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## Short Communication

# Durability enhancement of chirally modified metallic nickel catalysts for enantioselective hydrogenation

Tsutomu Osawa <sup>a,\*</sup>, Tomoko Kizawa <sup>a</sup>, I-Yin Sandy Lee <sup>a</sup>, Shinji Ikeda <sup>b</sup>, Takayuki Kitamura <sup>b</sup>, Yoshihisa Inoue <sup>c</sup>, Victor Borovkov <sup>b,c,\*\*</sup>

<sup>a</sup> Graduate School of Science and Engineering for Research, University of Toyama, Gofuku, Toyama 930-8555, Japan

<sup>b</sup> Metek Kitamura Co., Ltd., 1 Warada-cho, Kamitoba, Minami-ku, Kyoto 601–8133, Japan

<sup>c</sup> Department of Applied Chemistry, Osaka University, 2-1 Yamada-oka, Suita 565-0871, Japan

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### 1. Introduction

Developing facile method for preparing optically pure compounds is one of the most important and challenging tasks in current synthetic chemistry. Amongst various chemical and biochemical methods to prepare optically active compounds, the use of heterogeneous chiral catalysts is promising in particular for large-scale production in industry [1]. This type of catalysts can be readily prepared, recovered and reused, yet less expensive and ecologically benign. For enantio-differentiating heterogeneous hydrogenation, two major catalytic systems, i.e. alkaloidmodified precious metals [2-4] and tartaric acid (TA)-modified nickels [5-8], are known to give high enantio-selectivities. Thus, alkaloidmodified platinum catalysts are used for the hydrogenation of prochiral  $\alpha$ -ketoesters, while alkaloid-modified palladium catalysts for prochiral alkenes. On the other hand, nickel catalysts co-modified with TA and NaBr are successful in hydrogenating prochiral ketones, such as  $\beta$ -ketoesters and 2-alkanones, to the corresponding chiral alcohols in high enantio-purities.

In applying a heterogeneous catalyst to practical hydrogenation reactions, there are several important factors to be taken into

#### ABSTRACT

Metallic Ni catalysts co-modified with (R,R)-tartaric acid and NaBr showed high enantioselectivity and durability upon hydrogenation of methyl acetoacetate to give methyl 3-hydroxybutyrate. The chirally modified catalyst prepared from 3-µm Ni powder was highly robust to maintain the hydrogenation activity and enantiodifferentiating ability for ca. 3 months under dry condition, which enables long-term storage and hence facilitates commercial distribution and industrial application.

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consideration: (1) the enantio-selectivity upon hydrogenation; (2) the durability upon repeated use; (3) the shelf life of activity and selectivity. However, apart from the enantio-selectivity, the durability and shelf life have rarely been investigated in detail. For example, in the case of alkaloid-modified precious metal catalysts, the cinchonidine (commonly used as the most effective modifier) adsorbed on platinum is liable to leach out from the catalyst surface upon repeated use, and hence the chiral modifier has to be added after each hydrogenation run to keep the original enantio-selectivity [9]. In contrast, the durability of TA-modified nickel catalyst can be greatly improved by embedding the catalyst in silicone polymer, while retaining the 75% enantio-selectivity for repeated 27 runs [10]. More recently, we demonstrated that in situ TA/NaBr modification of metallic nickel prepared by reducing nickel oxide leads to a durable nickel catalyst that maintains the enantioselectivity of 80% for 30 catalytic cycles [11]. Chen et al. also reported that TA-modified Raney nickel catalyst keeps the enantio-selectivity of >60% even after 11 repeated runs, provided that a small amount of NaBr is added after each catalytic cycle [12].

