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Facile Synthesis of Optically-Active γ-Valerolactone from Levulinic Acid and Its Esters Using a Heterogeneous Enantio-Selective Catalyst

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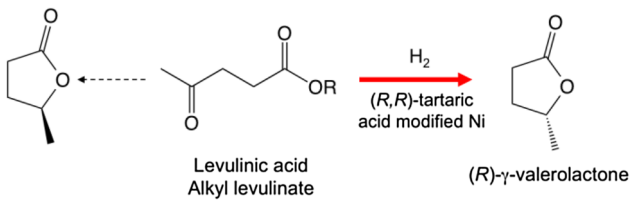
Abstract
Optically-active γ-valerolactone was synthesized by the enantio-selective hydrogenations of levulinic acid and its esters. A tartaric acid-NaBr-modified nickel catalyst produced the optically-active γ-valerolactone with a 60% enantiomeric excess (ee), almost quantitative conversion and chemoselectivity. The synthesis of the optically-active γ-valerolactone using the enantio-selective heterogeneous catalyst would be promising for the large-scale industrial production from levulinic acid and its esters, which can be obtained by the acid-catalyzed dehydration of cellulosic fraction of biomass.

Graphical Abstract



Keywords Optically-active γ-valerolactone · Levulinic acid · Alkyl levulinate · Tartaric acid modified Ni · Enantio-differentiating hydrogenation

1 Introduction

The application of γ-valerolactone (GVL) as a sustainable liquid for carbon-based chemicals was first proposed by Horvath et al. [1]. In recent years, much attention has been paid for the facile synthesis of GVL for the production of various kinds of materials. For example, the application of GVL is a raw material for liquid alkanes [2, 3], and a precursor of bio-polymers [4–7]. GVL is also proposed as a renewable solvent [8–12], as well as a fuel additive [1]. Especially, the optically-active GVL can be a chiral starting compound for the synthesis of chiral fine chemicals [13–17].

The GVL can be produced by the hydrogenation of alkyl levulinate or levulinic acid that is obtained by the hydrolysis of cellulosic biomass [18, 19]. Concerning the production of the racemic GVL, intensive studies have already been reported using various homogeneous catalysts [20–23] and heterogeneous catalysts [24, 25]. Meanwhile, the research studies for the production of the optically-active GVL have not made much progress compared to that of the racemic ones. Especially, the development of enantio-selective heterogeneous catalysts has lagged behind the homogeneous ones [16, 26–29].

The enantio-selective modified heterogeneous catalysts (solid catalysts which have an intrinsic catalytic activity and the surface of which is modified by optically-active compounds) are promising for the facile industrial synthesis of optically-active compounds. Modified solid catalysts have the characteristics of easy and low cost preparation, easy separation from the reaction mixture, and easy reuse. The tartaric acid (TA)-NaBr-modified

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nickel catalyst is one of the successful enantio-selective heterogeneous catalysts [30, 31]. This catalyst produces a high enantio-selectivity of over 98% during the hydrogenation of β-ketoesters [32, 33] and 85% during 2-alkanone hydrogenations [34, 35]. The enantio-selective hydrogenation of levulinic acid and alkyl levulinates to GVL would be an environmentally benign approach for the efficient transformation of biomass waste into a value-added chiral building block.

In the present study, the enantio-differentiating hydrogenations of levulinic acid and various alkyl levulinates (Scheme 1) were carried out over the modified nickel catalyst. The effects of the catalyst preparation methods and the hydrogenation conditions on the selectivity and the enantioselectivity of GVL were investigated.

2 Experimental

Hydrogen gas (99.99%) and nitrogen gas (99.999%) were obtained from Takachiho Trading Co., Ltd. Ion exchanged water was used for preparation of the catalysts.

