Vapor-phase conversion of γ-valerolactone over copper-based catalysts

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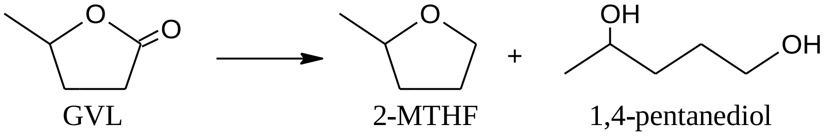
Abstract: Vapor-phase conversion of γ-valerolactone was performed over Cu-based catalysts such as Cu/Al_2O_3 in a pressured H_2 flow. γ-Valerolactone was converted to 2-methyltetrahydrofuran and 1,4-pentanediol depending on the calcination and reaction temperatures. Calcination temperature greatly affects the selectivity to products: high calcination temperature at 900 °C prefers the formation of 1,4-pentanediol, and low calcination temperature at 700 °C or lower prefers 2-methyltetrahydrofuran. In the formation of 2-methyltetrahydrofuran, the best performance was obtained over Cu/Al_2O_3 calcined at 700 °C: the selectivity was higher than 97% at a conversion of 81.1% at an H_2 pressure of 1.5MPa and 170 °C.

Keywords: γ-Valerolactone, 2-methyltetrahydrofuran, 1,4-pentanediol.

1. Introduction

Application of biomass resources for producing either energy or chemicals has attracted much attention in recent years[1]. γ-Valerolactone (GVL) is an attractive raw material to produce various important chemicals, and it can be derived from biomass resources such as cellulose and hemicellulose via levulinic acid[2]. GVL can be converted into 2-methyltetrahydrofuran (2-MTHF) and 1,4-pentanediol. Among these chemicals, 2-MTHF can be used as a bio-fuel and 1,4-pentanediol has a potential use to produce polyesters. Some researches have been made for the formation of 2-MTHF and 1,4-pentanediol from GVL[3-6], in which all the reactions are performed in liquid phase under H_2 pressures higher than 5 MPa. However, in the vapor phase, Cu/ZnO catalyst exhibits the conversion of GVL to 1,4-pentanediol at 140 °C and 1.5 MPa H_2 pressure[7]. Cu/ZnO calcined at 500 °C showed the highest 1,4-pentanediol selectivity over 99% at 82.3 % conversion. Only a few reports, as mentioned above, addressed the catalytic conversion of GVL to value-added chemicals. In this paper, we examined the vapor-phase conversion of GVL over several Cu-based catalysts under H_2 pressure, and found that Cu/Al_2O_3 catalysts had interesting catalytic features on this reaction.



2. Experimental

The hydrogenation of GVL was carried out using a fixed-bed stainless tube reactor under H_2 pressure. Prior to the reaction, a catalyst sample was preheated at 250 °C in an ambient H_2 flow in order to reduce the CuO species. After that, pure GVL was introduced to the reactor together at a feed rate of 0.4 g h^{-1} together with an H_2 flow at 1.5 MPa. The liquid effluents were collected in a dry ice-acetone trap every hour, and they were analyzed using a FID-GC (GC-2014, Shimadzu, Japan) with a 30-m capillary column of RtxR-Wax (GL-Science, Japan).

3. Results and discussion

In the previous report[7], calcination of Cu/ZnO at 500 °C is important for the selectivity to each product. Cu effectively catalyzes the hydrogenolysis of GVL to 1,4-pentanediol, and ZnO support exists without catalyzing other side reactions at 140 °C. Thus, the 1,4-pentanediol selectivity remains high value over 99%. At higher temperatures than 140 °C, however, 2-MTHF and 1-pentanol are produced. The reaction temperature as well as calcination temperature is an important factor for the selectivity.

