Enantio-differentiating Hydrogenation of Methyl Acetoacetate over Asymmetrically Modified Supported Nickel Catalyst Prepared from Nickel Acetylacetonate

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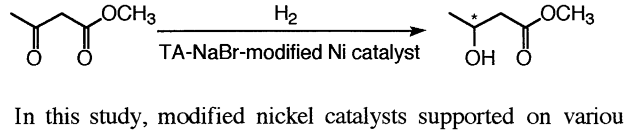
Various supported nickel catalysts were prepared from nickel acetylacetonate in a solvent-free condition, and then these catalysts were modified in the solution containing tartaric acid and NaBr. Enantio-differentiating hydrogenation of methyl acetoacetate was carried out over the resulting tartaric acid-NaBr-modified supported Ni catalysts. Maximal optical yield 86% was attained when zeolite was used as a support.

The enantio-differentiating hydrogenation over asymmetrically modified heterogeneous catalysts has been attracting much attention. In the hydrogenation of β-ketoesters and alkanones, tartaric acid (TA)-NaBr-modified Raney nickel catalysts gave the highest optical yield [1,2] in the asymmetrically modified heterogeneous catalysts. In the case of modified Raney nickel catalysts, it is known that a number of catalyst preparation variables affect the optical yield. Raney nickel alloy has several Ni-Al phases and optical yield depends on the composition of these phases.[3] The temperature and pH of the modification solution affect the content of residual aluminum on the surface of the catalyst. The residual aluminum on the surface reduces the optical yield, but aluminum on Raney catalysts could not be removed completely.[4] Therefore, although tartaric acid-NaBr-modified Raney nickel catalysts gave high optical yields in the hydrogenation of β-ketoesters and alkanones, there would be a limit in attaining higher optical yield than the reported values using Raney nickel catalysts. On the other hand, nickel catalysts on various supports were also used for the preparation of asymmetrically modified nickel catalysts and the preparation variables were studied for attaining high optical yield, but the optical yields were lower than those obtained by modified Raney nickel catalysts.[5-8]

For preparing a catalyst having higher activity in hydrogenation reaction and higher enantio-differentiating ability than those of the catalysts reported so far, breakthrough in the catalyst preparation method is needed.



In this study, modified nickel catalysts supported on various supports were prepared from the mixture of nickel acetylacetonate and supports in a solvent-free condition. Hydrogenation of methyl acetoacetate was carried out over these catalysts. The optical yields with these catalysts were comparable to those obtained by the modified Raney nickel as shown below.

The typical preparation method of asymmetrically modified supported nickel catalyst is as follows. Nickel acetylacetonate (3.3 g) and a support (1 g) (40 wt% Ni loading) were mixed well and treated with an Ar stream at 270 °C for 2 h and 370 °C for 1 h. After the decomposition of nickel acetylacetonate, the mixture was treated with a H_2 stream at 500 °C for 3 h. The supported nickel catalyst thus obtained was soaked in a 100 ml of aqueous solution containing *(R,R)*-tartaric acid (1 g) and NaBr (1 g) at 100 °C for 1 h. The pH of the modification solution was adjusted to 3.2 with 1 mol dm^{-3} NaOH solution in advance. After the modification, the solution was removed by decantation and the resultant catalyst was washed successively once with 45-ml distilled water, once with 45-ml methanol, and twice with 45-ml THF.

The modified catalyst was employed for the hydrogenation of methyl acetoacetate (10 g) in THF (20 ml) containing acetic acid (0.2 g) in an autoclave. The initial hydrogen pressure was 10 MPa and the reaction temperature was 100 °C. The hydrogenation was completed within 12 h, when α-Al_2O_3 and zeolites were used as supports. The modified catalysts prepared from γ-Al_2O_3 needed 3 days and that from SiO_2 needed 5 days for the completion of hydrogenation. The hydrogenation products were obtained by simple distillations with chemical purity of more than 98%. Optical purity of methyl 3-hydroxybutyrate was determined by polarimetry. The specific optical rotation of optically pure *(R)*-methyl 3-hydroxybutyrate was +22.95° (neat).[4]

Figure 1 shows the relation between initial Ni weight percentage of a Ni-α-Al_2O_3 catalyst and the optical yield. Optical yield was

