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Study of the properties of nickel oxide and nickel as precursors for the tartaric acid-NaBr-modified nickel catalyst

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Nickel oxide was prepared by the decomposition of nickel hydroxide and then the nickel oxide was reduced to form the nickel catalyst. The properties of the nickel oxide and the reduced nickel were studied in relation to the enantio-differentiating ability (e.d.a.) of a tartaric acid-NaBr-modified reduced nickel catalyst. The modified nickel catalyst prepared from nickel oxide with less non-stoichiometric oxygen produced a high e.d.a. for the hydrogenation of methyl acetoacetate. The high crystallinity of the nickel oxide and the resultant nickel would be required to attain a high e.d.a.

KEY WORDS: non-stoichiometric oxygen; BET surface area; enantio-differentiating ability; modified nickel catalyst; nickel hydroxide.

1. Introduction

A tartaric acid-NaBr-modified nickel catalyst has a high enantio-differentiating ability (e.d.a.) for the enantio-differentiating hydrogenation of β-ketoesters [1–4]. Many types of activated nickel catalysts are used for preparing the modified catalyst, that is, Raney nickel, a supported nickel, nickel obtained by the reduction of nickel oxide (reduced nickel), and fine nickel powder. Two preparation methods have been reported for the modified catalyst. One is a pre-modification and the other is an *in-situ* modification. The pre-modification is a conventional method for preparing the modified nickel catalyst, i.e., the activated nickel is modified in an aqueous solution of tartaric acid and NaBr at pH 3.2 and 373 K [5]. The *in-situ* modification method has been recently applied to the preparation of a modified nickel catalyst [6]. The *in-situ* modification has the following several advantages compared with the pre-modification: (i) very simple preparation procedure (only the addition of tartaric acid and NaBr to the reaction mixture), (ii) high e.d.a. and its high durability during the repeated use of the recovered catalyst, and (iii) no waste containing nickel ions [7]. However, only the reduced nickel and fine nickel powder attain a high e.d.a. and durability [6]. Furthermore, the e.d.a. of the modified reduced nickel catalyst was influenced by the nickel oxide manufacturers [8–9]. As the preparation details of the commercial nickel oxides are rarely reported, it is difficult to examine the difference in the resulting modified nickel catalyst. In a previous paper, we reported the enantio-differentiating hydrogenation over the modified reduced nickel catalyst prepared by the reduction of nickel oxide, which was prepared by the decomposition of nickel hydroxide and nickel carbonate [10]. It was revealed that a higher decomposition temperature of the nickel compounds resulted in a higher e.d.a. of the resulting modified nickel catalyst. In this study, in order to clarify the reason for the effect of the decomposition temperature of nickel salt on the resulting e.d.a., the properties of nickel oxide and reduced nickel were studied by thermogravimetric (TG) analyses, BET surface area measurements, and the surface composition analyses, in relation to the e.d.a. of the modified catalyst.

2. Experimental

The BET surface area was measured using a Micromeritics Gemini 2375 by N_2 adsorption at 77 K. Thermal analyses were carried out using Seiko TG/DTA 300. Qualitative analyses of the surface of nickel and nickel oxide were carried out using an electron probe microanalyzer Shimadzu EPMA-1500.

Nickel oxide. The nickel oxide was prepared by the decomposition of nickel hydroxide (Wako Pure Chemical Industries, Ltd., lot TPG6939) under a mixed stream of nitrogen (40 ml/min) and oxygen (10 ml/min) for 3 h at 773, 973, 1173, and 1373 K. These nickel oxides were designated NIO-773, −973, −1173, and −1373, respectively.

Reduced nickel catalyst. The nickel oxide prepared from the nickel hydroxide was reduced at 623 K in a hydrogen stream (40 ml/min) for 1 h.

Determination of the amount of non-stoichiometric oxygen in nickel oxide. TG analyses of NIO-773, −973,

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−1173, and −1373 were carried out from 323 to 1373 K (ramping rate: 40 K/min). The weight loss was determined after the sample was cooled to room temperature in order to eliminate the buoyancy effect. The amount of non-stoichiometric oxygen in the nickel oxide was calculated by the assumption that the weight loss of the sample was the release of non-stoichiometric oxygen.

