Effects of reaction variables on enantioselectivity of modified Raney nickel catalyst

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Abstract

The effects of reaction variables (temperature, pressure, solvent type, substrate to catalyst ratio and substrate concentration) on enantioselectivity of methyl acetoacetate hydrogenation were studied. Raney nickel modified with (2R,3R)-(+)-tartaric acid was used as a catalyst. The reactions were carried out in a liquid phase, under atmospheric and increased hydrogen pressure. It was found that the reaction variables have a significant effect on the resulting enantioselectivity. A decrease of enantioselectivity either occurred at low substrate concentration in the reaction mixture or related to a catalyst. Changes of enantioselectivity were monitored during the reaction. The highest values of enantioselectivity were achieved under high hydrogen pressures (10 MPa), at a temperature of 60 °C and with tetrahydrofuran as the solvent. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

The synthesis of optically pure substances has recently become a very important and essential part of chemical procedures, especially in the production of pharmaceuticals, agrochemicals and, fragrant and flavour substances [1]. During the production of optically pure chiral substances, several different strategies are applied. One of these is heterogeneous asymmetric catalysis, which offers unique advantages compared to the others. The primary advantage of this strategy is the multiple enantioresolution of the reactant on a single chiral active center, resulting in the production of a relatively high amount of chiral product using only a small amount of catalyst as the source of chirality.

From a technical point of view, it enables an easier manipulation and separation of the reaction mixture [1].

Nickel catalysts modified using tartaric acid can be applied during hydrogenation of various β-ketoesters and β-diketones to produce optically active mixtures of appropriate alcohols [2–5]. In this case, the source of chirality is the chiral molecule of tartaric acid, which is suitably implemented to the surface of a nickel catalyst. Many different types of nickel catalysts have been tested for enantioselectivity in hydrogenation: Raney nickel [2,3], several supported nickel catalysts [6–14], bimetallic supported catalysts [15–22] and nickel powder [2,4,23]. A large number of studies have been dedicated to the method of the catalyst modification by tartaric acid and the effects of individual modification parameters on the catalyst enantioselectivity [7–14]. As it was already found [5,24–26], corrosive chemisorption of tartaric acid, and the production of a complex of nickel and tartaric acid occur on the catalyst surface during the modification.

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This complex functions probably as an enantioselective active site, on which a stereospecific adsorption or a steroselective reaction occurs.

Enantioselective hydrogenation is almost exclusively performed in the liquid phase as a batch process. During the reaction in the gaseous phase, significantly lower optical yields were achieved [27]. Opinions on the dependence of selectivity on the reaction conditions vary in the available literature [28–36]. For instance, with regard to enantioselectivity temperature dependence, some published studies claim optimization through temperature control [28–31] while others claim no influence [32] or even decreases in enantioselectivity with temperature [33]. Published papers show a similar situation regarding the effects of pressure, the substrate to catalyst ratio, and the substrate concentration. Various types of dependencies have been described [9,28,30,31,34–36]. Several papers [28,32,36] also focused on the study of the solvent effects. Although nowadays there is a general agreement that higher optical yields are obtained when aprotic semi-polar solvents are used, the disaccord in published papers appears especially for modified Raney nickel catalysts.

The considerable differences in the published dependencies of enantioselectivity on reaction variables can be primarily attributed to the use of various types of nickel catalysts and different modes of modification, which significantly influence the arrangement on the catalyst surface [26]. Moreover, the ranges of experimental conditions, which have been studied, vary in each paper. The influence of modification conditions and reaction conditions on the reaction rate and enantioselectivity has already been studied systematically [36], but this was done with silica supported modified nickel catalyst and the experiments were performed only at low hydrogen pressure in a bubble reactor. Therefore, the resulting enantioselectivities are considerably lower when compared with modified Raney nickel experiments. Comparable work has not yet been published for modified Raney nickel catalyst, even though the enantioselectivity of modified Raney nickel catalyst is usually much higher than that supported nickel catalysts. The main reasons for discrepancy in the results obtained in pervious studies with modified Raney nickel can be attributed to the different modes of preparation of the catalyst, the different modification procedures, the low reproducibility of the

modification process and last but not least, the different reaction conditions. Due to the character of Raney nickel type catalysts, it is also difficult to control their structural properties, particularly after modification, and so the comparison of the catalysts is limited in this way.

