The Enantioface-differentiating (Asymmetric) Hydrogenation of the C=O Double Bond with Modified Raney Nickel. XXXIV. The Adsorption Mode of 2-Hydroxy Acid on Raney Nickel

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The adsorbed species of the modifying reagent and the surface states of the catalyst caused by the modification of a Raney nickel with 2-hydroxy acid at various pH regions were investigated. The adsorption mode of 2-hydroxy acid was proposed in each modifying-pH region; that is, (1) in a pH region intrinsic to the solution of the free 2-hydroxy acid, nickel salt of 2-hydroxy acid was adsorbed on the catalyst surface corroded by the acid; (2) under weakly acidic conditions, nickel salt and sodium salt of 2-hydroxy acid were adsorbed on the catalyst surface partially corroded by the acid; (3) under neutral conditions, the sodium salt was adsorbed on the surface of the fresh Raney nickel, and (4) under strongly basic conditions, the sodium salt and NaOH were adsorbed on the surface of the fresh Raney nickel.

The modification of the metal surface to yield an enantioface-differentiating (asymmetric) hydrogenation catalyst has been intensively studied since 1962.[1] Among those substances examined, 2-hydroxy acids were found to be some of the most effective modifying reagents. In the course of the study, the enantioface-differentiating step was found to occur prior to the hydrogen addition to the adsorbed substrate.[2] That is, the interaction of the substrate with the modifying reagent adsorbed on the catalyst causes the substrate to face the catalyst surface predominantly with one of the enantiofaces. Therefore, the investigation of the adsorption mode of 2-hydroxy acid on Raney nickel (RNi) is essential to an understanding of the mechanism of the enantioface-differentiation.

Recently, the adsorptions of hydroxy acids on nickel were investigated by employing physicochemical techniques. Groenwegen *et al.* studied the adsorption of hydroxy acids from the vapor onto silica-supported nickel and inferred from their IR spectra that hydroxy acids were adsorbed as carboxylates.[3] Suetaka *et al.* studied the orientation of hydroxy acids on nickel plate and assumed, from their reflection IR spectra, that hydroxy acids were adsorbed as undissociated forms.[4]

Physicochemical techniques are not always relevant to studies of the modified Raney nickel catalyst (MRNi), because these techniques are mostly applied under conditions quite different from those of the modification or reaction processes. With this in view, some workers have studied the adsorption modes of hydroxy acids in connection with the enantioface-differentiating ability of MRNi. Tatsumi suggested that tartaric acid was adsorbed on the surface of RNi with two carboxyl groups under acidic conditions and with the 2-hydroxyl group and the 1-carboxyl group under neutral conditions.[5] Tanabe *et al.* studied the effect of the bases used for the pH adjustment of the modifying solution on the enantioface-differentiating ability of the catalyst, and concluded that, in the case of tartaric acid at pH 5, one of the carboxyl groups participated in the adsorption onto the catalyst, while the other was free from the catalyst surface.[6] Yasumori *et al.* investigated the effect of the modifying pH on the optical yield and the amount of tartrate adsorbed on a nickel powder catalyst, and inferred that, when the catalyst was modified with tartaric acid, tartrate dianion was the most effective species for the enantioface-differentiation, without reference to the counter-ion.[7] Harada proposed that the adsorption mode of 2-hydroxy acid was influenced by the pH value of the modifying solution and that the enantioface-differentiating ability of MRNi was directly governed by the adsorption mode of 2-hydroxy acid.[8]

This paper will describe our studies of the adsorbed species of 2-hydroxy acid at various pH regions of the modifying solution and on the change in the surface state of the catalyst caused by the modification.