Nickel is much less expensive than platinum or palladium, but has an inherent drawback that its metallic surface is liable to be oxidized upon exposure to air. It is believed therefore that the chirally modified nickel catalyst should be used immediately after the preparation to achieve the optimal activity and enantio-selectivity. Consequently, little is known about the shelf life of TA-modified catalyst. Nevertheless, Sugimura et al. reported that 1,2,4-butanetriol as an additive enables longer storage of the cinchonidine modified palladium catalyst under nitrogen atmosphere [13]. Tai et al. also have shown that TA-modified

<sup>\*</sup> Corresponding author. Tel.: +81 76 445 6611; fax: +81 76 445 6549.

<sup>\*\*</sup> Correspondence to: V. Borovkov, Department of Applied Chemistry, Osaka University, 2-1 Yamada-oka, Suita 565-0871, Japan. Tel.: +81 6 6879 4128; fax: +81 6 6879 7923.

*E-mail addresses:* osawa@sci.u-toyama.ac.jp (T. Osawa), victrb@chem.eng.osaka-u.ac.jp (V. Borovkov).

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nickel embedded in silicone polymer can be stored in the air for 6 months without any accompanying decline of the enantio-selectivity upon hydrogenation [10]. However, the silicone polymer easily swells to absorb part of the reaction mixture under the hydrogenation conditions (at 373 K and 9 MPa of hydrogen), and the absorbed product is difficult to retrieve from the swelled silicone. This reveals the limitation of such a strategy to extend the shelf life and a more straightforward method to prepare a durable catalyst of long shelf life is highly desired.

In the present study to obtain a highly active and enantiodifferentiating, yet durable, chirally modified nickel catalyst, we prepared the TA-modified nickel catalysts not only from Raney nickel alloy but also from fine nickel powder and compared their performance upon hydrogenation of methyl acetoacetate after varying periods of storage under wet and dry conditions (Scheme 1).

#### 2. Experimental

For the preparation of modified Raney nickel catalyst, 1.24 g of Raney nickel alloy (Ni:Al = 41:59) (Kawaken Fine Chemicals, Saitama, Japan) was digested for 1 h in 13 cm<sup>3</sup> of 20% aqueous NaOH solution at 373 K. After removal of the alkaline solution by decantation, the catalyst was washed 15 times with 15-cm<sup>3</sup> portions of deionized water. For the activation of metallic nickel powder (Aldrich, 3 µm in diameter), 0.5 g of nickel powder was treated for 0.5 h in a hydrogen stream at 473 K. The activated nickel catalyst, i.e. Raney nickel or nickel powder, was immersed in a 50-cm<sup>3</sup> aqueous solution containing (R,R)-tartaric acid (0.5 g) and NaBr (0.5 g for Raney nickel and 0.01 g for nickel powder) at 373 K for 1 h. The pH of the modifier solution was adjusted in advance to 3.2 with a 1 M aqueous NaOH solution. For the hydrogenation reaction immediately after the modification (without any storing), the solution was removed by decantation and the catalyst was successively washed once with 10 cm<sup>3</sup> of deionized water, twice with 25 cm<sup>3</sup> of methanol, and then twice with 10 cm<sup>3</sup> of tetrahydrofuran (THF). For the hydrogenation reaction after the storage for a given period of time under the wet condition, the modifying solution was removed by decantation and the catalyst was washed twice with 10 cm<sup>3</sup> of deionized water, and stored under nitrogen atmosphere in a minimum amount of deionized water to cover the catalyst. Before use the catalyst was washed twice with 25 cm<sup>3</sup> of methanol and then twice with 10 cm<sup>3</sup> of THF. For the hydrogenation reaction after the storage under the dry condition, the modifying solution was removed by decantation and the catalyst was successively washed once with 10 cm<sup>3</sup> of deionized water and twice with 25 cm<sup>3</sup> of ethanol. The washed catalyst was then dried under vacuum (4.0 kPa) for 18.5 h and stored under nitrogen in a glass vial. The stored dry catalyst was used for the hydrogenation reaction without any further treatment.

