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IMPROVED MODIFIED RANEY NICKEL CATALYST FOR ENANTIOFACE-DIFFERENTIATING (ASYMMETRIC) HYDROGENATION OF METHYL ACETOACETATE

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The enantioface-differentiating ability of the modified Raney nickel was enhanced by the use of an inorganic salt as an ingredient of the modifying solution. An optical yield of near 90 % was attained in the hydrogenation of methyl acetoacetate to methyl 3-hydroxybutyrate when tartaric acid and sodium bromide were chosen as the modifying reagents.

Among the catalysts for enantioface-differentiating (asymmetric) reactions, the asymmetrically modified metal catalyst is the simplest one. It can easily be prepared when the metal catalyst is soaked in the solution of an optically active substance.1) The enhancement of the enantioface-differentiating ability of this catalyst is of quite importance for the practical purpose. The tartaric acid-modified reduced nickel oxide2) and the tartaric acid-modified nickel-palladium-kieselguhr3) have been reported to be excellent as the catalysts for enantioface-differentiating hydrogenation of methyl acetoacetate (MAA) to methyl 3-hydroxybutyrate (MHB).

Modified Raney nickel (MRNi) is advantageous in its high hydrogenation activity and its preparative convenience in large scale production. In this regard, efforts have been made for the improvement of enantioface-differentiating ability of MRNi without sacrificing its catalytic activity. In the course of these studies, it was frequently noticed that the optical yield of the reaction was influenced by the presence of minor supplementary compounds in the reaction system.4) Especially the effect of Cl^- and SO_4^{--} in the supplied water used for the modification process was significant. This finding led us to the idea that the effective enantioface-differentiating catalyst would be prepared by modifying RNi with the solution containing not only tartaric acid but also supplementary compound. Now we have succeeded in improving a method of preparation of MRNi which has higher enantioface-differentiating ability than the conventionally prepared ones.1) In the present method, an inorganic salt was used as the supplementary modifying reagent.

Optical yields in the enantioface-differentiating hydrogenation with the Raney nickel catalyst modified with the solution consisting of tartaric acid and inorganic salt are listed in Table 1. Among the inorganic salts examined, sodium bromide gave the best result with respect to hydrogenation activity and enantioface-differentiating ability.

The representative experimental procedures are as follows;

(1) Modifying solution. Tartaric acid (1 g) and inorganic salt (the amount was given in Table 1) were dissolved in deionized water (100 ml), and the pH of the solution was adjusted to 3.2 with N sodium hydroxide.

(2) Preparation of the Raney nickel. Into an alkaline solution (4.5 g of sodium hydroxide in 20 ml of deionized water) was added 1.9 g of a well pulverized Raney nickel alloy (Ni : Al = 42 : 58) in small portions over two minutes. The resulting suspension was kept at 100°C for 1 hr. After removal of the alkaline solution by decantation, the catalyst was washed 15 times with 30 ml portions of deionized water.

(3) Modification. The Raney nickel (0.8 g) was soaked in the modifying solution at 100°C. After the mixture was kept at this temperature for 1 hr with occasional shaking, the solution was removed by decantation and the residue was washed with 10 ml of deionized water. The above procedure was carried out twice and three times in the experiment No. 3 and 4 respectively. The deionized water suspending the catalyst was replaced by methanol and then by methyl propionate. Two 50 ml portions of methanol and a 25 ml portion of methyl propionate were used for this procedure.

(4) Hydrogenation. After removal of the solvent by decantation, MRNi suspended in 23 ml of methyl propionate, 11.5 ml of MAA, and 0.2 ml of acetic acid was placed in an autoclave (100 ml capacity). Hydrogen was charged until the pressure reached 90 Kg/cm^2 and then heating was commenced under shaking. The temperature of the reaction mixture was raised to 100°C within 1 hr and this temperature was maintained until no more hydrogen uptake was observed. In these conditions, the reactions were completed within 10 hr.

(5) Determination of optical yield. After removal of the catalyst by filtration, the fractional distillation of the filtrate gave MHB. The optical purity of the product was calculated based on the value of $[\alpha]_D^{20}$ = 22.95 (neat) for optically pure MHB.5)

Detailed presentation of the process leading to the present improvement and the function of inorganic salts will be publisned elsewhere in near future.

Table 1. Enantioface-differentiating hydrogenation of MAA with improved MRNi

No.	Inorganic salt in the modifying solution(g)	Times of the modification procedure	$[\alpha]_D^{20}$ of the product	Optical yield of the reaction(%)
1	None	1	-8.99	39.2
2	NaBr (10)	1	-19.07	83.1
3	NaBr (10)	2	-19.77	86.1
4	NaBr (10)	3	-20.34	88.6
5	NaF (3)	1	-13.95	60.8
6	NaCl (10)	1	-16.55	72.1
7	NaI (5 x 10^{-4})	1	-11.74	51.2
8	Na_2SO_4 (10)	1	-12.95	56.4
9	$NaH_2PO_4.2H_2O$ (1)	1	-8.19	35.7
10	$NaNO_3$ (0.1)	1	-12.17	53.0
11	$NiBr_2$ (1)	1	-14.36	62.6

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References and Notes

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3) Y. Orito, S. Niwa, and S. Imai, *Yuki Gosei Kagaku Kyokai shi*, **35**, 753 (1977) and references therein.

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5) Based on this optical rotation, the highest optical yield of 99.4 % reported by Orito et al3) has to be reduced to 90.6 %. The maximum optical yield (85 %) listed in our preceding communication2) also goes down to 81.7 %. The details on the optical properties of MHB will be published elsewhere.

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