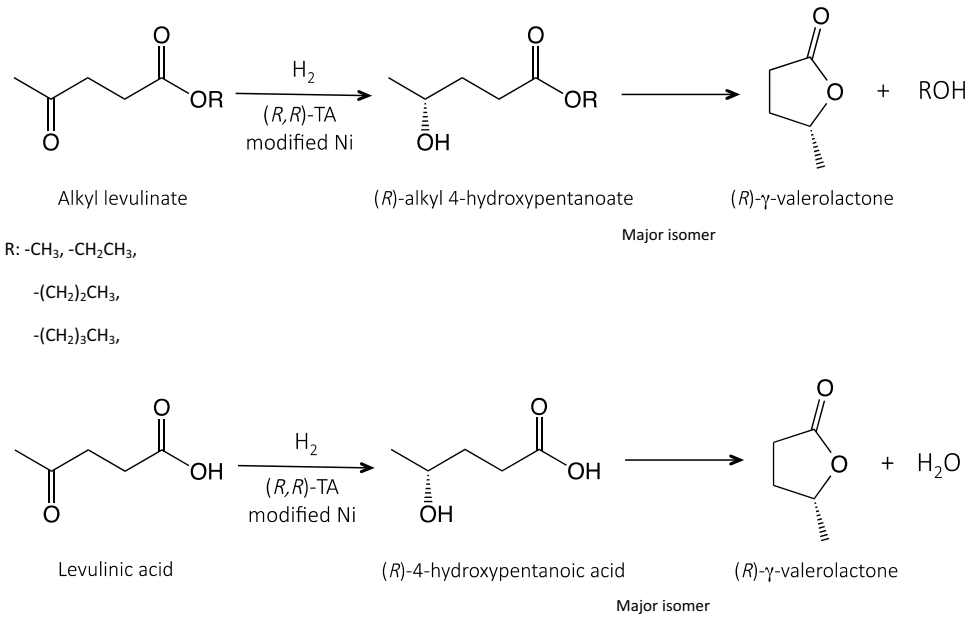
Levulinic acid (> 95% Wako Pure Chemical Ind., Ltd.) was used after distillation. Methyl levulinate and ethyl levulinate were synthesized from levulinic acid and the corresponding alcohols using an ion exchange resin (Amberlite 15). Propyl, butyl, 1-methyl-propyl, 2-methyl-propyl, and cyclohexyl esters were synthesized using levulinic acid and the corresponding alcohols and a Dean–Stark apparatus.

2.1 Enantio-Differentiating Hydrogenation of Alkyl Levulinates

The hydrogenation of the various esters of levulinic acid was carried out using an in situ modification method, i.e., modifier and auxiliary modifier were added to the reaction media [36, 37]. A 0.94 g sample of nickel oxide (Wako Pure Chemical Industries, Ltd.) was treated at 623 K for 1 h under a H_2 stream (30 mL min^{-1}) to obtain the reduced nickel catalyst. Sodium bromide in 50 μL H_2O and (*R,R*)-tartaric acid (TA) (the amounts are stated in the text) were added to a mixture of levulinate (2.9×10^{-2} mol), acetic acid (0.065 g), and the solvent (7 mL). This substrate solution and the reduced nickel catalyst were placed in a magnetically-stirred autoclave [OM Lab-Tech Co., Ltd. (Tochigi, Japan)]. Hydrogenation was carried out under the initial hydrogen pressure of 9 MPa for 20 h. The stirring rate of the autoclave was 1130 rpm.

