Low Temperature Synthesis of Hydrogen Titanate Nanotubes and Their Solid Acidity for Conversion of Glucose into 5-(hydroxymethyl)furfural

Misaki Ota[a], **Yuichiro Hirota**[a], **Yoshiaki Uchida**[a], **and Norikazu Nishiyama**[a*]
[a]*Division of Chemical Engineering, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan*
**Corresponding author: +81-6-6850-6257, nisiyama@cheng.es.osaka-u.ac.jp*

Abstract: In this work, hydrogen titanate ($H_2Ti_3O_7$) nanotubes were synthesized at low temperature via a new simple method. Firstly a raw material of amorphous titanium dioxide (TiO_2) nanoparticles with a high surface area were prepared at room temperature. The $H_2Ti_3O_7$ nanotubes were obtained by introducing Na^+ into the amorphous TiO_2 nanoparticles at room temperature and ion exchange reaction between Na^+ and H^+. The $H_2Ti_3O_7$ nanotubes had nanopores less than 1 nm and a high surface area of 735 m^2/g. The $H_2Ti_3O_7$ nanotubes acted as an efficient solid acid catalyst for glucose conversion into 5-(hydroxymethyl)furfural.

Keywords: hydrogen titanate nanotube, biomass, 5-(hydroxymethyl)furfural.

1. Introduction

Alternative resources of carbohydrate biomass have a potential for sustainable supply of valuable production through the platform chemicals. 5-(hydroxymethyl)furfural (HMF) can be obtained from glucose or fructose with acid catalyst and it has been well known as one of the platform chemicals[1]. HMF can be converted into a series of derivatives such as fran-2,5-dicarboxylic acid and levulinic acids, which can be used as raw materials of fuels, plastics and drugs.

Hydrogen titanate ($H_2Ti_3O_7$) nanotubes have attracted considerable interest as adsorbents, electrochemical cells and catalyst supports since Kasuga *et al*. reported its synthesis method[2]. However, little has been reported on the catalytic properties of $H_2Ti_3O_7$ nanotubes themselves[3]. Moreover the synthesis process requires severe conditions with heat treatment at 120°C and high pressure.

In our previous work, we have developed a method for synthesizing amorphous TiO_2 (a-TiO_2) nanoparticles with a high specific surface area and high reactivity at low temperature[4]. The a-TiO_2 can be used as precursor for synthesizing various titanate nanomaterials. Here, we reported a low temperature synthesis method of $H_2Ti_3O_7$ nanotubes by using the a-TiO_2 as a raw material. The $H_2Ti_3O_7$ nanotubes were used as an acid catalyst for biomass conversions. The acidic properties of the $H_2Ti_3O_7$ nanotubes are characterized by conducting the conversion of glucose and fructose to HMF.

2. Experimental

First, titanium isopropoxide (TTIP) was mixed with tetrahydrofuran (THF) at room temperature. Next, water was added to cause a hydrolysis reaction and precipitate of TiO_2 was immediately formed. Finally, a-TiO_2 was collected by centrifugation and drying. The hydrogen titanate nanotubes were synthesized via a simple route using a-TiO_2 at room temperature. The synthetic procedure is as follows: First, a-TiO_2 was mixed with 10 M NaOH aqueous solution for 48 h. The precipitate, $Na_2Ti_3O_7$ was acid-washed with 0.1 M HCl solution until the pH value reached 1 by ion exchange between Na^+ and H^+. As a reference, $H_2Ti_3O_7$ nanotubes were obtained via a conventional hydrothermal treatment at 120°C by using commercially available P25-TiO_2 as a raw material. The $H_2Ti_3O_7$ samples prepared at room temperature from a-TiO_2 and by hydrothermal treatment from P25-TiO_2 were labeled as HTO-RT and HTO-HT, respectively.

The catalytic reaction was carried out in 15 mL of aqueous solution containing 0.1 wt% glucose or fructose as an initial reactant, and 0.03 g of catalyst at 80°C for 24 h. After filtration, the solution was analyzed using HPLC to determine the concentration of HMF. As references, hydrochloric acid (HCl) and a commercially-available acid resin (Amberlyst-15 in hydrogen form) were used as acid catalysts.