This study is focused on the effects of reaction conditions on the enantioselectivity. Systematic study of the effects of reaction conditions on the reaction course is essential to optimize optical yields. Comparison of the data available in the literature with that generated in this study was also of interest. The preparation and the characterization of the catalyst used in this work have been described in detail in previous publications [26,37]. The scope of this work includes the effect of temperature, pressure, solvent type, substrate to catalyst ratio and substrate concentration on enantioselectivity of methyl acetoacetate hydrogenation. The study of the effects of the reaction conditions on the enantioselectivity provides sufficient information for a successive, more sophisticated selection of reaction conditions, so that the maximal values of enantioselectivity could be achieved.

2. Experimental

2.1. Catalyst preparation

Commercial Raney nickel, Actimet M (Engelhard) was used for the preparation of modified catalysts. The Raney nickel was stored in an alkaline environment under water. The total catalyst surface declared by the manufacturer is $75 \, m^2/g$, size of pores is $0.12 \, cm^3/g$ and particle size ranging between 5 and 101 μm. Some of the main properties of the catalyst were also tested in previous work [26,37]. The Raney nickel catalyst (usually 10 g of suspension in water) was washed three times with 50 ml of distilled water and then with a so-called pre-modification solution, 1% aqueous solution of (2R,3R)-(+)-tartaric acid (p.a., Lachema Brno). This washing procedure was carried out with stirring, using a magnetic stirrer for a period of 10 min. The catalyst was again washed with 50 ml of distilled water and introduced to a modifying solution (100 ml, $c_{TA} = 0.2 \, mol/l$) for the modification. In the case of modification with a co-modifier, 50 g of sodium bromide (p.a., Lachema Brno) were added to the

modifying solution. pH of the modifying solution was adjusted to 4.95 using a potentiometric titration with 20% solution of sodium hydroxide (p.a., Lachema Brno). The suspension of the catalyst and the modifying solution was stirred in an Erlenmeyer flask equipped with a reflux cooler and a magnetic stirrer at the constant temperature of 100 °C for a period of 90 min. During the modification, the suspension pH was monitored. The modifying solution was decanted and the catalyst was gradually washed with methanol and tetrahydrofuran (p.a., Penta Prague). The modified catalyst prepared in this manner was characterized using various methods—X-ray powder diffractometry (XRD), atomic absorption spectrometry (AAS), organic elemental analysis, spectroscopies in infrared (FT-IR) and ultra-violet, and visible (UV–VIS) region, X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy equipped with X-ray microanalyzer (SEM-EDAX). The results of the characterization of modified catalysts are included in the previous papers [28,37].

2.2. Apparatus and procedure

Hydrogenation reactions were carried out in the liquid phase in a glass apparatus or in an autoclave under an increased pressure of hydrogen. Methyl-acetoacetate was used as the substrate. The reactions were carried out in various solvents: methanol, ethanol, butanol and tetrahydrofuran. The glass hydrogenation apparatus is described in another work [12] in detail. The effect of the temperature on the enantioselectivity of hydrogenation in a glass apparatus was measured within a range from 15 to 55 °C. The reactions were maintained isothermally. Higher temperatures were not considered because the high partial pressure (vapour pressure) of solvent did not allow maintainance of the same hydrogen partial pressure. The volume of the reaction mixture, in which stirring was still efficient was 10 ml. Experiments were carried out in 8 ml of solvent (methanol p.a., tetrahydrofuran p.a.) with the starting amount of substrate ranging from 0.1 to 0.3 ml. The weight of modified catalyst used was in the range of 0.5–1.0 g. A high substrate to catalyst ratio had to be used in order to reach a complete conversion of the substrate in reasonable reaction time. The catalyst was activated directly in the reactor, prior to the reaction, in

a flow of hydrogen (15 min) under constant stirring. The reaction was started by the injection of substrate and solvent mixture (usually 1 ml) to the reactor and turning on the stirrer. Samples of reaction mixture were withdrawn regularly during the course of the reaction and were analyzed using GLC.

