Effect of Single-walled Carbon Nanotube Catalysts on Hydrothermal Pretreatment of Cellulose

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1. Introduction

Second-generation bioethanol, which is obtained from lignocellulosic biomass, has attracted considerable attention as a substitute for fossil fuel because of the problems related to energy and environmental issues. To produce bioethanol, glucose must be obtained first from lignocellulosic biomass through hydrolysis of cellulose. Typical hydrolysis employs enzymatic, hydrothermal, or acidic treatment. Among these, hydrothermal pretreatment uses only water, and thus can be an inexpensive and environment-friendly process.

For the hydrolysis of cellulose in lignocellulosic biomass, removal of hemicellulose and lignin is important. Hydrothermal treatment is also effective for this purpose. For example, hydrothermal treatment is often employed as pretreatment to the enzymatic hydrolysis so that the accessibility of cellulose for the enzyme is enhanced by removing hemicellulose and lignin. Without this hydrothermal pretreatment, glucose yield from enzymatic hydrolysis is limited, and thus, hydrothermal pretreatment is an important step for effective enzymatic hydrolysis. In hydrothermal pretreatment, lignin and hemicellulose are first removed to isolate cellulose, and the remaining cellulose is hydrolyzed.

To further improve this effect, utilization of solid catalysts such as sulfonated amorphous carbon, activated carbon, zeolite, zirconia, and carbon nanohorns has been investigated. By using a catalyst in the hydrothermal pretreatment reaction, isolation of cellulose and the ensuing hydrothermal pretreatment could be accelerated. As is well known, both acids and bases can catalyze the hydrolysis of holocellulose, especially hemicellulose. Thus, solid acids or solid bases can facilitate the removal of hemicellulose from the biomass structure, leaving cellulose behind. A carbonaceous catalyst is expected to be particularly effective, considering its durability under hydrothermal conditions and possible modification of its surface. Kitano et al. showed that a graphene-based amorphous solid acid catalyst achieved a faster cellobiose hydrolysis rate than beta-glucosidase.

Since effective surface area is important for catalysis, among carbonaceous catalysts, nanocarbon catalysts...
should be more effective. Because of its nanostructure, a high specific surface area can be achieved. However, carbon nanomaterials of good quality are expensive. From a commercial viewpoint, cheap nanocarbon catalysts are desired. Fortunately, carbon nanotubes (CNTs) have been commercialized recently, and are expected to meet this criterion. Of course, it is much more expensive compared to activated carbon. Single-walled carbon nanotube is 66,000 JPY/g, and multi-walled carbon nanotube is 12,000 JPY/g while activated carbon is 0.080 JPY/g. However, the price is going down. Considering that we could not even purchase single wall carbon nanotube, much reduction in its price is expected. By using CNTs as a hydrothermal pretreatment catalyst, a cheap and effective catalyst may be realized. However, CNTs have not been employed as a catalyst for hydrothermal pretreatment. They have been applied as catalysts for other purposes\(^{10}\), but their effectiveness as a catalyst in enhancing hydrothermal pretreatment has not been elucidated. Thus, the purpose of this study was to experimentally determine the effect of CNTs on the hydrothermal pretreatment of lignocellulosic biomass.

2. Experimental

2.1. Catalyst Preparation

Four types of single-walled carbon nanotube (SWCNT) catalyst were prepared: untreated SWCNTs (SW), those with oxidation treatment (Ox-SW), those with acid treatment (Acid-SW), and those with both oxidation and acid treatment (Ox-Acid-SW). The SWCNTs were obtained from Meijo Nano Carbon Co., Ltd. (MEIJO eDIPS EC2.0). Multi-walled carbon nanotube is less expensive, but in this study, SWCNT was employed for its higher effective specific surface area.

For the oxidation treatment, SWCNTs were placed in a ceramic crucible and then heated using an electric furnace in air at 500°C for 30 min. Acid treatment was performed as follows: 1.3 g of SWCNTs was immersed in 30 cm\(^3\) of sulfuric acid (96 %) in a Teflon container. Then, the entire container was heated in an oven at 200°C for 18 h. After heating, the SWCNTs were washed with distilled water on a nylon membrane until the pH of the filter water was the same as that of distilled water. After washing, they were dried at room temperature.

The produced catalyst was analyzed using Fourier transform infrared spectroscopy (FT-IR, Thermo Scientific, Nicolet 6700 FT-IR Spectrometer) and thermogravimetric analysis (TGA, Shimadzu, TA-60WS). To quantify the density of acid functional groups on the SWCNTs (acid site density), ion-exchange titration was conducted using an auto-titration apparatus (Mettler Toledo, T50). First, a 500 mol/m\(^3\) (0.5 M) NaOH solution and 50 mol/m\(^3\) (0.05 M) HCl solution were prepared. Then, 50 mg of catalyst was immersed in 30 cm\(^3\) of the NaOH solution at room temperature with stirring for 24 h. The liquid samples (20 cm\(^3\)) were diluted by five times using distilled water. Finally, this solution was titrated with the 50 mol/m\(^3\) HCl solution using the auto-titration apparatus.