2.2 Enantio-Differentiating Hydrogenation of Levulinic Acid

The hydrogenations of levulinic acid were carried out using an in situ modification method and a pre-modification method [38]. The hydrogenation using the in situ modification was almost the same as that of the alkyl levulinates. The hydrogenation procedure using a pre-modification was as follows. A 0.94 g sample of nickel oxide (Wako Pure Chemical Industries, Ltd.) was treated at 623 K for 1 h under a H_2 stream (30 mL min^{-1}) to obtain the reduced nickel catalyst. The aqueous solution of (*R,R*)-TA and NaBr (the amounts are stated in the text)



Scheme 1 Enantio-differentiating hydrogenation of alkyl levulinates and levulinic acid

was adjusted to pH 3.2 using a 1 M NaOH solution (modification solution). The reduced nickel catalyst was soaked in the modification solution and stored for 1 h at 373 K. The catalyst was successively washed with water (10 mL), twice with methanol (25 mL), and twice with the reaction solvent (10 mL). The mixture of the levulinic acid, acetic acid, and the solvent (the amounts are mentioned at the footnote of the table) and the reduced nickel catalyst were placed in a magnetically-stirred autoclave [OM Lab-Tech Co., Ltd. (Tochigi, Japan)]. Hydrogenation was carried out under the initial hydrogen pressure of 9 MPa for 20 h. The stirring rate of the autoclave was 1130 rpm.

2.3 Analysis of the Hydrogenated Product

The enantiomeric excess (ee) was determined by GLC.

$$ee = \frac{|(R) - (S)|}{(R) + (S)}$$

(*R*) and (*S*) are the peak areas of the (*R*) and (*S*) enantiomers, respectively. For both the hydrogenations of levulinic acid and its esters, as the product was mainly GVL, the ee values were calculated from the peak integration of the corresponding enantiomers of the GVL. They were determined without any pre-derivatization of the hydrogenated product. Analyses were carried out using a chiral capillary gas chromatograph [Shimadzu GC-18A, CP Chirasil DEX-CB (0.25 mm × 25 m)] at 333–413 K (5 K min^{-1}), then at 413–433 K (10 K min^{-1}). The reproducibility of the ee value was with an error of ≤ 2%. The conversion and lactone selectivity were also determined by the same column and analysis conditions.

3 Results

3.1 Enantio-Differentiating Hydrogenation of Alkyl Levulinates Over an In Situ Modified Nickel Catalyst

In order to synthesize the optically-active GVL by the hydrogenation of alkyl levulinates using an in situ modified nickel catalyst, the effects of the types of solvent on the hydrogenation rate, the conversion and chemoselectivity, and the ee were initially examined. In the case of the in situ modification method, most of the TA and NaBr added to the reaction media are adsorbed on the nickel surface during the initial stage of the reaction [39] as well as the in situ modified cinchonidine modified Pt catalysts [40, 41]. These modifier and the auxiliary modifier should be dissolved in the reaction media in order to be uniformly adsorbed on the nickel surface [37]. This is the reason why NaBr was dissolved in a small amount of deionized water (50 μL). Table 1 shows the effects of the types of solvents during the enantio-differentiating hydrogenation of methyl levulinate as a representative example of the alkyl levulinates.

The examined solvents, except for methanol, gave almost a 100% conversion in a 20-h reaction, although the hydrogenation rates in the alcoholic solvents were higher than those in the aprotic solvents. While the selectivity of GVL was more than 95% for all the solvents, the ee depended on the types of solvents. Aprotic solvents, such as THF, 1,4-dioxane, and methyl propionate, gave a higher ee than the alcoholic solvents. As THF produced the highest ee, it was selected as the solvent in this study.

As has been reported that the addition of NaBr as an auxiliary modifier increased the ee for the hydrogenations

Table 1 Effects of the types of solvents during the enantio-differentiating hydrogenation of methyl levulinate

Solvent	Conversion (%)	Hydrogenation rate (mmol h^{-1})	Selectivity (%)			ee (%)
			GVL	Alcohol	Transesterified alcohol	
THF	100	3	95	5	–	46
1,4-Dioxane	100	2	99	1	–	40
Methyl propionate	100	2	99	1	–	41
Methanol	82	2	93	7	–	2[a]
Ethanol	99	7	96	2	2	17
1-Propanol	100	7	98	1	1	27
2-Poropanol	100	8	98	1	1	38
1-Butanol	100	14	98	2	0	35
2-Butanol	100	5	98	2	0	39
2-Methyl-1-propanol	100	7	98	1	1	34

