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The Enantioface-differentiating (Asymmetric) Hydrogenation of the C=O Double Bond with Modified Raney Nickel. XXXVI.
The Development of Modified Nickel Catalysts with High Enantioface-differentiating Abilities

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Various types of modified nickel catalysts were prepared and their enantioface-differentiating (asymmetric) abilities were examined. It was found that the presence of aluminum or related metal compounds in the catalyst was unfavorable for the effective enantioface-differentiating catalyst. The modification with a solution containing tartaric acid and inorganic salt gave a high enantioface-differentiating ability to Raney nickel and reduced nickel catalyst. Among the modified nickel catalysts examined, the Raney nickel modified with tartaric acid and sodium bromide gave the best result with respect to the hydrogenation activity and enantioface-differentiating ability (optical yield 88%). NaBr adsorbed on Raney nickel was found to inhibit the nonenantioface-differentiating hydrogenation.

An asymmetrically modified Raney nickel catalyst (MRNi) is easily prepared by soaking Raney nickel catalyst (RNi) in a solution of an optically active substance.[1] This is the most suitable catalyst for the enantioface-differentiating (asymmetric) hydrogenation because of its high hydrogenation activity and its preparative convenience. Our research group has been continuing the studies to improve the enantioface-differentiating ability (e.d.a.) of MRNi.

Recently, we succeeded in obtaining an improved MRNi with a sufficient e.d.a.[2] The improved catalyst can be prepared by the modification of RNi with a solution containing tartaric acid (TA) and NaBr (TA–NaBr–MRNi). An optical yield of near 90% was attained in the hydrogenation of methyl acetoacetate (MAA) to methyl 3-hydroxybutyrate (MHB) over this catalyst.

This paper will present our approach leading to the development of TA–NaBr–MRNi and the role of adsorbed NaBr in the enantioface-differentiating process.

Results and Discussion

TA–MNi and TA–NaBr–MHNi. Asymmetrically modified nickel catalysts (MNi) can be prepared from many kinds of nickel catalysts.[3] The e.d.a.'s of various TA–MNi's are listed in Table 1. The degrees of e.d.a.'s were evaluated by the optical yields (%) of the hydrogenation of MAA to MHB.

The use of the activated nickel prepared by the liquid phase reaction (Entries 1—5) resulted in poor optical yields (below 44%), while the use of the catalyst activated by a dry process (Entries 6—9) resulted in high optical yields (55—82%).

It is well known that Raney type catalysts (Entries 1—3) and Urushibara catalyst (Entry 4) contain some amounts of impurities (Al, Mg, Si, Zn, or derivatives of their cations). The rather poor results listed in Entries 1—4 could be considered to be caused by existence of these impurities in the catalyst. When RNi was modified with a solution containing TA and $NaAlO_2$, the resulting TA–MRNi (Entry 5) showed a lower e.d.a. than that of the conventional TA–MRNi (Entry 1). From the facts mentioned above, it can be concluded that the uses of nickel catalysts containing either Al, Mg, Si, Zn, or related metal compounds are not desirable for obtaining TA–MNi with high e.d.a.

The activated nickels prepared by thermal decomposi-

Table 1. Enantioface-differentiating hydrogenations of MAA over various types of TA–MNi's

No.	Source of activated Ni	Modifying conditions		Amount of MNi/g	Reaction conditions				Degree of e.d.a.[a]
		pH	Temp/°C		MAA ml	Solvent ml	AcOH ml	Temp °C	
1	Ni-Al alloy	5.0	100	0.6	17.5			60	44
2	Ni-Mg alloy	5.0	100	0.6	17.5			60	6
3	Ni-Si alloy	5.0	100	0.6	17.5			60	44
4	Urushibara Ni-A	4.1	85	1.0	11.5	THF/23	0.2	100	4
5	Ni-Al alloy	5.0[b]	100	0.6	17.5			60	30
6	$Ni(HCO_2)_2 2H_2O$	5.0	100	0.6	17.5			100	55
7	NiO	5.0	100	0.6	17.5			100	59
8	NiO	4.1	85	0.8	11.5	THF/23	0.2	100	65—82
9	$Ni(CO)_4$[c]	4.1	85	0.6	11.5	THF/23	0.2	85	58—75

a) Degree of e.d.a. was evaluated by optical yield (%) of hydrogenation of MAA over MNi. b) The pH of modifying solution was adjusted with $NaAlO_2$ instead of NaOH. c) The Ni powder prepared from $Ni(CO)_4$ was supplied by Metal Foil and Powder MFG Co..

