Mechanochemical Preparation of a H$_3$PO$_4$-Based Solid Catalyst for Heterogeneous Hydrolysis of Cellulose

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ABSTRACT: Cellulose saccharification to produce glucose is considered as an important approach for application of biomass resources. Solid acids as catalysts for this purpose have attracted much attention with the advantages of environmental friendliness, easy separation of products, and recyclability. In this work, a new method was introduced to prepare a H$_3$PO$_4$-based solid acid catalyst by simply grinding with kaolinite. Characterizations of the prepared products based on a set of analytical methods as well as cellulose hydrolysis were investigated and optimized. Loading H$_3$PO$_4$ on kaolinite with a mass ratio of 20% was used as a high-stability green catalyst. Cellulose hydrolysis occurred on the prepared catalyst even at much mild conditions with a low temperature of 343 K, and a yield of glucose products at 6.85% was achieved at optimized conditions. A catalytic activity of 82% remained after three cycles of use. The possible hydrolysis of cellulose under very low temperature demonstrates a potential approach for promoting biomass conversion into useful materials.

1. INTRODUCTION

Ensuring supply of resources and energy remains a serious global problem toward the sustainable development of our society and economy in the 21st century. Among several renewable resources, including wind energy and solar energy, biomass is the only one in the form of material and stores solar energy in the form of chemical energy through photosynthesis. Cellulose is the most abundant existence in biomass materials, and the main point of efficient use of cellulose is the conversion into soluble high-value-added oligomers, especially monomeric glucose, through depolymerization. It remains a very difficult task due to the existence of a large number of hydroxyl groups (−OH) inside the cellulose molecules and the large number of hydrogen bonds formed between them, although many research studies have been performed with various efforts based on enzymes or inorganic acids in order to promote the hydrolysis and conversion of cellulose. Elaborate efforts are strongly required to overcome the remaining difficulties of both the enzyme process and the acidic process.

The use of solid acid catalysts to replace the concentrated acidic solution is known as a green process that is conducive to recover the product without the concern over the treatment of acidic wastewater. Table 1 summarizes the recently reported results with various types of solid acid catalysts. Due to the mass transfer limitation between cellulose and heterogeneous catalysts, solid acids with a large specific surface area, large pore size, and strong acid centers are expected to exhibit better catalytic performance. The selection and preparation of supporting materials are key factors in improving the performance of the catalysts, including clays, carbonaceous materials, and mesoporous aluminosilicates. Zhuo et al. soaked the calcined kaolin at 600 °C into 20 wt % sulfuric acid for 4 h to obtain the highest acid number on the surface. It was found that the proper Si−Al structure of the dealumination-retained part can greatly produce acidic strength. Carbon-based solid acids are usually prepared in concentrated sulfuric acid or fuming concentrated acid by heating to introduce a sulfonic acid group with higher catalytic activity. Qi et al. synthesized a solid acid cellulose simulant with sulfonic acid as the cellulose-hydrolyzable group (CHG) and hydroxyl and carboxyl groups as the cellulose-binding group (CBG). It was found that the hydroxyl group can also serve as CHG, namely, oxygen-containing functional groups (−OH and −COOH) on weakly acidic surfaces to effectively catalyze the hydrolysis of cellulose.

H$_3$PO$_4$-based catalysts are widely used as solid acids for propylene oligomerization and benzene alkylation. Among them, diatomite-H$_3$PO$_4$ catalysts have become the most important type of H$_3$PO$_4$ salt catalysts due to their wide industrial use and good performance. Studies have shown that the active component of the diatomite-H$_3$PO$_4$ catalyst is the free H$_3$PO$_4$ dispersed on the catalyst. Based on the
properties of the hydroxyl-rich ore with natural solid acid, kaolinite with various active functional groups (interlayer Si–O–Al, Al–OH groups, and Lewis acid sites on the edges) is selected as the carrier material. H3PO4 was used as the CHG to prepare a solid acid catalyst.23 Most traditional methods for preparing cellulose-hydrolyzed solid acids are the two-step roasting-acid-leaching method. Although the prepared catalyst has a large specific surface area and high conversion efficiency, its preparation process requires large energy consumption and complicated acid-leaching processes, and the formation of acidic wastewater cannot be avoided.24 A mechanical ball-milling method may avoid such problem when loading H3PO4 on kaolinite to achieve high potassium-fixation ability, and the prepared material has uniform texture and high stability.23 As a common physical and chemical preparation method of composite materials, mechanical force ball-milling has a simple, efficient, and extensible application prospect,25 but there are few reports on solid acid preparation and biomass energy conversion application.

