

Enantio-differentiating hydrogenation of methyl acetoacetate over asymmetrically modified reduced nickel catalysts

The effects of the nickel sources on the enantio-differentiating ability

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Abstract

The enantio-differentiating hydrogenation of methyl acetoacetate was carried out over a tartaric acid–NaBr-modified reduced nickel catalyst. Nickel hydroxide and nickel carbonate were used as the precursors of the nickel oxide. They were calcined to nickel oxides, then reduced to nickel metal (reduced nickel catalyst). It was revealed that the calcination temperature of the precursors was an important variable for attaining the high enantio-differentiating ability (e.d.a.) of the catalyst. The nickel surface with the least lattice defects would be appropriate for attaining a high e.d.a.

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1. Introduction

It is well known that the tartaric acid–NaBr-modified nickel is a solid catalyst, which hydrogenates β -ketoesters and 2-alkanones with high enantio-selectivity. Many types of the base nickel catalysts for preparing modified catalysts have been investigated, that is, Raney nickel [1–11], supported nickel [1–5,12–16], nickel obtained by the reduction of nickel oxide (reduced nickel) [7,17–20], nickel obtained by the decomposition of nickel formate [7,17,21], nickel powder [19,22], and intermetallic catalysts [23,24]. Among them, Raney nickel is widely used for preparing enantio-differentiating catalysts, because of its high hydrogenation activity and high enantio-differentiating ability. The tartaric acid–NaBr-modified Raney nickel catalyst has been prepared in an aqueous solution of tartaric acid and NaBr at pH 3.2 and 373 K (pre-modification). This pre-modification process generated a large amount of waste solution containing nickel ions and bromide ions [17]. We recently reported that an in situ modification (tartaric acid and NaBr

were directly added to the reaction media) was applicable for the tartaric acid–NaBr-modified nickel catalysts with a high enantio-differentiating ability (e.d.a.) [25]. The in situ modification is environmentally benign, because it saves energy for the modification process and generates no waste solution. When the in situ modification was applied to the preparation of a tartaric acid–NaBr-modified nickel catalyst, the reduced nickel prepared by the reduction of nickel oxide or fine nickel powder was needed for attaining a high e.d.a. [26,27]. However, it was demonstrated that the e.d.a. of the modified reduced nickel catalyst was influenced by the nickel oxide manufacturers [18–20]. As the preparation details of the commercial nickel oxides are scarcely known, nickel oxides were prepared from nickel hydroxide or nickel carbonate and used for the preparation of a modified nickel catalyst in this study. The effects of the preparation variables of the nickel oxide and nickel on e.d.a. were investigated.

2. Experimental

The GLC measurements of the hydrogenated products were carried out using a Hitachi 263-30 gas chromatograph.

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graph. The optical rotations were measured with a JASCO DIP-1000 polarimeter. The X-ray diffraction patterns of the nickel oxide and nickel were measured using a Shimadzu XD-3A diffractometer.

2.1. Nickel oxide

Nickel oxide was prepared by the calcination of nickel hydroxide (Wako Pure Chemical Industries Ltd., lot TPG6939) or nickel carbonate (approximately $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, Wako Pure Chemical Industries Ltd., lot SKG2014) under a stream of nitrogen (40 ml/min) and oxygen (10 ml/min) for 3 h at the specified temperatures.

2.2. Reduced nickel catalyst

Nickel oxide (1 g) was reduced at the specified temperatures in a hydrogen stream for 1 h.

2.3. Enantio-differentiating hydrogenation of methyl acetoacetate

Modification of the reduced nickel catalyst was carried out by an in situ modification method [27]. The reaction mixture of methyl acetoacetate (3.3 g), THF (6.7 ml) and acetic acid (0.067 g) containing (*R,R*)-tartaric acid (3.3 mg) and NaBr (0.3 mg in 50 mm³ of H₂O) was subjected to hydrogenation over the reduced nickel catalyst. The hydrogenation was carried out at 373 K and the initial hydrogen pressure was 9 MPa. Simple distillation gave a product of more than 98% in chemical yield (GLC analyses: 5% Thermon 1000 on Chromosorb W at 383 K).

