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Vapor-phase hydrogenation of levulinic acid to γ -valerolactone over Cu-Ni bimetallic catalysts

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Abstract:

Vapor-phase hydrogenation of levulinic acid (LA) to γ -valerolactone (GVL) was performed over SiO₂-supported Cu-Ni bimetallic catalysts with different Cu/Ni weight ratios under ambient H₂ pressure. Characterization of the catalysts was carried out using powder X-ray diffraction, temperature programmed reduction and thermogravimetric analysis. In contrast to the monometallic catalysts i.e. Ni/SiO₂ and Cu/SiO₂, the Cu-Ni/SiO₂ bimetallic catalyst with a Cu/Ni weight ratio of 6/14 exhibits an excellent catalytic activity, and gave a GVL yield higher than 99% with a productivity of 1.64 kg_{GVL} kg_{cat}.⁻¹ h⁻¹ at 250 °C and at a high WHSV of 1.65 h⁻¹ for 50 h.

Keywords: levulinic acid, γ -valerolactone, hydrogenation, Cu-Ni bimetallic catalyst.

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1. Introduction

The depletion of fossil fuel resources and the increasing global environmental problems motivate the application of renewable biomass carbon resources for producing useful chemicals as well as energy [1]. LA is a material derivable from cellulose and hemicellulose present in lignocellulosic feedstocks [1,2], and has applications as a food flavoring agent and also as a starting material for the production of pharmaceutical compounds. LA has high reactivity due to the presence of both ketone and carboxyl groups, and LA is also an attractive platform molecule to produce various compounds such as GVL, 2-methyltetrahydrofuran (MTHF) and 1,4-pentanediol (1,4-PDO) [3]. Among these compounds, GVL is attractive because of its importance as a solvent and an intermediate in the chemical industry [4].

The hydrogenation of LA into GVL has to date mostly been investigated in liquid-phase reactions under high H_2 pressure conditions [4]. Supported precious metal catalysts were applied for the hydrogenation of LA into GVL in some previous reports. Manzer performed reactions over active carbon-supported Ru, Ir, Pt, Rh, Re, and Pd catalysts [5]. Among these catalysts, Ru/C showed the highest catalytic activity for GVL formation and a 97% yield of GVL was obtained at 150 °C and an H_2 pressure of 55 bar. Non-noble metal such as Cu and Ni also showed high activity for the GVL formation from LA [6-9], and a quantitative yield of GVL was obtained over Cu/ZrO₂ or Cu/Al₂O₃ at 200 °C under 34 bar H_2 pressure [6].

From a viewpoint of industrial application, a continuous process for GVL production is attractive and the use of earth abundant non-noble metal-based catalysts is preferable. Continuous vapor-phase hydrogenation of LA into GVL over non-noble metal-based catalysts has been reported by several groups in recent years [10-16]. In the report of Mohan *et al.*, Ni/SiO₂ provided a GVL productivity of 0.87 kg_{GVL}kg_{cat}.⁻¹ h⁻¹ with a GVL selectivity of 87% under ambient H₂ pressure conditions [14]. In contrast to Ni/SiO₂, Upare *et al.* reported a Cu/SiO₂ catalyst, which showed a lower GVL productivity of 0.51 kg_{GVL}kg_{cat}.⁻¹ h⁻¹, while the selectivity to GVL was as high as 99.9% [11]. Since Ni is active for the LA conversion and Cu is selective for the GVL formation, we reasoned that the preparation of Ni-Cu bimetallic catalysts would be an effective method for the efficient formation of GVL from LA.

In this study, the hydrogenation of LA to GVL over Cu-Ni bimetallic catalysts has been investigated using a fixed-bed down-flow reactor under ambient H_2 flow conditions. A series of Ni-Cu bimetallic catalysts supported on SiO₂ with different Cu/Ni weight ratios were examined and we show that the bimetallic catalysts give a superior performance when compared with the monometallic Cu and Ni catalysts.

2. Experimental

2.1 Materials and catalyst preparation

LA was purchased from Wako Pure Chemical Industries, Japan, and was used for the catalytic reaction without further purification. SiO₂ (CARiACT Q10 with mean pore diameters of 10 nm) was supplied by Fuji Silycia Chemical Ltd. Cu(NO₃)₂· $3H_2O$ and Ni(NO₃)₂· $6H_2O$, which were used as the precursors of the corresponding metals, were purchased from Wako Pure Chemical Industries, Japan.

