

Sodium Ion as the Most Essential and Effective Element for the Enantio-Differentiating Hydrogenation of Prochiral Ketones over Tartaric Acid Modified Ni Catalyst

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Abstract In order to investigate the role of metal ions on a tartaric acid modified nickel catalyst, the enantio-differentiating hydrogenations of methyl acetoacetate and methyl levulinate were carried out. The effects of the addition of 17 metal salts of acetic acid on the enantio-selectivity and the hydrogenation rate were investigated during the hydrogenation of methyl acetoacetate. Among the examined metal salts, the addition of NaBr caused the great increase in the enantio-selectivity and the hydrogenation rate during the hydrogenations of both methyl acetoacetate and methyl levulinate. Based on the strength of the interaction between the metal salts of tartaric acid and the substrate, the sodium salts would have the strongest interaction with the substrate, hence, this would be attributed to the highest enantio-selectivity and hydrogenation rate for the sodium salts of tartaric acid.

Graphical Abstract



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1 Introduction

In the field of pharmaceuticals, flavor and aromachemicals, and agrochemicals, the synthesis of optically-active compounds is a key issue for the production of the target compounds with the view of both obtaining the medicine without side effects and economically producing the target compounds. Many strategies, such as enantioselective homogeneous catalysts (organometallic complexes, enzymes, or organocatalysts) [1–7] and enantioselective heterogeneous catalysts (modified solid catalysts, heterogenized organometallic complexes or enzymes, metal-organic frameworks) [8-15] have been widely studied for this purpose. Among them, the enantioselective modified solid catalysts (solid catalysts which have an intrinsic catalytic activity and the surface of which is modified by optically-active compounds) are promising, because modified solid catalysts have the characteristics of easy and low cost preparations, easy separation from the reaction mixture, and easy reuse.

A tartaric acid-NaBr-modified nickel catalyst is one of the successful enantio-differentiating solid catalysts for the hydrogenation of β -ketoesters [16, 17] and 2-alkanones [18, 19]. Although this catalyst is easily prepared by adsorbing tartaric acid and NaBr on an activated nickel catalyst, it has been reported that many factors affect the enantio-selectivity [11, 20–22]. It is known that the addition of sodium bromide to the reaction system increases the enantio-selectivity during the hydrogenation of methyl acetoacetate [23–25]. One of the explanations for increasing the enantio-selectivity by the addition of NaBr is that Br⁻ inhibits the hydrogenation on the nonenantio-differentiating sites, where the tartaric acids are not adsorbed and racemic products are produced [26]. On the other hand, sodium ions in the reaction system are mandatory for attaining a high enantio-selectivity during the hydrogenation of β -ketoesters [27, 28] and 2-alkanones [29, 30]. These sodium ions are introduced to the reaction system either through the preparation process of the base nickel catalyst (leaching process by NaOH solution in the case of the Raney nickel catalyst), or the modification process (pH adjustment by NaOH solution in the case of premodification method, or additives, such as NaBr or sodium salts of carboxylic acid, to the reaction media in the case of in situ-modification) [31-33]. Although the presence of lithium or potassium ions is less effective for increasing the enantio-selectivity [27], the reason for this has not yet been clarified.

In the present study, the enantio-differentiating hydrogenations of methyl acetoacetate and methyl levulinate (Scheme 1) were carried out in the presence of various metal ions. The effects of these ions on the enantio-selectivity and the hydrogenation rate were studied and the specificity of the sodium ions is discussed.

2 Experimental

The hydrogen gas (99.99%) and nitrogen gas (99.999%) were obtained from Takachiho Trading Co., Ltd. Ion exchanged water was used for the preparation of the catalysts.

2.1 Enantio-Differentiating Hydrogenation

The enantio-differentiating hydrogenation in this study was carried out using the in situ modification method, i.e., a modifier and auxiliary modifier were added to the reaction media [31, 34].



Scheme 1 Enantio-differentiating hydrogenations of methyl acetoacetate and methyl levulinate

2.1.1 Hydrogenation of Methyl Acetoacetate

A 1.3 g sample of nickel oxide (Wako Pure Chemical Industries, Ltd.) was treated at 623 K for 1 h under a H_2 stream (30 cm³ min⁻¹) to obtain a reduced nickel catalyst. Various salts of acetic acid or alkali bromides in 50 mm³ H₂O and (*R*,*R*)-tartaric acid (the amounts are stated in the text) were added to a mixture of methyl acetoacetate (5.0 g), acetic acid (0.1 g), and THF (10 cm³). This substrate solution and the reduced nickel catalyst were placed in a magnetically-stirred autoclave [OM Lab-Tech Co., Ltd. (Tochigi, Japan)]. Hydrogenation was carried out under the initial hydrogen pressure of 9 MPa at 373 K for 20 h. The stirring rate of the autoclave was 1130 r.p.m.

