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 SiO_2-supported Cu-Ni bimetallic catalysts with different Cu/Ni weight ratios under ambient H_2 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/SiO_2 and Cu/SiO_2, the $Cu-Ni/SiO_2$ 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 ℃ and at a high WHSV of 1.65 h^{-1} for 50 h.

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

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 ℃ 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/ZrO_2 or Cu/Al_2O_3 at 200 ℃ 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/SiO_2 provided a GVL productivity of 0.87 $kg_{GVL} kg_{cat.}^{-1} h^{-1}$ with a GVL selectivity of 87% under ambient H_2 pressure conditions [14]. In contrast to Ni/SiO_2, Upare et al. reported a Cu/SiO_2 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 SiO_2 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. SiO_2 (CARiACT Q10 with mean pore diameters of 10 nm) was supplied by Fuji Silycia Chemical Ltd. $Cu(NO_3)_2 \cdot 3H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$, which were used as the precursors of the corresponding metals, were purchased from Wako Pure Chemical Industries, Japan.

SiO_2-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 SiO_2 was fixed at 20 wt.%. After impregnation, the samples were dried (110 ºC, 12 h) and calcined (300 ºC, 3 h). Hereafter, the prepared catalysts are expressed as xCu-yNi/SiO_2, where x and y indicate the weight percentage of the Cu and Ni metals, respectively. For example, 6Cu-14Ni/SiO_2 indicates 6 wt.% Cu and 14 wt.% Ni loaded on SiO_2.

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 H_2. Prior to the reaction, a catalyst (0.250g or 1.00g) was placed in the catalyst bed and reduced in H_2 flow at 300 ºC; although 400 ºC was used for 20Ni/SiO_2 for 1 h. LA was then fed through the top of the reactor at a liquid feed rate of 1.65 cm^3 h^{-1} together with H_2 (30 cm^3 min^{-1}). The liquid effluents were collected in a dry ice-acetone trap (-78 ºC) every hour and were analyzed by a FID-GC (GC-14B, Shimadzu) with a
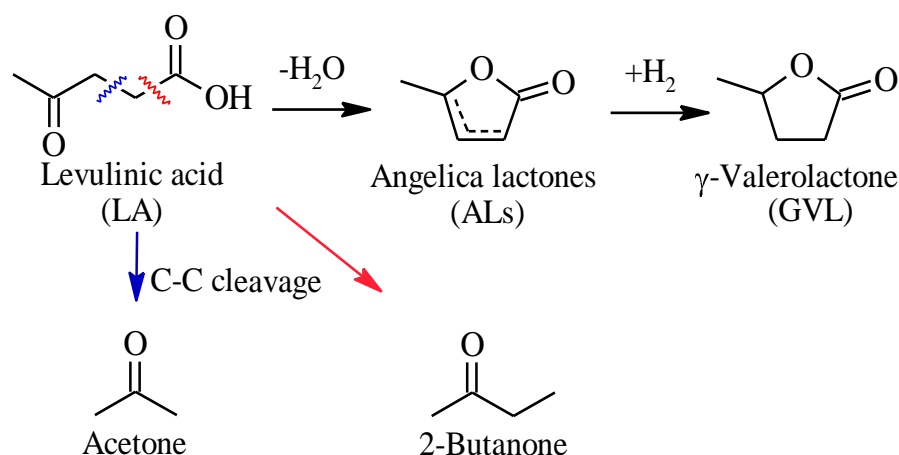
60-m capillary column of TC-WAX (GL-Science, Japan). A GC-MS (QP5050A, Shimadzu) was used for identification of the products in the effluent. n-Butanol was used as an internal standard.