SiO₂-supported metal catalysts were prepared by an incipient wetness impregnation method using a solution with a prescribed amount of Cu and Ni nitrate dissolved in distilled water. The weight percentages of metal in the support were calculated using the weight of Cu and Ni metal in the calcined catalysts. Total metal loading on SiO₂ was fixed at 20 wt.%. After impregnation, the samples were dried (110 °C, 12 h) and calcined (300 °C, 3 h). Hereafter, the prepared catalysts are expressed as xCu-yNi/SiO₂, where x and y indicate the weight percentage of the Cu and Ni metals, respectively. For example, 6Cu-14Ni/SiO₂ indicates 6 wt.% Cu and 14 wt.% Ni loaded on SiO₂.

2.2 Catalytic reaction

Vapor-phase hydrogenation of LA was performed in a fixed-bed down-flow glass reactor with an inner diameter of 17 mm at an ambient pressure of H₂. Prior to the reaction, a catalyst (0.250g or 1.00g) was placed in the catalyst bed and reduced in H₂ flow at 300 °C; although 400 °C was used for 20Ni/SiO₂ for 1 h. LA was then fed through the top of the reactor at a liquid feed rate of 1.65 cm³ h⁻¹ together with H₂ (30 cm³ min⁻¹). The liquid effluents were collected in a dry ice-acetone trap (-78 °C) every hour and were analyzed by a FID-GC (GC-14B, Shimadzu) with a

60-m capillary column of TC-WAX (GL-Science, Japan). A GC-MS (QP5050A, Shimadzu) was used for identification of the products in the effluent. n-Butanol was used as an internal standard.

2.3 Characterization of catalysts

The XRD patterns of samples were recorded on a D8 ADVANCE (Bruker, Japan) using Cu K α radiation. The thermogravimetry (TG) analysis was performed using Thermoplus 8120E2 (Rigaku) under the conditions: sample weight, *ca.* 10 mg; the rate of temperature increment, 5 °C min⁻¹ from the room temperature to 900 °C. Temperature-programmed reduction (TPR) was conducted for characterizing the metal state of the prepared catalysts. The measurements were performed in a mixed flow of H₂/N₂ (1/9, 10 cm³ min⁻¹) with a heating rate of 5 °C min⁻¹ and a temperature range from 25 to 900 °C, and the details are described elsewhere [17].

3. Results and discussion

Before conducting the catalytic reactions, TPR analyses of the Cu, Ni, and Cu-Ni bimetallic catalysts were performed. As shown in Fig. 1, 20Ni/SiO₂ shows a broad signal at *ca*. 350 °C, while 20Cu/SiO₂ and Cu-Ni bimetallic catalysts show a sharp signal at *ca*. 220 °C. It is obvious that the existence of Cu can decrease the reduction temperature of NiO, indicating the interaction between Ni and Cu metal. Spillover effect on Cu-Ni bimetallic catalysts has been widely reported [18-20], therefore, it is considered that CuO is reduced to Cu, and the hydrogen associated with Cu shifts to NiO by a spillover effect that leads to reduction of NiO. Based on the TPR analysis, the reduction temperature of 20Cu/SiO₂ and Cu-Ni/SiO₂ catalysts was determined to be 300 °C, while that of 20Ni/SiO₂ and 6Cu-14Ni/SiO₂ catalysts after reduction. The diffraction reflections observed at 43.5° and 51.8° are attributed to Ni metal. No reflections assigned to metal oxides were observed in these catalysts, indicating that the metal oxides were successfully reduced to metal before the reaction. No reflections assigned to Cu-Ni alloy were observed in the profile of 6Cu-14Ni/SiO₂, which suggests that Cu-Ni alloy was either highly dispersed or not formed.



Scheme 1 The major products in the hydrogenation of LA.

The hydrogenation of LA to GVL was conducted over Cu, Ni, and Cu-Ni bimetallic catalysts with different Cu/Ni weight ratios in H₂ flow with a flow rate of 30 ml min⁻¹ at 250 °C and a WHSV of 6.60 h⁻¹. Table 1 shows the reaction results in the initial 8 h where the conversion and selectivity were averaged for 8 h. Scheme 1 shows the major products in the reactions. Except for the 20Cu/SiO₂ catalyst, the main product was GVL, and the by-products included acetone, methyl ethyl ketone (MEK), and angelicalactones (ALs). The ALs included α -, β - and γ -angelicalactone isomers. ALs were produced by the cyclodehydration of LA, while MEK and acetone were the decomposition products of LA.