NiO 0.94 g (13 mmol), reaction mixture: 29 mmol methyl levulinate, 1.1 mmol acetic acid, 7 mL solvent, 0.025 mmol (*R,R*)-TA and 5.8×10^{-3} mmol NaBr in 50 μL H_2O. Hydrogenation temperature: 373 K

[a](*S*)-isomer in excess

of β-ketoesters and alkanones [42, 43], the effects of the amount of NaBr added to the reaction media was investigated in the methyl levulinate case. The results are shown in Fig. 1.

The conversions of 100% were attained by the addition of 1.5–5.8 μmol NaBr. Less and greater amounts of NaBr produced lower conversions. In the absence of NaBr or below 0.5 μmol, almost racemic products were obtained. The increase in the amount of NaBr increased the ee and a 5.8 μmol addition resulted in a 46% ee.

The effects of the hydrogenation temperature from 353 (333) to 413 K were also investigated for the hydrogenation of various alkyl levulinates over the in situ modified reduced nickel catalyst. Table 2 shows the results.

An over 96% lactone selectivity was attained at > 393 K for all the substrates (except 2-methyl-propyl levulinate). The highest ee was attained for the 373–393 K hydrogenation of all the examined substrates. Ester groups with a longer alkyl chain had a tendency for producing a higher ee. The highest 60% ee was attained for the *n*-butyl levulinate at 373 K. Branching of the alkyl group did not affect the ee. The ee of the substrates with 2-methyl-propyl and iso-butyl groups was the same as that with the propyl group (57% ee).

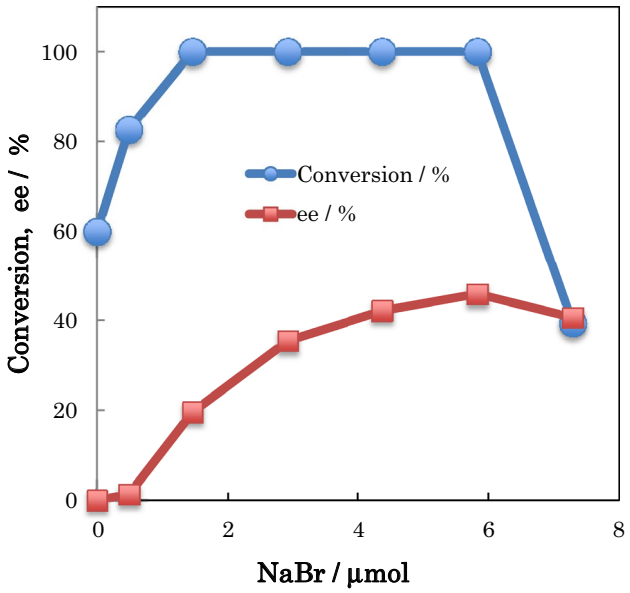


Fig. 1 Effects of the amount of NaBr in the modification solution on the conversion and the enantio-selectivity. NiO 0.94 g (13 mmol), reaction mixture: 29 mmol methyl levulinate, 1.1 mmol acetic acid, 7 mL THF, 0.025 mmol (*R,R*)-tartaric acid, and NaBr in 50 μL H_2O. Hydrogenation temperature: 373 K

3.2 Enantio-Differentiating Hydrogenation of Levulinic Acid Over Modified Nickel Catalyst

The one-pot conversion of levulinic acid to GVL is favorable for the industrial large-scale synthesis of GVL using levulinic acid prepared from biomass waste [16]. Table 3 shows the enantio-differentiating hydrogenation of levulinic acid over the modified reduced nickel catalyst.

