

Enantio-Differentiating Hydrogenation of 2-Octanone over Modified Nickel Catalysts Prepared by an In Situ Modification

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The enantio-differentiating hydrogenation of 2-octanone was carried out over a tartaric acid-modified reduced nickel catalyst. It was shown that the in situ modification of the Ni surface was available for the hydrogenation of 2-octanone in the presence of a large amount of pivalic acid in the reaction media. An optical yield of 74% was attained with the in situ modified reduced Ni catalyst.

An (*R,R*)-tartaric acid (TA)–NaBr-modified Ni catalyst was conventionally prepared by immersing a Ni catalyst in an aqueous solution of pH 3.2 containing TA and NaBr at 373 K before the hydrogenation reaction (*pre*-modification). This *pre*-modified catalyst hydrogenates two kinds of prochiral ketones with high optical yields. That is, they are β -functionalized ketones and dialkyl ketones.^{1–3} The feature of the reaction medium for attaining high optical yields for the hydrogenation of dialkyl ketones was different from that for the β -functionalized ketones. An acidic mixture of pivalic acid and tetrahydrofuran (THF) was needed for the hydrogenation of dialkyl ketones, while THF was used for the hydrogenation of β -functionalized ketones.⁴ Although the addition of pivalic acid to the reaction media greatly increased the optical yield for the hydrogenation of 2-octanone, pivalic acid produced the desorption of Na ions from the TA–NaBr-*pre*-modified Raney Ni (RNi) catalyst; this decreased the enantio-differentiating ability of the catalyst for repeated runs (the first run, 59% optical yield; the second run, 4%; the third run, 0%).⁵ We recently reported that the use of a reduced Ni catalyst prepared by the reduction of NiO enabled the application of an in situ modification (TA and NaBr were directly added to the reaction media) to the enantio-differentiating hydrogenation of methyl acetoacetate, and that the in situ modified reduced Ni catalyst gave a 90% optical yield.⁶ The added TA and NaBr were adsorbed on the nickel surface during the initial stage of the reaction and created an enantio-differentiating catalyst. The in situ modification has greater advantages compared with *pre*-modification, especially for industrial applications of this catalyst,

because the *pre*-modification process in an aqueous solution in advance of hydrogenation can be omitted, and the in situ modification does not produce a waste modification solution containing Ni ions. The possibility of applying the in situ modification to the hydrogenation of 2-octanone is of significant interest, because the reaction media is an acidic organic solution containing a large amount of pivalic acid, while *pre*-modification was carried out in an aqueous solution. In this paper, we report on the hydrogenation of 2-octanone over an in situ modified reduced Ni catalyst. The parameters affecting the optical yield were examined.

Figure 1 shows the effect of the amount of TA added to the reaction media on the optical yield. A reduced Ni catalyst was prepared by the reduction of NiO at 623 K in a hydrogen stream. The optical yield increased significantly with the addition of 2 mg of TA, and gradually increased with up to a 10-mg addition of TA. Figure 2 shows the effect of the NaBr amount

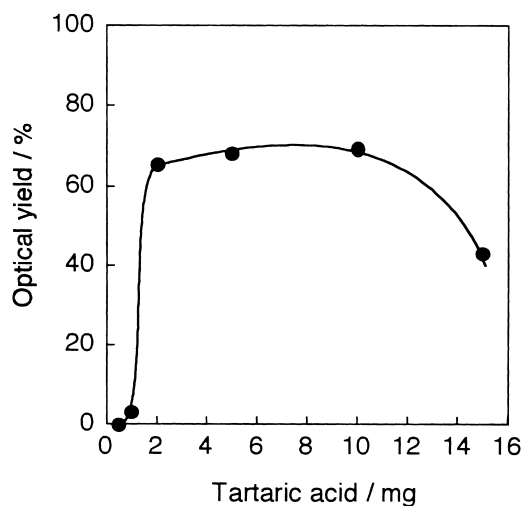


Fig. 1. Effect of the in situ added TA on the optical yield NaBr 1.5 mg, Hydrogenation 373 K.

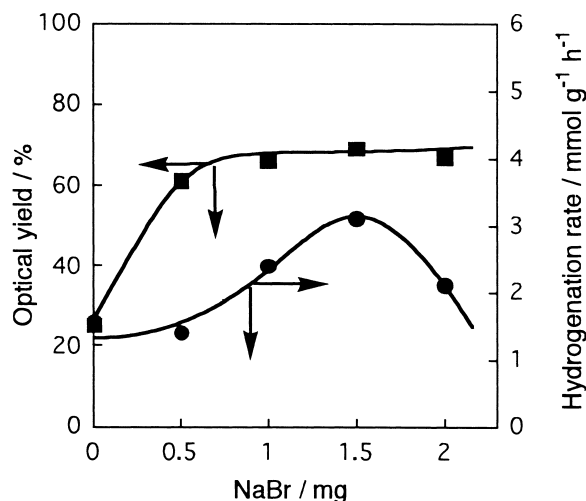


Fig. 2. Effect of the in situ added NaBr on the optical yield and the hydrogenation rate TA 10 mg, Hydrogenation 373 K.

on the optical yield and hydrogenation rate. The addition of appropriate amounts of TA (10 mg) and NaBr (1.5 mg) gave a 70% optical yield for hydrogenation at 373 K. When the hydrogenation temperature was lowered to 333 K, the optical yield increased to 74% (NaBr: 1.5 mg). These results indicated that TA and NaBr added to the reaction media were adsorbed on the Ni surface during the initial stage of the reaction to create an enantio-differentiating catalyst in spite of the presence of a large amount of pivalic acid in the reaction media. The amount of NaBr also affected the hydrogenation rate. The rate increased with the increase in the amount up to 1.5 mg of NaBr, and then decreased. The repeated use of the in situ modified reduced Ni for the hydrogenation of 2-octanone was also investigated. An optical yield of 62% was maintained after the third run at 373 K (the first run, 67% optical yield; the second run, 67%; the third run; 62%). A distinct improvement in the durability compared with the case of the *pre*-modified RNi can be attributed to the combination of the in situ modification and the reduced Ni catalyst, analogous to the hydrogenation of methyl acetoacetate.⁷ Because the surface of the reduced Ni has a more regularly arranged Ni domain than that of RNi,⁸ TA and NaBr would be more stably adsorbed on the reduced Ni than on RNi. The in situ-modified reduced Ni is a promising catalyst for practical applications of the enantio-differentiating hydrogenation of dialkyl ketones.

Experimental

A typical enantio-differentiating hydrogenation of 2-octanone over an in situ modified reduced nickel catalyst was carried out as follows: six grams of commercially available nickel(II) oxide

(Wako Pure Chemical Industry Co., Ltd.) were reduced in a hydrogen stream at 623 K for 1 h before use. TA and an aqueous solution of NaBr (in 50 μ L distilled water) were added to the reaction mixture of 2-octanone (4.1 g), THF (10 mL), and pivalic acid (8.2 g). The hydrogenation of 2-octanone was carried out over reduced nickel at 333 to 373 K and at an initial hydrogen pressure of 9 MPa. For repeated use of the catalyst, it was separated from the reaction mixture and washed three times with THF. The hydrogenation was carried out without the addition of TA and NaBr after the second run. The optical yield of the reaction was determined by polarimetry. The specific optical rotation of the optically pure (*S*)-2-octanol was +9.76° (neat).

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