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HYDROGEN PRESSURE DEPENDENCE OF THE ASYMMETRIC HYDROGENATION OF METHYL ACETOACETATE WITH MODIFIED NICKEL/SiO_2 CATALYST

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The optical yield of methyl 3-hydroxybutyrate in the asymmetric hydrogenation of methyl acetoacetate with tartaric acid-modified Ni/SiO_2 catalyst decreased linearly with an increase in the hydrogen pressure up to 10 kg/cm^2 in contrast to the data under higher hydrogen pressures.

Among various tartaric acid-modified nickel catalysts for the enantioface-differentiating(asymmetric) hydrogenation of methyl acetoacetate(MAA), silica-supported nickel catalyst was found to have very high hydrogenation activity and considerably high enantioselectivity,[1)] which promise a convenient catalyst for the study of the reaction mechanism. Using this catalyst, we investigated the effect of the hydrogen pressure and the concentration of MAA on the optical yield of methyl 3-hydroxybutyrate(MHB) under mild reaction conditions.

Klabunovskii et al. reported that the optical yield of ethyl 3-hydroxybutyrate in the asymmetric hydrogenation of ethyl acetoacetate increased linearly with an increase in the hydrogen pressure up to 60 atm with tartaric acid-modified ruthenium catalyst[2)] and up to 20 atm with modified Raney-cobalt catalyst,[3)] but they also reported that the optical yield hardly changed on varying the hydrogen pressure from 25 to 100 atm with modified Raney-nickel catalyst.[4)] Yasumori et al. reported that, in the vapor phase hydrogenation of MAA, the reaction orders with respect to hydrogen were zero both with modified and with unmodified nickel catalyst.[5)] With regard to the liquid phase hydrogenation of MAA, the effect of the hydrogen pressure on the optical yield of MHB or on the reaction rate remains ambiguous especially under lower hydrogen pressure around atmospheric pressure.

Silica-supported nickel catalyst($Ni:SiO_2=1:1$) was prepared by a precipitation method with Na_2CO_3 from a mixture of a $Ni(NO_3)_2$ solution and a weighed amount of commercial silica gel(600 m^2/g, Nakarai Chemicals), followed by filtration, washing, drying at 110°C for 24 h, and reduction in hydrogen stream of 8 l/h at 500°C for 1 h. The modification of the catalyst and the analysis of the reaction products were carried out according to the method described previously.[6)]

10 ml of MAA in 10 ml of ethyl acetate(EA) was hydrogenated with 1.5 g of the modified catalyst at 60°C in a glass autoclave(TEM-U-50, Taiatsu Glass Industry Co.) equipped with a vigorous stirring system under a constant hydrogen pressure in the range of 1.5 to 10 kg/cm^2. It was also hydrogenated under higher hydrogen pressures

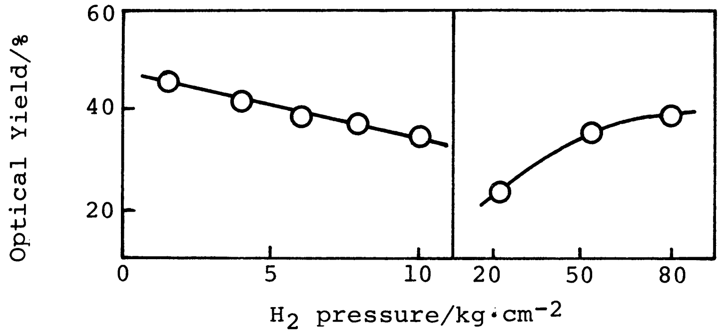

Fig. 1 Effect of hydrogen pressure on the optical yield of MHB

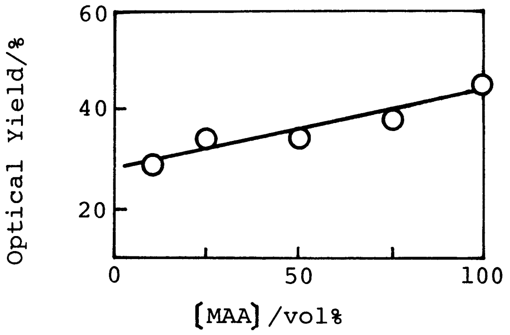

Fig. 2 Effect of concentration of MAA on the optical yield of MHB

for comparison by using another autoclave.

As shown in Fig. 1, the optical yield of MHB decreased linearly with an increase in the hydrogen pressure up to 10 kg/cm^2 in contrast to the data observed under higher hydrogen pressures and to the published data mentioned above. The optical yields were reproducible to about ±2% on repeated runs. The reactions were completed within 12 h at the most. Accordingly, we can easily attain a high optical yield of MHB in a hydrogenation under an atmospheric H_2 pressure rather than under a high H_2 pressure, e.g. 80 kg/cm^2, by using the highly active Ni/SiO_2 catalyst.

Figure 2 shows the effect of the concentration of MAA in EA(total volume=20 ml) on the optical yield of MHB produced in the reaction under a H_2 pressure of 10 kg/cm^2. An increase in the concentration of MAA resulted in the increase in the optical yield of MHB.

Taking into account the reaction rates, these experimental results suggest that the apparent reaction orders on the modified and unmodified sites are different from each other, which seems very important in order to establish the reaction mechanism for this hydrogenation reaction on the modified Ni catalyst. Further investigations on this point are now in progress.

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