Ruthenium loaded on alumina catalytically active for one-pot synthesis of 2-pyrrolidone from pyroglutamic acid

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Abstract: The influences of Ru precursor, reduction treatment and calcination temperature on the catalytic activity of Ru/Al_2O_3 for the reaction of pyroglutamic acid into 2-pyrrolidine were studied. Difference of the Ru precursor (chloride or nitrate) little affected the catalytic activity. The reduction treatment in H_2 after calcination in air converted RuO_2 into Ru metal and increased 2-pyrrolidone, while pyroglutaminol in the product decreased. The Ru crystallite size increased with increasing the calcination temperature, and simultaneously, 2-pyrrolidone decreased, while pyroglutaminol increased. The catalyst, which was calcined at 300 °C and then reduced, exhibited the highest yield (63%) of 2-pyrrolidone.

Keywords: pyroglutamic acid, 2-pyrrolidone, ruthenium

1. Introduction

Nitrogen-containing compounds in biomass resources must be valuable and renewable feedstocks for the chemicals. Glutamic acid, the most abundant amino acid constituent of plant biomass, is rapidly converted into pyroglutamic acid over 120 °C. [1] De Vos et al. reported the decarboxylation of pyroglutamic acid into 2-pyrrolidone using Pd-based catalysts at 250 °C under 0.6 MPa of inert atmosphere. [2] We found the conversion of pyroglutamic acid with supported Ru catalysts under high pressure of H_2 (Figure 1). [3] In this work, we studied the influences of Ru precursor, reduction treatment and calcination temperature on the catalytic activity for the reaction of pyroglutamic acid into 2-pyrrolidine. Through the analysis by powder X-ray diffraction (XRD), the active species was investigated.

2. Experimental

Ru/Al_2O_3 was prepared through impregnation method in an aqueous solution of $RuCl_3$ or $Ru(NO_3)_3$ possessing the metal corresponding to the loading 8 wt% on the final catalyst. Al_2O_3 (JRC-ALO-6, Catalyst Society of Japan) was stirred in the solution for 1 h at room temperature. Subsequently, the solvent was evaporated at >110 °C, followed by drying the obtained solid overnight at 110 °C. The catalyst was then calcined at 300-500 °C for 3 h in air, and the thus prepared sample is hereafter termed "Ru/Al_2O_3". The "Ru/Al_2O_3-H_2" sample was prepared by the reduction at 400 °C for 3 h in a flow of 2 mL min^{-1} H_2 in a Pyrex tube. In a typical reaction, an aqueous solution of pyroglutamic acid (0.026 mol L^{-1}, 50 mL) and the catalyst (0.2 g) were put into an autoclave (120 mL) as the batch reactor. Then, the gaseous space was purged with H_2. After filling the reactor with 2 MPa of H_2, the mixture was stirred at 500 rpm and kept at 160 °C for 2 h. The catalyst was separated from the solution by centrifugation, and the products were analyzed by FID-GC.

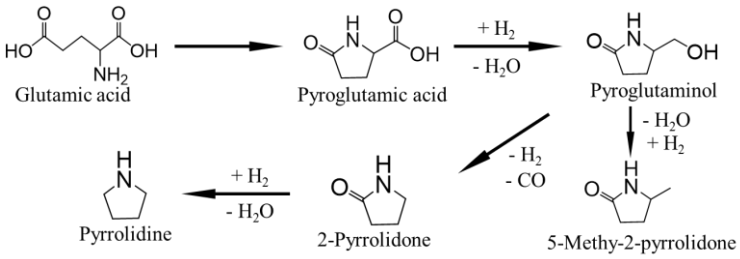

Figure 1. Reaction pathways for hydrogenation-decarbonlyation of glutamic acid to 2-pyrrolidone

3. Results and discussion

Figure 2 compares the effects of Ru-precursors ($RuCl_3$ and $Ru(NO_3)_3$) and the reduction treatment on the yield of products. The Ru/Al_2O_3 catalysts were calcined at 500 °C. Both of Ru/Al_2O_3 catalysts prepared

from $RuCl_3$ and $Ru(NO_3)_3$ brought a small amount of 2-pyrrolidone and high yield of pyroglutaminol. On the Ru/Al_2O_3-H_2 catalysts (reduced), the conversion of pyroglutamic acid was high (100%), and the yield of 2-pyrrolidone was >50%. The reduction of catalyst increased the activity for the step from pyroglutaminol into 2-pyrrolidone, as well as the conversion of pyroglutamic acid. Therefore, it is presumed that Ru-metal was the active species. On the other hand, negligible difference was caused by the different precursors.