Results and Discussion

Effect of the Modifying pH *on the Adsorbed Species and the Surface States.* When RNi was soaked in the modifying solution, some amounts of metallic nickel were corroded by the modifying reagent and were dissolved into the modifying solution as the nickel ion. The amounts of the nickel ion produced during the

Table 1. Amounts of the nickel ion in the recovered modifying solutions (Ni(II)/mol)

Modifying reagent	Modifying pH			
	2.3	5.1	7.4	10.0
(*RS*)-Mandelic acid	2.9×10^{-4}	—	0.0×10^{-4}	0.0×10^{-4}
(*RS*)-Lactic acid	3.7×10^{-4}	—	0.2×10^{-4}	0.0
Glycolic acid	4.4×10^{-4}	1.1×10^{-4}	0.2×10^{-4}	0.0

Catalyst: 1.5 g as the alloy (Ni: Al=42: 58). Modifying solution: 100 ml of a 1% aqueous solution of the modifying reagent. The pH was adjusted with 1 M NaOH. Modification: at 0 °C for 90 min.

Table 2. Amounts of adsorbed modifying reagents

No.	Reagent for acid treatment (g in 100 ml H_2O, pH)	Modifying reagent (g in 100 ml H_2O, pH)	Adsorbed glycolate
			mol
1	(*RS*)-Mandelic acid (1, pH 2.3)	Nickel glycolate[a] (0.1, pH 6.8)	1.1×10^{-4} (Mandelate: 0.1×10^{-4})
2	—	Nickel glycolate[a] (0.1, pH 6.8)	0.9×10^{-4}
3	Glycolic acid (1, pH 2.3)	Nickel glycolate[a] (0.1, pH 6.8)	1.3×10^{-4}
4	—	Glycolic acid (1, pH 2.3)	1.3×10^{-4}

Catalyst: 1.5 g as the alloy (Ni: Al=42: 58). Acid-treatment and modification: at 0 °C for 90 min, using 100 ml of an acid-treating or modifying solution. a) The concentration (0.1%) of the nickel glycolate solution is comparable to that of the nickel glycolate found in the modifying solution after the modification with a 1% solution of glycolic acid at pH 2.3 (Table 1).

modification with 2-hydroxy acids at various modifying pH regions are listed in Table 1. Only trace amounts of nickel metal were corroded by the modification under neutral or basic conditions. Thus, no appreciable changes in the modifying reagent (*i.e.*, sodium salt to nickel salt of 2-hydroxy acid) or in the surface state of RNi were assumed during the modification under neutral or basic conditions.

The formation of the nickel ion in large amounts by soaking the catalyst in a 2-hydroxy acid solution suggested that the modifying reagent was no longer the free acid, but the nickel salt of the acid in the neighborhood of the catalyst surface, and also that the surface state of RNi was drastically changed by the corrosion. Thus, the MRNi prepared under acidic conditions was assumed to be quite different from those prepared under neutral or basic conditions with respect to the surface state of the catalyst and the species of the adsorbed modifying reagent.

In order to make clear the above-mentioned differences, modifications with nickel glycolate or glycolic acid were carried out using two types of RNi catalysts. One was prepared by a method reported before (fresh RNi),[9] while the other was prepared by the treatment of fresh RNi with 2-hydroxy acid (acid-treated RNi). The amounts of the glycolate adsorbed on the two types of catalysts are compared in Table 2. As is shown in Entry 1, most of the mandelate used for the preparation of the acid-treated RNi was replaced by glycolate on modification with nickel glycolate. By a comparison of the result shown in Entry 1 with that shown in Entry 2, it is apparent that the loading capacity of the catalyst for nickel glycolate was increased by prior treatment with 2-hydroxy acid.

As is shown in Entries 3 and 4, the modification of fresh RNi with a 1% solution of glycolic acid (pH 2.3) and the modification of an acid-treated RNi with a 0.1% solution of nickel glycolate (pH 6.8) gave the same results with respect to the amount of adsorbed glycolate. This fact strongly suggests that the modification of RNi with glycolic acid under acidic conditions consists of two processes; that is, the conditioning process of the RNi surface with the acid, and the following adsorption process of the nickel salt produced *in situ.*

After the modification of fresh RNi was performed with a solution of nickel glycolate, the molar ratio of the glycolate to the nickel ion adsorbed on the catalyst was found to be 1.8: 1 (Table 3). This value is close to that for $Ni(CH_2(OH)CO_2)_2$. Therefore, in this case the major adsorbed species is found to be $Ni(CH_2(OH)CO_2)_2$.