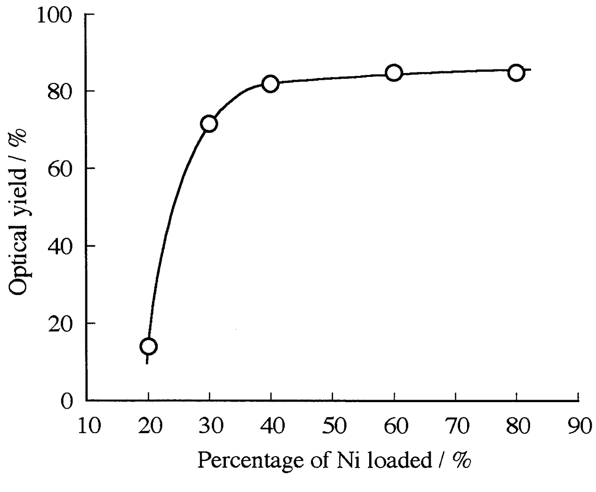


Figure 1. The relation between the Ni weight percentage of a Ni-α-Al_2O_3 catalyst [a)] and the optical yield.

a) This was the initial Ni weight percentage in the preparation of supported nickel catalyst. Small amount of Ni was dissolved into the solution during the modification.

Table 1. Effects of Ni source on optical yield

Ni source	Support [a]	Optical yield / %
Ni acetylacetonate	without support	---[b]
Ni acetylacetonate	α-Al_2O_3	81
Ni acetylacetonate	γ-Al_2O_3	50
Ni acetylacetonate	zeolite (Si/Al = 15) [c]	86
Ni acetylacetonate	zeolite (Si/Al = 46) [d]	83
Ni acetylacetonate	zeolite (Si/Al = 123) [e]	84
Ni acetylacetonate	zeolite (Si/Al = 215) [f]	84
Ni acetylacetonate	SiO_2	73
$Ni(NO_3)_2$ [g]	α-Al_2O_3	71
Raney nickel	without support	86

[a] Initial Ni percentage loaded: 40% (w/w)

[b] Hydrogenation reaction did not take place.

[c] Süd Chemie, H-type Pentasil powder (EX-122).

[d] Süd Chemie, H-type Pentasil powder (T-4480).

[e] Süd Chemie, H-type Pentasil powder (EX-717).

[f] Süd Chemie, H-type Pentasil powder (EX-504).

[g] The catalyst was prepared by the precipitation method.

increased with the increase in Ni loading percentage, and reached a plateau. It is recognized that more than 40% of Ni loading is necessary to attain more than 80% optical yield.

Asymmetrically modified supported nickel catalysts were prepared using various supports with 40% Ni loading. Table 1 shows the results of enantio-differentiating hydrogenation of methyl acetoacetate over these catalysts. The results of the hydrogenation over the modified RNi catalyst and the modified supported nickel catalyst prepared from $Ni(NO_3)_2$ solution by the precipitation method were also listed for comparison. When α-Al_2O_3 or zeolite was used as a support, optical yield over 80% was attained. The ratio of Si to Al in zeolites little affected the optical yield. Maximal optical yield 86% was achieved over the catalyst with zeolite support. This is the highest optical yield in the reported values using asymmetrically modified supported Ni catalyst so far and is comparable to the values obtained by the modified Raney nickel catalysts. The modified nickel catalyst prepared from $Ni(NO_3)_2$ by precipitation method, which is the conventional method for preparing supported catalysts, gave only 71% optical yield. When a nickel catalyst was prepared from nickel acetylacetonate without support, the resulting modified catalyst had very low hydrogenation activity.

It has been demonstrated that large mean crystallite size of nickel was generally favorable for attaining high optical yield.[9] In this study, large mean crystallite size of about 60 nm was obtained for the zeolite supported nickel catalyst. Optical yields attained by this study were much higher than those obtained by the conventional modified supported nickel catalysts prepared in Ni ion solution.[5-8] The results obtained by the present work demonstrate that a preparation from nickel acetylacetonate in a solvent-free condition is a promising method for the preparation of asymmetrically modified nickel catalyst. This method would produce nickel particles, the surfaces of which are suitable for the formation of enantio-differentiating sites by the aid of tartaric acid, on the surface of the supports.

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