2.3 Characterization of catalysts

The XRD patterns of samples were recorded on a D8 ADVANCE (Bruker, Japan) using Cu Kα 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 $^{\circ}$C min^{-1} from the room temperature to 900 $^{\circ}$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 H_2/N_2 (1/9, 10 cm^3 min^{-1}) with a heating rate of 5 $^{\circ}$C min^{-1} and a temperature range from 25 to 900 $^{\circ}$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/SiO$_2$ shows a broad signal at *ca.* 350 $^{\circ}$C, while 20Cu/SiO$_2$ and Cu-Ni bimetallic catalysts show a sharp signal at *ca.* 220 $^{\circ}$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/SiO$_2$ and Cu-Ni/SiO$_2$ catalysts was determined to be 300 $^{\circ}$C, while that of 20Ni/SiO$_2$ was determined to be 400 $^{\circ}$C. Fig. 2 shows the XRD patterns of 20Ni/SiO$_2$, 20Cu/SiO$_2$ and 6Cu-14Ni/SiO$_2$ catalysts after reduction. The diffraction reflections observed at 43.5° and 50.4° are attributed to Cu metal, while the reflections observed at 44.5° 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/SiO$_2$, which suggests that Cu-Ni alloy was either highly dispersed or not formed.

4

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 H_2 flow with a flow rate of 30 ml min^{-1} at 250 ℃ 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/SiO$_2$ 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/SiO$_2$ gave a GVL selectivity of 99.9% at a WHSV of 0.513 h^{-1} under 1 MPa H_2 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 H_2 flow conditions, SiO$_2$-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 SiO$_2$ efficiently catalyzed the cyclodehydration of LA to ALs in the vapor phase at a temperature range of 250-300 ℃ [21]. Therefore, it is reasonable that the ALs are generated over SiO$_2$ as an intermediate, whereas the hydrogenation ability of Cu is insufficient to efficiently convert ALs to GVL under ambient H_2 pressure and high WHSV conditions. In order to confirm the speculation,

the reaction over $20Cu/SiO_2$ 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 $20Cu/SiO_2$, $20Ni/SiO_2$ 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 γ-butyrolactone were formed as by-products over $20Ni/SiO_2$ and this decreased the observed selectivity to GVL. In the case of $20Cu/SiO_2$, however, no decomposition product was detected, indicating the inactivity of Cu for the C-C cleavage of LA. The SiO_2-supported Cu-Ni bimetallic catalysts showed different catalytic activity depending on the Cu/Ni weight ratio. Compared with $20Ni/SiO_2$, 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 $14Cu-6Ni/SiO_2$ and $16Cu-4Ni/SiO_2$ 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/SiO_2 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 $20Cu/SiO_2$, $20Ni/SiO_2$ and Cu-Ni/SiO_2 with different Ni and Cu loadings. $20Cu/SiO_2$ showed low conversions as well as a low stability: the conversion over Cu/SiO_2 gradually decreased from 25.6% to 9.7% during 8 h. Since ALs easily polymerize to form coke [21], the catalytic deactivation of $20Cu/SiO_2$ is considered to be attribed to the large amount of intemediate ALs due to low hydrogenation ability of Cu. Cu-Ni/SiO_2 bimetallic catalysts showed enhanced catalytic activity compared to $20Cu/SiO_2$, 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 $20Ni/SiO_2$, $6Cu-14Ni/SiO_2$, and $20Cu/SiO_2$. 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 $20Ni/SiO_2$, $6Cu-14Ni/SiO_2$, and $20Cu/SiO_2$ was found to be 3.2, 5.5, and 9.0 wt.%, respectively. This indicates that coke is easily accumulated on $20Cu/SiO_2$, but difficult to be accumulated on the catalysts with high Ni loadings such as $20Ni/SiO_2$ and $6Cu-14Ni/SiO_2$. As the $20Cu/SiO_2$ catalyst deactivated rapidly compared to both the $20Ni/SiO_2$ and $6Cu-14Ni/SiO_2$ catalysts, the formation of coke is considered to cause the catalytic deactivation primarily.

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/SiO_2 [11], and Ni/TiO_2 [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, $6Cu-14Ni/SiO_2$ 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/SiO$_2$ catalyst gave a high activity for the hydrogenation of LA to GVL at high WHSV conditions under ambient H$_2$ 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/SiO$_2$ catalyst exhibited high catalytic performance: GVL yield higher than 99% with a high productivity of 1.64 kg$_{GVL}$ kg$_{cat.}^{-1}$ h^{-1} at 250 ^{o}C and a WHSV of 1.65 h^{-1} for 50 h.

Acknowledgement

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Table 1 The hydrogention of LA to GVL over SiO_2-supported Cu, Ni and Cu-Ni bimetallic catalysts.