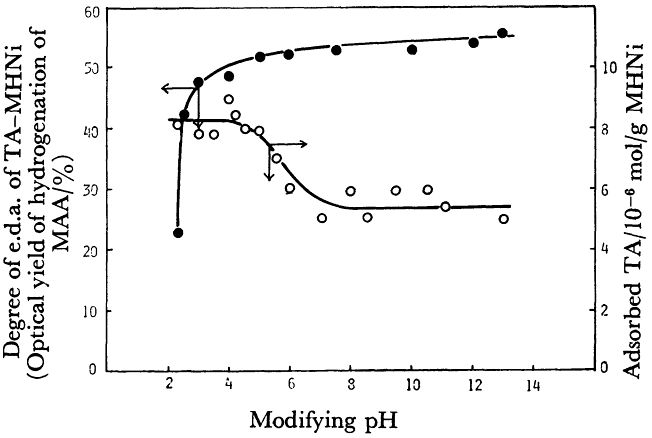

Fig. 1. Relationship between modifying pH and degree of e.d.a. of TA-MHNi(optical yield of hydrogenation of MAA over TA-MHNi) or amount of adsorbed TA. HNi was prepared from NiO supplied by Wako Pure Chemical Industries, Ltd. Amount of HNi: 0.8 g. Modification: at 0 °C for 1 h. Hydrogenation :MAA (17.5 ml) was subjected to hydrogenation at 100 °C.

tion of nickel formate, by hydrogenolysis of nickel oxide (HNi), and by decomposition of nickel carbonyl gave TA-MNi's with rather high e.d.a.'s. Among the catalysts examined, HNi modified with TA (TA-MHNi) gave the best result with respect to the e.d.a.

It was known that the e.d.a. of TA-MRNi was strongly affected by the modifying pH.[4] Thus, the relation between the modifying pH and the e.d.a. of TA-MHNi was examined in order to find out the optimal modifying pH. The results are shown in Fig. 1. Figure 1 also shows the relation between the modifying pH and the amount of TA adsorbed on HNi. The e.d.a. of TA-MHNi was found to increase steeply with increasing pH and settle down at a constant value at the pH range from 3 to 13. The adsorbed amount of TA at below pH 4 is greater than that at above pH 4. Thus, the poor e.d.a. of TA-MHNi at below pH 3 cannot be explained on the basis of the amount of adsorbed TA. It is reasonable to assume that the difference between the e.d.a. at below pH 3 and that at the pH range from 3 to 13 results from the difference in the adsorption mode of TA.[5] The counter ions of adsorbed TA are expected to be Ni^{2+} and H^+ in the pH region intrinsic to the solution of the free TA and to be Na^+ under neutral and basic conditions.

TABLE 2. ENANTIOFACE-DIFFERENTIATING HYDROGENATION OF MAA OVER TA-MHNi

NiO		$[\alpha]_D^{20}$ of the product	Degree of e.d.a.[a]
Manufacturer	Lot No.		
Wako Pure Chemical Industries, Ltd.	LDJ 1657	−18.60	81
Wako Pure Chemical Industries, Ltd.	117-1	−15.51	68
Nihon Kagaku Sangyo, Co., Ltd.		−16.15	70
Mitsuwa Pure Chemicals, Ltd.	34491	−17.30	79

Amount of HNi: 0.8 g. Modification: at pH 4, 100 °C for 1 h. Hydrogenation: MAA (11.5 ml) in THF (23 ml) and AcOH (0.2 ml) was subjected to hydrogenation with each catalyst at 120 °C. a) Optical yield (%) of hydrogenation of MAA over TA-MHNi.

The e.d.a. of TA-MHNi was found to be sensitive to the preparative variations and purity of NiO. That is, differences in the manufacturer and the lot number of NiO caused a significant difference in the e.d.a. of TA-MHNi (Table 2). There was a relation between the colour of NiO powder and the e.d.a. of the resulting TA-MHNi. In general the light green NiO powder tended to give TA-MHNi with high e.d.a., while the dark green one tended to give TA-MHNi with low e.d.a.

TABLE 3. ENANTIOFACE-DIFFERENTIATING HYDROGENATION OF MAA OVER TA-MHNi ON SUPPORT

Support	$[\alpha]_D^{20}$ of the product	Degree of e.d.a.[c]
Kieselguhr[a]		
Shimalite SP-17	−12.39	54
Shimalite SP-25	−10.09	44
Shimalite SP-35	−8.48	37
Shimalite SP-55	−8.61	38
Activated alumina[b]		
Woelm acidic	−15.33	67
W 200 basic	−15.53	68
W 200 neutral	−15.55	68
TiO_2	−16.07	70
ZrO_2	−14.46	63

Weight ratio of Ni to support=50 to 50. Amount of supported Ni: 1.2 g. Modification: at pH 4.1, 85 °C for 1 h. Hydrogenation conditions were the same as those described in Footnote of Table 2 except for the hydrogenation temperature (85 °C). a) Kieselguhr was supplied by Wako Pure Chemical Industries, Ltd. b) Activated alumina was supplied by ICN Woelm Laboratories, Inc. c) Optical yield (%) of hydrogenation of MAA over TA-MNi.

Orito and his coworkers reported that Ni-Pd catalyst supported on kieselguhr gave an excellent catalyst for the enantioface-differentiating hydrogenation of MAA to MHB.[6] More than 90% of the optical yield was reported when the catalyst was modified with TA. We also prepared HNi's supported on various kinds of supports and the effects of supports were examined. As found in Table 3, no significant increase of e.d.a. was attained by the uses of nickel catalysts supported on kieselguhr, TiO_2, ZrO_2, and Al_2O_3. The e.d.a. of TA-MHNi supported on kieselguhr was observed to be affected by the sort of kieselguhr. Kieselguhrs well purified by acid or/and alkali washing (Shimalite SP-25, -35, and -55) gave TA-MHNi's with lower e.d.a.'s than that of unpurified one (Shimalite SP-17). It is reasonable to assume that minor components in kieselguhr are dissolved into the modifying solution and some of them serve as supplementary modifying reagents to increase the e.d.a.