2.4. Determination of e.d.a.

The e.d.a. of the catalyst was evaluated using the optical purity of the hydrogenated product determined by polarimetry.

$$\text{e.d.a. (\%)} = \frac{[\alpha]_{\text{D}}^{20} \text{ of methyl 3-hydroxybutyrate}}{[\alpha]_{\text{D}}^{20} \text{ of pure enantiomer}} \times 100$$

The specific optical rotations $[\alpha]_{\text{D}}$ of the optically pure (*R*)-methyl 3-hydroxybutyrate is $[\alpha]_{\text{D}}^{20} = -22.95^\circ$ (neat) [17].

2.5. Measurement of crystallite size

The mean crystallite sizes of nickel oxide and nickel metal were obtained from the half-width of the NiO(1 1 1) or Ni(1 1 1) peak using Scherrer's method. Nickel oxide prepared by the calcination of nickel carbonate at 1373 K and nickel metal prepared by the reduction of nickel oxide at 873 K for 5 h in a hydrogen stream were used as the references, respectively.

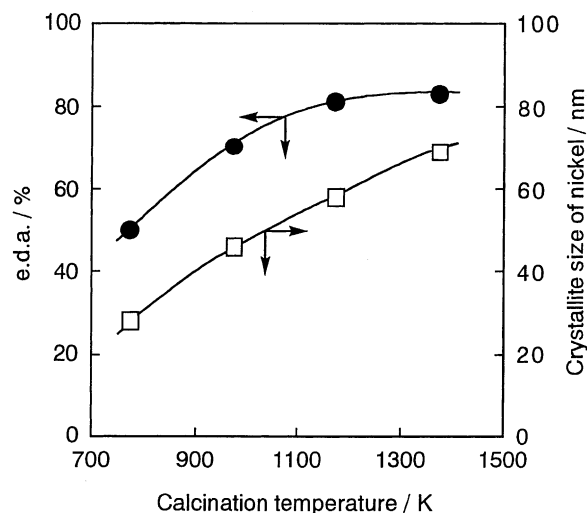


Fig. 1. Effect of the calcination temperature of nickel hydroxide on e.d.a. and crystallite size of nickel. Reduction temperature of nickel oxide was 623 K.

3. Results and discussion

3.1. Effect of the calcination temperature of nickel hydroxide

The nickel oxide was prepared by the calcination of nickel hydroxide from 773 to 1373 K. The nickel oxides were then reduced at 623 K for 1 h under a hydrogen stream for preparing a reduced nickel catalyst. Fig. 1 shows the effects of the calcination temperature on the e.d.a. of the modified reduced nickel catalysts. When the calcination temperature was raised, the e.d.a. of the modified reduced nickel increased and the maximal e.d.a. was attained for the 1373 K calcination of nickel oxide.

It was demonstrated that the e.d.a. of the modified nickel catalyst depended on the nickel crystallite size and that a larger sized nickel crystallite was preferable for attaining a high e.d.a. [7,15,16]. Therefore, the relation between the mean crystallite size of nickel and the calcination temperature was investigated. The values of the crystallite size of nickel are also shown in Fig. 1. The higher calcination temperature of nickel hydroxide gave the reduced nickel with the larger nickel crystallite size after the reduction of nickel oxide.