Hydrogenation under an increased hydrogen pressure was carried out in a 300 ml stainless steel autoclave. This autoclave was equipped with a manometer with range of 0–25 MPa, a double-propeller with a magnetic transmission, a thermocouple probe and a heating mantle with a temperature control. The temperature was recorded digitally. The volume of substrate (MAA) used ranged between 1 and 20 ml. The reactions were carried out in various solvents (MeOH, EtOH, BuOH and THF). The volume used in the reactions was 60–79 ml. The total volume of the reaction mixture in the autoclave was always maintained at a level of 80 ml. After the autoclave was closed, it was purged three times with hydrogen and the appropriate pressure was set. The stirring and the heating were switched on. Pressure increased with temperature. The start of the reaction was signified by the first decrease of hydrogen pressure in the autoclave. The hydrogen pressure permanently decreased further during the reaction. After a decrease of 0.5 MPa, the pressure in the autoclave was adjusted to the original value. The reaction temperature was varied between 40 and 100 °C and the hydrogen pressure from 2 to 12 MPa. Temperature and pressure were maintained at constant values during the reaction course. All the reactions were carried out under such conditions as to obtain 100% conversion of the substrate. Samples of the reaction mixture were withdrawn during the reactions and analyzed using gas chromatography.

Having performed separate experiments, it was confirmed that in the selected experimental arrangements, the hydrogenation reactions proceeded in the kinetic region. Since the reaction rate is directly proportional to the catalyst weight, the hydrogen transport within the liquid–gas interface was not the rate-determining step. A significant diffusion effect in the stationary phase on the liquid–gas interface was also not probable, due to the efficient stirring intensity and thus, the negligible thickness of the stagnant layer. The effect of the inner diffusion in the catalyst pores was eliminated using fine powders with an essentially low mean size of the particles.

2.3. Analysis

The samples withdrawn during the reactions were analyzed using gas chromatography on the chromatograph HP 5890 *Series II Plus* from Hewlett & Packard (USA) with FID detector and enantioselective capillary column β-DEX-325 (30 m × 0.25 mm × 0.25 μm) from Supelco. During the analyses, a temperature program of 80–160 °C was used with a starting constant temperature maintained for 7 min, the first temperature increase rate of 10 °C/min up to the temperature of 95 °C and the second temperature increase rate of 70 °C/min up to the temperature of 160 °C. The pressure of the carrier gas $p(N_2)$ was 79 kPa, the flow rate of the carrier gas 1.0 ml/min and the split ratio 1:100. Using these chromatographic conditions and the above mentioned enantioselective column, a separation of the produced (R)- and (S)-enantiomers of methyl-3-hydroxybutyrate was achieved. Due to a difficult separation of these enantiomers, the analysis was carried out with the lowest possible concentration of the measured substances, i.e. with a very low input of the reaction mixture of 0.1–0.2 μl and a pre-set maximal detector sensitivity. The following equation was used for the calculation of the reaction enantioselectivity:

$$\text{e.e.} = \text{oy}(\%) = \frac{[(R) - \text{MHB}] - [(S) - \text{MHB}]}{[(R) - \text{MHB}] + [(S) - \text{MHB}]} \times 100$$

