One-pot synthesis of 2-pyrrolidone from pyroglutamic acid and glutamic acid using Ru/Al_2O_3

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Abstract: Pyroglutaminol was selectively converted into 2-pyrrolidone over Ru/Al_2O_3 catalyst in 1 MPa of H_2, while this reaction did not proceed under 1 MPa of N_2. It is proposed that methylol group in pyroglutaminol was eliminated through oxidative dehydrogenation into aldehyde groups, followed by rapid decarbonylation. One-pot synthesis of 2-pyrrolidone from pyroglutamic acid was examined to show that Ru/Al_2O_3 brought high yield of 2-pyrrolidone (62.6 %) in 2 MPa of H_2. The reaction from glutamic acid was also observed.

Keywords: glutamic acid, 2-pyrrolidone, ruthenium.

1. Introduction

Nitrogen-containing organic compounds have been produced through the insertion of ammonia into fossil-based and bio-based molecules in high pressure and temperature. In place of these processes consuming energy and resources, amino acid constituents are believed to be converted into the important chemical compounds. Glutamic acid is commercially produced through fermentation of saccharides extracted from sugarcane, corn, cassava, *etc.*[1]. In addition, the chemical process and the extraction from plant biomass can increase the mass of glutamic acid. Therefore, glutamic acid has potential as a raw material of nitrogen-containing organic compounds.

Herein, we describe an approach to produce 2-pyrrolidone from pyroglutamic acid, which is easily formed through non-catalytic cyclocondensation of glutamic acid under high pressure of hydrogen at 433 K without adjustment of pH (Figure 1). 2-pyrrolidone has been utilized as a solvent, and feedstock of polymers and pharmaceutical medicines in the chemical industry. In this study, the activities of noble metal catalysts were compared in the reaction of pyroglutaminol. Ru/Al_2O_3 showed remarkably high yield of 2-pyrrolidone, and therefore, one-pot synthesis from pyroglutamic acid and glutamic acid was examined.

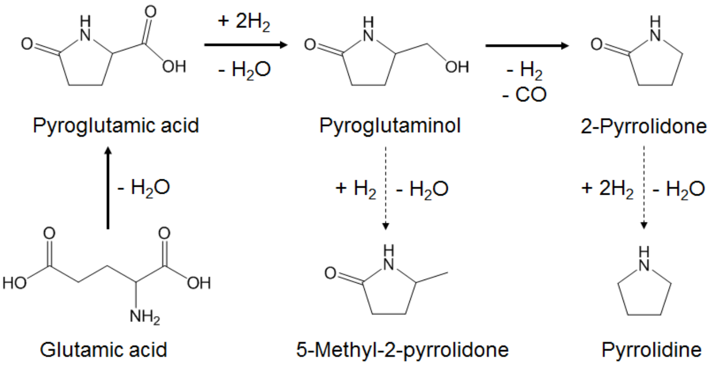

Figure 1. Proposed reaction pathways in conversion of pyroglutamic acid into 2-pyrrolidone

2. Experimental

The catalysts were prepared by impregnation method in aqueous solutions of metal chlorides of Ru, Pt, Pd and Rh. Al_2O_3 (JRC-ALO-6, Catalyst Society of Japan) was stirred in the solution for 1 h at room temperature. After evaporation of water at 343 K, the catalysts were dried at 383 K overnight and calcined at 773 K for 3 h in air. The metal loading on catalysts was 8 wt.%. In a typical reaction, an aqueous solution of pyroglutaminol or pyroglutamic acid (0.026 mol L^{-1}, 50 mL) and a catalyst (0.2 g) were mixed in an autoclave reactor (120 mL). After sealing, the interior atmosphere was purged and filled with H_2 or N_2. The solution was stirred and heated for 4 h at the desired reaction temperature. The catalyst was separated from the solution by centrifugation, and the product solution was analyzed by FID-GC.

3. Results and discussion

Figure 2 shows the yields of products over the supported metal catalysts under 1 MPa of N_2 and H_2 at 423 K. In N_2, Pt/Al_2O_3 exhibited moderate yields of 2-pyrrolidone and 5-methyl-2-pyrrolidone, while the other catalysts showed no activity. However, in H_2 atmosphere, even Pt/Al_2O_3 did not show catalytic activity, whereas Ru/Al_2O_3 exhibited extremely high yield of 2-pyrrolidone and formed a small amount of pyrrolidine and 5-methyl-2-pyrrolidone. It tells us that the elimination of methylol group in pyroglutaminol proceeded on Ru/Al_2O_3 in H_2 atmosphere but difficult in N_2. It is speculated that the methylol group in pyroglutaminol was converted into aldehyde group through oxidative dehydrogenation, followed by rapid decarbonylation of the aldehyde groups, and therefore 2-pyrrolidone was formed over Ru/Al_2O_3.