We have often noticed that small amounts of impurities in the supplied water used for the modification

Table 4. ENANTIOFACE-DIFFERENTIATING HYDROGENATION OF MAA OVER TA–INORGANIC SALT–MHNi

Inorganic salt in the modifying solution (g)	$[\alpha]_D^{20}$ of the product	Degree of e.d.a.[a]
None	−16.85	73
NaI (1.0×10^{-3})	−18.34	80
NaBr (20)	−19.75	86
NaCl (10)	−17.83	78

Amount of HNi: 0.8 g. Modification: at pH 4.0, 100 °C for 1 h. Hydrogenation: MAA (11.5 ml) in methyl propionate (23 ml) and AcOH (0.2 ml) was subjected to hydrogenation at 100 °C. a) Optical yield (%) of hydrogenation of MAA over MHNi.

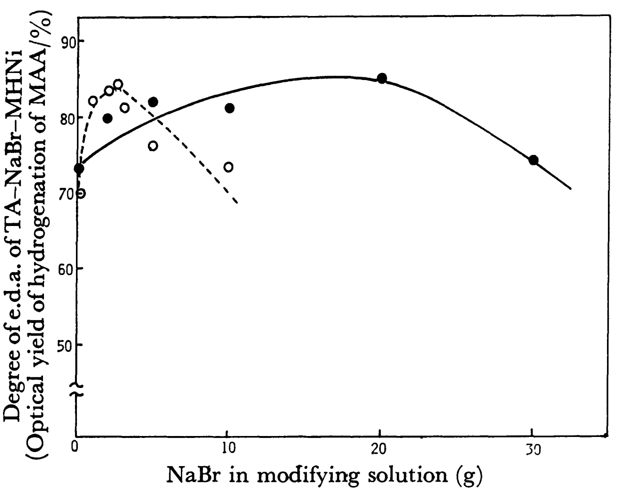

Fig. 2. Relationship between amount of NaBr in modifying solution and degree of e.d.a. of TA–NaBr–MHNi (optical yield of hydrogenation of MAA over TA–NaBr–MHNi).
TA–NaBr–MHNi: NiO was supplied by Wako Pure Chemical Industries, Ltd. (—●—) or Nihon Kagaku Sangyo, Co., Ltd. (—○—). Modification: at pH 4, 100 °C for 1 h. Hydrogenation was carried out under the same conditions as those described in footnote of Table 2.

process affected significantly the e.d.a. of the resulting catalyst. This finding led us to the idea that investigation of supplementary compounds in the modifying solution would enable us to develop a more effective enantioface-differentiating catalyst.

In the course of studies on the effect of supplementary modifying reagents on the e.d.a. of MHNi, it was found that the use of some kinds of inorganic salts increased the e.d.a. (Table 4). Among inorganic salts examined, NaBr was the best supplementary compound in giving a high e.d.a. As shown in Fig. 2, the e.d.a. of TA–NaBr–MHNi increased with the amount of NaBr in the modifying solution, reached a maximum value, and then decreased. The optimal amount of NaBr in the modifying solution was affected by the sort of NiO sample. Under the optimal conditions, TA–NaBr–MHNi showed a sufficient e.d.a. (optical yield, 86%). However, the main disadvantage of TA–NaBr–MHNi is the lack of high hydrogenating activity. The hydrogenation of MAA over TA–MHNi had to be performed at above 100 °C. Under these conditions, the yield of MHB can never be satisfactory because of the formation of by-products (*e.g.*, methyl 3-(3-hydroxybutyryloxy) butyrate). Thus, the preparation of an aluminum free catalyst with high hydrogenating activity was strongly required.

In this regard, our investigation attempted to develop a procedure for elimination of aluminum from the RNi surface in order to prepare a highly active and aluminium free catalyst.

Acid-treated RNi (RNi–A). Aluminium easily dissolves into water by the reaction with hydroxy acids to give highly water soluble products (aluminium chelates). Therefore, the selective elimination of aluminium from RNi was expected, when RNi was treated with a large amount of aqueous solution of hydroxy acid such as TA or glycolic acid (GA) under acidic conditions at a high temperature. A significant decrease of aluminium content was observed on this treatment (from 6% of Al content of the conventional RNi to less than 3% of Al content of GA-treated RNi (RNi–A (GA)) or TA-treated RNi (RNi–A (TA)).[7] Since the corrosion of nickel also took place during this treatment, the surface state of the resulting catalyst was no longer the same as that of RNi.