3. Results and discussion

The dependence of the reaction enantioselectivity on temperature under atmospheric and increased hydrogen pressure is shown in Fig. 1. The enantioselectivity of the hydrogenation at atmospheric hydrogen pressure was much lower than that at increased hydrogen pressure. The difference in the enantioselectivity is caused not only by the difference of hydrogen pressure, but probably also by the different substrate to catalyst ratios used for the hydrogenation at atmospheric and increased hydrogen pressure. This assumption was proved later in the experiment, where all the reaction conditions were kept constant and only substrate to catalyst ratio was changed (see below). During the hydrogenation of methyl-acetoacetate under atmospheric pressure, the reaction enantioselectivity increased with
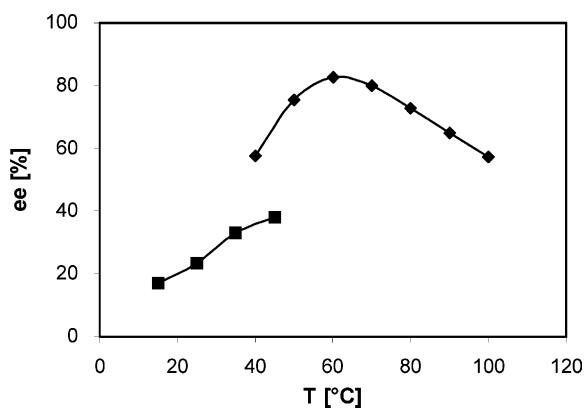

Fig. 1. Dependence of reaction enantioselectivity on temperature under atmospheric and increased hydrogen pressure. (■) atmospheric pressure of hydrogen, THF, $c_{\text{MAA}} = 0.25 \, \text{mol} \, l^{-1}$; (◆) hydrogen pressure 10 MPa, THF, $c_{\text{MAA}} = 2.31 \, \text{mol} \, l^{-1}$).

temperature over the measured interval of 15–55 °C. Hydrogenation under an increased hydrogen pressure also showed a dependence with the maximum in a region of 60 °C. This is in good agreement with the published results for modified Raney nickel and hydrogenation of ethyl acetoacetate [30] as well as for the atmospheric hydrogenation of methyl acetoacetate [29]. A similar dependence was recorded even with the use of a supported nickel catalyst (Ni/SiO$_2$) in the work [36]. It is necessary to mention that in all the studies [29,30,36] the maximum enantioselectivities obtained were considerably lower than those achieved in this study. An explanation of the occurrence of a maximum at the enantioselectivity dependence on temperature was already suggested in the literature [29,36]. The lower enantioselectivity at lower temperature can be caused by the dependence of the spatial arrangement of contributing molecules on temperature. Maximum values of enantioselectivity are achieved at approximately 60 °C. This temperature corresponds to the starting temperature, at which the hydrogen bonds start to break down. At temperatures higher than 60 °C, an enantioselectivity decreases due to a break down of interactions between methyl-acetoacetate and tartaric acid, which are responsible for a stereospecific reaction course.

Fig. 2 shows the dependence of the reaction enantioselectivity on the hydrogen pressure. The measured dependence was obtained using reactions carried
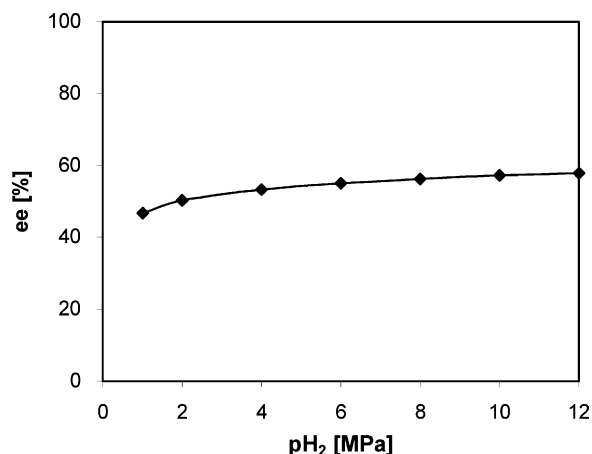
Fig. 2. Dependence of reaction enantioselectivity on hydrogen pressure. (◆) 100 °C, THF, $c_{MAA} = 2.31 \, mol \, l^{-1}$.

