolite catalyst prepared in this study was smaller than that of the modified Raney nickel catalyst.

4. Conclusions

The optical yields attained in this study were much higher than those obtained using the conventional modified supported nickel catalysts prepared in a nickel ion solution. When sumico rundum or zeolite (Pentasil powder) was used as a support, the maximum optical yield of 87% was achieved. The results obtained by the present work demonstrated that nickel acetylacetonate is a promising precursor for the preparation of an asymmetrically modified nickel catalyst. This method would produce the nickel particles, whose surfaces are suitable for the formation of enantio-differentiating sites with the aid of TA.

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