3.2. Effect of the reduction temperature of nickel oxide

Fig. 2 shows the effect of the reduction temperature of nickel oxide on the e.d.a. and the crystallite size of nickel. The nickel oxide was prepared by the calcination of nickel hydroxide at 1373 K. The e.d.a. significantly decreased from 83 to 57% with an increase in the reduction temperature of the nickel oxide from 598 to 673 K, while the nickel crystallite size was almost constant at ca. 60 nm. These results show that the e.d.a. is significantly related to the reduction

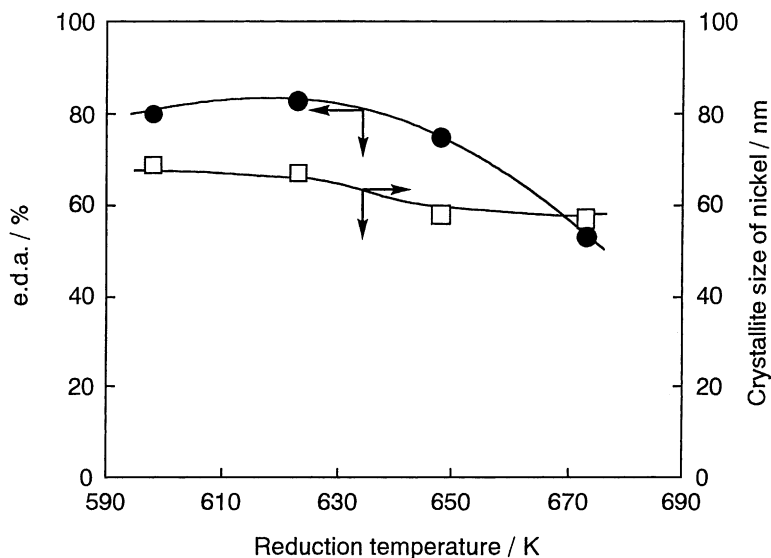


Fig. 2. Effect of the reduction temperature of nickel oxide on e.d.a. and crystallite size of nickel. Nickel oxide was prepared from nickel hydroxide at 1373 K calcination.

temperature but that nickel crystallite size is not affected by the reduction temperature of 598–673 K. The reduction at 673 K could result in enhanced sintering of the nickel surface and the surface of nickel would become unsuitable for the effective enantio-differentiation. The results of Fig. 2 could be explained by the crystallite size distribution of nickel. Nitta et al. demonstrated that the reduction at a high temperature would cause the broad crystallite size distribution of nickel and decrease the e.d.a. At high reduction temperature, nickel with small crystallite size with low e.d.a. and high hydrogenation activity would be governed by the reaction [28,29].

3.3. Effect of the types of the precursors of nickel oxide

In order to study the relation between the crystallite size of nickel and e.d.a. in more detail, nickel oxide was also prepared from nickel carbonate and used for the preparation of the modified reduced nickel. Fig. 3 shows these results. For both precursors (nickel hydroxide and nickel carbonate), the e.d.a. of the catalysts increased with the nickel crystallite sizes. However, the nickel crystallite size giving an e.d.a. of 80% depended on the type of the precursor. That is, as for the catalyst prepared from nickel hydroxide, the e.d.a. of 80% was attained with the nickel crystallite size of ca. 60 nm, but as for the catalyst prepared from nickel carbonate, the catalyst with a nickel crystallite size of ca. 40 nm gave an 80% e.d.a. These findings reveal that there could exist factor(s) determining the e.d.a. other than the crystallite size of the nickel, because the appropriate nickel crystallite size for attaining a high e.d.a. depended on the type of precursor. It was demonstrated that the different types of the modified nickel (Raney nickel, reduced nickel, and nickel obtained by the decomposition of nickel formate) showed the same e.d.a. with different nickel crystallite size [7]. Our present study revealed that the same e.d.a. was attained over

the modified reduced nickel catalysts with different nickel crystallite size when nickel oxides were prepared from the different precursors.

The relation between the nickel oxide crystallite size prepared from both precursors (nickel hydroxide and nickel carbonate) and e.d.a. were also investigated. These results are shown in Table 1. For both precursors, the crystallite size of the nickel oxides increased with an increase in the calcination temperatures. The e.d.a. values also increased with the increase in the crystallite size of the nickel oxides. At the low calcination temperatures of 773 and 973 K, the e.d.a. values significantly differed between the two precursors. However,

