Application of an in situ modification of nickel catalysts to the enantio-differentiating hydrogenation of methyl acetoacetate

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Abstract

In situ modification ((R,R)-tartaric acid and NaBr were directly added to the reaction media) of fine Ni powder (FNiP) and reduced Ni catalysts was applied to the enantio-differentiating hydrogenation of methyl acetoacetate (MAA). The high optical yield of 89% was attained by the reduced Ni catalyst. This is the highest value reported so far for the hydrogenation of methyl acetoacetate using the in situ modification. The addition of a small amount of NaBr to the reaction media increased both the optical yield and hydrogenation rate, while the hydrogenation rate decreased with the addition of NaBr to the modification solution for the conventional modification method. NaBr added to the reaction media for the in situ modification would have both of the following roles: (i) Na^+ increased the optical yield and the hydrogenation rate; and (ii) Br^- increased the optical yield and decreased the hydrogenation rate. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The technique of in situ modification (modifiers are directly added to the reaction media) is now a common method for the enantio-differentiating hydrogenation with cinchona-modified Pt ([1,2] and references therein) or Pd ([3,4] and references therein) catalysts. When Orito discovered the cinchona-modified Pt in 1979, he prepared it by immersing supported Pt in the ethanolic solution of a modifier [5]. In the 1980s, the European groups began to use the in situ modification technique for cinchona-modified Pt and Pd systems. On the other hand, the in situ modification technique had not been applied to the tartaric acid

(TA)-modified Ni system, because the addition of TA to the reaction media retarded the hydrogenation rate and gave a very low optical yield for the hydrogenation of methyl acetoacetate (MAA) over Raney Ni catalysts [6]. Only a few studies concerning the in situ modification have been reported in the case of the TA-modified Ni systems. An optical yield of 32% was reported for the Ni–Ce oxide catalysts [7]. We recently demonstrated that the in situ modification could be applied to the enantio-differentiating hydrogenation over fine Ni powder (FNiP) catalysts [8].

In this paper, we show the results of the enantio-differentiating hydrogenation of methyl acetoacetate over FNiP catalysts and reduced Ni catalysts with the in situ modification. The parameters affecting the optical yield and hydrogenation rate are discussed.

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2. Experimental

All chemicals used were as-received. The GLC measurement of the products was carried out using a Hitachi 263-30 gas chromatograph. The optical rotations were observed using a JASCO DIP-1000 polarimeter.

2.1. Catalyst

2.1.1. Fine nickel powder (FNiP) catalyst

A total of 1 g of commercially available FNiP (Vacuum Metallurgical Co. Ltd., Chiba, Japan, mean particle diameter: 20 nm) was treated in a hydrogen stream at 280°C for 0.5 h before use.

2.1.2. Reduced nickel catalyst

A total of 3 g of commercially available nickel oxide (Nacalai Tesque, lot M3F86790) was reduced in a hydrogen stream at 350°C for 1 h before use.

2.2. Enantio-differentiating hydrogenation using in situ modification method

TA and NaBr were directly added to the reaction mixture of MAA (10 g), THF (20 ml), and acetic acid (0.2 g). TA could be dissolved in THF. NaBr was added as an aqueous solution of the stated amount of distilled water. For the in situ modification, no pH adjustment was necessary. The hydrogenation of MAA was carried out over the hydrogen-treated Ni catalysts at 100°C and at the initial hydrogen pressure of 9 MPa. The hydrogenation products obtained by simple distillations showed more than a 98% chemical purity (GLC analyses: 90°C, 5% Thermon 1000 on Chromosorb W).

2.3. Determination of optical yield

The optical yield of the product was obtained using the following equation:

Optical yield (%)

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

The specific optical rotation of the optically pure (*R*)-methyl 3-hydroxybutyrate is −22.95° (neat) [9].

2.4. Determination of hydrogenation rate

The hydrogenation rate was obtained from the amount of hydrogen consumption during the MAA hydrogenation reaction after the temperature of the autoclave reached the reaction temperature of 100°C (from 1.5 to 2.5 h after the reaction started).

3. Results and discussion

3.1. Enantio-differentiating hydrogenation over FNiP

In a preceding paper, for the in situ modification using FNiP, we demonstrated that the addition of only tartaric acid to the reaction media produced a negligibly small optical yield and that the addition of both the sodium salt and tartaric acid resulted in increasing the optical yield. Among the sodium salts examined, NaBr was the most effective one [8].