Qualitative analyses of the surface of nickel and nickel oxide. Qualitative analyses of the nickel and nickel oxide surfaces were carried out by electron probe microanalysis (EPMA). The EPMA was carried out with an accelerating voltage of 15 kV, a probe current of ca. 1.5×10^{-8} A, and an electron beam diameter of 50 μm. The samples were initially pressed into pellets at 30 MPa. Platinum was sputtered onto the pellet of the nickel oxide to ensure an adequate conductivity.

3. Results and discussion

3.1. Thermal analysis of the decomposition of nickel hydroxide

In the present study, nickel oxide was prepared by the thermal decomposition of nickel hydroxide at various temperatures. The features of the decomposition of nickel hydroxide were first examined by a thermal analysis. Figure 1 shows the results of the TG and DTA of nickel hydroxide. Most of the nickel hydroxide endothermically decomposed from 523 K to 623 K.

3.2. Characterization of nickel oxide and reduced nickel

3.2.1. Non-stoichiometric oxygen in nickel oxide

In a previous paper, we reported that the decomposition temperature of nickel hydroxide affected the e.d.a. of the resultant modified catalyst and that the higher decomposition temperature produced a higher e.d.a. [10]. In order to investigate the difference in the nickel oxides prepared at the various decomposition temperatures of nickel hydroxide, TG analyses of the nickel oxides were carried out from 323 K to 1373 K (figure 2). Nickel oxide obtained by the decomposition at 773 K (NIO-773) showed a weight loss over the entire range of increasing temperature. NIO-973 showed a slight weight loss and NIO-1173 and NIO-1373 showed almost no weight loss.

To determine the origin of the weight loss, qualitative analyses of the surface of the nickel oxide were carried out by EPMA. Although the EPMA analysis gives information about the surface, this method is useful for surveying the existence of minor elements from Be to U in a sample. The results of the nickel oxides are shown in figure 3(a) and (b). Both NIO-773 and NIO-1373 showed the existence of Ni, C, O, and Co. Cobalt would be an impurity of nickel hydroxide. Nickel is usually contaminated by a small amount of cobalt. The detected carbon would be an impurity of nickel hydroxide or would come from the environment. Although the attribution of the weight loss (figure 2) to the contaminated carbon species cannot be completely excluded, it is reasonable to assume that the weight loss would be attributed to the release of non-stoichiometric oxygen from the nickel oxide, because carbon was detected in NIO-1373 which showed no weight loss, and nickel oxide with a darker color showed a higher weight loss. Table 1 shows the effect of the decomposition temperature on the color of the nickel oxide, the percent weight loss, and the chemical formula of nickel oxide calculated based on the percent weight loss. It has been reported that black nickel oxide is a non-stoichiometric compound with excess oxygen and has lattice defects including vacancies [11]. In the present study, a lower decomposition temperature produced a black-colored nickel oxide (NIO-773) and a higher temperature produced an olive-green nickel oxide (NIO-1373). The

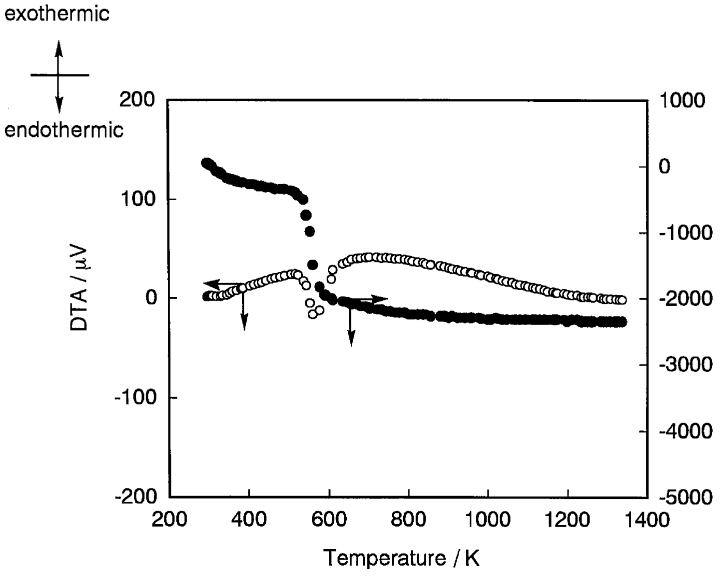

Figure 1. Thermal analysis of nickel hydroxide A 10 mg sample was used for the analysis.