In contrast to the hydrogenation of various alkyl levulinates, levulinic acid was difficult to be hydrogenated using the in situ modified reduced nickel catalyst, i.e., low conversions of less than 10% were attained. In contrast, a pre-modified reduced nickel catalyst attained a much higher conversion. Hence, the effects of the amount of NaBr in the modification solution and the amount of acetic acid in the reaction media were investigated over pre-modified nickel catalysts. The modification with a solution containing 5 mmol TA and 22 mmol NaBr, and the addition of 1.7 mmol acetic acid to the reaction mixture produced the highest ee of 60% with a 100% conversion. The selectivity of GVL was 100% irrespective of the conversion value. The effects of the hydrogenation temperature (353–413 K) on the conversion and the ee were also investigated. The results are shown in Table 4.

As in the alkyl levulinate case, a 60% ee was attained at 373 K at 100% conversion. No product other than GVL was obtained.

4 Discussion

The in situ modification method is more attractive for the synthesis of optically-active compounds in industry than the pre-modification method, because the independent modification process can be omitted and the industrial waste solution containing nickel ions as heavy metals does not occur. We previously reported the enantio-differentiating hydrogenation of methyl levulinate over pre-modified Raney nickel and reduced nickel catalyst, and attained a 51% ee of GVL using the pre-modified reduced nickel [44]. In this study, the in situ modified system, which is more preferable for the industrial production of GVL, was investigated. For attaining a high ee using the in situ modification method, the modifier and auxiliary modifier should be completely dissolved in the reaction media [37]. In this regard, as TA can be dissolved in the evaluated solvent (Table 1), it can be added to the reaction media without dissolving in water. On the contrary, NaBr should be dissolved in 50 μL of water, because of its low solubility in aprotic solvents such as THF. Based on the results in Table 1, although the solubilities of TA and NaBr are higher in alcoholic solvents than in aprotic solvents, the ee was higher for the aprotic solvents than for the alcoholic solvents. Among the primary alcohols examined, the alcohol

Table 2 Enantio-differentiating hydrogenation of various 4-oxopentanoates

Substrate $CH_3CO(CH_2)_2COO$–	Hydrogenation temperature (K)	Conversion (%)	Lactone selectivity (%)	ee (%)
–CH_3	333	3	38	25
	353	29	64	35
	373	100	93	46
	393	100	97	44
	413	100	98	42
–CH_2CH_3	353	22	52	35
	373	29	91	48
	393	100	98	53
	413	100	99	49
–$(CH_2)_2CH_3$	353	22	74	40
	373	59	88	54
	393	100	97	57
	413	100	98	50
–$(CH_2)_3CH_3$	353	37	51	46
	373	95	86	60
	393	100	96	59
	413	100	97	53
–$CH(CH_3)CH_2CH_3$	353	23	16	41
	373	52	52	55
	393	97	89	57
	413	100	100	52
–$CH_2CH(CH_3)_2$	353	19	54	45
	373	69	78	57
	393	100	96	57
	413	100	97	48
–Cyclohexyl	353	24	58	52
	373	82	81	59
	393	97	96	59
	413	100	99	53

NiO 0.94 g (13 mmol), reaction mixture: 29 mmol levulinic acid ester, 1.1 mmol acetic acid, 7 mL THF, 0.025 mmol (*R,R*)-TA and 5.8×10^{-3} mmol NaBr in 50 µL H_2O

with a longer alkyl chain gave a higher ee. The secondary alcohol produced a higher ee than the primary alcohol. These tendencies were the same as the methyl acetoacetate case [45–47], and indicated that the effective stronger interactions between the TA and substrate by hydrogen bond and ion–dipole interaction (TA is actually adsorbed as a sodium salt [48]) were achieved in the aprotic solvent.

