



Editor's choice paper

Vapor-phase hydrogenation of levulinic acid and methyl levulinate to γ -valerolactone over non-noble metal-based catalysts



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ABSTRACT

Vapor-phase hydrogenation of levulinic acid (LA) and methyl levulinate (ML) to γ -valerolactone (GVL) was performed over non-noble metal-based catalysts such as Cu/Al₂O₃, Ni/SiO₂ and Co/SiO₂. The catalytic activity and stability of the Cu-, Ni- and Co-based catalysts for the formation of GVL from ML and LA were investigated and compared at a low contact time of 0.3 h. In the hydrogenation of ML to GVL, the order of the catalytic activity for the conversion of ML was Cu/Al₂O₃ > Co/SiO₂ > Ni/SiO₂. Cu/Al₂O₃ was the most selective for the formation of GVL, whereas it was unstable in contrast to the other catalysts. In the hydrogenation of LA to GVL, the order of the catalytic activity for the conversion of LA was Ni/SiO₂ > Cu/Al₂O₃ > Co/SiO₂, which is the same as the order of the catalyst stability, while Cu/Al₂O₃ was the most selective for the formation of GVL from LA. The reactions were also performed in N₂ atmosphere in order to study the reaction pathways. Methyl 4-hydroxypentanoate was supposed to be the intermediate in the hydrogenation of ML to GVL, whereas the reaction pathways in the hydrogenation of LA to GVL were dependent on the catalyst species. Based on the TG analysis of the used catalysts, it was found that LA led to more severe catalyst deactivation than ML did.

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1. Introduction

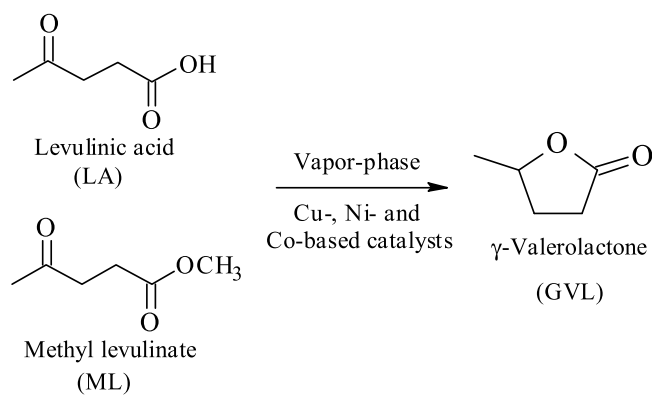
Currently, the energy and chemical industries are highly dependent on the use of fossil resources, which have caused serious global environmental problems. Renewable biomass is attractive as an alternative resource for the production of either energy or chemicals, and many efforts in relation to the application of biomass have been made for the last decade [1–3]. Biomass-derivable levulinic acid (LA) is an attractive platform molecular for producing various useful chemicals including γ -valerolactone (GVL), which has many uses as either a solvent or an intermediate [4–7]. Liquid-phase hydrogenation of LA to GVL were intensively reported over either noble metals, such as Ru [8–16], Ir [17], and Pd [18–20], or non-noble metals such as Cu [21–24] and Ni [21,25]. Higher than 97% yield of GVL was achieved over Ru [8], Pd [20], or Cu [23] catalyst, whereas Ru and Pd could work at temperatures lower than Cu. Levulinic acid ester (levulinate), which can be easily synthesized by the esterification of LA with an alcohol even at room temperature [26], is also considered as an attractive feedstock of GVL. Transi-

tion metals such as Ru [27,28], Pd [29], Cu [30] and Co [31] have been reported to be effective for the liquid-phase hydrogenation of levulinate to GVL, and ca. 90% yield of GVL are obtained.