In the report of Uprare *et al.*, 5Cu/SiO₂ gave a GVL selectivity of 99.9% at a WHSV of 0.513 h⁻¹ under 1 MPa H₂ pressure conditions [11], indicating Cu was selective for the formation of GVL under low WHSV conditions. However, in the present study at a high WHSV of 6.60 h⁻¹ under ambient H₂ flow conditions, SiO₂-supported Cu catalyst showed a low GVL selectivity of 25.5%, but a high ALs selectivity of 57.1%. In a recent study of our group, it was found that SiO₂ efficiently catalyzed the cyclodehydration of LA to ALs in the vapor phase at a temperature range of 250-300 °C [21]. Therefore, it is reasonable that the ALs are generated over SiO₂ as an intermediate, whereas the hydrogenation ability of Cu is insufficient to efficiently convert ALs to GVL under ambient H₂ pressure and high WHSV conditions. In order to confirm the speculation,

the reaction over 20Cu/SiO₂ was performed at a low WHSV of 3.30 h⁻¹: the conversion of LA and the selectivity to GVL increased to 73.4% and 75.4%, respectively, while the selectivity to ALs decreased to 9.9%. In contrast to 20Cu/SiO₂, 20Ni/SiO₂ gave a high conversion of 94.2% with a high GVL selectivity of 92.2% and a low ALs selectivity of 0.3%. It is obvious that the hydrogenation ability of Ni is higher than Cu. However, LA decomposition products such as acetone, MEK and y-butyrolactone were formed as by-products over 20Ni/SiO₂ and this decreased the observed selectivity to GVL. In the case of 20Cu/SiO₂, however, no decomposition product was detected, indicating the inactivity of Cu for the C-C cleavage of LA. The SiO₂-supported Cu-Ni bimetallic catalysts showed different catalytic activity depending on the Cu/Ni weight ratio. Compared with 20Ni/SiO₂, the Cu-Ni bimetallic catalysts with Cu loadings lower than 8 wt.% showed both high LA conversions and GVL selectivities, indicating that the activity of Ni was improved by the interaction with Cu. On the other hand, the Cu-Ni bimetallic catalysts with high Cu/Ni weight ratios such as 14Cu-6Ni/SiO2 and 16Cu-4Ni/SiO2 gave relatively low LA conversions. This is possibly caused by the relatively low hydrogenation activity of Cu. The catalyst with a Cu/Ni weight ratio of 6/14 showed the best catalytic performance, and provided a LA conversion of 99.1% with a high GVL selectivity of 99.2%. Upare et al. also reported a vapor-phase hydrogenation of LA using Cu-Ni/SiO₂ catalysts with a total metal loading of 80 wt.%, and the reactions were performed at a WHSV of 0.512 h⁻¹ using formic acid as a hydrogen donor and 1,4-dioxane as the solvent [16]. The suitable Cu/Ni weight ratio was determined to be 3/1, which is much different from the present results. This difference could be attributed to the different total metal loadings as well as the different reaction conditions.

Fig. 3 shows the changes in LA conversion and GVL selectivity in the reactions over the 20Cu/SiO₂, 20Ni/SiO₂ and Cu-Ni/SiO₂ with different Ni and Cu loadings. 20Cu/SiO₂ showed low conversions as well as a low stability: the conversion over Cu/SiO₂ gradually decreased from 25.6% to 9.7% during 8 h. Since ALs easily polymerize to form coke [21], the catalytic deactivation of 20Cu/SiO₂ is considered to be attribed to the large amount of internediate ALs due to low hydrogenation ability of Cu. Cu-Ni/SiO₂ bimetallic catalysts showed enhanced catalytic activity compared to 20Cu/SiO₂, while the catlytsts with large Cu contents still deactivated rapidly.