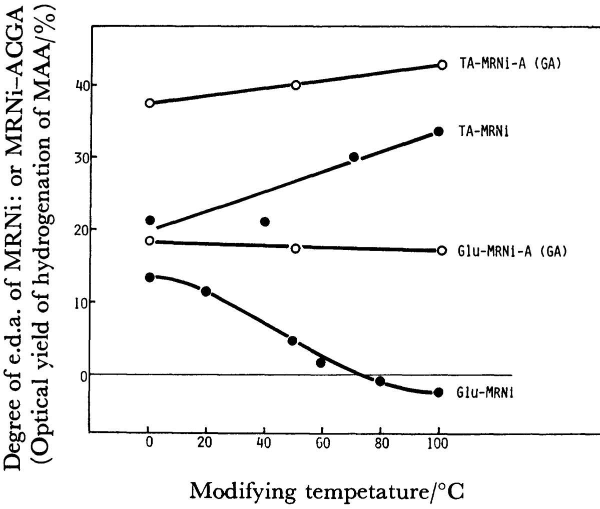

Fig. 3. Relationship between modifying temperature and degree of e.d.a. of MRNi (optical yield of hydrogenation of MAA over MRNi) or MRNi–A (GA). Amount of RNi or RNi–A (GA): 0.6 g. Modification: at pH 5 for 1.5 h. Hydrogenation: MAA (17.5 ml) was subjected to hydrogenation at 60 °C.

Figure 3 shows the e.d.a. of RNi–A (GA) modified with glutamic acid (Glu–MRNi–A (GA)) or TA–MRNi–A (GA), together with the e.d.a. of the conventional Glu–MRNi or TA–MRNi.[8] The e.d.a. of Glu– or TA–MRNi–A (GA) was higher than that of RNi modified with the same modifying reagent. The e.d.a. of MRNi–A (GA) was not affected by the modifying temperature, while that of the conventional MRNi changed significantly with the change in the modifying temperature. The results indicated that the GA-treatment gave a well stabilized and favorable catalyst

Table 5. Effect of TA-treatment on e.d.a. of TA-MRNi

Catalyst	Modifying conditions pH	Modifying conditions Temp/°C	$[\alpha]_D^{20}$ of the product	Degree of e.d.a.[a]
RNi-A (TA)	5.0	0	−14.23	62
RNi	5.0	0	−9.05	40
RNi	3.2	100	−8.99	39

Amount of catalyst: 0.8 g. Hydrogenation conditions were the same as those described in the Footnote of Table 4. a) Optical yield (%) of hydrogenation of MAA.

for the enantioface-differentiating hydrogenation. The hydrogenating activity of RNi–A (GA) was found to be high enough to carry out the hydrogenation of MAA at 60 °C.

The treatment with TA instead of GA functions as acid-treatment as well as modification. Table 5 shows the e.d.a. of TA–MRNi–A (TA) prepared in the following sequence: TA-treatment at 100 °C→water-washing→TA-modification at pH 5, 0 °C. It can be seen that the TA-treatment resulted in a significant increase of e.d.a. The hydrogenation over TA–MRNi–A (TA) was completed in 3—5 h at 100 °C, while the hydrogenation over TA–MHNi required 10—15 h to be completed at the same temperature. The TA- or GA-treatment of RNi was found to be effective for improvement of the e.d.a. of MRNi without sacrificing the hydrogenating activity. The nature of this catalyst was also found to be very close to that of HNi. It was expected that the TA–NaBr modification of RNi–A gave a catalyst with higher e.d.a. than that of TA–MRNi–A. With this expectation, RNi–A (TA) was modified with an aqueous solution containing TA and NaBr at pH 5.0, 0 °C. The resulting catalyst (TA–NaBr–MRNi–A) exhibited a high e.d.a. (optical yield 82%) and a high hydrogenating activity.

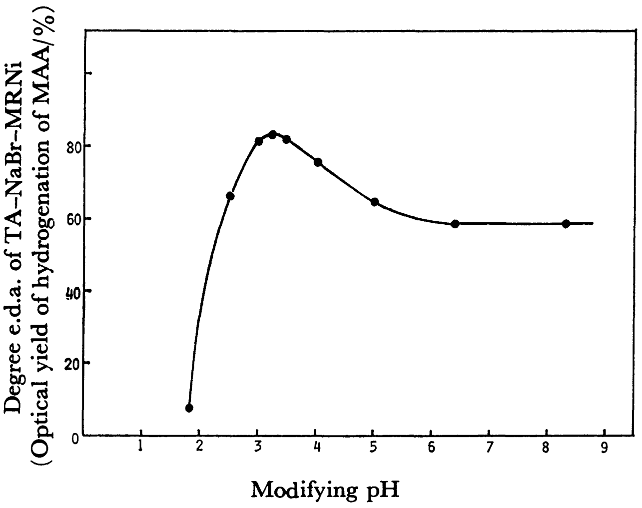

Fig. 4. Relationship between modifying pH and degree of e.d.a. of TA–NaBr–MRNi (optical yield of hydrogenation of MAA).
RNi (0.8 g) was modified with a solution containing TA (1 g) and NaBr (10 g) at 100 °C. The hydrogenation of MAA was carried out under the same conditions as those described in footnote of Table 4.

TA–NaBr–MRNi. In order to prepare TA–NaBr–MRNi–A directly from the conventional RNi, we treated RNi with an acidic aqueous solution containing TA and NaBr at 100 °C. The e.d.a. of TA–NaBr–MRNi thus obtained was examined by the enantioface-differentiating hydrogenation of MAA to MHB.