Catalyst	Conversion /mol%	Selectivity/mol%					GVL yield /mol%
		GVL	Acetone	MEK	ALs	others	
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

Conversion and selectivity were averaged between 0-8 h of TOS. Reaction conditions: H_2 flow rate, 30 cm^3 min^{-1}; reaction temperature, 250 $^\circ$C; WHSV, 6.60 h^{-1}. The catalyst was reduced in H_2 flow at 300 $^\circ$C except 400 $^\circ$C for 20Ni/SiO$_2$ 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}.

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

Catalyst	Temp. (^{o}C)	H$_2$ pressure (bar)	WHSV (h^{-1})	TOS (h)	GVL select. (%)	GVL yield (%)	Productivity kg$_{GVL}$ kg$_{cat.}^{-1}$ h^{-1}	Ref.
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

[a] GHSV, cm^3 g$_{cat}^{-1}$ s^{-1};

[b] Cu:Ni:SiO$_2$=60:20:20 weight ratio;

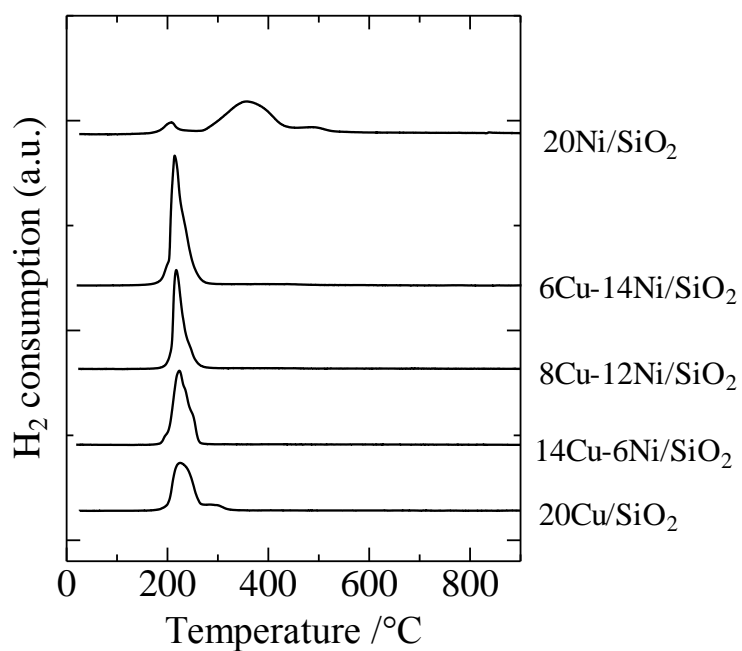[c] Formic acid and nitrogen were used instead of hydrogen.

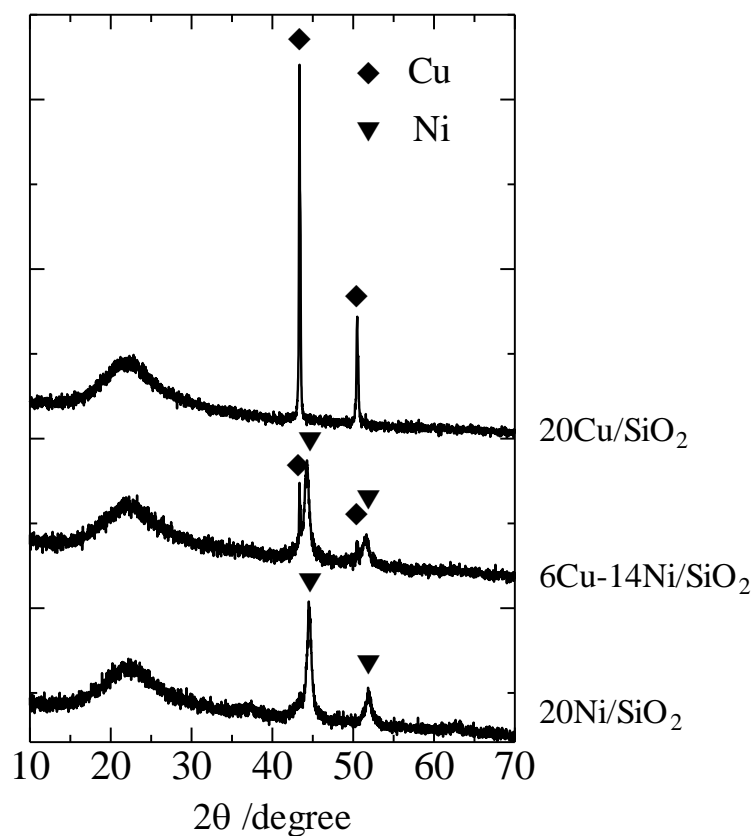Fig. 1 TPR profiles of the $20Ni/SiO_2$, $20Cu/SiO_2$ and $Ni-Cu/SiO_2$ with different Ni and Cu loadings.