Fig. 1 shows the effect of the amount of NaBr on the optical yield in the presence of 200 mg of TA. NaBr dissolved in the 50 μl of distilled water was added to the reaction media. With no addition of NaBr, an almost racemic hydrogenation was obtained. However, 0.5 mg of NaBr significantly increased the optical yield. The optical yield passed through a maximum of 79% at about 4 mg of NaBr.
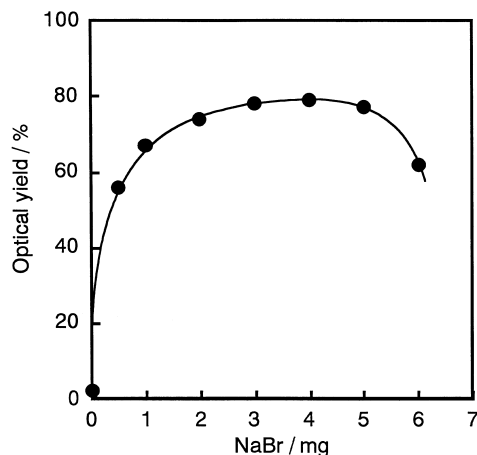

Fig. 1. Effect of the amount of NaBr on the optical yield. Catalyst: FNiP; additives to the reaction media: TA 200 mg and NaBr (dissolved in 50 μl of H₂O).

In the conventional modification method, the modification solution containing TA and NaBr was neutralized to above pH 3.2 by a NaOH solution for attaining a high optical yield. The modification solution with no neutralization produced a catalyst having a low enantio-differentiating ability and a low hydrogenation activity [9]. It was demonstrated that the sodium salts of TA on the Ni surface contributed to the differentiation of the enantio-face of the substrates [10]. Recently, we proposed a new model of enantio-differentiation, i.e. sodium tartrate interacted with methyl acetoacetate through sodium ions [11]. It was also demonstrated that NaBr was adsorbed on the non-enantio-differentiating sites and retarded the hydrogenation rate in order to raise the optical yield [12]. Thus, both sodium tartrate and NaBr were necessary for attaining a high optical yield for the conventional modification method.

The present study indicated that the addition of only TA to the reaction media gave a low optical yield for the in situ modification. This finding showed that the in situ modification has the same tendency as the conventional modification. However, the addition of TA and NaBr (no addition of NaOH) gave the high optical yield for the in situ modification. This result indicates that NaBr for in situ modification played the roles of both NaBr and NaOH for the conventional modification. In other words, NaBr in the in situ modification would have two roles. One is for Br^- to deactivate the non-enantio-differentiating sites and the other is for Na^+ to enhance the enantio-differentiation.

This argument was supported by the results shown in Fig. 2. This figure shows the effect of the amounts of NaBr on the hydrogenation rate. The hydrogenation rate significantly increased with the addition of 0.5 mg of NaBr. The rate gradually increased with the addition of up to 1 mg of NaBr, but decreased with more than
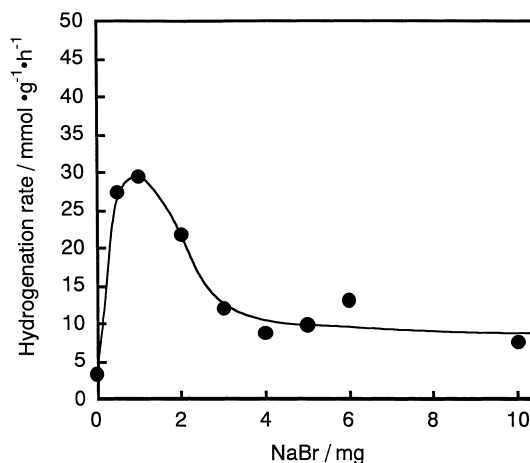
Fig. 2. Effect of the amount of NaBr on the hydrogenation rate. Catalyst: FNiP; additives to the reaction media: TA 200 mg and NaBr (dissolved in 50 μl of H_2O).

1 mg. The phenomenon that a small amount of NaBr increased the hydrogenation rate was not observed in the conventional modification. The hydrogenation rate decreased with the addition of NaBr [9,13] or the hydrogenation rate was almost constant with the addition of a small amount of NaBr [14] in the conventional modification. Judging from the fact that Na carboxylate added to the reaction media increased the hydrogenation rate using the conventional modified Ni catalysts [15,16], the increase in the hydrogenation rate by the addition of small amount of NaBr for the in situ modification would be attributed to the function of Na^+ from the NaBr. The hydrogenation rate would be determined by the competition of Na^+ (increases the rate) and that of Br^- (decreases the rate).

Considering that sodium tartrate played an important role in the effective enantio-differentiation

Table 1
Effect of the amount of monosodium tartrate in the reaction system on an optical yield and hydrogenation rate

Monosodium tartrate·H_2O (mg)	NaBr (mg)	Amount of water (μl)[a]	Optical yield (%)	Hydrogenation rate (mmol g^{-1} h^{-1})
30	0	420	50	32
50	0	700	46	28
30	1	470	65	33
30	2	470	73	29
30	4	470	66	33

[a] Catalyst: FNiP; additives to the reaction media: Na tartrate and NaBr (dissolved in the stated amount of H_2O^a).