In contrast to the Cu-rich catalysts, $20Ni/SiO_2$ and the Ni-rich catalyts showed relatively stable catalytic activities. This inicates that the Ni component is responsible for the catalytic stability. On the other hand, in the reactions over $4Cu-16Ni/SiO_2$ and $6Cu-14Ni/SiO_2$ catalysts, slight decrease in converion was observed after 6 h. We further performed a long-run test using $6Cu-14Ni/SiO_2$ at a lower WHSV of 1.65 h⁻¹ (Fig. 4). The catalytic activity was stable during 50 h: the conversion was maintained at 100% and the GVL selectivity gradually increased to 99.7% at time on stream (TOS) of 25 h. It has to be mentioned that the WHSV of 1.65 h⁻¹ in the present study is higher than that reported in previous studies [10-16].

In the LA hydrogenation, catalyst deactivation is confirmed (Fig. 3). In order to evaluate the amount of coke deposited on the catalysts, TG analyses of fresh and used catalysts were performed. Fig. S1 depicts TG profiles for the fresh and used 20Ni/SiO₂, 6Cu-14Ni/SiO₂, and 20Cu/SiO₂. The reaction conditions for the used catalysts were the same as those shown in Table 1, and the fresh catalysts were also reduced before the TG analysis. Because the TG analyses were performed in air atmosphere, the weight increase in the profiles of fresh catalysts is attributed to the oxidation of Cu and/or Ni metal to the corresponding metal oxide(s). The weight attributed to coke was calculated by subtracting the weight loss of the fresh catalyst from that of the used one. The weight of coke in 20Ni/SiO₂, 6Cu-14Ni/SiO₂, and 20Cu/SiO₂ was found to be 3.2, 5.5, and 9.0 wt.%, respectively. This indicates that coke is easily accumulated on 20Cu/SiO₂, but difficult to be accumulated on the catalysts with high Ni loadings such as 20Ni/SiO₂ and 6Cu-14Ni/SiO₂ and 6Cu-14Ni/SiO₂ and 6Cu-14Ni/SiO₂ and focu-14Ni/SiO₂ focu-14Ni/SiO₂ focu-14Ni/SiO₂ and focu-14Ni/SiO₂ f

Table 2 compares the reaction result in this study with those in the previous reports. Although almost quantitative yields of GVL are obtained over Ru/C [10], Cu/SiO₂ [11], and Ni/TiO₂ [15], the productivities of these catalysts are low. The highest GVL productivity in previous reports is 0.91 kg_{GVL} kg_{cat}.⁻¹ h⁻¹ achieved over Ni/ZSM-5 [13], whereas the selectivity to GVL is relatively low. In contrast, in the present study, 6Cu-14Ni/SiO₂ gave GVL yield higher than 99% with a high productivity of 1.64 kg_{GVL} kg_{cat}.⁻¹ h⁻¹ for 50 h.

4. Conclusions

A 6Cu-14Ni/SiO₂ catalyst gave a high activity for the hydrogenation of LA to GVL at high WHSV conditions under ambient H₂ pressure. The enhanced activity of Cu-Ni bimetallic catalysts would be attributed to both inhibition of carbon accumulation by Ni and inhibition of LA decomposition by Cu. In contrast to the catalysts in previous reports, the 6Cu-14Ni/SiO₂ catalyst exhibited high catalytic performance: GVL yield higher than 99% with a high productivity of 1.64 $kg_{GVL} kg_{cat}$.⁻¹h⁻¹ at 250 °C and a WHSV of 1.65 h⁻¹ for 50 h.

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Catalyst	Conversion		GVL yield				
	/mol%	GVL	Acetone	MEK	ALs	others	/mol%
20Ni/SiO ₂	94.2	92.2	0.6	0.3	0.3	4.7	86.8
4Cu-16Ni/SiO ₂	97.8	98.2	0	0.3	0	1.5	96.1
5Cu-15Ni/SiO ₂	98.2	97.9	1.0	0.4	0	0.7	96.2
6Cu-14Ni/SiO ₂	99.1	99.2	0.1	0.2	0	0.6	98.2
7Cu-13Ni/SiO ₂	98.5	99.3	0.1	0.2	0	0.4	97.8
8Cu-12Ni/SiO ₂	98.1	98.3	0.6	0.1	0	1.0	96.5
14Cu-6Ni/SiO ₂	83.8	99.0	0.1	0	0.3	0.5	83.0
16Cu-4Ni/SiO ₂	66.7	96.6	0.5	0	1.5	1.3	64.6
20Cu/SiO ₂	22.0	25.5	0	0	57.1	9.6	6.4
20Cu/SiO ₂ ^a	73.4	75.4	0	0	9.9	13.7	55.3

Table 1 The hydrogention of LA to GVL over SiO₂-supported Cu, Ni and Cu-Ni bimetallic catalysts.