Fig. 3. Dependence of enantioselectivity and total reaction rate on solvent type. 100 °C, 10 MPa, $c_{MAA} = 2.31 \, mol \, l^{-1}$.

out in an autoclave under a constant temperature of 100 °C. It is apparent from Fig. 2 that the reaction enantioselectivity is almost independent on the pressure. This result is in agreement with that obtained by Lipgart et al. [30], who found that the optical yield of the ethyl-acetoacetate hydrogenation over modified Raney nickel was hardly changed by varying the hydrogen pressure from 2.5 to 10 MPa. However, the optical yields obtained in their work were lower than 17%, which is significantly less than in our case. Nevertheless, a slight trend could be observed during our measurements, in which the enantioselectivity increased with an increasing pressure, but at pressures higher than 10 MPa it remained almost constant. This trend can be explained by the assumption that there are two types of active sites (selective and non-selective) on the catalyst surface and the reaction rate on the selective and non-selective active sites depends on the hydrogen pressure in different ways. The reason could be a stronger adsorption of the substrate or a higher reaction rate on the selective sites than on the non-selective ones. Thus, the reaction on selective sites is preferred with an increase of hydrogen pressure. The opposite character of the dependence of enantioselectivity on the hydrogen pressure, i.e. enantioselectivity decreasing with an increasing pressure, was recorded [38] in the region from 0.1 to 5 MPa with the use of a supported nickel catalyst (Ni/SiO₂).

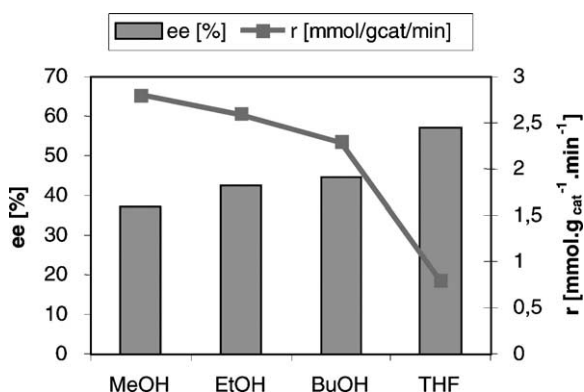The effect of selected solvents on the reaction rate and ultimate enantioselectivity can be seen in Fig. 3.

Reaction rates as well as enantioselectivity are clearly dependent on the type of reaction medium. While the reaction rate decreases as follows, MeOH > EtOH > BuOH > THF, the dependence of enantioselectivity is opposite. Higher the polarity of the solvent the lower enantioselectivity of the reaction. This is in contrast to the findings of Smith and Musoiu [28], who reported no significant solvent effect on changes in enantioselectivity. In our study the changes in enantioselectivity were significant, and also the change of the reaction rate by changing the solvent was large; in the reaction carried out in THF the rate was almost five times lower than in the case of the use of MeOH. The enantioselectivity was the highest with the use of THF. The effectiveness of THF was already reported [32], but mainly for the hydrogenation of 2-alkanones. On contrary, Lipgart et al. [30] claimed the higher optical yield for MeOH than for THF, over modified Raney nickel and Keane [36], also reported higher optical yield for BuOH over Ni/SiO₂. However, as it has been already mentioned above, in both these papers [30,36] the enantioselectivity was lower than 19 and 27% respectively and thus its changes with different solvents which were smaller.

The reaction rate dependence on a solvent type was compared to a dielectric constant for the reaction mixture. The dielectric constants of the mixture containing methyl-acetoacetate and the appropriate solvent were calculated in accordance with the following equation:

$$\varepsilon_{reaction\text{-}mixture} = \frac{(\varepsilon_{MAA} V_{MAA} + \varepsilon_{solvent} V_{solvent})}{(V_{MAA} + V_{solvent})}$$

Table 1
Effects of reaction solvent and dielectric constant of reaction mixture on total reaction rate and reaction enantioselectivity

Solvent	$\varepsilon_{\text{reaction-mixture}}$	r (mmol/g_{cat}/min)	ee (%)
MeOH	16.2	2.8	37.3
EtOH	13.5	2.6	42.7
BuOH	8.5	2.3	44.5
THF	4.6	0.8	57.2