Figure 4 shows the relationship between the modifying pH and the e.d.a. of TA–NaBr–MRNi. The modification at pH 1.8 resulted in a low e.d.a. and low hydrogenating activity. The modification at pH 3.0—3.5 gave the best result with respect to the e.d.a. (optical yield 83%). The RNi modified with a mixture of TA and NaBr at above pH 3.5 exhibited a lower e.d.a. than that of RNi modified at pH 3.0—3.5 with the same modifying reagents.

Further improvement of e.d.a. was attained when the modification procedure was repeated. Thus, RNi treated three times with a solution containing TA and NaBr at pH 3.2, 100 °C, gave a catalyst with the highest e.d.a. The optical yield of the hydrogenation of MAA to MHB reached 88%. Table 6 shows e.d.a.'s of the catalysts prepared by repeated modifications together with the amount of Al^{3+} and Ni^{2+} eliminated from RNi by repeated modifications.

Table 6. Amounts of ions eliminated by multi-modifications and e.d.a. of multi-modified RNi

Times of modification	Amounts of eliminated ions Ni^{2+}(mg)	Amounts of eliminated ions Al^{3+}(mg)	Degree of e.d.a.[a]
1	137	27	83
2	257	30	86
3	368	32	88

RNi (0.8 g) was modified with an aqueous solution of TA (1 g) and NaBr (10 g) at pH 3.2, 100 °C. Hydrogenation conditions were the same as those described in the Footnote of Table 4. a) Optical yield (%) of hydrogenation of MAA over MRNi.

As can be seen in Table 6, only a small amount of Al^{3+} was found in the modifying solution at the second and third steps. This fact indicates that most of the aluminium and its derivatives on the catalyst surface were eliminated by a single treatment of RNi with TA and NaBr at pH 3.2, 100 °C.

Figure 5 shows the relationship between the amount of NaBr in the modifying solution (pH 3.0, 4.0, or 5.0) and the e.d.a. of the resulting catalyst. The optimal amount of NaBr was affected by the modifying pH. In our research, increasing the modifying pH value tended to increase the optimal amount of NaBr. The use of an excess amount of NaBr resulted in a remarkable decrease of the e.d.a. The e.d.a. of TA–NaBr–MRNi prepared under the optimal amount of NaBr at each modifying pH increased in the following order: pH 5<pH 4< pH 3.

The effects of various kinds of inorganic salts on the e.d.a. of MRNi were examined with the intention of

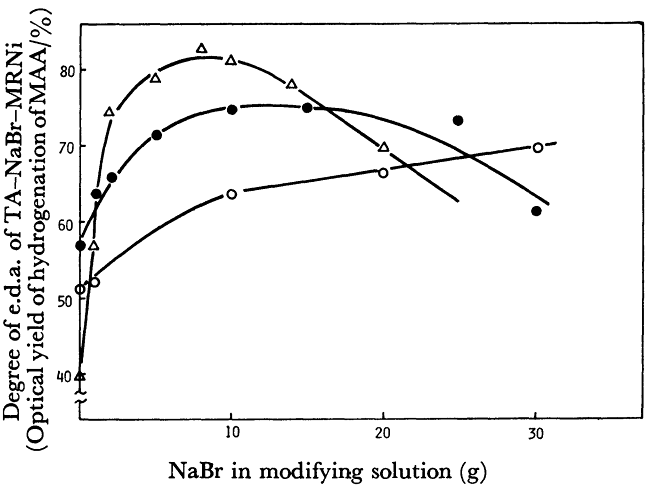

Fig. 5. Relationship between amount of NaBr in modifying solution and degree of e.d.a. of TA–NaBr–MRNi (optical yield of hydrogenation of MAA over TA–NaBr–MRNi).
Amount of RNi: 0.8 g. Modifying pH: at pH 3.0 (—△—), pH 4.0 (—●—), and pH 5.0 (—○—).
Modifying temperature: at 100 °C.
The hydrogenation was carried out under the same conditions as those described in Foothnote of Table 4.

TABLE 7. ENANTIOFACE-DIFFERENTIATING HYDROGENATION OF MAA OVER TA–INORGANIC SALT–MRNi

Inorganic salt in the modifying solution(g)	$[\alpha]_D^{20}$ of the product	Degree of e.d.a.[a]
None	−8.99	39
NaBr (10)	−19.07	83
NaF (3)	−13.95	61
NaCl (10)	−16.55	72
NaI (5×10^{-4})	−11.74	51
Na_2SO_4(10)	−12.95	56
$NaH_2PO_4\cdot2H_2O$ (1)	−8.19	36
$NaNO_3$ (0.1)	−12.17	53
$NiBr_2$ (1)	−14.36	63
$LiBr\cdot H_2O$ (10)	−14.25	62

Amount of RNi: 0.8 g. Modification: at pH 3.2, 100 °C for 1 h. Hydrogenation conditions were the same as those described in the footnote in Table 4. a) Optical yield (%) of hydrogenation of MAA over MRNi.

finding out the best compound to use as the supplementary modifying reagent. The modification was carried out with a mixture of TA and inorganic salt at the optimal modifing pH (pH 3.2) deduced from the results shown in Figs. 4 and 5. Table 7 shows the e.d.a.'s of TA-inorganic salt-MRNi's together with e.d.a. of TA-MRNi. In general the enhancements of the e.d.a.'s were observed by the addition of inorganic salt. The results shown in Table 7 indicate that the kinds of cations in the supplementary modifying reagents affect the e.d.a.'s of the resulting catalysts like the kinds of anions do. These results are in accord with the fact that there are large effects of the alkali ions on the e.d.a. of TA-MRNi.[4] In the case of NaI, a large amount of NaI in the modifying solution resulted in the loss of the hydrogenating activity of the catalyst. Among inorganic salts examined, NaBr was found to be the most effective inorganic salt in giving TA-inorganic salt-MRNi with high e.d.a.