2.1.2 Hydrogenation of Methyl Levulinate

A 0.94 g sample of nickel oxide (Wako Pure Chemical Industries, Ltd.) was treated at 623 K for 1 h under a H_2 stream (30 cm³ min⁻¹) to obtain a reduced nickel catalyst. Alkali bromides in 50 mm³ H₂O and (*R*,*R*)-tartaric acid (the amounts are stated in the text) were added to a mixture of methyl levulinate (3.82 g), acetic acid (0.065 g), and THF (7 cm³). This substrate solution and the reduced nickel catalyst were placed in a magnetically-stirred autoclave [OM Lab-Tech Co., Ltd. (Tochigi, Japan)]. Hydrogenation was carried out under the initial hydrogen pressure of 9 MPa at 373 K for 20 h. The stirring rate of the autoclave was 1130 r.p.m.

2.1.3 Determination of enantio-selectivity

The enantio-selectivity was expressed using the enantiomer excess (e.e.) determined by GLC. The e.e. of the hydrogenated product of methyl acetoacetate was determined by the analyses of the acetyl derivatives of the product. After distillation of the reaction mixture at a reduced pressure, the product was acetylated using acetyl chloride and pyridine. A portion of the acetylated sample was subjected to analysis using a chiral capillary gas chromatograph [Shimadzu GC-18A, CP Chirasil DEX-CB (0.25 mm × 25 m) at 363 K, (R)-isomer: 9.7 min, (S)-isomer: 10.4 min]. The e.e. was calculated from the peak integration of the corresponding enantiomers. In the case of the hydrogenation of methyl levulinate, as the product of the hydrogenation was mainly 4-pentanolide, the e.e. was determined without acetylation of the product. The e.e. was calculated from the peak integration of the corresponding enantiomers of 4-pentanolide. After the distillation of the reaction mixture at a reduced pressure, the product was analyzed using a chiral capillary gas chromatograph [Shimadzu GC-18A, CP Chirasil DEX-CB (0.25 mm \times 25 m) at 333–413 K (5 K min⁻¹), then at 413–433 K (10 K min⁻¹), (*R*)-isomer: 10.1 min, (*S*)-isomer: 10.3 min].

3 Results and Discussion

3.1 Effects of the Types of Metal Ions in the Reaction Media During the Enantio-Differentiating Hydrogenation of Methyl Acetoacetate

In order to examine the effect of the metal ions in the reaction system, a reduced nickel catalyst (the nickel catalyst prepared by the reduction of nickel oxide) as the base nickel catalyst and an in situ-modification method were used in this study, because the reduced nickel catalyst does not contain sodium ions, which is in contrast to a Raney nickel catalyst, and the in situ-modification can exclusively introduce specific metal ions to the reaction system [35].

Seventeen metal acetates $(7.8 \times 10^{-6} \text{ mol})$ were separately added to the reaction media for investigating the effects of the types of metal ions on the enantio-selectivity and the hydrogenation rate. As the various types of salts are commercially available, the salts of acetic acid were used for this purpose. The results are shown in Fig. 1.

Based on the Fig. 1 results, the following points were revealed. (i) The salts of acetic acid, which increased the hydrogenation rate, also increased the enantio-selectivity during the enantio-differentiating hydrogenation of methyl acetoacetate. (ii) Among the alkali metal ions, only the salts of Na and K increased both the enantio-selectivity and the hydrogenation rate. (iii) In spite of the alkali metal ions, the salts of Rb and Cs had no effect on the hydrogenation rate and the enantio-selectivity, as well as the salts other than the alkali metal ions.