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 ℃, respectively.
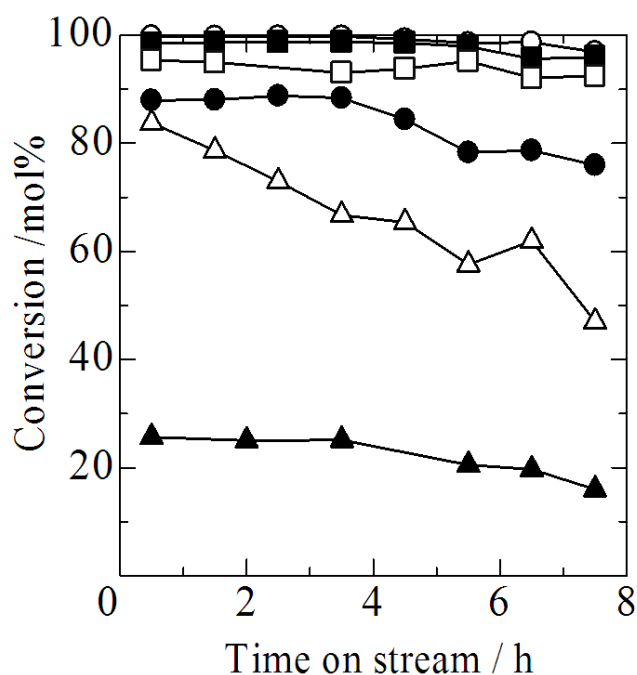
Fig. 3 Change in the conversion in–the reactions over different catalysts with time on stream. Open square, 20Ni/SiO$_2$; closed square, 4Cu-16Ni/SiO$_2$; open circle, 6Cu-14Ni/SiO$_2$; closed circle, 14Cu-6Ni/SiO$_2$; open triangle, 16Cu-4Ni/SiO$_2$, closed triangle, 20Cu/SiO$_2$.

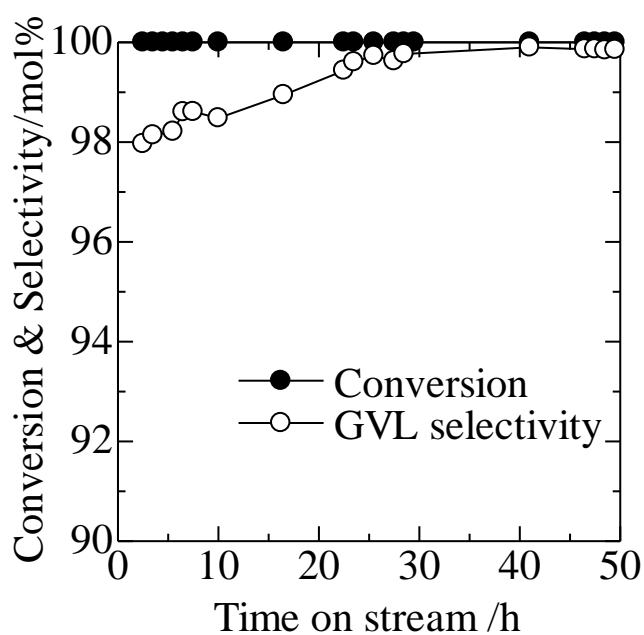Reaction conditions: H$_2$ flow rate, 30 cm^3 min^{-1}; reaction temperature, 250 °C; WHSV, 6.60 h^{-1}.

Fig. 4 Change in the conversion and selectivity in a long-run reaction over 6Cu-14Ni/SiO$_2$.

Reaction conditions: H$_2$ flow rate, 30 cm^3 min^{-1}; reaction temperature, 250 °C; WHSV, 1.65 h^{-1}.