# Catalytic conversion of N-containing sugar alcohol from chitin

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**Abstract:** Chitin is the most abundant nitrogen-containing biomass on Earth and is a potential feedstock for organonitrogen compounds. We report a new method of depolymerization of chitin, which is the hydrolytic hydrogenation to synthesize 2-acetamido-2-deoxysorbitol (ADS). We demonstrated the catalytic conversion of chitin to oligomers using mechanocatalytic hydrolysis in presence of $H_2SO_4$. Selective ADS synthesis is achieved by dividing hydrolytic hydrogenation of the oligomers into two steps: hydrolysis at high temperature at pH 2, and hydrogenation under low temperature at pH 3-4. We accomplished 52% yield of ADS by optimizing the reaction condition for each step.

**Keywords:** Chitin, Hydrolytic hydrogenation, $Ru/TiO_2$ catalyst.

## 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, currently efficient conversion of chitin to monomeric compounds has not been achieved. We propose a new method of depolymerization, which is the combination of mechanocatalytic hydrolysis by $H_2SO_4$ and hydrolytic hydrogenation of the products by $Ru/TiO_2$ catalyst to synthesize ADS (Figure 1). ADS can be a feedstock for the production of polyester amides, nylon resins and commodity chemicals such as alkylamine and acetoamide. Despite the usefulness of ADS, its synthesis from pristine chitin is challenged[1], because chitin is insoluble in typical solvents and its reactivity is low due to rigid crystal structure. Therefore, it is necessary to solve this problem. Our group recently reported that mechanical force and $H_2SO_4$ enhanced the hydrolysis of chitin to NAG and its oligomers[2]. These small fragments are completely soluble in water and can be easily hydrolyzed. We aimed for high yield synthesis of ADS by hydrolytic hydrogenation of this oligomer.

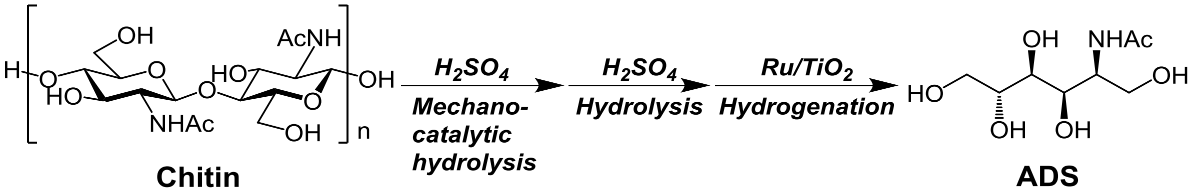

**Figure 1.** Proposed reaction scheme of chitin conversion

## 2. Experimental

Chitin was impregnated with $H_2SO_4$ (S/C 3.8), and subsequently milled by a planetary ball-mill at 500 rpm for 6 h. This sample is denoted as Oligomer-$H_2SO_4$. The hydrolytic hydrogenation of Oligomer-$H_2SO_4$ was performed at 453 K under $H_2$ pressure of 4 MPa by metal/$TiO_2$ catalysts prepared by an impregnation method.

## 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 after the pretreatment. Oligomer-$H_2SO_4$ contained NAG (19%) and oligomers (DP$\geqq$2) (64%). $^1$H- and $^{13}$C-NMR measurement showed that oligomer has $\beta$-1,4- and $\alpha$-1,6-glicosidic bonds. This suggests the formation of a branched structure in the molecules.

The hydrolytic hydrogenation of Oligomer-$H_2SO_4$ gave ADS in 25% yield in the presence of 5 wt% $Ru/TiO_2$. Other products were NAG (5%), oligomers (22%) and unknown products (48%). 5 wt% $Pt/TiO_2$ and 70 wt% $Ni/TiO_2$ showed low catalytic performance in this reaction.