Fig. 1 Effects of the types of metal acetates on the enantio-selectivity and the hydrogenation rate (Substrate: methyl acetoacetate) (*R*,*R*)-tartaric acid (1.3 mg) and metal salts of acetic acid (7.8×10^{-6} mol) in 50 mm³ H₂O were added to the reaction media. *a* As Ag acetate and Zn acetate were difficult to dissolve in 50 mm³ of water, these salts were added to the reaction media as suspensions

3.2 Effects of the Types of Alkali Bromides During the Enantio-Differentiating Hydrogenation of Methyl Acetoacetate and Methyl Levulinate

Based on the results in Sect. 3.1, only the addition of the sodium and potassium salts increased both the enantio-selectivity and the hydrogenation rate. The effects of the addition of various alkali bromides on the enantio-selectivity and the hydrogenation rate were investigated in detail during the hydrogenations of methyl acetoacetate and methyl levulinate. Figures 2 and 3 show the effects of the amount of alkali bromides on the enantio-selectivity and the hydrogenation rate, respectively, during the hydrogenation of methyl acetoacetate.

When no alkali bromide was added to the reaction media, a 20% enantio-selectivity was attained. The addition of 1.9×10^{-6} mol of alkali bromides, except for CsBr, increased the enantio-selectivity. The increase in the enantio-selectivity was most significant with the addition



Fig. 2 Effects of the amount of alkali bromides on the enantioselectivity (substrate: methyl acetoacetate) *filled square* LiBr, *filled diamond* NaBr, *filled triangle* KBr, *filled circle* RbBr, *asterisk* CsBr (R,R)-tartaric acid (5 mg) and alkali bromide in 50 mm³ H₂O were added to the reaction media



Fig. 3 Effects of the amount of alkali bromide on the hydrogenation rate (substrate: methyl acetoacetate) *filled square* LiBr, *filled diamond* NaBr, *filled triangle* KBr, *filled circle* RbBr, *asterisk* CsBr (R,R)-tartaric acid (5 mg) and alkali bromide in 50 mm³ H₂O were added to the reaction media

of NaBr, and in the order of NaBr>KBr>RbBr>LiBr. The addition of 9.7×10^{-6} mol of NaBr resulted in an 88% enantio-selectivity. On the other hand, in the case of KBr, RbBr, and LiBr, the maximum enantio-selectivity was obtained with a smaller amount of the salts than the addition of NaBr. The addition of an excess amount of the salts decreased the enantio-selectivity. The hydrogenation rates increased with the addition of 1.9×10^{-6} mol of NaBr or KBr. The addition of RbBr or LiBr slightly increased the hydrogenation rate. On the contrary, the addition of CsBr decreased the hydrogenation rate. Of all the examined alkali bromides, NaBr increased the hydrogenation rate the highest. In the cases of NaBr, KBr, and RbBr, the addition of 3.9×10^{-6} mol of the salts produced the maximum hydrogenation rate. The increase in both the enantio-selectivity and the hydrogenation rate was observed only by the addition of NaBr or KBr. It has been reported that the modification of the nickel surface by tartaric acid and NaBr increases the hydrogenation rate [36, 37]. The previously reported results and the present results would indicate the attractive interaction occurring between the sodium tartrate and the substrate.

The effects of the addition of alkali bromides on the enantio-selectivity and the hydrogenation rate during the hydrogenation of methyl levulinate are shown in Figs. 4 and 5, respectively.

In contrast to the hydrogenation of methyl acetoacetate, the enantio-selectivity was almost zero without the addition of alkali bromides during the hydrogenation of methyl levulinate. The addition of NaBr, KBr, and RbBr increased the enantio-selectivity. Especially, the addition of 5.8×10^{-6} mol of NaBr attained the enantio-selectivity of 46%. The effect of KBr was almost the same as that of RbBr. Although the addition of 1.5×10^{-6} mol of CsBr slightly increased the enantio-selectivity. The addition of LiBr resulted in the production of the (*S*)-isomer in excess. The



Fig. 4 Effects of the addition of alkali bromide on the enantio-selectivity (substrate: methyl levulinate) *filled square* LiBr, *filled diamond* NaBr, *filled triangle* KBr, *filled circle* RbBr, *asterisk* CsBr (R,R)-tartaric acid (3.7 mg) and alkali bromide in 50 mm³ H₂O were added to the reaction media



Fig. 5 Effects of the addition of alkali bromide on the hydrogenation rate (substrate: methyl levulinate) *filled square* LiBr, *filled diamond* NaBr, *filled triangle* KBr, *filled circle* RbBr, *asterisk* CsBr (R,R)-tartaric acid (3.7 mg) and alkali bromide in 50 mm³ H₂O were added to the reaction media

hydrogenation rate was increased by the addition of only NaBr and the maximum rate was attained by the addition of 1.5×10^{-6} mol.