By using the chirally modified catalyst prepared from 1.24 g of Raney nickel alloy or prepared from 0.5 g of nickel powder, the hydrogenation reaction was carried out. The hydrogenation of methyl acetoacetate (5 g) dissolved in a mixture of acetic acid (0.1 g) and THF (10 cm<sup>3</sup>) was run for 20 h at 373 K and the initial hydrogen pressure of 9 MPa in an autoclave equipped with a magnetically coupled mechanical stirrer. The hydrogenation product, methyl 3-hydroxybutyrate, was isolated from the reaction mixture by distillation. The enantio-differentiating ability (e.d.a.) of the catalyst was evaluated by the optical purity of

the hydrogenation product determined by polarimetry; i.e., e.d.  $a = optical purity (\%) = 100 \times ([\alpha]_D^{20} of methyl 3-hydroxybutyrate obtained by hydrogenation)/([\alpha]_D^{20} of optically pure enantiomer), where the specific rotation ([\alpha]_D^{20}) of optically pure ($ *R* $)-methyl 3-hydroxybutyrate is <math>-22.95^{\circ}$  (neat) [14]. When the conversion of the methyl 3-hydroxybutyrate was not 100%, the e.d.a. was evaluated by using gas-liquid chromatography (GLC). Acetylation of the sample was carried out using acetyl chloride and pyridine. A portion of the acetylated sample was subjected to the analysis using a chiral capillary gas chromatograph equipped with CP Chirasil DEX-CB (0.25 mm × 25 m, column temperature: 363 K). The e.d.a was calculated from the peak integration of the corresponding enantiomers.

### 3. Results and discussion

The effects of storage period on the hydrogenation activity and enantio-differentiating ability (e.d.a.) of the catalysts were examined by using the TA-modified Raney nickel and 3-µm nickel powder catalysts stored for 0–21 days under the wet condition at ambient temperature.

As can be seen from Table 1, quantitative conversions were achieved even after 7 and 21 days of storage with the modified Raney nickel and modified 3-µm nickel powder, respectively, indicating the hydrogenation activity is kept at least for 1-3 weeks under the wet condition. However, the e.d.a. of the modified Raney nickel catalyst showed a sudden drop from 75% to 36% after 1 day and was kept low thereafter, as anticipated from the previous research [10,15–17]. In contrast, the e.d.a. of the modified 3-µm nickel powder catalyst was much more persistent for a longer period of time, exhibiting only slow decrease from 84% to 79% after 1 day, then to 75% after 1 week, and eventually to 69% even after 3 weeks of storage. The longer shelf life of the nickel powder catalyst, compared to the modified Raney nickel catalyst, may be attributed to the absent of aluminum remnant, which is readily oxidized under the condition employed (vide infra), causing the overall reduction of the enantioselectivity. The smaller, but noticeable, decrease of e.d.a. observed for 3-µm nickel powder catalyst may be ascribed to the slower oxidation and the subsequent structural changes of the nickel surface under the wet condition (vide infra). These results prompted us to further examine the effect of drying catalyst on the e.d.a. The modified Raney nickel and nickel power catalysts were dried at different temperatures of 323 K and 353 K, and the results of hydrogenation were compared with those obtained with the freshly prepared catalysts (Table 2).

It is somewhat unexpected that both the catalysts kept the original hydrogenation activity even after drying for 18.5 h at 353 K to give the quantitative conversions. However, the e.d.a. was much more susceptive to drying in particular for the Raney nickel catalyst to give a significantly reduced e.d.a. of 53% upon drying at 353 K. In sharp contrast, the nickel powder catalyst was more robust to maintain the originally high e.d.a. even after drying. Thus, the e.d.a. obtained with the nickel powder catalyst dried at 323 K or 353 K showed only a slight decrease from 84% to 82% or to 78%, respectively. These results reveal the great advantages of the chirally modified nickel powder catalyst over the Raney nickel catalyst in all aspects of hydrogenation activity, e.d.a., shelf life, and durability.