In this work, CuO/Al_2O_3 catalysts were calcined at various temperatures. The catalysts were tested at 140 °C and 1.5 MPa H_2. The conversion of GVL was as low as 12 -14%, as the selectivity to 2-MTHF and 1,4-pentanediol is changed with calcination temperature, as shown in **Fig. 1**. At a calcination lower than 900 °C, the catalyst is composed of CuO crystallites and amorphous Al_2O_3 phase. At 900 °C, the catalyst sample was crystalized to $CuAl_2O_4$ phase, which was hardly reduced to metallic Cu species. After reduction at 250 °C, it is reasonable that the catalyst consists of Cu metal and Al_2O_3 or $CuAl_2O_4$. Cu metals efficiently work as hydrogenation catalyst to produce 1,4-pentanediol, as has been reported in the Cu/ZnO catalyst[7]. Al_2O_3 in the Cu/Al_2O_3 plays a role for cyclization of 1,4-pentanediol to produce 2-MTHF, whereas $CuAl_2O_4$ species has low acidity, which could not cyclize 1,4-pentanediol to 2-MTHF.

Fig. 2 shows the changes in conversion of GVL over CuO/Al_2O_3 calcined at 700 °C. At temperatures higher than 140 °C, the conversion of GVL increased with increasing the reaction temperature. The selectivity to 2-MTHF also increased with the increase in the reaction temperature while 1,4-pentanediol was readily cyclized to 2-MTHF. At a high temperature of 200 °C, 1-pentanol as a decomposition product was increased. A high 2-MTHF selectivity of 97.9% at the GVL conversion of 81.1% was attained at a low WHSV of 0.2 h^{-1} and 170 °C.

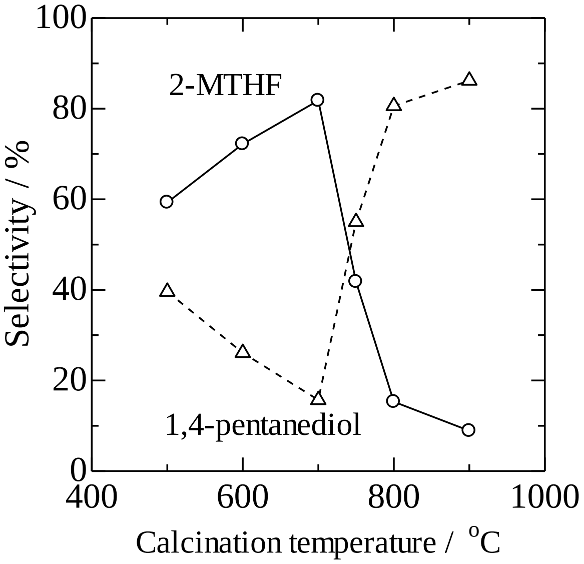


Figure 1. Effect of calcination temperature of CuO/Al_2O_3 at 140 °C (WHSV = 0.8 h^{-1}).

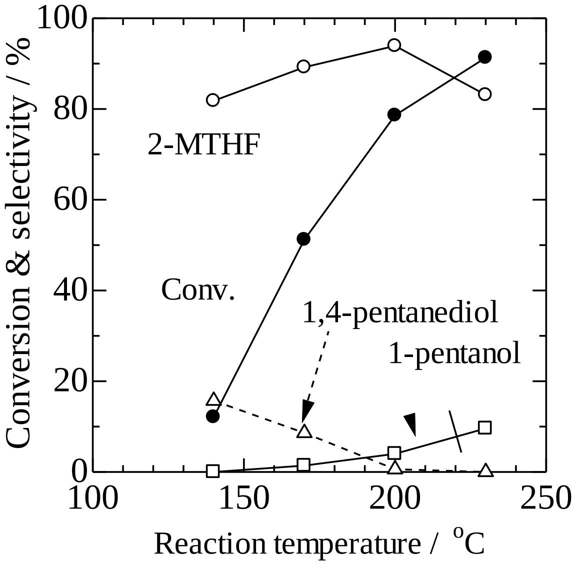


Figure 2. Effect of reaction temperature over Cu/Al_2O_3 calcined at 700 °C (WHSV = 0.8 h^{-1}).

4. Conclusions

Vapor-phase conversion of GVL was performed under H_2 pressure of 1.5 MPa using Cu/Al_2O_3 catalyst. Product selectivity was dependent on the calcination temperature of the catalyst. High selectivity to 2-MTHF was obtained over CuO/Al_2O_3 catalyst calcined at 700 °C, while high selectivity to 1,4-pentanediol was attained over the catalyst calcined at 900 °C. A high 2-MTHF selectivity of 97.9% was obtained over CuO/Al_2O_3 catalyst calcined at 700 °C with the GVL conversion of 81.1% at 170 °C.

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