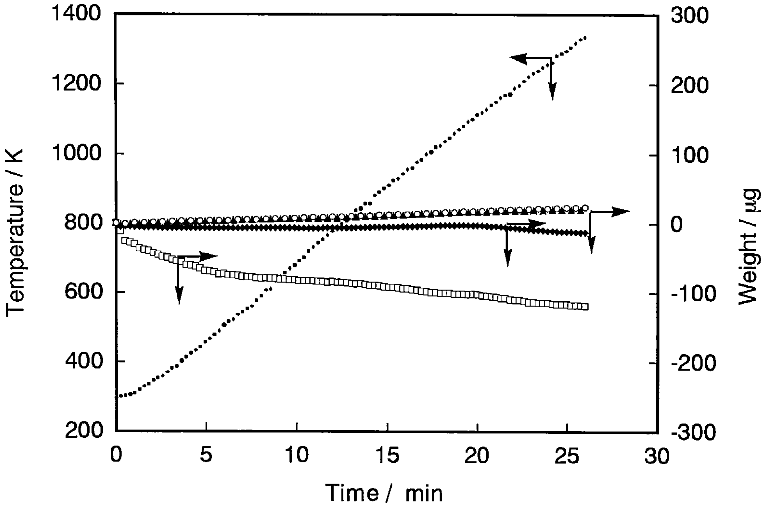

Figure 2. Thermal analysis of nickel oxide prepared by the decomposition of nickel hydroxide at different temperatures. Each sample of 10 mg was used for the analysis ● = Temperature, □ = NIO-773, ◆ = NIO-973, ▲ = NIO-1173, ○ = NIO-1373.

result that the black nickel oxide has a greater amount of non-stoichiometric oxygen as shown in table 1 is in accord with the literature.

Figure 4 shows the effect of the percent of non-stoichiometric oxygen in the nickel oxide on the e.d.a. of the modified nickel catalyst for the hydrogenation of methyl acetoacetate. The modified nickel catalyst prepared from nickel oxide with less non-stoichiometric oxygen produced a higher e.d.a. The EPMA results (figure 3) showed that nickel oxide had no poisonous elements,