Optimization of the amount of NaBr in the modification process is also of critical importance for attaining a high ee when reduced nickel was used as the base nickel material, because its optimal amount depended on the manufacturer or even the lot number of the nickel oxide, a precursor of the reduced nickel catalyst [44]. The effects of the amount of NaBr for the hydrogenation of methyl levulinate over the in situ modified nickel catalyst (Fig. 1) showed a tendency similar to the hydrogenation of methyl acetoacetate using the pre-modified Raney nickel [42, 49, 50]. However, it was revealed that the effects of the addition of NaBr during the hydrogenation of methyl levulinate were more significant than for the methyl acetoacetate case. An almost racemic product was produced without the addition of NaBr to the reaction system, meanwhile, the addition of a small amount significantly increased the ee. As the addition of 2.9×10^{-6} mol of sodium 2-ethylhexanoate instead of NaBr also increased the enantio-selectivity to 16%, the sodium ion would play an essential role in the enantio-differentiation of the prochiral face of methyl levulinate [48]. As the addition of NaBr attained a higher ee than that of sodium 2-ethylhexanoate, Br^- also contributed to increasing the enantio-selectivity. The role of Br^- would be the same as the hydrogenation of methyl acetoacetate, i.e., blocking the hydrogenation on the non-enantio-differentiating sites where racemic products were produced [38, 51].

Table 3 Enantio-differentiating hydrogenation of levulinic acid over modified Ni catalyst

Modification method	TA (mmol)	NaBr (mmol)	Acetic acid (mmol)	Conv. (%)	ee (%)
in situ[a]	0.025	5.8×10^{-3}	1.1[c]	8	13
in situ[a]	0.025	5.8×10^{-3}	1.7[d]	4	28
pre[b]	5	0	1.7[e]	100	10
pre[b]	5	7.3	1.7[e]	100	20
pre[b]	5	22	1.7[e]	97	60
pre[b]	5	51	1.7[e]	41	47
pre[b]	5	22	0[e]	100	53
pre[b]	5	22	1.7[e]	100	60
pre[b]	5	22	3.3[e]	99	55
pre[b]	5	22	5.0[e]	93	58
pre[b]	5	22	6.7[e]	100	43
pre[b]	5	22	8.3[e]	96	30

[a]Modification reagents were added to the reaction mixture

[b]Modification solution: 5 mmol (*R,R*)-TA and NaBr in 75 mL H_2O (pH 3.2, 373 K)

[c]Reaction mixture: 29 mmol levulinic acid, 1.1 mmol acetic acid, 7 mL THF, 0.025 mmol (*R,R*)-TA, and 5.8×10^{-3} mmol NaBr in 50 μL H_2O

[d]Reaction mixture: 8.6 mmol levulinic acid, 1.7 mmol acetic acid, 10 mL THF, 0.025 mmol (*R,R*)-TA, and 5.8×10^{-3} mmol NaBr in 50 μL H_2O

[e]Reaction mixture: 8.6 mmol levulinic acid, acetic acid, and 10 mL THF.

Hydrogenation temperature: 373 K

Table 4 Effects of the hydrogenation temperature on the conversion and ee during the hydrogenation of levulinic acid

Hydrogenation temperature (K)	Conversion (%)	ee (%)
353	77	56
373	97	60
393	100	55
413	100	39

NiO 0.94 g, modification solution: 5 mmol (*R,R*)-TA and 22 mmol NaBr in 75 mL H_2O (pH 3.2, 373 K), reaction mixture: 8.6 mmol levulinic acid, 1.7 mmol acetic acid, and 10 mL THF

Concerning the effects of the hydrogenation temperature during the hydrogenation of various alkyl levulinates, the higher ee was attained at 373–393 K than at 353–413 K for each substrate. This tendency was different from our previous results over the modified Raney nickel catalyst (ee was independent of the hydrogenation temperature [44]). This could be partly attributed to the difference in the hydrogenation activity of the catalyst. The hydrogenation activity of the modified reduced nickel is lower than that of the modified Raney nickel catalyst. The enantio-differentiating mechanism could be changed according to the hydrogenation temperature. The studies of this aspect are now in progress. The 60% ee was attained for the hydrogenation of butyl levulinate, which was the highest value attained by the enantio-selective heterogeneous catalyst reported, to the best of our knowledge.