In order to further improve the ADS yield, we separated and optimized hydrolysis and hydrogenation processes for the following reason. High temperature and low pH promote hydrolysis, but at the same time also promote side reactions in hydrogenation conditions. On the other hand, low temperature and high pH suppressed the side reactions in hydrogenation, but hydrolysis did not proceed at the temperature. Based on the strategy, the NAG yield reached 61% by hydrolyzing the Oligomer-$H_2SO_4$ at 448 K. The pH of the solution was 3 after hydrolysis, the solution was neutralized by adding $NaHCO_3$, followed by hydrogenation by adding $Ru/TiO_2$ and $H_2$ 4 MPa. The side reactions were greatly suppressed by lowering the reaction temperature to 393 K and neutralizing the solution to pH 3, whereby ADS can be obtained in a high yield of 52%.

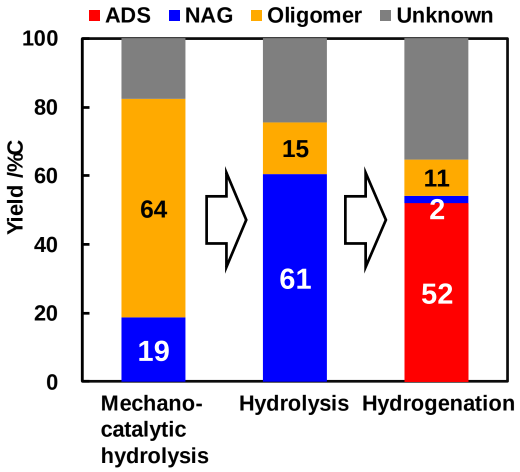

**Figure 2.** Hydrolytic hydrogenation of chitin

We evaluated the effect of pH for hydrogenation. Table 1 shows the pseudo first order rate constants for respective reaction steps. We assumed that NAG is converted to ADS and by-products in parallel, and the rate constants were named $k_1$ and $k_2$, respectively. The other reaction is decomposition of ADS to by-products with $k_3$. These rate constants were determined by curve fitting time courses of the reaction. Between pH 2-5, the value of $k_1$ and $k_3$ decreased with increasing pH, and $k_2$ was the smallest at pH 3. $k_1/k_2$ ratio was maximized at pH 4, and $k_1/k_3$ ratio was almost same at pH 3-5. These result showed that neutralization suppressed generation of by-products at mild acidic conditions, and pH 3-4 was the best condition for the hydrogenation. At pH 6.8, these ratios were drastically different because the presence of bases enhanced retro-aldol reaction of NAG. As a result, erythritol and acetamide ethanol were generated in reaction solution at pH 6.8 due to retro-aldol reaction.

| pH | ADS yield /% | $k_1$ /$h^{-1}$ | $k_2$ /$h^{-1}$ | $k_3$ /$h^{-1}$ | $k_1/k_2$ | $k_1/k_3$ |
|---|---|---|---|---|---|---|
| 2 | 37 | 1.4 | 0.56 | 0.05 | 2.6 | 29 |
| 3 | 52 | 1.3 | 0.08 | 0.03 | 17 | 44 |
| 4 | 51 | 1.0 | 0.05 | 0.025 | 20 | 40 |
| 5 | 46 | 0.95 | 0.15 | 0.02 | 6.3 | 48 |
| 6.8 | 5 | 0.60 | 4.9 | 0.10 | 0.12 | 6.0 |

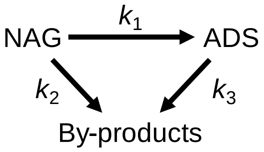

**Table 1.** Pseudo first order rate constants for hydrogenation.

## 4. Conclusions

We reported new method of chitin conversion to nitrogen-containing sugar alcohol using a combination of mechanocatalytic hydrolysis and hydrolytic hydrogenation. Mechanical force and presence of $H_2SO_4$ hydrolyzed chitin to soluble oligomers, and these oligomers can be easily hydrolyzed to NAG in 61% yield at 448 K and pH 2. After hydrolysis, subsequent hydrogenation was performed without purification of the product solution containg NAG. The pH of the solution was adjusted to be pH 3, which improved the ADS overall yield to 52%. This is the first report of ADS production from chitin. This result will promote the future use of chitin and it will be of great help to build up a sustainable society.

## References

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