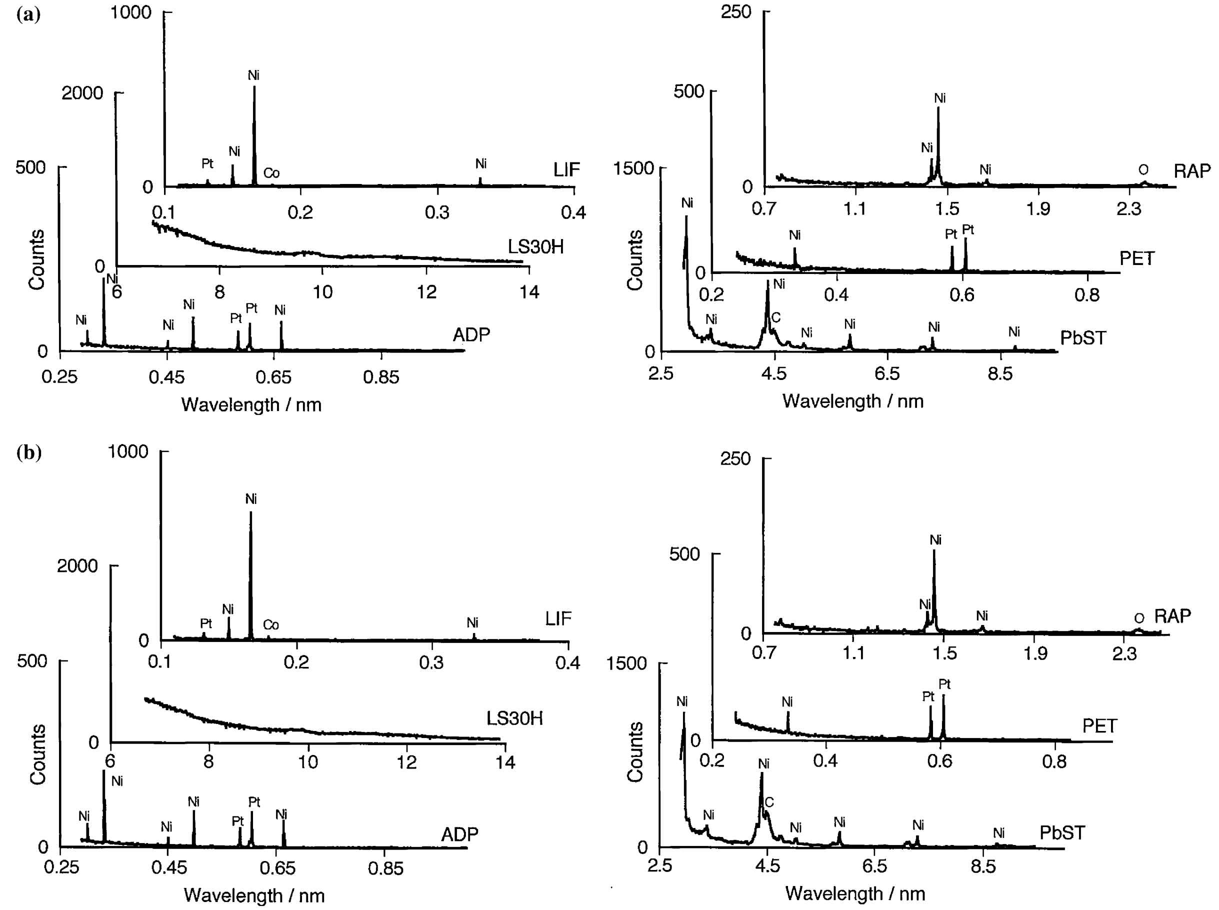

Figure 3. (a) Qualitative analysis of NIO-773 ADP = Ammonium dihydrogenphosphate, LS30H = Layered stracture analyzer, LIF = Lithium fluoride, PbST = Lead stearate, PET = Pentaerythritol, RAP = Rubidium acid phtharate (b) Qualitative analysis of NIO-1373.

Table 1
Degree of weight loss of nickel oxide and its chemical formula

Nickel oxide	Color of nickel oxide	Weight loss/%	Chemical formula of nickel oxide
NIO-773	black	1.32	$Ni^{2+}_{0.88}Ni^{3+}_{0.12}O^{2-}_{1.06}$
NIO-973	olive gray	0.30	$Ni^{2+}_{0.98}Ni^{3+}_{0.02}O^{2-}_{1.01}$
NIO-1173	grayish olive green	0.10	$Ni^{2+}_{0.99}Ni^{3+}_{0.01}O^{2-}_{1.006}$
NIO-1373	olive green	0.038	$Ni^{2+}_{1.00}Ni^{3+}_{0.00}O^{2-}_{1.00}$

such as sulfur, for the hydrogenation activity and e.d.a. The EPMA experiment of reduced nickel prepared from NIO-773 and NIO-1373 also showed the existence of no poisonous elements on both these reduced nickels (data not shown). Therefore, the high e.d.a. of the modified nickel catalyst prepared from NIO-1373 was not attributed to the release of poisonous elements from the nickel oxide during the high temperature decomposition. The increase in the e.d.a. by those higher decomposition temperature nickel hydroxide would be attributed to the lower non-stoichiometric oxygen in the resultant nickel oxide.

It has been demonstrated that the large crystallite size nickel produces a high e.d.a. [12]. The present study revealed that the high crystallinity of nickel oxide (slight non-stoichiometric oxygen) produced a modified nickel catalyst with a high e.d.a. This means that the high crystallinity of nickel oxide would produce a highly crystalline nickel, which is suitable for preparing the modified nickel catalyst with a high e.d.a. 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 characteristic of the parent nickel oxide such as the lattice defects.