As for the hydrogenation of levulinic acid using the in situ modification method, a lower conversion was attained compared to the alkyl levulinate case. This would be attributed to the acid characteristics of the substrate. Levulinic acid would be competitively adsorbed on the nickel surface with TA during the initial stage of the reaction. Large amount of levulinic acid (8.6×10^{-3} mol) compared to TA (2.5×10^{-5} mol) in the reaction mixture would hinder the TA adsorption. It is known that modification of the nickel surface by TA increases the hydrogenation rate [52]. Therefore, the decrease in the amount of TA could result in a decreased conversion and ee. Meanwhile, the pre-modification method, by which TA is firmly adsorbed before the reaction in the appropriate surface coverage, afforded almost quantitative conversions. Concerning the effects of the addition of acetic acid to the reaction media, it was reported that the acetic acid accelerated the hydrogenation rate on the enantio-differentiating sites through the interaction with TA, which was revealed during the hydrogenation of methyl acetoacetate [52]. This could be also applied to the hydrogenations of levulinate and levulinic acid. The results that the hydrogenation rate of levulinic acid was higher than that of levulinate (Tables 2, 3) partly support the above idea. The carboxyl acid with smaller alkyl group (acetic acid) was effective for increasing in ee with a smaller amount of the acid compared to the carboxylic acid with larger alkyl group (pivalic acid) [44]. This could explain the present results that small amount of acetic acid increased the ee in the hydrogenation of levulinic acid. The highest ee of 60% with a 100% conversion was attained for the enantio-differentiating hydrogenation of levulinic acid as well as the alkyl levulinate. This is also the highest value so far obtained over the heterogeneous enantio-selective catalyst.

The direct asymmetric reduction of levulinic acid and its esters to GVL is rather difficult even using homogeneous catalysts compared to the reductions of α-ketoesters, α-ketoacids, and β-ketoesters. For example, 82% ee was attained by the hydrogenation of levulinic acid over the ruthenium complex at 423 K [16], while the hydrogenation of the α-ketoesters and β-ketoesters produced more than a 95% ee at 298 K [41, 53] and 337 K [54], respectively. Although the ee obtained by the TA-NaBr-modified nickel catalyst was now rather lower (60%) than those obtained by the homogeneous complex catalysts, this value was attained at 373–393 K with an almost quantitative chemoselectivity and conversion, as well as having the typical advantages of heterogeneous catalysts, i.e., easy preparation, easy recovery

and reuse, and particularly, resource savings (not using precious metals for the present catalyst). As for the isolation of GVL from the product solution, almost the quantitative yield of GVL was attained after the removal of the catalyst using magnet and a simple distillation, in the case of the conversion and the chemoselectivity of GVL was 100%. The study of the development of the catalyst for ring closure of alkyl 4-hydroxypentanoate is in progress. Hence, the TA-NaBr-modified nickel catalyst would be promising for the industrial production of the optically-active GVL from bio-mass waste.

5 Conclusion

The optically-active GVL was synthesized by the enantio-selective hydrogenations of levulinic acid and its esters, which can be obtained by the degradation of biomass. The optically-active GVL with 60% ee was produced from both levulinic acid and its esters in almost quantitative conversion and chemoselectivity using the TA-NaBr-modified nickel catalyst. The enantio-selective hydrogenation of levulinic acid required a pre-modified catalyst. This would be attributed to the acid characteristics of the substrate. Meanwhile, the enantio-selective hydrogenations of alkyl levulinates proceeded by the in situ modified catalysts, which is more favorable for the industrial applications. The synthesis of optically-active GVL from levulinic acid and its esters using enantio-selective heterogeneous catalysts would be promising for its large-scale industrial production.

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