Conversion and selectivity were averaged between 0-8 h of TOS. Reaction conditions: H_2 flow rate, 30 cm³ min⁻¹; reaction temperature, 250 °C; WHSV, 6.60 h⁻¹. The catalyst was reduced in H_2 flow at 300 °C except 400 °C for 20Ni/SiO₂ for 1 h prior to the reaction.

GVL, γ -valerolactone; MEK, methyl ethyl ketone; ALs, angelicalactones. Others included pentanoic acid, pentenoic acid, and γ -butyrolactone.

^a The reaction was performed at a WHSV of 3.30 h^{-1} .

Catalyst	Temp.	H ₂ pressure	WHSV	TOS	GVL select.	GVL yield	Productivity	Ref.
	(°C)	(bar)	(h ⁻¹)	(h)	(%)	(%)	$kg_{GVL} kg_{cat.}^{-1} h^{-1}$	
Pd/C	265	1	0.512	50	90	90	0.46	10
Ru/C	265	1	0.512	50	98.6	98.6	0.50	10
Cu/SiO ₂	265	10	0.513	100	99.9	99.9	0.51	11
Cu/Al ₂ O ₃	265	1	0.169	-	87	85	0.14	12
Ni/ZSM-5	250	1	1.13	-	92.2	92.2	0.91	13
Ni/SiO ₂	250	1	1.13	-	87	87	0.87	14
Ni/TiO ₂	270	1	3.25 ^a	-	99.1	99.1	0.58	15
Cu-Ni/SiO ₂ ^b	285	1 ^c	0.512	100	96	95.0	0.49	16
6Cu-14Ni/SiO ₂	250	1	1.65	50	100	99.4	1.64	This study
6Cu-14Ni/SiO ₂	250	1	6.60	8	99.2	98.2	6.48	This study

Table 2 Vapor-phase hydrogention of LA to GVL over various catalysts.

 a GHSV, cm³ g_{cat}⁻¹ s⁻¹;

^bCu:Ni:SiO₂=60:20:20 weight ratio;

^c Formic acid and nitrogen were used instead of hydrogen.



Fig. 1 TPR profiles of the 20Ni/SiO₂, 20Cu/SiO₂ and Ni-Cu/SiO₂ with different Ni and Cu loadings.



Fig. 2 XRD patterns of $20Cu/SiO_2$, $6Cu-14Ni/SiO_2$ and $20Ni/SiO_2$ after reduction. The reduction temperature of $20Cu/SiO_2$, $6Cu-14Ni/SiO_2$, and $20Ni/SiO_2$ was 300, 300, 400 °C, respectively.



Fig. 3 Change in the conversion in-the reactions over different catalysts with time on stream. Open square, 20Ni/SiO₂; closed square, 4Cu-16Ni/SiO₂; open circle, 6Cu-14Ni/SiO₂; closed circle, 14Cu-6Ni/SiO₂; open triangle, 16Cu-4Ni/SiO₂, closed triangle, 20Cu/SiO₂.

Reaction conditions: H₂ flow rate, 30 cm³ min⁻¹; reaction temperature, 250 °C; WHSV, 6.60 h⁻¹.



Fig. 4 Change in the conversion and selectivity in a long-run reaction over 6Cu-14Ni/SiO₂. Reaction conditions: H_2 flow rate, 30 cm³ min⁻¹; reaction temperature, 250 °C; WHSV, 1.65 h⁻¹.

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Highlights

- 1. Hydrogenation of levulinic acid to γ -valerolactone was performed over Cu-Ni bimetallic catalyst.
- 2. SiO₂-supported Cu-Ni bimetallic catalysts shows stable catalytic activity in H₂ flow at 250 °C.
- 3. An excellent γ -valerolactone yield higher than 98% was obtained at Cu/Ni weight ratio of 6/14.
- 4. A high γ -valerolactone productivity of 1.64 kg kg_{cat}⁻¹ h⁻¹ was obtained at a high WHSV of 1.65 h⁻¹.
- 5. Inhibition of carbon deposition by Ni and high selectivity of Cu improved the catalyst performance.

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