2.2. Feedstock

Commercial cellulose (Sigma-Aldrich, Product No. 435236-1KG) and eucalyptus (Eucalyptus globulus) from Thailand were used in this study as feedstock. Cellulose was in the form of microcrystalline powder, and its particle size ranged from approximately 74 to 250 μm. To analyze the chemical composition of eucalyptus, quantitative acid hydrolysis was conducted according to a modified laboratory analytical procedure from the National Renewable Energy Laboratory (NREL)\(^{11}\). The composition was determined to be 0.590 kg/kg of cellulose, 0.285 kg/kg of hemicellulose, and 0.100 kg/kg of lignin. Elementary analysis of the feedstock was conducted using a CHN analyzer (LECO, CHN 628), giving ratios of carbon in eucalyptus and cellulose of 0.350 kg/kg and 0.409 kg/kg, respectively. Since the theoretical carbon content of cellulose is 0.444 kg/kg, this result has a relative error of 0.08 and should be reliable.

2.3. Hydrothermal Pretreatment

For hydrothermal pretreatment, an autoclave reactor, as shown in Fig. 1, was used. The inner diameter and depth of the Teflon liner were 32 mm and 104 mm, respectively (the inner volume was approximately 84 cm\(^3\)). Specific amounts of feedstock (cellulose or eucalyptus), SWCNT catalyst, and water were placed in the autoclave, and after closing the lid, the reactor was heated by a jacket heater at a heating rate of approximately 4 °C/min. The reactor was cooled using iced water as soon as the temperature reached 200°C. After cooling, the product was recovered and analyzed.

![Schematics of the Experimental Setup](image-url)
The liquid product was analyzed using a total organic carbon (TOC) analyzer (Shimadzu, TOC-VCPH) and a high-performance liquid chromatography (HPLC, Shimadzu, Prominence LC-20A) apparatus equipped with UV-Vis and refractive index detectors. A Bio-Rad column (Aminex HPX-87H) was used for organic acid analysis, with an eluent of 5 mol/m³ (5 mM) sulfuric acid in water at a flow rate of 0.6 cm³/min. A Shodex column (SP0810) was used for sugar analysis, with an eluent of Type I-deionized (DI) water, at a flow rate of 0.6 cm³/min. The solid product was analyzed using the CHN analyzer. Experimental conditions are shown in Table 1. For the case of eucalyptus, 1.0 g was placed in the reactor. For the case of commercial cellulose, 0.6 g of cellulose was used so that the amount of cellulose in the reactor was the same as that in the eucalyptus treatment.

3. Results and Discussion

3.1. Catalyst Characterization

Figure 2 shows the FT-IR spectra of the SWCNT catalysts. A broad peak of –OH stretching at 3440 cm⁻¹ was observed. The peak at 1630 cm⁻¹ is the stretching mode of C=C. The change in the obtained spectrum was not large after oxidation or acid treatment, indicating that the basic structure of SWCNTs was not changed after these treatments. Small peaks observed at 1040 cm⁻¹ and 1120 cm⁻¹ for acid-treated SWCNTs may be from the combination of water with the sulfonic acid group.

Figure 3 shows TGA results for the SWCNT catalysts. Again, the change in the TGA curve is small, supporting the idea that the basic structure of SWCNTs was not changed after these treatments. Reduction of ash content was observed for acid-treated SWCNTs, which should be due to dissolution of ash in sulfuric acid.

The result obtained from ion-exchange titration is shown in Table 2. It is noted that Acid-SW and Ox-Acid-SW, which were treated with sulfuric acid, had positive acid site densities. Hence, SO₃H functional groups should have been successfully attached to SWCNTs. These SWCNTs originally had some base functional groups. As shown by the higher base site density of Ox-SW than that of SW, some base functional groups were added to the catalyst surface owing to the oxidation treatment, although it was not intentional. The acid site density of Acid-SW was higher than that of Ox-Acid-SW. This tendency was confirmed in previous research.

The molar ratio of number of acid sites to that of carbon atoms is roughly estimated to range from 0.007 to 0.017 mol-(acid site)/mol-C. This small ratio explains the negligible differences in the FT-IR and TGA curves of the different SWCNT catalysts.

3.2. Hydrothermal Pretreatment

The carbon yield after hydrothermal pretreatment is shown in Fig. 4. Carbon yields from the experimental results were calculated on the basis of the carbon content in the feedstock. For all runs, the obtained carbon balance was higher than 0.8. For the case of eucalyptus, the carbon yield in the liquid phase was higher than that of cellulose. This is because eucalyptus contains lignin and hemicellulose, which are easier to dissolve than cellulose. Note that the carbon yield in the solid is close to the original carbon distribution in cellulose.