Table 3. Amounts of adsorbed glycolate and adsorbed nickel ion on modification with nickel glycolate

	Modifying solution (solute/mol)		Adsorbed solute
	Initial	Final	mol
Ni(II)	4.9×10^{-4}	4.4×10^{-4}	0.5×10^{-4}[a]
Glycolate	10.6×10^{-4}	—	0.9×10^{-4}

Catalyst: 1.5 g as the alloy (Ni: Al=42: 58). Modifying solution: 100 ml of an aqueous solution of nickel glycolate. Modification: at 0 °C for 90 min. a) Caculated value.

Table 4. Amounts of adsorbed glycolate and adsorbed potassium ion on modfication with potassium glycolate

	Modifying solution (solute/mol)		Adsorbed solute
	Initial	Final	mol
K(I)	2.0×10^{-4}	1.8×10^{-4}	0.2×10^{-4}[a]
Glycolate	2.0×10^{-4}	—	0.2×10^{-4}

Catalyst: 1.5g as the alloy (Ni: Al=42: 58). Modifying solution: 50 ml of an aqueous solution of potassium glycolate. Modification: at 0°C for 90 min. a) Calculated value.

The adsorbed species on modification under neutral conditions were examined in the same way as in the modification with nickel glycolate. Table 4 shows the amounts of the adsorbed glycolate and the adsorbed potassium ion when the fresh RNi was modified with a solution of potassium glycolate (pH 6.8). The molar ratio of the glycolate to the potassium ion adsorbed on the catalyst was found to be exactly 1: 1. Therefore, the species adsorbed on modification with potassium glycolate is found to be potassium glycolate. Similarly, when sodium glycolate is used as the modifying reagent, sodium glycolate is assumed to be the adsorbed species.

Under weakly acidic modifying conditions, RNi was partially corroded by the acid to form a mixture of the catalyst with a fresh surface and with an acid-treated surface. The species adsorbed under this modifying conditions are expected to form a mixture of nickel glycolate and sodium glycolate.

Under strongly basic modifying conditions, the adsorbed species are considered to be the alkali salt

TABLE 5. EFFECTS OF ACID TREATMENT ON THE ENANTIOFACE-DIFFERENTIATING ABILITY OF THE CATALYSTS

No.	Reagent for acid treatment (g in 100 ml H_2O)	Modifying reagent (g in 100 ml H_2O)	$[\alpha]^{20}_{D}$ of Methyl 3-hydroxybutyrate/°
1	(*S*)-3-Phenyllactic acid (1)	Nickel (*S*)-3-phenyllactate (0.1)	+0.58
2	(*RS*)-Lactic acid (1)	Nickel (*S*)-3-phenyllactate (0.1)	+0.62
3	—	Nickel (*S*)-3-phenyllactate (0.1)	+0.30
4	—	(*S*)-3-Phenyllactic acid (1)	+0.60
5	Sodium (*S*)-3-phenyllactate (1)	Nickel (*S*)-3-phenyllactate (0.1)	+0.36
6	—	Sodum (*S*)-3-phenyllactate (1)	+0.15
7	—	(*S*)-3-Phenyllactic acid (1)+NaOH (pH 5)	+0.30
8	—	(*S*)-3-Phenyllactic acid (1)+NaOH (pH 12)	−0.35

Catalyst: 1.5 g as the alloy (Ni: Al=42: 58). Acid-treatment and modification: at 0 °C for 90min. Substrate: 17.5 ml of methyl acetoacetate. Hydrogenating conditions: at 60 °C under an initial H_2 pressure of 90 kg/cm^2.

of 2-hydroxy acid and the alkali hydroxide. This consideration is supported by the fact that the amount of the adsorbed salt of 2-hydroxy acid was drastically decreased when the modifying pH was increased.[8]

The Effect of the Modifying pH *on the Enantioface-differentiating Ability of MRNi.* In the preceding section, MRNi was classified into four types on the basis of the adsorbed species and the surface states: that is, MRNi prepared in a pH region intrinsic to the solution of the free 2-hydroxy acid, under weakly acidic conditions, under neutral conditions, and under strongly basic conditions. Each type of MRNi was examined in order to elucidate the relationship between the enantioface-differentiating ability of MRNi and the adsorption mode of 2-hydroxy acid. (*S*)-3-Phenyllactic acid and its salts were used as the optically active modifying reagents. The ability of MRNi was evaluated by means of the optical yield of the hydrogenation of methyl acetoacetate to methyl 3-hydroxybutyrate. The results are summarized in Table 5.