In contrast to the liquid-phase reactions, vapor-phase hydrogenation of LA to GVL was less studied. Vapor-phase continuous processes have been reported using non-noble metals such as Cu and Ni as the catalysts [32–37], and GVL yields higher than 90% could be obtained over Cu- [32] and Ni-based catalysts [35,37]. However, because the above reported vapor-phase processes were performed under low WHSV conditions with low GVL productivities, it is difficult to distinguish and compare the activity and the stability of these catalysts. In a recent report of our group, SiO₂-supported Cu-Ni bimetallic catalyst showed a high and stable catalytic activity at a high WHSV of 1.65 h⁻¹, and the yield of GVL was higher than 99% at a time on stream of 50 h [38]. In the case of the hydrogenation of levulinate to GVL, however, vapor-phase continuous processes have not been reported. In addition, the catalytic behavior of Co in the hydrogenation of either LA or levulinate to GVL is less reported although Co is well used as a metal catalyst. The use of base metal catalysts with low cost is the realistic way for industrial applications, therefore, we consider that it is necessary and important to compare the activity of the base metals under the same severe reaction conditions.

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Scheme 1. Formation of γ -valerolactone from levulinic acid and methyl levulinate.

In this study, as shown in [Scheme 1](#), vapor-phase hydrogenation of either LA or methyl levulinate (ML) to GVL was studied using Cu-, Ni- and Co-based catalysts at a low contact time, W/F, of 0.3 h where W and F are the catalyst weight and the feed rate of reactant, respectively. The catalytic activity and stability of these catalysts in each reaction were compared. Furthermore, the reaction pathways in the formation of GVL from LA and ML over different catalysts were investigated and proposed.

2. Experimental

2.1. Samples

LA and ML were purchased from Tokyo Chemical Industries Co., Ltd, and they were used for the catalytic reaction without further purification. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, which were used as the precursors of the corresponding metals, were purchased from Wako Pure Chemical Industries, Ltd. SiO_2 (CARIACT Q10 with mean pore diameters of 10 nm, $S_{\text{BET}} = 295 \text{ m}^2 \text{ g}^{-1}$) was supplied by Fuji Silicia Chemical Ltd. Al_2O_3 (N611N, $S_{\text{BET}} = 210 \text{ m}^2 \text{ g}^{-1}$) and $\text{SiO}_2\text{-Al}_2\text{O}_3$ (N631L, $S_{\text{BET}} = 440 \text{ m}^2 \text{ g}^{-1}$) were purchased from Nikki Chemical Co., Ltd. Active carbon (A-BAC-LP, $S_{\text{BET}} = 1100\text{--}1300 \text{ m}^2 \text{ g}^{-1}$) was supplied by Kureha Corporation.

Metal-loaded catalysts were prepared by an incipient wetness impregnation method. An aqueous solution (ca. 15 cm^3) of metal nitrate with a prescribed amount was firstly prepared. About 0.3 cm^3 of the solution was dropped onto ca. 4 g of the support (pore volume, ca. $1 \text{ cm}^3 \text{ g}^{-1}$) in an operation, and then the water was evaporated at 70°C by illuminating samples using a 350-W electric light bulb at ambient pressure. Such an operation was repeated until all of the solution was dropped. After the impregnation process, the samples were dried at 110°C for 12 h, and then calcined at 300°C for 3 h. Hereafter, the prepared catalysts are named as x-A/B, where A indicates the species of the supported metal; B indicates the support; x means the weight percentage of the supported metal A. For example, 20-Co/ Al_2O_3 means a catalyst with 20 wt.% Cu loaded on Al_2O_3 support.

2.2. Catalytic reaction

Vapor-phase hydrogenation of LA and ML was conducted using a fixed-bed down-flow glass reactor with an inner diameter of 17 mm at ambient H_2 pressure conditions. Before starting the reaction, 0.5 g catalyst was placed on the catalyst bed and preheated in H_2 flow at a prescribed temperature for 1 h in order to reduce the metal oxide species, and then the temperature was controlled to a determined reaction temperature. The reduction temperature for Cu-, Ni- and Co-based catalysts were 260, 380 and 380°C , respectively.

Table 1
Hydrogenation of ML over Co-supported catalysts^a.