In Fig. 5, glucose and cellobiose yields from liquid samples are shown. The measurement error determined by HPLC calibration curve was 0.4 %, and too small to put error bars. These product yields were calculated on the basis of the carbon content of cellulose in the feedstock. The actual obtained yield is very low compared to this theoretical value. This is because the catalyst amount was not adjusted in this study owing to the limitation of CNT treatment facilities, but the effectiveness of the catalysts can be compared.

Table 1 Experimental Conditions of Hydrothermal Pretreatment

| Feedstock   | Eucalyptus | Cellulose |
|-------------|------------|-----------|
| Feedstock amount | 1.0 g | 0.6 g |
| Particle size  | 45-90 μm | 51 μm |
| Catalyst weight | 0.10 g | |
| Total weight including water | 30 g | |
| Temperature   | 200 °C | |
| Holding time  | 0 s | |
| Catalyst      | No catalyst, SW, Ox-SW | Acid-SW, Ox-Acid-SW |

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Acid-SW, the highest yields of glucose and cellobiose were obtained for both eucalyptus and cellulose. This means that Acid-SW was the most effective catalyst among the SWCNT catalysts employed in this study. Considering the high acid site density observed for Acid-SW, this may be due to the acid effect of the Acid-SW catalyst.

Figure 6 shows the relationship between acid site density and yields of glucose and cellobiose. The measurement error determined by HPLC calibration curve was 0.4 %, and too small to put error bars. Both yields increased with acid site density (positive value), while the yields hardly depended on base site density (negative value). This confirms that the acid site density of the catalyst plays a key role. This is understandable considering the fact that an acid is more effective than a base as a hydrolysis catalyst.

| Sample   | Acid site density [mmol/g-cat] |
|----------|---------------------------------|
| SW       | −0.720                          |
| Ox-SW    | −2.19                           |
| Acid-SW  | 1.44                            |
| Ox-Acid-SW | 0.623                        |

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**Table 2** Acid Site Density (negative value indicate base site density)

**Fig. 3** TGA Curves for SWCNT Catalysts

**Fig. 4** Carbon Balance of (a) Eucalyptus and (b) Cellulose
4. Conclusion

The following conclusions were obtained. 
(1) Four types of SWCNT catalyst, SW, Ox-SW, Acid-SW and Ox-Acid-SW, were prepared by oxidization and acid treatment. 
(2) Catalysts treated with sulfuric acid, Acid-SW and Ox-Acid-SW, had acid site density. 
(3) Higher acid site resulted in higher yield of glucose and cellobiose.

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References
1) Sabiha-Hanim, S., Noor, M. A. M., Rosma, A., Bioresour. Technol., 102, 1234 (2011).
2) Moeller, M., Nilges, P., Harnisch, F., Schroeder, U., ChemSusChem, 4, 566 (2011).
3) Zakaria, M. R., Hirata, S., Hassan, M. A., Bioresour. Technol., 176, 142 (2015).
4) Nakajima, K., Hara, M., ACS Catal., 2, 1296 (2012).
5) Onda, A., Ochi, T. Yanagisawa, K., Top. Catal., 52, 801 (2009).
6) Fukuhara, K., Nakajima, K., Kitano, M., Hayashi, S., Hara, M., Phys. Chem. Chem. Phys., 15, 9343 (2013).
7) Corma, A., Martinez, A., Adv. Mater., 7, 137 (1995).
8) Poonjarernsilp, C., Sano, N., Tamon, H., Appl. Catal. B: Environ., 147, 726 (2014).
9) Kitano, M., Sato, K., Narai, K., Kaneko, N., Hara, M., J. Jpn. Inst. Energy, 92, 675 (2013).
10) Yu, H., Jin, Y., Li, Z., Peng, F., Wang, H., I. Solid State Chem., 181, 432 (2008).
11) Sluieter, A., Hames, B., Ruiz, R., Sitler, J., Templeton, D., Crocker, D., “Determination of structural carbohydrates and lignin in biomass,” Laboratory Analytical Procedure (LAP), National Renewable Energy Laboratory (NREL)/TP-510-42618, 2008.


要　旨

セルロースの水熱加水分解に及ぼすシングルウォールカーボンナノチューブ触媒の効果

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水熱加水分解によってリグノセルロースからグルコースを効率良く得るためにシングルウォールカーボンナノチューブ（SWCNT）を用いた。ウーティルとセルロースの水熱加水分解をSWCNT触媒を添加した場合と添加しない場合で行った。さらに、SWCNT触媒は酸化／酸処理を行った場合と行っていない場合について比較した。酸化処理は500℃の空気中で30分、酸処理は200℃の96％硫酸中で18時間行った。水熱加水分解は0.6 gのセルロースを含む試料を84 mLのオートクレーブ反応器を用い、200℃まで4℃/minで加熱してすぐに冷却して行った。そのままでの状態ではSWCNTは塩基性を示し、酸化処理は塩基性をさらに増加させ、酸処理はSWCNTの酸点濃度を高める結果となった。グルコース収率は酸点濃度とともに増加することが確認され、酸処理SWCNTの有効性が示された。

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