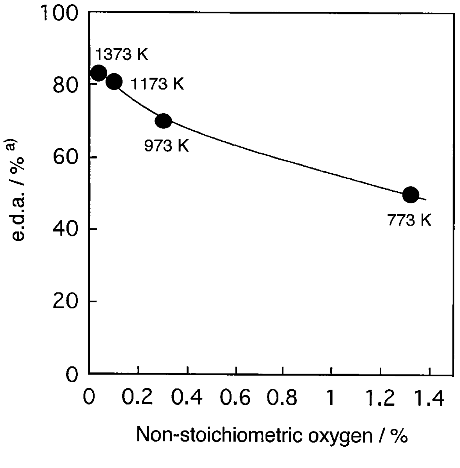

Figure 4. Effect of non-stoichiometric oxygen percentage of on e.d.a. of modified reduced nickel catalyst. Temperatures in the figure indicate the decomposition temperature of nickel hydroxide (a) Reference [10] Reaction conditions: methyl acetoacetate (3.3 g), THF (6.7 cm^3), and acetic acid (0.067 g) containing (R,R)-tartaric acid (3.3 mg) and NaBr (0.3 mg in 50 mm^3 of H_2O) was subjected to hydrogenation over reduced nickel catalyst (0.79 g).

3.2.2. BET surface area of nickel oxide and reduced nickel

Figure 5 shows the effect of the decomposition temperature of the nickel hydroxide on the BET surface area of the nickel oxide and that of the reduced nickel. This figure also indicates the e.d.a. of the modified nickel catalyst prepared from NIO-773, −973, −1173, and −1373. All the nickel oxide samples were reduced at the same temperature of 623 K to obtain the reduced nickel catalyst. Regarding the surface area of nickel oxide, it significantly decreased with the increase in the decomposition temperature. However, the surface area of the reduced nickel was almost the same (about 4.5–5.0 m^2 g^{-1}) irrespective of the decomposition temperature of the nickel hydroxide. That is, the surface area of NIO-773 significantly decreased during the reduction to nickel, while the surface area of NIO-1173 and that of NIO-1373 increased during the reduction to nickel. As the hydrogenation activities of the modified reduced nickel catalysts prepared from NIO-773, −973, −1173, and −1373 were almost the same, it is better to decompose nickel hydroxide at a higher temperature to attain a higher e.d.a. When nickel oxide was reduced at a high temperature to obtain a nickel catalyst with high crystallinity (large crystallite size), the hydrogenation activity decreases because the sintering of nickel resulted in a low surface area. From a practical view

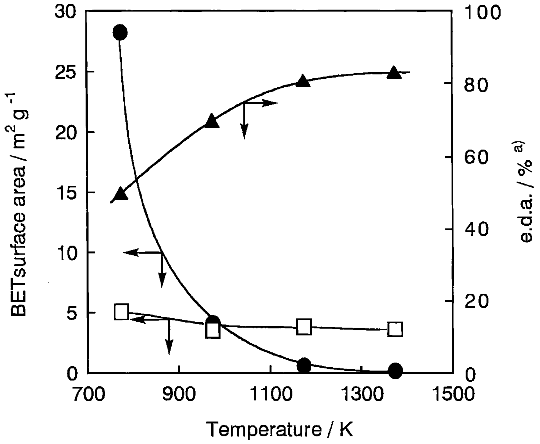

Figure 5. BET surface area of nickel oxide and reduced nickel. ● = surface area of nickel oxide, □ = surface area of reduced nickel, ▲ = e.d.a. of modified reduced nickel catalyst. (a) Reference [10].

point, the combination of the decomposition of nickel hydroxide at a high temperature (1373 K) and the reduction of nickel oxide at a moderate temperature (623 K) is significant for producing a modified nickel catalyst with a high e.d.a. without loss in hydrogenation activity.

4. Conclusion

The properties of nickel oxide prepared by the decomposition of nickel hydroxide and the reduced nickel catalyst were studied in relation to the e.d.a. of a tartaric acid-NaBr-modified reduced nickel catalyst. A high decomposition temperature of nickel hydroxide resulted in slight non-stoichiometric oxygen in nickel oxide. It was revealed that this low non-stoichiometric oxygen in the nickel oxide (i.e., high crystallinity of nickel oxide) would be significant for attaining a high e.d.a. for the resultant modified nickel catalyst. Although the BET surface area of the nickel oxide significantly decreased with the increase in the decomposition temperature of the nickel hydroxide, the BET surface area of the reduced nickel was almost unchanged irrespective of the decomposition temperature of the nickel hydroxide. The combination of the decomposition of nickel hydroxide at a high temperature and the reduction of the resultant nickel oxide at a moderate temperature is significant for producing a modified nickel catalyst with a high e.d.a. without loss in hydrogenation activity.

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