3. Results and discussion

The TEM images are shown in Figure 1. The particle size of the a-TiO_2 is about 3.0 nm which is smaller than the commercially available P25-TiO_2 of 20-30 nm. The HTO-HT showed nanotube structure with outer diameter of 8.0 nm and an inner diameter of 3.5 nm, while the nanotubes with outer diameter of 3.0 nm and an inner diameter of 0.7 nm were observed for HTO-RT calculated by 1D profile analysis. The size of titanate nanotubes should depend on the particle size of the raw material of TiO_2, which can be explained based on the following proposed formation mechanism. The formation of nanotubes involves peeling and scrolling processes. First, nanosheets of $Na_2Ti_3O_7$ are formed on TiO_2 particles, and then the nanosheets of $Na_2Ti_3O_7$ delaminate from TiO_2 particles in NaOH solution. Finally, the nanosheets are rolled up into nanotubes during the ion-exchange reaction between Na^+ ions and H^+ ions. The specific surface areas of HTO-RT and HTO-HT calculated from the N_2 adsorption isotherms were S_{BET} = 735 and 408 m^2/g, respectively.

According to XRD pattern, the peaks attributed to the $H_2Ti_3O_7$ crystal structure are observed for both HTO-RT and HTO-HT. This result indicates that $H_2Ti_3O_7$ could be successfully synthesized using a-TiO_2 as a raw material without high pressure and heat treatment showing a high reactivity of a-TiO_2. On the other hand, when the P25-TiO_2 was used as raw material under the same reaction condition, without heat treatment and the pressure, a $H_2Ti_3O_7$ crystal structure was not formed and its nanostructure did not change. When the P25-TiO_2 was used, hydrothermal conditions at 120°C and autogenous pressure were required for the phase transition from TiO_2 to the $H_2Ti_3O_7$ structure.

Figure 2 shows HMF yield from glucose or fructose under the catalysts. Glucose isomerizes into fructose under base site or Lewis acid site followed by the conversion by dehydration of fructose to HMF under Brønsted acid site. The HTO samples showed a high yield of HMF from glucose suggesting that the $H_2Ti_3O_7$ nanotube has both of Lewis and Brønsted acid sites. When HCl and Amberlyst-15 with only Brønsted acid site were used as the catalyst, the HMF yield from glucose was lower than HTO samples. In addition, HTO-RT showed a higher HMF yield from fructose than HTO-HT. This result indicated that HTO-RT had more Brønsted acid sites on the surface of nanotube than HTO-HT due to the high surface area of HTO-RT.

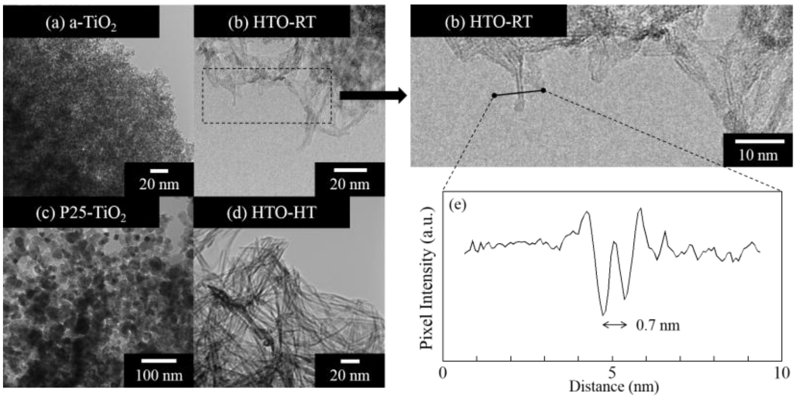

Figure 1 TEM images of TiO_2 and HTO samples

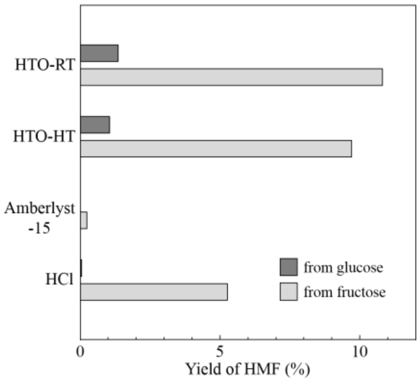

Figure 2 HMF yield

4. Conclusions

$H_2Ti_3O_7$ nanotubes were successfully synthesized at low temperature without heat and high pressure treatment by using a-TiO_2 nanoparticles with a high surface area. The high surface area of the $H_2Ti_3O_7$ nanotubes enhanced the solid acid catalytic activity for the conversion of glucose and fructose to HMF.

References

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