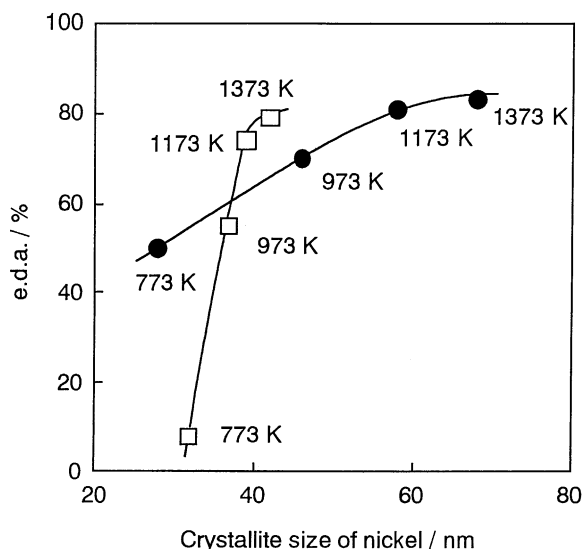


Fig. 3. Effect of the crystallite size of nickel on e.d.a. (●) Precursor: nickel hydroxide; (□) precursor: nickel carbonate. Temperature in the figure indicates calcination temperature of the precursors. Reduction temperature of nickel oxide was 623 K.

Table 1
Relation between the nickel oxide crystallite size and e.d.a.

Calcination temperature (K)	Precursor		Precursor	
	Nickel hydroxide		Nickel carbonate	
	Crystallite size of nickel oxide (nm)	e.d.a. (%)	Crystallite size of nickel oxide (nm)	e.d.a. (%)
773	54	50	50	8
973	121	70	132	55
1173	141	81	>200	74
1373	>200	83	>200	79

Reduction temperature of nickel oxide was 623 K.

at the higher calcination temperature of 1373 K, a greater than 80% e.d.a. was attained for both precursors.

Nickel oxide prepared by the calcination at 1373 K has a olive green color, but the color depended on the calcination temperatures. A lower calcination temperature produced a black color. It is known that black nickel oxide is a non-stoichiometric compound with excess oxygen and has lattice defects including vacancies [30]. On the other hand, the olive green nickel oxide has a lower amount of excess oxygen and a lower amount of lattice defects compared with the black nickel oxide. As the reduction of nickel oxide at 623 K for 1 h would not be enough for the rapid bulk agglomeration of the nickel particles and the rearrangement of the lattice atoms, nickel produced by the reduction of nickel oxide would inherit the characteristics of the parent nickel oxide such as the lattice defects. It has been reported that a nickel surface with less disorder would be favorable for the regularly arranged adsorption of tartaric acid thus giving a high e.d.a. [7]. For the two precursors, the higher calcination temperature would be favorable for forming a lattice of nickel oxide with less defects. This would result in the formation of a smooth nickel surface with less defects after the reduction of nickel oxide. A smooth nickel surface would be appropriate for the effective enantio-differentiation.

From the results of Figs. 1–3 and Table 1, the e.d.a. of the modified reduced nickel catalyst is not determined only by the crystallite size of nickel. The e.d.a. also depended on the characteristics of the parent nickel oxide, that is, the type of the precursor of nickel oxide and the calcination temperature of the precursor. The types of precursors could contribute to the surface structure, adsorption species on the surface, and/or contamination of nickel oxide and nickel. It is not clear at present that what factor affects the e.d.a. of modified reduced nickel catalyst most significantly. However, for attaining a high e.d.a., the calcination temperature of the precursor of nickel oxide was the very important issue for obtaining the appropriate nickel surface for the effective enantio-differentiation.

4. Conclusion

The enantio-differentiating hydrogenation of methyl acetate was carried out over a tartaric acid–NaBr-modified

reduced nickel catalyst. Nickel hydroxide and nickel carbonate were calcined and the resulting nickel oxides were reduced to nickel catalysts. The value of the nickel crystallite size was not directly correlated with the e.d.a. The calcination temperature of the nickel oxide precursor was the important issue for attaining a high e.d.a. A smooth nickel surface without the lattice defects would be appropriate for attaining a high e.d.a.

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