Based on the results from Figs. 1, 2, 3, 4 and 5, it was revealed that the existence of sodium ions in the reaction system is indispensable for attaining a high enantio-selectivity and hydrogenation rate during both the hydrogenation of methyl acetoacetate and methyl levulinate.

3.3 Interaction Between Substrate and Sodium Tartrate on the Catalyst Surface

3.3.1 Enantio-Differentiating Model Including Sodium Ions

Based on the results of Figs. 2, 3, 4 and 5, the addition of NaBr produced the highest enantio-selectivity and hydrogenation rate during both the hydrogenation of methyl acetoacetate and methyl levulinate. We propose the following mechanisms of the enantio-differentiating hydrogenation on the tartaric acid-NaBr-modified nickel catalyst. The added Na⁺ would form sodium tartrate on the catalyst surface [31]. The sodium tartrate could increase the substrate concentration on the enantio-differentiating site and hence increase the hydrogenation rate and the enantio-selectivity. The remarkable effects of the addition of Na⁺ compared to the other alkali metal ions would indicate that the attractive interaction between the substrate and Na⁺ was stronger than those between the substrate and alkali ions other than Na⁺.

The tartaric acid-NaBr-modified Ni differentiates the enantio-face of the substrate through the interaction between the tartaric acid (salt) and the substrate. Various types of modes of the interaction between the tartaric acid and the substrate have been proposed [9, 32, 38–44]. Among them, only the model we proposed explained the enantio-differentiation based on the role of the sodium ions [29]. This model is based on the following interaction (Fig. 6).

- (*R*,*R*)-tartaric acid adsorbed on the nickel surface as a mono or disodium salt.
- One of the hydroxyl groups of tartaric acid interacts with the carbonyl group to be hydrogenated in the substrate through hydrogen bonding.
- Na⁺ in the sodium tartrate interacts with the ester carbonyl group of the substrate through an ion-dipole interaction.

In this study, based on this model, we discussed the reasons for the effectiveness of the Na^+ addition compared to the other metal ions for increasing the enantio-selectivity and hydrogenation rate.

3.3.2 Effective Nuclear Charge of Alkali Metal Ions and the Strength of the Interaction Between the Substrate and Tartaric Acid Salt

As has been mentioned in Sect. 3.3.1, the addition of Na^+ resulted in an increased enantio-selectivity and hydrogenation rate. This would be attributed to the stronger interaction between the sodium tartrate and the substrate than the other alkali salts of the tartaric acids.

Based on the results of Fig. 1, only alkali metal ions, especially Na^+ and K^+ , affected the enantio-selectivity and hydrogenation rate. The enantio-selectivity and hydrogenation rate obtained with the addition of other metal ions were almost the same as or lower than those without additives. One of the reasons for explaining these results would be the difference between the alkali metal ions as monovalent ions and the other metal ions



Fig. 6 Enantio-differentiating model including sodium ions [29]

as di- or trivalent ions (except Ag⁺). As the substrate needs to interact with the modifier on the nickel surface. the proper space around the tartaric acid is needed for accessing the substrate to the modifier. The adsorption mode of the multivalent ion salts of tartaric acid on the nickel surface is not clear, but it would not be suitable for the appropriate interaction with the substrate for attaining a high enantio-selectivity. For example, it would be difficult for the substrate to approach the tartaric acid salts of multivalent ions, because more than two molecules of tartaric acid could exist around the multivalent ions. Therefore, a stable complex cannot be made from the substrate and tartaric acid. The result that the addition of multivalent ions did not increase the hydrogenation rate would also suggest that the interaction between the cation and the substrate cannot form a stable substrate-tartaric acid complex.

The reason for attaining a low enantio-selectivity with the addition of Ag^+ ions could be due to the phenomena that Ag^+ changes into Ag^0 with the change of Ni⁰ to Ni²⁺ as well as the low solubility of silver acetate in the reaction solution.

Concerning the discussion of the strength of the interaction between the modifier and the substrate, the following assumptions were developed.

• The stronger interaction between an alkali metal ion and the ester carbonyl group of the substrate produces a more stable tartaric acid-substrate complex, hence a higher enantio-selectivity and hydrogenation rate are attained.

