Vapor-phase lactonization of levulinic acid into angelicalactones

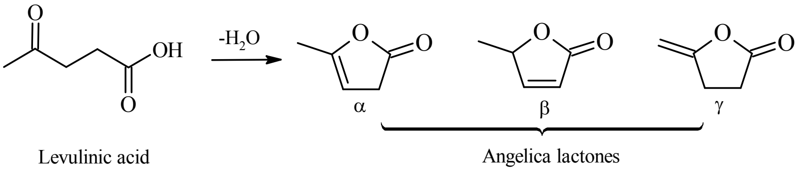
Daolai Sun,[a,b] **Yuta Takahashi,**[a] **Yasuhiro Yamada,**[a] **Satoshi Sato**[a,*]
[a]*Graduate School of Engineering, Chiba, 263-8522, Japan*
[b]*School of Chemical Engineering and Technology, Tianjin, 300130, China*
**Corresponding author. Fax number: +81 43 290 3401; E-mail address: satoshi@faculty.chiba-u.jp*

Abstract: Levulinic acid is an attractive chemical, which can be produced from lignocellulosic biomass, and it can be converted to many useful C5 chemicals including angelica lactones. Angelica lactones have a potential as raw materials for producing fuels and useful chemicals such as γ-valerolactone. In this study, we report a vapor-phase lactonization of levulinic acid to angelica lactones over solid catalysts under continuous flow conditions using a fixed-bed down flow reactor. The active species for angelica lactones formation from levulinic acid was investigated and the effect of the reaction conditions was also studied.

Keywords: levulinic acid, angelica lactones, cyclodehydration.

1. Introduction

Applications of renewable biomass provide facile routes to alleviate the shortage of fossil fuels as well as to reduce CO_2 emission. Levulinic acid (LA) is an attractive chemical, which can be produced from cellulose and hemicellulose as well as sugars presented in agricultural and forest residues. Many useful C5 chemicals, such as angelica lactones (ALs), γ-valerolactone, 1,4-pentanediol and 2-methyltetrahydrofuran, can be derived from LA. Among these chemicals, ALs have important uses in various fields, whereas the selective conversion of LA to ALs has rarely been reported.



Scheme 1 Lactonization of levulinic acid to angelica lactones.

ALs include three kinds of isomers, α-, β- and γ-angelica lactone. Recently, the conversion of ALs to C6-C13 gasoline-like hydrocarbons has attracted much attention[1,2]. As a result, ALs are expected to be a novel feedstock for the production of chemicals and fuels. In some previous studies, production of ALs from LA was performed under distillation conditions, and ALs yields higher than 90% could be achieved in the presence of either montmorillonite clay[1] or H-ZSM5[2].

In this study, we firstly report a vapor-phase lactonization of LA to ALs over solid catalysts under continuous flow conditions using a fixed-bed down flow reactor. The active species for ALs formation from LA was investigated and the effect of the reaction conditions was also studied.

2. Experimental

Various commercial catalysts, such as SiO_2, Al_2O_3, SiO_2-Al_2O_3, TiO_2, and ZrO_2 were tested in the reactions. Typically, the reactions were performed in a fixed-bed down-flow glass reactor with an inner diameter of 17 mm at an ambient pressure of N_2. Prior to the reaction, a catalyst of 0.5 g was placed in the catalyst bed and heated at a prescribed temperature for 1 h. After that, LA or its aqueous solution was fed through the top of the reactor at a liquid feed rate of 1.2 g h^{-1}. In the reactions under reduced pressure conditions, a vacuum pump was connected with the bottom of the reactor without using a carrier gas. The liquid effluents collected every hour were analyzed by a FID-GC. A GC-MS was used for identification of the collected products. Temperature-programmed desorption (TPD) of adsorbed NH_3 and diffuse reflectance infrared Fourier-transform (DRIFT) analysis were performed for characterizing the catalysts.