From the results described in this section, it turned out that the modification of RNi with TA and NaBr under acidic conditions gave TA–NaBr–MRNi with a rather higher e.d.a. than that of TA–NaBr–MRNi–A. This simple preparative method of TA–NaBr–MRNi is easily applicable for large scale production.

Role of NaBr Adsorbed on RNi. The preceding section dealt with the preparative method of TA–NaBr–MRNi for practical purposes. As can be seen in Fig. 5, the e.d.a. of the catalyst was very much affected by the modifying pH, modifying temperature, and the amount of NaBr in the modifying solution. RNi is an unstable catalyst and the e.d.a. of the resulting MRNi is very sensitive to the modifying conditions whereas RNi–A is a well stabilized one (Fig. 3). Thus, the complicated results shown in Fig. 5 may be caused, at least in part, by the unstability of RNi. Apart from the practical purposes, it is necessary to use a stabilized catalyst such as RNi–A for the studies on the role of adsorbed NaBr in improvement of the e.d.a.

In this regard, the catalysts used for this experiment were prepared from RNi–A under mild modifying conditions. TA–MRNi–A and TA–NaBr–MRNi–A for this experiment were prepared as follows: RNi was pretreated with an aqueous solution of TA at pH 3.2, 100 °C and then modified with a solution of TA or that of TA and NaBr at pH 5, 0 °C. The surface states of TA–MRNi–A and TA–NaBr–MRNi–A can be considered to be similar to that of RNi–A. The e.d.a.'s of these types of the catalysts were high and comparable to those of TA–MRNi and TA–NaBr–MRNi prepared in one step at pH 3.2, 100 °C.

Figure 6 shows the relationship between the amount of NaBr in the modifying solutions and the amount of adsorbed NaBr or TA. The addition of the first small amount of NaBr in the modifying solution resulted in a noticeable decrease of adsorbed TA. However, no further decrease of adsorbed TA was observed with the further addition of NaBr in the modifying solution.

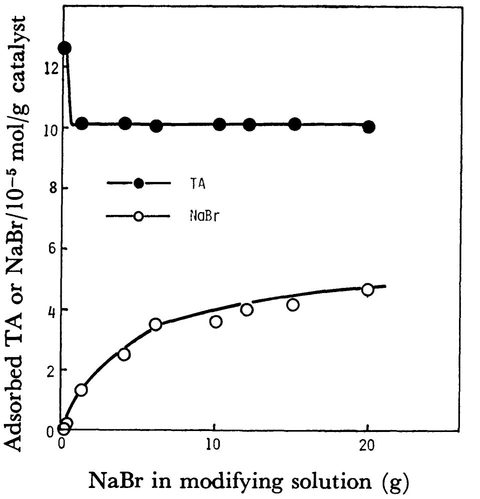

Fig. 6. Relationship between amount of NaBr in modifying solution and amount of adsorbed TA or NaBr.
Catalyst: a 1 g portion of RNi–A (TA). Modification: at pH 5, 0 °C for 1 h.

On the other hand, the amount of adsorbed NaBr increased with the amount of NaBr in the modifying solution. These results can be explained well on the basis of the idea that there are at least two types of areas on RNi–A: one (area-I) prefers to adsorb TA, and the other (area-II) prefers to adsorb NaBr. The increment of adsorbed TA in the absence of NaBr in the modifying solution (Fig. 6; at the point of NaBr=0) may be caused by the adsorption of TA on area-II. On hydrogenation over TA–NaBr–MRNi–A, the enantioface-differentiating hydrogenation may take place over area-I with the aid of adsorbed TA and the non-enantioface-differentiating hydrogenation may take place over area-II. The e.d.a. of TA–MRNi–A was on the line of TA–NaBr–MRNi–A, as will be seen in Fig. 7. This finding suggests that optically active MHB can not be produced over area-II, even when TA was adsorbed on this area.

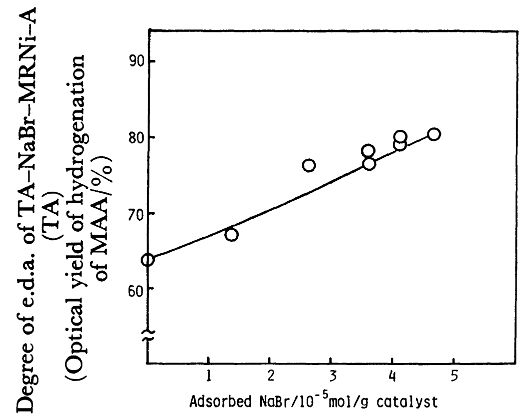

Fig. 7. Relationship between amount of adsorbed NaBr and degree of e.d.a. of TA–NaBr–MRNi–A (TA) (optical yield(%) of hydrogenation of MAA).
Amount of catalyst and modifying conditions were same as those described in Footnote of Fig. 6. The hydrogenation was carried out under the same conditions as those described in Footnote of Table 4.