As is shown in Entries 1 and 4, the same ability was obtained by MRNi prepared from an acid-treated RNi and a solution of nickel (*S*)-3-phenyllactate (pH 6.8), and MRNi prepared from fresh RNi and a solution of (*S*)-3-phenyllactic acid (pH 2.3). In addition, the difference in the acid used for the acid-treatment of fresh RNi did not influence the ability of MRNi (Entries 1 and 2). On the other hand, MRNi prepared from fresh RNi and a solution of nickel (*S*)-3-phenyllactate (pH 6.8) showed a lower ability (Entry 3).

The above results are well compatible with the results obtained in the adsorption studies. That is, MRNi prepared from fresh RNi and a solution of free 2-hydroxy acid is equivalent to that prepared from an acid-treated RNi and a solution of nickel salt of the acid. The difference in the ability between the nickel salt–MRNi prepared from the acid-treated RNi and that prepared from the fresh RNi indicates that the ability of MRNi depends not only on the adsorbed species of the modifying reagent, but also on the surface state of RNi.

The treatment of fresh RNi with a solution of sodium (*S*)-3-phenyllactate (pH 8.2) prior to the modification did not influence the ability of nickel (*S*)-3-phenyllactate–MRNi (Entries 3 and 5). This fact is in accordance with the result obtained in the preceding section; that is, the treatment of fresh RNi with sodium salt of 2-hydroxy acid resulted in no detectable change in the surface state of the catalyst.

Sodium (*S*)-3-phenyllactate–MRNi prepared from fresh RNi showed a different ability from that of nickel (*S*)-3-phenyllactate–MRNi prepared from fresh RNi (Entry 6). The difference can be explained in terms of the difference in the adsorbed species.

The ability of the catalyst modified with a solution containing both 2-hydroxy acid and its sodium salt (pH 5.1) was intermediate between that of 2-hydroxy acid–MRNi and that of its sodium salt–MRNi (Entry 7).

The ability of the catalyst modified under strongly basic conditions was quite different from that of the sodium salt–MRNi (Entry 8). In this case, the direction of the enantioface-differentiation was different from that of the sodium salt–MRNi. This fact indicates that the adsorbed sodium hydroxide drastically affects the adsorption mode of methyl acetoacetate on the catalyst.

As a whole, it can be concluded that the pH-dependence of the enantioface-differentiating ability can also be explained by common factors: the adsorbed species of the modifying reagent and the surface states of the catalyst.

Experimental

The preparation of the modified Raney nickel catalyst, the determination of the absorbed (*RS*)-mandelate and glycolate, the hydrogenation of methyl acetoacetate, and the measurement of the enantioface-differentiating ability of the catalyst were all carried out by the use of the procedures described in a previous paper.[9]

The Preparation of an Acid-treated RNi. A Raney-nickel catalyst obtained from 1.5 g of the alloy[9] was soaked in 100 ml of a 1% aqueous solution of the reagent for acid treatment at 0 °C for 90 min. The mixture was shaken every 15 min. After the acid treatment, the solution was removed by decantation and the catalyst was washed once with 10 ml of deionized water and then with three 50 ml portions of methanol. The resulting catalyst was used for the modification.

The Determination of Ni(II). The nickel ions in the modifying solution were determined by the EDTA titration method at pH 10—12, using murexide as the indicator and triethanolamine as the masking reagent for the aluminium ion.[10]

The Determination of K(I). The potassium ions in the modifying solution were determined by the gravimetric technique using sodium tetraphenylborate.[11]

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