The strength of the interaction between an alkali metal ion in the tartrate and an oxygen atom in the ester carbonyl group of the substrate (F) is estimated. The strength would be proportional to the $\frac{Z_{eff}}{r^2}$ value calculated by Eq. 1 using Coulomb's law.

$$F = k \frac{Z_{eff} e^2}{r^2} \propto \frac{Z_{eff}}{r^2} \tag{1}$$

where Z_{eff} , effective nuclear charge of an alkali metal ion [45]; *e*, elementary charge; *r*, radius of valence shell s-orbital of alkali metal [46].

Table 1 $\frac{Z_{eff}}{r^2}$ values of various alkali metal ions

Alkali metal ion	Effective nuclear charge	Radius of valence shell s-orbital of alkali metal/ pm	$rac{Z_{eff}}{r^2}$	
Li ⁺	1.3	164	4.8×10^{-5}	
Na ⁺	2.2	179	6.9×10^{-5}	
K^+	2.2	230	4.2×10^{-5}	
Rb ⁺	2.2	249	3.5×10^{-5}	
Cs ⁺	2.2	282	2.8×10^{-5}	

Table 2 Effect of the addition of alkali metal salts on the enantioselectivity and the hydrogenation rate	Substrate	Additive	Enantioselectivity	Hydrogenation rate
	Methyl acetoacetate	Alkali acetate	$Na^+ > K^+ > Rb^+ \approx Li^+ > Cs^+$	$Na^+ > K^+ \approx Li^+ > Rb^+ > Cs^+$
		Alkali halide	$Na^+ > K^+ > Rb^+ > Li^+ > Cs^+$	$Na^+ > K^+ > Rb^+ > Li^+ > Cs^+$
	Methyl levulinate	Alkali halide	$Na^+ > K^+ \approx Rb^+ > Cs^+ > Li^+$	$Na^+ > K^+ \approx Rb^+ \approx Li^+ > Cs^+$

The values of the effective nuclear charge are well known based on those by Slater [45] and those by Clementi et al. [47, 48]. In the present study, the values by Slater were used, because the attractive force when the valence electron of the oxygen atom of the substrate approaching the position of the valence s-electron of the alkali metal ion is to be calculated. As for the values by Clementi et al. when considering the penetration effects of the s-orbitals, it would not be appropriate for the present purpose. The calculated values for the various alkali metal ions are shown in Table 1.

Based on the results of Table 1, the order of the $\frac{Z_{eff}}{r^2}$ value was Na⁺>Li⁺>K⁺>Rb⁺>Cs⁺. The strongest interaction between sodium tartrate and the substrate would result in the most stable modifier–substrate complex, hence the highest enantio-selectivity and hydrogenation rate.

Meanwhile, the order of the effect of the addition of the alkali metal salts on the enantio-selectivity and hydrogenation rate of methyl acetoacetate and those of methyl levulinate are summarized in Table 2. The orders shown in Tables 1 and 2 agree except for the lithium ion. The lithium ion tends to be more solvated than the other alkali metal ions [49]. This could be the reason for the inconsistency of the orders in Tables 1 and 2 concerning the lithium ion.

4 Conclusion

In order to investigate the role of metal ions on a tartaric acid modified nickel catalyst, the enantio-differentiating hydrogenations of methyl acetoacetate and methyl levulinate were carried out. The effects of the addition of 17 metal salts of acetic acid on the enantio-selectivity and hydrogenation rate were investigated during the hydrogenation of methyl acetoacetate. Among the examined metal salts, only the salts of Na⁺ and K⁺ affected both the enantio-selectivity and hydrogenation rate. Especially, sodium acetate significantly increased the enantio-selectivity and hydrogenation rate. The effects of the significant increase in the enantio-selectivity and hydrogenation rate by the addition of Na⁺ were also observed by the addition of alkali halides during the hydrogenation of both methyl acetoacetate and methyl levulinate. The role of the sodium ion was discussed in view of the strength of the interaction between the alkali metal salts of tartaric acid and the substrate. The strength of the interaction of the alkali metal ion and the oxygen atom of the ester carbonyl group of the substrate was estimated using Coulomb's law. It was revealed that the interaction involving the sodium ion was the strongest. This would result in the production of the most stable sodium tartrate–substrate complex on the nickel surface, hence, the highest concentration of the substrate and the highest hydrogenation rate on the enantio-differentiating site. This would be the reason that the highest enantio-selectivity was attained by the addition of sodium ions. The order of the enantio-selectivity and hydrogenation rate agreed with the order of the strength of the interaction between the alkali metal ion and the oxygen atom of the ester carbonyl group, except for the lithium ion.

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