Figure 7 shows the relationship between the adsorbed amount of NaBr and the e.d.a. of the catalyst. The e.d.a. increased monotonously with the amount of adsorbed NaBr. When the fact that the amount of adsorbed TA is constant under the experimental conditions is taken into account, it is reasonable to assume that the amounts of the optically active MHB produced are not changed by the increase of NaBr adsorbed on the catalyst. The enhancement of the e.d.a. with the amount of adsorbed NaBr results from the decrease of racemic MHB produced over unmodified area-II, because of the deactivation of area-II by the adsorption of NaBr.

In order to compare the hydrogenating activities of TA–MRNi–A and TA–NaBr–MRNi–A, the rates of hydrogenations of acetone over these two catalysts were compared. The time courses of the hydrogenation is shown in Fig. 8. The hydrogenation over TA–NaBr–MRNi–A was found to proceed more slowly than that over TA–MRNi–A. This finding is consistent with the above ideas that NaBr is adsorbed on a different area (area-II) from that (area-I) on which TA is adsorbed and that the adsorbed NaBr reduces the formation of MHB over area-II.

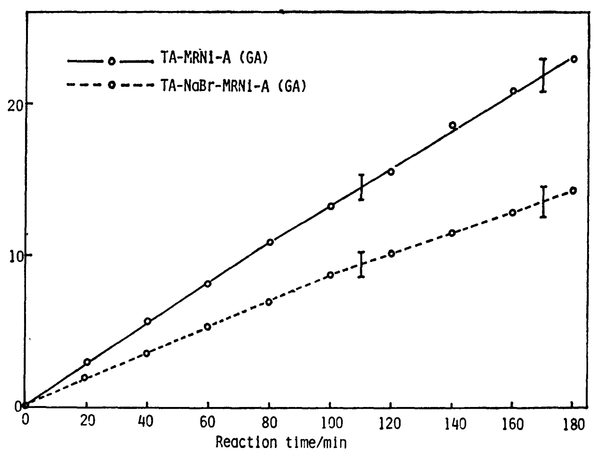

Fig. 8. Time courses of hydrogenation of acetone.
Modifying solution: TA (2 g) or TA (2 g)+NaBr (20 g) were dissolved in deionized water (200 ml). Modification: at pH 5, 0 °C for 1 h.

The areas occupied by TA, MAA, and TA···MAA complex can be assumed to be $2—4\times10^{-19}$, $2—4\times10^{-19}$, and $4—8\times10^{-19}$ m^2/molecule, respectively, which are the silhouette areas of their CPK models. The areas are variable, depending on the adsorption modes of these molecules, and cannot be determined unequivocally at the present stage. When the results of adsorption studies by Welch *et al.*[9] are taken into account, these molecules are too large to cover the parts of small pores and capillaries in the catalyst. Thus, it is difficult to evaluate the e.d.a. of TA–NaBr–MRNi–A simply based on the surface area measured with the BET method and the amounts of adsorbed TA and NaBr.

Although the concepts of areas-I and -II are not directly related to the real surface area of the catalyst, they are informative for understanding the surface state of the catalyst under working conditions.

As a whole, it can be concluded that NaBr adsorbed on RNi inhibits the non-enantioface-differentiating hydrogenation to improve the e.d.a. of TA–MRNi.

Experimental

The optical rotations and visible spectra were measured with a Perkin-Elmer 241 Polarimeter and Hitachi 124 Spectrophotometer, respectively.

Raney Nickel Catalyst. The Ni–Al alloy (Ni/Al=42/58) was leached by adding it portion by poriton to 20 ml of a 20% aqueous solution of NaOH. The Ni–Si alloy (Ni/Si=50/50) was also leached by adding it to 30 ml of a 20% aqueous solution of NaOH. The resulting suspension was kept at 100 °C for 1 h. After removal of the alkaline solution by decantation, the catalyst was washed 15 times with 30 ml portions of deionized water. The Ni–Mg alloy (Ni/Mg=50/50) was leached, using 300 ml of a 3% aqueous solution of tartaric acid. The resulting suspension was kept at room temperature for 45 min. The catalyst was washed 15 times with 30 ml portions of deionized water.

Unless otherwise stated the Ni–Al alloy was used as the Raney alloy in this study.

Reduced Nickel Catalyst. Greenish NiO was reduced for 1 h at 350 °C under a hydrogen stream of 8 l/h.

Catalyst from Nickel Formate. Well-dried nickel formate prepared from nickel chloride and sodium formate was thermally decomposed at 250—300 °C under a pressure of 20—25 mmHg for 1 h.