Since the modified 3-µm nickel powder catalyst dried at 323 K showed almost the same e.d.a. as the freshly modified catalyst, the effects



Scheme 1. Enantio-differentiating hydrogenation of methyl acetoacetate.

Table 1
Effects of the storage period on the conversion and e.d.a. under wet condition

Storage period/day	Modified Raney nickel		Modified 3-µm nickel	
	Conv./%	E.d.a./%	Conv./%	E.d.a./%
0 <sup>a</sup>	100	75	100	84
1	100	36	100	79
7	100	36	100	75
14	-	-	99	64
21	-	-	99	69

<sup>a</sup> Hydrogenation was carried out just after the modification.

#### Table 2

Effects of the drying temperature on the conversion and e.d.a.<sup>a</sup>

Drying temperature/K	Modified Raney nickel		Modified 3	-µm nickel
	Conv./%	E.d.a./%	Conv./%	E.d.a./%
b	100	75	100	84
323	100	63	100	82
353	100	53	100	78

<sup>a</sup> Dried for 18.5 h at the designated temperature.

<sup>b</sup> The catalyst was kept wet and used immediately after the modification.

of storage period on its catalyst activity and e.d.a. were examined to give the results shown in Table 3.

The e.d.a. of the dried Raney nickel-based catalyst deteriorated from 75% to 63% only after 1 day, whilst the dried nickel powder-based catalyst nicely maintained the high e.d.a. of 82% after 21 days and of 79% even after 84 days of storage. These results clearly demonstrate that both of the chirally modified Raney and the powder nickel catalysts maintain the original e.d.a. for a longer period of time under the dry rather than wet condition. In particular, the TA-modified nickel powder is well suited for commercial purposes in view of the high e.d.a. and the facile storage and distribution.

The Raney nickel alloy (Ni:Al = 41:59 w/w) consists of NiAl<sub>3</sub>, Ni<sub>2</sub>Al<sub>3</sub>, and the Al/NiAl<sub>3</sub> eutetic. The initial treatment with 20% NaOH solution does not fully dissolve the aluminum component from these phases, as the existence of aluminum is detected in the activated Raney nickel catalyst [18]. The subsequent chiral modification in a pH 3.2 solution at 373 K further dissolves the residual aluminum, but a certain amount of aluminum still remains in the modified Raney nickel catalyst [14]. The noticeable decrease of e.d.a. observed for the modified Raney nickel upon storage could be attributed to the oxidation of catalyst surface under the wet and dry conditions and/or the dissolution of aluminum into the remaining water under the wet condition. Furthermore, the possible change on the catalyst surface is likely to alter the spatial orientation of the TA adsorbed on the nickel surface, thus reducing the enantio-selectivity upon hydrogenation. The better e.d.a. obtained with such modified catalysts that were stored under dry, rather than wet, condition support this rationalization. Thus, the small decrease in e.d.a.

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Effects of the storage period on the conversion and e.d.a. under dry condition<sup>a</sup>.

Storage period/day	Modified Raney nickel		Modified 3-µm nickel	
	Conv./%	E.d.a./%	Conv./%	E.d.a./%
0 <sup>b</sup>	100	75	100	84
1	100	63	100	82
7	100	61	100	81
21	-	-	100	82
84	-	-	82	79

<sup>a</sup> Dried at 323 K for 18.5 h.

<sup>b</sup> The catalyst was kept wet and used immediately after the modification.

observed for the modified 3-µm nickel powder catalyst stored under the dry condition is considered to arise from the oxidation of nickel surface.

In conclusion, the TA-modified nickel catalyst prepared from 3-µm nickel powder showed a remarkably high e.d.a. even after 84 days of storage under the dry condition. Metallic nickel powder was shown to be a promising starting material for modified nickel catalysts for asymmetric hydrogenation, which are active, efficient, durable, yet inexpensive.

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