The values of the dielectric constants of pure solvent were found in the literature [39] and re-calculated to the reaction temperature of 100 °C. Table 1 offers a comparison of calculated dielectric constants of reaction mixtures with the total reaction rates and the reaction enantioselectivity obtained under the following reaction conditions: $V_{\text{MAA}}:V_{\text{solvent}} = 1:3$; total volume of the reaction mixture, 80 ml; temperature, 100 °C; pressure 10 MPa. It is apparent that with a decreasing value of the dielectric constant of the reaction mixture, the total reaction rate decreased and simultaneously, the reaction enantioselectivity increased. Thus, the total reaction rate of methyl-acetoacetate hydrogenation and the ultimate enantioselectivity is in a very strong relation with the polarity of the reaction environment. The higher solvating power of the more polar alcohols obviously negatively influences the interaction between a modifier and the substrate, which results in a lower reaction enantioselectivity. Similarly, it is necessary to consider the solvent effects on the tautomeric equilibrium of the substrate [40].

The effect of substrate to catalyst molar ratio on the enantioselectivity is illustrated in Fig. 4. The dependence was obtained by varying the amount of catalyst, while the concentration of methyl-acetoacetate was kept constant. A significant decrease of enantioselectivity was observed at low substrate to catalyst ratios. At molar ratios higher than 4 (68 mmol MAA/g_{Ni}), the enantioselectivity began to plateau and no further change in enantioselectivity occurred. The low optical yields below the substrate to catalyst ratio 2.5:1 were also reported by Smith and Musoiu [28]. On contrary, Lipgart et al. [30] observed the dependence passing through a maximum when the substrate to catalyst ratio was varied in asymmetric hydrogenation of ethyl-acetoacetate over modified Raney nickel. The effect of varying the MAA/Ni ratio on enantioselectivity was also studied over modified Ni/SiO₂ catalyst.
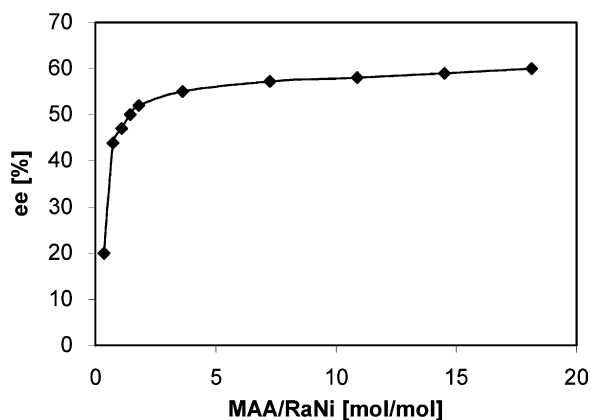

Fig. 4. Dependence of enantioselectivity on initial molar ratio MAA/RaNi. 100 °C, 10 MPa, THF, $c_{\text{MAA}} = 1.16 \, \text{mol} \, l^{-1}$.

Nitta et al. [35] reported a constant increase in enantioselectivity with increasing concentration of MAA in ethyl acetate, and Keane [36] obtained the dependence where the optical yield increased with the reactant concentration and then remained constant in the region from 100 to 310 mmol MAA/g_{Ni}. Also other works [23,34] reported the independence of enantioselectivity from the substrate to catalyst ratio in the range of 70–170 mmol MAA/g_{Ni}.

Enantioselectivity dependence, similar to that shown in Fig. 4, was observed when the starting concentration of methyl-acetoacetate was changed and the amount of catalyst was kept constant (Fig. 5). The
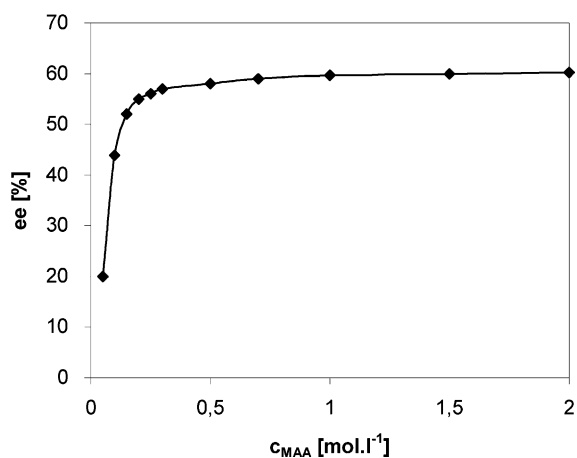