Urushibara Nickel-A. This was prepared by the procedure of Urushibara *et al.*[10]

Supported Nickel Catalyst. The various types of supported nickel catalysts (weight ratio of Ni to support=50/50) were prepared by a precipitation method. $Ni(NO_3)_2 \cdot 6H_2O$ and the corresponding quatity of kieselguhr, activated alumina, TiO_2, or ZrO_2 were mixed in deionized water. Into the suspension was added dropwise an aqueous solution of Na_2CO_3 with vigorous stirring. After the end of addition of Na_2CO_3, stirring was continued for 1 h. The precipitate was collected by filtration and washed 3 times with water. The residue was dried at 110 °C for 24 h and pulverized in a mortar. The powder was heated to 500 °C and allowed to stand for 3 h at this temperature. The supported NiO thus obtained was reduced for 1 h at 350 °C under a hydrogen stream (8 l/h) just before the modification.

GA-treated Raney Nickel Catalyst. After treatment of RNi (0.8 g) with 100 ml of a 1% aqueous solution of GA at pH 3.2, 100 °C for 1 h, the catalyst was washed 3 times with 30 ml portions of water. Subsequently, the catalyst was treated with 30 ml of 1 M NaOH at 100 °C for 1 h and washed 15 times with 30 ml portions of water.

TA-treated Raney Nickel Catalyst. RNi (0.8 g) was treated with TA under the same conditions as above. The resulting catalyst was washed 3 times with 30 ml portions of water and then subjected to the modification with TA or TA+NaBr.

Modifying Solution. *1)*: TA (1 g) or TA (1 g) and an appropriate amount of inorganic salt were dissolved in deionized water (100 ml), and the pH of the solution was adjusted with 1 M NaOH (the amount of inorganic salt and the value of pH were specified in the text in each case).

2): (*S*)-Glutamic acid (1 g) was dissolved in deionized water (100 ml), and the pH of the solution was adjusted to pH 5 with 1 M NaOH.

Modification. The nickel catalyst was soaked in the modifying solution for 1 h under the conditions stated in the table in the text. After removal of the solution by decantation, the modified catalyst was washed successively with a 10 ml portion of water, two 50 ml portions of methanol, and a 25 ml portion of the reaction solvent.

Hydrogenation of MAA. The hydrogenation of MAA was carried out in a 100 ml autoclave under 110—130 kg/cm^2 of initial hydrogen pressure at the specified temperature. After removal of the catalyst, fractional distillation gave MHB. The optical purity of the product was calculated based on the value of $[\alpha]^{20}_{D}=22.95$ (neat) for optically pure MHB.

Optically Pure MHB. The quinine salt of 3-hydroxybutyric acid, obtained by hydrolysis of MHB ($[\alpha]^{20}_{D}$ -19.50 (neat)), was recrystallized five times from water.[11] Decomposition of the quinine salt and esterification of the free acid with diazomethane gave (*R*)-(−)-MHB with $[\alpha]^{20}_{D}$ -22.95 (neat) (the observed value (l=1 dm); α^{20}_{D} -24.23 (neat), and the specific gravity; $d_{20}=1.056$[6]). Optically pure (*S*)-(+)-MHB was obtained from MHB ($[\alpha]^{20}_{D}$ $+19.50$ (neat)) in the same procedure as described above, except for the use of acetone as the solvent for recrystallization.[11] The value of $[\alpha]^{20}_{D}$ of (*S*)-isomer was $[\alpha]^{20}_{D}$ $+22.77$ (neat) (the observed value (l=1 dm); α^{20}_{D} $+24.05$ (neat)).

Determinations of Ni^{2+} and Al^{3+} in the Modifying Solution. The combined Ni^{2+} and Al^{3+} content in the modifying solution was determined by the EDTA titration method at pH 3.0—3.3, 95—100 °C, using Cu-PAN as the indicator.[12] The Ni^{2+} content in the solution was determined by the EDTA titration method at pH 10—12, using murexide as the indicator and triethanolamine as the masking reagent for Al^{3+}.[12] The difference between these two determinations represented the Al^{3+} content in the modifying solution.

Determination of TA Adsorbed on the Catalyst. A 1 g portion of MRNi-A (TA) or a 10 g portion of TA-MHNi was suspended in 25 ml of 1 M NaOH solution at 100 °C for 1 h. The supernatant was collected by decantation and the remaining catalyst was washed with four 15 ml portions of water. After combination of the supernatant and the washings, the solution was acidified with 10 ml of 1.5 M H_2SO_4 and then was made up to 100 ml with water. The amount of TA was determined colorimetrically by the method reported by G. R. Christian.[13]

Determination of NaBr Adsorbed on the Catalyst. The amount of NaBr adsorbed on the catalyst was determined by Volhard's titrimetric method.[14] A 1 g portion of TA-NaBr-MRNi-A (TA) was decomposed with 15 ml of 60% HNO_3 in the presence of a known amount of $AgNO_3$. The resulting solution was back-titrated with NH_4SCN.

Hydrogenation of Acetone. A 1.6 g portion of RNi-A (GA) was modified with TA or TA+NaBr and then washed successively with a 20 ml portion of water, two 100 ml portions of methanol, and a 50 ml portion of acetone. After removal of the solution by decantation, the modified catalyst suspended in acetone (30 ml) was introduced into an autoclave (100 ml capacity). The hydrogenation of acetone was conducted under 90 kg/cm^2 of initial hydrogen pressure at 28 °C. The conversion of acetone to 2-propanol was calculated based on the depression of hydrogen pressure.

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