of the conventional modification, the addition of monosodium tartrate and NaBr could attain a higher optical yield. Table 1 shows the effect of the addition of monosodium tartrate and NaBr on the optical yield and hydrogenation rate. The addition of only monosodium tartrate gave a 50% optical yield and the addition of NaBr increased the optical yield. However, the maximum optical yield of 73% was attained when 30 mg of Na tartrate and 2 mg of NaBr were added to the reaction media. This value of the optical yield was lower than that for 200 mg tartaric acid and 4 mg NaBr as shown in Fig. 1. This would be attributed to the water which initially dissolved the Na tartrate, because Na tartrate is not soluble in THF. It has been reported that the addition of water was not appropriate for attaining a high optical yield [17]. The hydrogenation rate with the addition of only monosodium tartrate was similar to that for the addition of both monosodium tartrate and NaBr. These results indicated that the Na^+ of monosodium tartrate played an important role in determining the hydrogenation rate for the addition of monosodium tartrate.

3.2. Enantio-differentiating hydrogenation over reduced Ni catalyst

During the enantio-differentiating hydrogenation using a reduced Ni catalyst, the optical yield was affected by the manufacturer of the nickel oxide used as the starting material for the catalyst [18–20]. The preliminary experiment showed that nickel oxide manufactured by Nacalai Tesque Co. Ltd., gave the highest optical yield in the present study. When 100 mg of TA and 4 mg of NaBr (standard condition in the case of FNiP) were added to the reaction media, the hydrogenation was very slow and the chemical yield after 20 h was <1%. This would be caused by the addition of too much TA to the reaction media. Therefore, 10 mg of TA was used for the reduced Ni catalysts. Figs. 3 and 4 show the effect of the amount of NaBr on the optical yield and the hydrogenation rate, respectively. The addition of NaBr increased the optical yield and the maximal optical yield of 89% was attained with the addition of 2 mg of NaBr. This is the highest value reported so far for the hydrogenation of methyl acetoacetate using the in situ modification. The hydrogenation rate increased
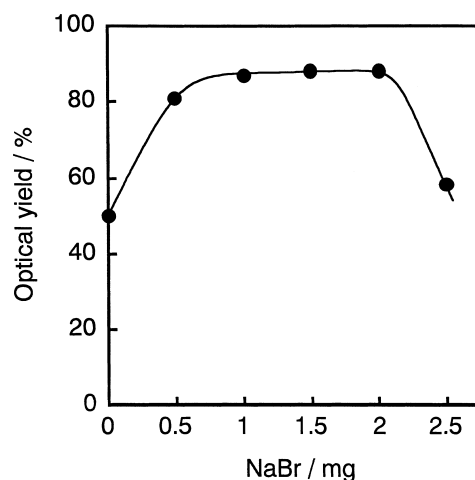

Fig. 3. Effect of the amount of NaBr on the optical yield. Catalyst: reduced Ni; additives to the reaction media: TA 10 mg and NaBr (dissolved in 50 µl of H_2O).

with the addition of up to 0.5 mg of NaBr, but then decreased above 0.5 mg. Much smaller amounts of TA and NaBr gave the high optical yield for the reduced Ni catalyst in comparison with the case of FNiP. This would be the result of the smaller surface area of the Ni catalyst prepared from NiO than that of FNiP.
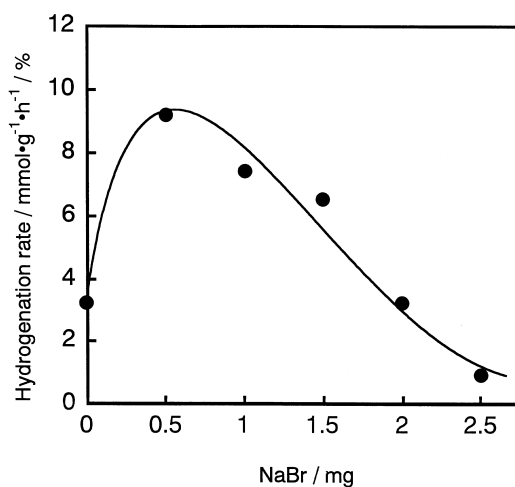

Fig. 4. Effect of the amount of NaBr on the hydrogenation rate. Catalyst: reduced Ni; additives to the reaction media: TA 10 mg and NaBr (dissolved in 50 µl of H_2O).

4. Conclusions

The method of in situ modification (addition of TA and NaBr to the reaction media) makes the enantio-differentiating hydrogenation procedure with a Ni catalyst very simple, because the process of modification in an aqueous solution prior to the hydrogenation can be omitted. When a reduced Ni catalyst was used, the maximal optical yield of 89% was attained for the hydrogenation of methyl acetoacetate. The addition of the appropriate amount of NaBr to the reaction media increased the hydrogenation rate and the optical yield. NaBr added to the reaction media used in the in situ modification would have both of these roles: (i) Na^+ increased the optical yield and the hydrogenation rate; and (ii) Br^- increased the optical yield and decreased the hydrogenation rate.

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