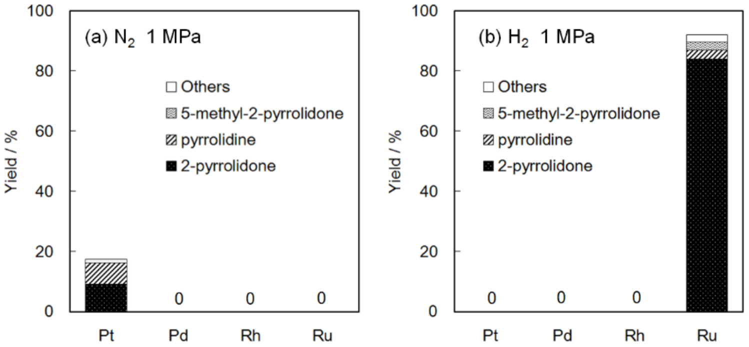

Figure 2. Yield of products in conversion of pyroglutaminol using supported metal catalysts in (a) N_2 or (b) H_2. Initial pressure: 1 MPa, temperature: 423 K.

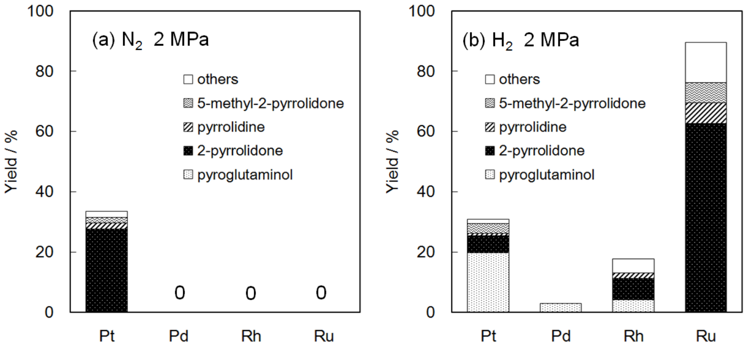

Figure 3. Yield of products in conversion of pyroglutamic acid using supported metal catalysts in (a) N_2 or (b) H_2. Initial pressure: 2 MPa, temperature: 448 K.

Figure 3 shows the yields of products of the reaction of pyroglutamic acid under 2 MPa of N_2 and H_2 at 448 K. In N_2, Pt/Al_2O_3 formed 2-pyrrolidone as a main product, but pyroglutaminol was not formed. The other catalysts did not show the catalytic activity. In H_2 atmosphere, Pt/Al_2O_3 formed pyroglutaminol as a main product, while the yield of 2-pyrrolidone was lower than that in N_2 atmosphere. Rh/Al_2O_3 showed higher catalytic activity than the supported Pd catalyst and formed 2-pyrrolidone as a main product. The highest yield of 2-pyrrolidone was attained by Ru/Al_2O_3, while 5-methyl-2-pyrrolidone and pyrrolidine were slightly formed. In addition, Ru/Al_2O_3 showed high yield of 2-pyrrolidone (63.5 %) also in the conversion of glutamic acid into 2-pyrrolidone (not shown here). One-pot synthesis of 2-pyrrolidone from pyroglutamic acid and glutamic acid was thus found to proceed on Ru/Al_2O_3 in H_2.

4. Conclusions

Ru/Al_2O_3 catalyzed the reaction forming 2-pyrrolidone from pyroglutaminol and that from pyroglutamic acid through formation of pyroglutaminol as an intermediate. In the conversion of pyroglutaminol into 2-pyrrolidone in H_2 atmosphere, Ru/Al_2O_3 exhibited extremely high yield of 2-pyrrolidone, while the other noble metal catalysts did not show activity. It is speculated that methylol group in pyroglutaminol was eliminated over Ru/Al_2O_3 through oxidative dehydrogenation into aldehyde group, and subsequent decarbonylation formed 2-pyrrolidone. Glutamic acid was also selectively transformed into 2-pyrrolidone.

References

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