In this report, a mechanochemical method was used to prepare H3PO4-based solid acid by loading it on kaolinite through a simple milling operation; thus, when the crystal structure of kaolinite is damaged, the crystal water or the hydroxyl group dehydrates to form an amorphous structure to obtain the activation effect to help H3PO4 incorporation.26 Proper regulations of milling conditions allowed the synthesis of H3PO4-based catalysts with high stability and high acid content, and an efficient hydrolysis of cellulose at very low temperature was obtained by using the product.

2. RESULTS AND DISCUSSION

2.1. Catalyst Characterization. Three kinds of inorganic acids HCl, H2SO4, and H3PO4 were compared for loading on kaolinite by ball-milling at the same mass ratio of 0.2 g/per 1 g kaolinite. The pH of the sample added into pure aqueous solution is used as an evaluation indicator of solid acid, which can directly reflect effective loading of the acid on the mineral, and a greater load can reduce the dissolution of free acid. The pH characterizations shown in Figure 1 indicated that compared with the loading effect of HCl and H2SO4, the H3PO4 loading effect proceeded well with less free acid released, which was confirmed by a higher pH value. Moreover, the phosphoric acid molecule can ionize three free hydrogen ions, which has the potential for solid acid preparation. This work focuses on the preparation of solid acid catalysts by ball-milling H3PO4 and kaolinite and the performance of the sample was investigated mainly by adjusting the ball-milling speed in the range of 250 to 600 rpm and the loading amount of H3PO4.

| catalyst       | acidity (mmolg⁻¹) | pretreatment method | assistance method | solvents | temp (K) | time (h) | glucose and TRSa yield% |
|----------------|------------------|---------------------|-------------------|----------|----------|----------|------------------------|
| Amberlyst-15   | 1.80             |                     |                   | [BMIm]Cl/H2O | 373      | 5        | 11                     |
| PCPs-SO3H     | 1.76             | milled/sieved       | microwave         | H2O      | 403      | 1        | 34.6                   |
| HNNbMoO6      | 1.90             | milled              |                   | H2O      | 403      | 12       | 8.5                    |
| CMK-3-SO3H    | 2.39             | milled              |                   | H2O      | 423      | 24       | 74.5                   |
| SimCn-SO3H    | 0.37             | milled              |                   | H2O      | 423      | 24       | 50.4                   |
| CaFe2O4       | 0.068            | milled              |                   | H2O      | 423      | 24       | 36                     |
| H3PW12O40     |                  |                     |                   | H2O      | 423      | 2        | 18                     |
| HSBW12O40     |                  |                     |                   | H2O      | 333      | 6        | 77                     |

Figure 1. Effect of three acids with kaolinite under the mechanical action.

Figure 2 shows XRD patterns of the coground sample of H3PO4 and kaolinite at different running speeds. In addition to the peaks of the impurity phase of quartz, peaks of the kaolinite phase appeared in the pattern of the raw ore sample. With an increase in the running speed, the peak intensity of the kaolinite phase became very weak and the peak existence in the pattern of the sample ground at 450 rpm was hardly observable and that in the pattern of the sample ground for 550 rpm disappeared with only small peaks of the quartz phase remaining. It is a well-known phenomenon that hydrated layered silicate minerals including kaolinite tend to become amorphous when undergoing intensively high-speed grinding. With the addition of H3PO4 to kaolinite for cogrinding here, a similar phenomenon of amorphization of the kaolinite phase was also observed, with the destruction of its crystalline structure. The pattern information of the ground sample indicated that a possible new phase between the H3PO4 and kaolinite reaction during the grinding operation was also in an amorphous state, not a crystalline phase, making it difficult to

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identify the reaction products. The degree of chemical bonding of H₃PO₄ on kaolinite was examined by measuring the pH value of the solution in distilled water with the sample dispersed. The lower pH value indicates the existence of more free H₃PO₄ molecules in the sample, implying less reaction happening during grinding. The results are shown in Figure 3, where data from the solutions of samples dispersed directly are shown in Figure 3a, and the data from the solutions after cellulose hydrolysis by sample addition are shown in Figure 3b, respectively. It was clear that with an increase in H₃PO₄ dosage, pH of the solutions decreased correspondingly with all the samples prepared at three running speeds. A higher H₃PO₄ dosage tended to have free H₃PO₄ in the sample, giving a lower pH value. Similarly, a higher pH value was observed for the sample prepared at a higher running speed. In other words, a higher running speed was required to prepare the sample with a higher dosage. The sample prepared by 20% H₃PO₄ dosage and 450 rpm grinding condition gave a pH of around 5, maybe an expectable candidate as a catalyst. The change patterns in pH from the filtrate after cellulose hydrolysis shown in Figure 3b are almost the same as that shown in Figure 3a, that is, a higher running speed for sample preparation gave less free H₃PO₄, therefore, higher pH of the solution. The sample at 450 rpm gave a solution of pH around 7, indicating no existence of free acid inside, therefore no need of the separation of free acid from the soluble hydrolysis products. The samples were feasible as a solid acid for cellulose hydrolysis when transformation yield was confirmed.