Figure 3 shows the XRD patterns of Ru/Al_2O_3 to after the calcination and reduction in different conditions. The samples were found to be RuO_2 after the calcination at 300-500 ˚C, while it was converted into the Ru metal by the reduction. The average crystallite size was calculated from RuO_2 (1 1 0) or Ru (1 1 0). It was increased with increasing the calcination temperature.

Figure 4 compares the influence of calcination temperature on the yields of products on the catalyst reduced after the calcination. All the employed catalysts showed 100% conversion. The yields of 2-pyrrolidone and pyrrolidine decreased with increasing the calcination temperature, while the yield of pyroglutaminol increased. The catalyst only reduced without calcination showed the highest yield of pyrrolidine as a byproduct. It is believed that the small crystallite size of Ru metal resulted in the prior formation of 2-pyrrolidone. Thus, the catalyst calcined at 300 ˚C exhibited the highest yield (63%) of 2-pyrrolidone.

4. Conclusions

The Ru precursor (chloride or nitrate) had negligible influence on the catalytic activity in the reaction of pyroglutamic acid. The reduction of catalyst converted the RuO_2 into Ru, resulted in the high yield of 2-pyrrolidone, and therefore the active species is presumed to the Ru metal. The low calcination temperature before the reduction contributed to give the small crystallite size and gave the high yield of 2-pyrrolidone. The Ru/Al_2O_3 catalyst calcined at 300 ˚C and then reduced in H_2 at 400 ˚C exhibited the highest yield (63%).

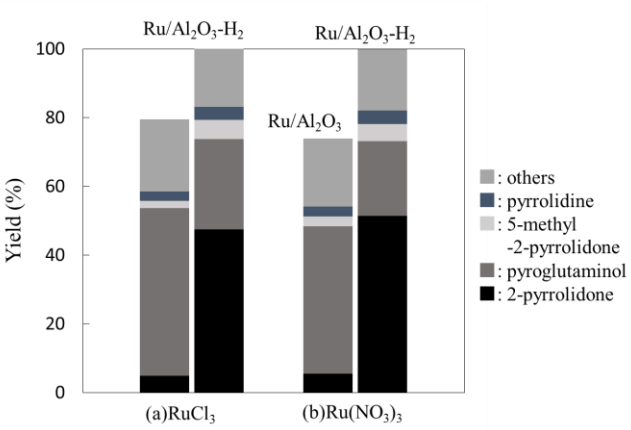

Figure 2. Influences of Ru precursors and reduction on yields of products in reaction of pyroglutamic acid.

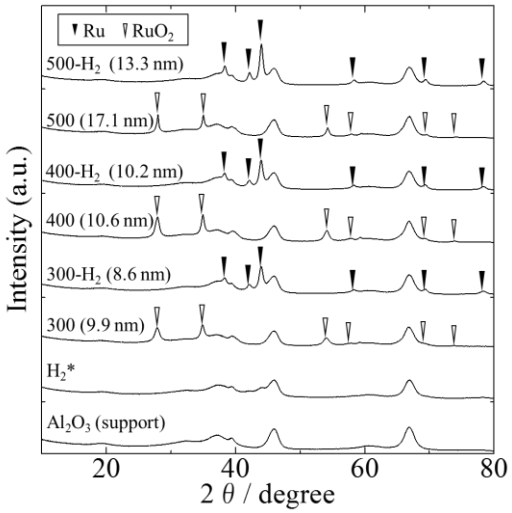

Figure 3. The XRD patterns of Ru/Al_2O_3 and Ru/Al_2O_3-H_2 prepared from $RuCl_3$. The digits indicate the calcination temperature (˚C), while "H_2" means that the sample was reduced at 400˚C. *The sample was only reduced at 400 ˚C. The digits in parentheses show the crystallite size.

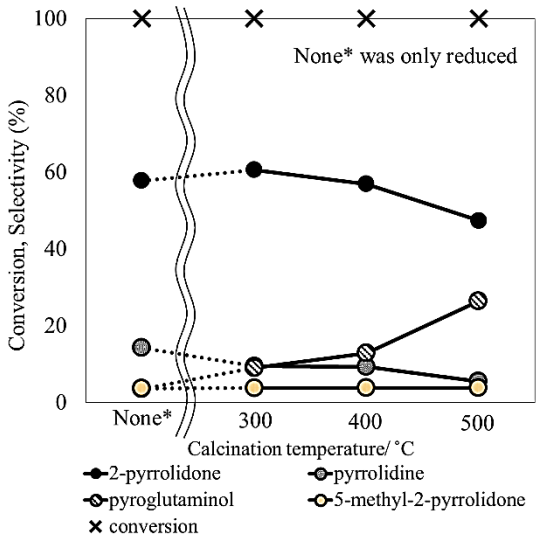

Figure 4. Yield of products in transformation of pyroglutamic acid using Ru/Al_2O_3-H_2.

References

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