Fig. 5. Dependence of enantioselectivity on initial MAA concentration. 100 °C, 10 MPa, THF, m(RaNi) = 1.0 g.
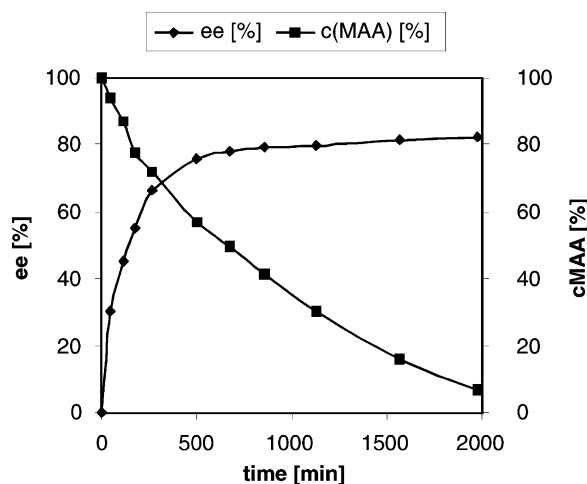
Fig. 6. Dependence of enantioselectivity and MAA concentration on reaction time. 60 °C, 10 MPa, THF, $c_{MAA} = 2.31 \, mol \, l^{-1}$.

reaction enantioselectivity depends on the starting concentration of MAA only in the region of concentrations lower than $0.3 \, mol \, l^{-1}$ (up to 48 mmol MAA/g_{Ni}). At the low concentration a smaller amount of MAA was probably adsorbed on the catalyst surface, which may have resulted in lower enantioselectivity.

Because of the reports that the enantioselectivity changes with the conversion of the substrate [4,9,36,41,42], we also studied this correlation. It was found that the enantioselectivity remained almost constant during the reaction course, except a short period in the beginning of the reaction. This induction period was observed especially at lower reaction rates. Fig. 6 shows the enantioselectivity dependence on time during hydrogenation of MAA at 60 °C. The figure also includes the development of MAA concentration in time. During the induction period the enantioselectivity sharply increased and when the conversion of MAA was higher than 40% the enantioselectivity remained constant. The induction period was found to be much shorter during reactions, which proceeded with higher reaction rates. We did not observe any decrease of enantioselectivity close to 100% conversion as it was described previously [41,42].

4. Conclusion

The data reported in this study showed that the reaction conditions had significant influence on the enantioselectivity. At the same time, a comparison of the effect of reaction variables on enantioselectivity between our catalyst and other reported systems was made. It was found that one of the essential parameters for obtaining a high optical yield is the hydrogen pressure. The enantioselectivity of MAA hydrogenation was much greater under a higher pressure than under atmospheric pressure. Another significant parameter is the selection of a reaction medium. When a suitable solvent was used in the reaction the enantioselectivity increased by as much as 20%. It was also showed that the solvent had a remarkable influence on the total reaction rate of hydrogenation and that there exist a strong relation between the dielectric constant of the reaction mixture and the total reaction rate. Furthermore, the molar ratio MAA/RaNi and the initial concentration of MAA affect the enantioselectivity. A decrease in the enantioselectivity either occurred at low concentration of MAA in the reaction mixture or related to the catalyst. Maximal values of enantioselectivity of MAA hydrogenation were achieved under the following reaction conditions: high hydrogen pressures (10 MPa), temperature (60 °C) and by use of THF as the solvent or without use of any solvent. Using a suitably modified catalyst and such optimal reaction conditions, enantioselectivity higher than 80% can be achieved, which represents more than 90% of the required enantiomer in the final product.

Acknowledgements

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