Catalyst	Conversion ^b /mol%	Selectivity ^b /mol%			
		GVL ^c	BL ^d	MP ^e	Others ^f
20-Co/ SiO_2	92.7	83.9	0.0	0.2	15.9
20-Co/ Al_2O_3	5.6	0	0	0	100
20-Co/ $\text{SiO}_2\text{-Al}_2\text{O}_3$	26.2	74.8	5.5	2.6	17.1
20-Co/C	75.7	76.8	0.0	0.0	23.2

^a Reaction conditions: reaction temperature, 240°C ; H_2 flow rate, $30 \text{ cm}^3 \text{ min}^{-1}$; W/F, 0.3 h.

^b Conversion and selectivity are averaged between 1–5 h.

^c GVL, γ -valerolactone.

^d BL, γ -butyrolactone.

^e MP, methyl pentanoate.

^f Others represent the unidentified products.

The reduction temperatures of these catalysts were determined according to the H_2 temperature-programmed reduction measurements [38]. After that, either pure LA or ML was fed through the top of the reactor with a liquid feed rate of 1.65 g h^{-1} together with an H_2 flow of $30 \text{ cm}^3 \text{ min}^{-1}$. The liquid effluents were collected in a dry ice-acetone trap (-78°C) every hour, and they were analyzed using a FID-GC (GC-14B, Shimadzu, Japan) with a 60-m capillary column of TC-WAX (GL-Science, Japan). The products in the effluents were identified using a GC-MS (QP5050A, Shimadzu). 1-Butanol was used as an internal standard substance.

2.3. Characterization of catalysts

The XRD patterns of the samples were recorded on a D8 ADVANCE (Bruker, Japan) using Cu $K\alpha$ radiation. The thermo gravimetry-differential thermal analysis (TG-DTA) was performed using Thermoplus 8120E2 (Rigaku, Japan) for analyzing the amount of coke accumulated on the catalyst surface. The analysis conditions are as followings: sample weight, ca. 10 mg; the rate of the temperature increase, 5°C min^{-1} ; heating range, from the room temperature to 900°C .

3. Results and discussions

3.1. Hydrogenation of ML to GVL over Co-based catalysts

The catalytic behavior of Co-based catalysts in the hydrogenation of ML to GVL was initially investigated. Co was loaded on various supports, such as SiO_2 , Al_2O_3 , $\text{SiO}_2\text{-Al}_2\text{O}_3$, and active carbon, where the loading of Co was fixed at 20 wt.%. Compared to SiO_2 and Al_2O_3 , $\text{SiO}_2\text{-Al}_2\text{O}_3$ has strong acidity and the large amount of acid sites, which is confirmed by $\text{NH}_3\text{-TPD}$ analysis in our previous studies [39–41]. The reactions were performed at 240°C with an H_2 flow rate of $30 \text{ cm}^3 \text{ min}^{-1}$ and a W/F of 0.3 h. [Table 1](#) shows the reaction results, which are the average values between 1–5 h of time on stream, and the corresponding time-on-stream profiles are shown in Fig. S1 in the supplementary file. It is obvious that the catalytic activity is dependent on the species of the support. 20-Co/ Al_2O_3 showed poor activity, and gave a low ML conversion of 5.6%. 20-Co/ $\text{SiO}_2\text{-Al}_2\text{O}_3$ gave a ML conversion of 26.2%, and the selectivity to GVL was only 74.8% due to the formation of γ -butyrolactone (BL), methyl pentanoate (MP), and other unidentified products. As shown in [Scheme 2](#), BL was produced by the decomposition of ML via C–C bond cleavage, and MP was produced by the hydrogenolysis of ML. The relatively high selectivity to BL and MP over 20-Co/ $\text{SiO}_2\text{-Al}_2\text{O}_3$ was considered to be attributed to the strong acidity of $\text{SiO}_2\text{-Al}_2\text{O}_3$. 20-Co/C showed a conversion of 75.7%, whereas the selectivity to other products was as high as 23.2%. SiO_2 support showed the best performance, and 92.7% conversion with 83.9%

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