3. Results and discussion

The reactions were performed at 250 °C. The main products were α-, β- and γ-AL in all the reactions. The total selectivity to ALs exceeded 50% in each reaction, and the residual selectivity was assigned to the undetectable products. The reaction did not proceed in the absence of a catalyst. SiO_2 catalyst showed the highest ALs selectivity of 95.0% among the catalysts. SiO_2-Al_2O_3 showed the highest conversion of LA and the highest ALs yield. TiO_2 was not so active, and the conversion of LA was as low as 10.6%. MFI and HY zeolites gave relatively high conversions of LA, whereas the selectivities to ALs were lower than 80%. ZrO_2 and γ-Al_2O_3, which have both acidic and basic property, showed poor activity and gave ALs selectivity lower than 60%. Because Brønsted acid catalysts such as SiO_2 and SiO_2-Al_2O_3 showed high acitivity, Brønsted acid sites are proposed to be efficient for catalyzing the lactonization of LA to ALs.

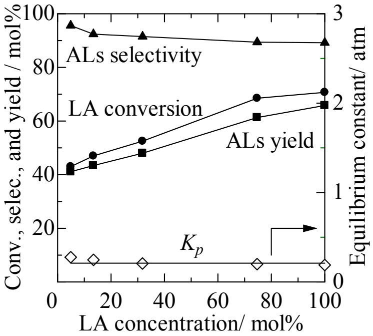


Figure 1 Changes in activity of SiO_2 with the concentration of LA aqueous solution at 275 °C.

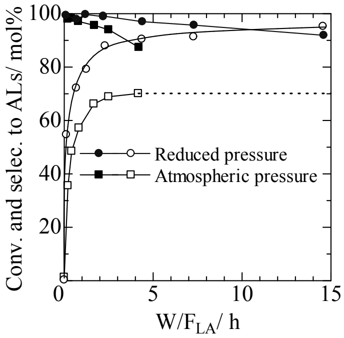


Figure 2 Changes in catalytic activity of SiO_2 with W/F_{LA} under atmospheric and reduced pressure conditions at 275°C. Open symbols, conversion of LA; Closed symbols, selectivity to ALs.

In order to study the reaction equilibrium in LA lactonization to ALs, reactions were performed over SiO_2 using aqueous LA solutions with different LA concentrations at 275 °C (Fig. 1). The catalyst weight was changed with the concentration of LA in order to achieve a constant W/F_{LA} (Weight of catalyst/ Feed rate of LA) of 3.6 h. Because decreasing the amount of water in the reaction system shifts the equilibrium from LA to ALs and water, the conversion of LA and the yield of ALs increases with increasing the concentration of LA. Each reaction showed similar values of pressure equilibrium constant, *ca.* 0.2 atm at 275 °C, which indicates that the equilibrium was achieved in the reactions at a W/F_{LA} of 3.6 h.

The lactonization of LA to ALs was also performed over SiO_2 under reduced pressure conditions. Fig. 2 compares the changes in catalytic activity of SiO_2 with W/F_{LA} under atmospheric and reduced pressure conditions. At a same W/F_{LA}, the conversion under reduced pressure conditions was much higher than that under atmospheric pressure conditions, which is because a reduced pressure is efficient for shifting the equilibrium from LA to ALs and water in such a reaction with increased molecule number. The selectivity to ALs under reduced pressure conditions was also higher than that under atmospheric conditions at a same W/F_{LA}. It is proposed that reduced pressures could induce the desorption of ALs from SiO_2, and this would inhibit the further oligomerization of ALs. At a W/F_{LA} of 14.6 h, a high ALs yield of 87.5% with a LA conversion of 95.3% was achieved under reduced pressure conditions.

4. Conclusions

Lactonization of LA was investigated in flow reactors. Lactonization of LA to ALs is an equilibrium reaction, and the pressure equilibrium constant is *ca.* 0.2 atm. Lactonization of LA to ALs can be efficiently catalyzed by SiO_2 catalyst at 275 °C. Reduced pressure conditions are effective for shifting the equilibrium from LA to ALs, and ALs yield of 87.5% could be achieved under reduced pressure conditions.

References

1. M. Mascal, S. Dutta, I. Gandarias, Angew. Chem. Int. Ed. 53 (2014) 1854.
2. J. Xin, S. Zhang, D. Yan, O. Ayodele, X. Lu, J. Wang, Green Chem. 16 (2014) 3589-3595.