# Three-step conversion of chitin to *N*-containing sugar alcohol

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## 1. Introduction

Chitin, a polymer of *N*-acetyl-D-glucosamine (NAG), is the most abundant nitrogen-containing biomass on Earth. Thus, chitin is expected to be a major feedstock for organonitrogen compounds. However, efficient conversion of chitin to monomeric compounds has not been achieved so far.

We propose a new method of depolymerization of chitin, which is the combination of mechanocatalytic hydrolysis by $H_2SO_4$ and hydrolytic hydrogenation of the product by $Ru/TiO_2$ catalyst to synthesize 2-acetamido-2-deoxysorbitol (ADS) (Fig. 1). ADS will be a feedstock for the production of polyester amides, nylon resins and commodity chemicals such as alkylamine and acetoamide. In this work, we aimed for high-yield synthesis of ADS by the combined process.

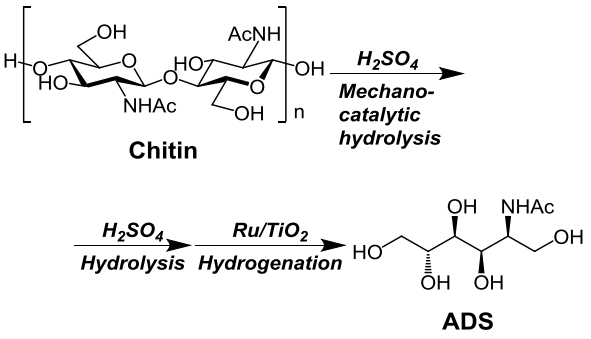


Fig. 1 Conversion of chitin to ADS.

## 2. Experimental

Chitin was impregnated with $H_2SO_4$ (substrate/ catalyst = 3.8), and subsequently milled by a planetary ball-milling at 500 rpm for 6 h to improve the reactivity. This sample is denoted Oligomer-$H_2SO_4$. Oligomer-$H_2SO_4$ was charged with 5 wt% $Ru/TiO_2$ and water into a high-pressure reactor. The reactor was pressurized with $H_2$ at 4 MPa, and heated to a designated temperature. After the reaction, the solution and catalyst were separated by centrifugation, and the liquid phase was analyzed by high performance liquid chromatography.

## 3. Results and discussion

Pristine and milled chitin samples were characterized to evaluate the effect of the pretreatment. Original chitin was insoluble in water, but it became soluble by the pretreatment. HPLC analysis showed that the pretreated chitin, Oligomer-$H_2SO_4$, contained NAG (19%) and oligomers (DP ≧ 2) (63%). This result indicates the mechanocatalytic hydrolysis of chitin during the milling process.

Direct hydrolytic hydrogenation of Oligomer-$H_2SO_4$ gave ADS in low yield (25%) by $Ru/TiO_2$ catalyst at 180 °C. High-yield synthesis of ADS was not achieved in the one step reaction.

Therefore, we investigated whether selective ADS synthesis can be achieved by dividing the reaction into two steps: hydrolysis and hydrogenation. For the hydrolysis, NAG was obtained at 61% by hydrolyzing Oligomer-$H_2SO_4$ at 175 °C. Afterwards, the hydrogenation at a low temperature of 120 °C and pH control to be pH 3 greatly suppressed side-reactions. ADS yield was increased to 52%.

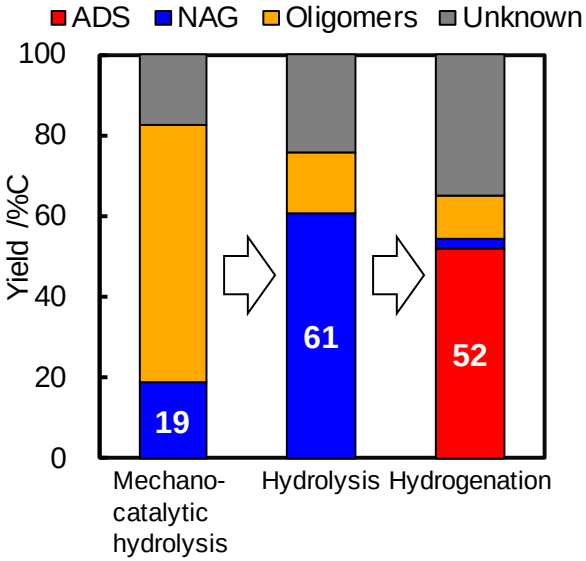


Fig. 2 Hydrolytic hydrogenation of chitin

## REFERENCES

[1] M. Yabushita, H. Kobayashi, K. Kuroki, S. Ito, A. Fukuoka, *ChemSusChem*, 8 (2015) 3760.