Changes in bonding states by Fourier transform infrared (FT-IR) analysis were conducted to examine what happened during the cogrinding process (Figure 4). The internal hydroxyl stretching vibration peaks of −OH in Al–OH appeared at 3694, 3620, and 913 cm⁻¹ from the kaolinite of the original ore sample. With addition of H₃PO₄ for cogrinding, the peak existence remained with intensity decreasing relatively. The reaction between H₃PO₄ and kaolinite changed the state of the crystalline structure of kaolinite; however, 20% H₃PO₄ addition at most did not consume all the Al–OH groups to fix the phosphate anion on the kaolinite sample. At the same time, with H₃PO₄ addition, the broadened peak around 3500 cm⁻¹ appeared from the −OH stretching vibration with strong hydrogen bonding, indicating the formation of water molecules from the reaction between H₃PO₄ and kaolinite, represented by eqs 1 and 2.

$$\text{Al}_2\text{SiO}_3\text{(OH)}_4 + H_3\text{PO}_4 \rightarrow \text{Al}_2\text{SiO}_3\text{(OH)}_3\cdot H_2\text{PO}_4 + H_2\text{O}$$

$$\text{Al}_2\text{SiO}_3\text{(OH)}_4 + H_3\text{PO}_4 \rightarrow \text{Al}_2\text{SiO}_3\text{(OH)}_3\cdot H\text{PO}_4 + H_2\text{O}$$

The agglomeration phenomenon is commonly observed particularly with the samples by intensive grinding. A small amount of water inside the sample will increase the agglomeration to a heavy state. Figure 5 shows the changes in morphology of the sample before and after ball-milling and confirmed the morphology change from a lamellar structure (Figure 5a) of the layered kaolinite to a heavy agglomeration of fine particles (Figure 5c). Also, the heavy state of agglomeration indicated existence of water in the sample, probably from the reaction during cogrinding. In addition to the existence of Si, Al, and O from kaolinite, existence of P was confirmed as shown in Figure 5b from H₃PO₄ addition. It was worth noting that the distribution of the P element was even in the mapping figure shown in Figure 5d, suggesting that the reaction occurred through all the samples, rather than local enrichment of H₃PO₄ composition, to serve as an effective catalyst for hydrolyzing cellulose.

2.2. Optimization of Hydrolysis Reaction Conditions. The phenomenon of active component dissolution from the biomass hydrolysis system is generally reported at high temperature hydrothermal treatment by carrier catalysts.

![Figure 3. Changes in the pH value of (a) solutions with the catalyst dispersed in water and (b) solutions after the hydrolysis reaction.](image)

![Figure 4. FT-IR spectra of kaolinite/H₃PO₄ with different weight ratios of H₃PO₄.](image)
Operation at mild conditions with a low temperature is expected to be beneficial for industrial utilization of cellulose biomass energy. A temperature range from 20 to 80 degrees was chosen for the experiment, and stability confirmation through weight loss due to the dissolution of catalyst components was conducted in this temperature range. Figure 6 shows the changes in the dissolution rate of the catalyst sample in distilled water and together with cellulose to temperature. Around 1% weight loss of the sample in water was observed, partly from the moisture inside and partly from real dissolution of some active compositions. However, when cellulose was added, the weight loss in general to the whole solid base was increased to more than 6%, indicating that certain amount of cellulose had changed into water soluble at 80 degrees. Most of the reported hydrolysis processes use high-pressure reaction conditions at high temperature to pursue highly efficient hydrolysis of cellulose. The data shown in Figure 6 confirmed possible transformation of cellulose into water soluble substances even at this mild condition. The key parameters for the optimization of cellulose hydrolysis process conditions were confined to temperature, time, solid–liquid ratio, and catalyst dosage ratio. Detailed experiments were performed to study the effects for increasing the yield of the glucose product and the results are shown in Figure 7. All data in the four figures showed clearly that treating cellulose in water only or in water with kaolinite only did not give noticeable formation of the glucose product. Kaolinite itself does not demonstrate evident catalytic ability toward cellulose hydrolysis. Only the phosphoric acid-loaded kaolinite had the ability to catalyze cellulose hydrolysis.

The change in the glucose yield with time is shown in Figure 7a. An increase in the glucose yield was observed until 12 h from 0 to near 3% and the increase rate slowed down after 12 h, with the glucose yield around 3% between 12 and 24 h. A prolonged hydrolysis time did not contribute to the increase in the glucose yield, possibly due to an easy degradation of the glucose product to adhere to the surface of unreacted microcrystalline cellulose and reduce the reaction surface of microcrystalline cellulose. The change in the glucose yield with hydrolysis temperature is shown in Figure 7b in the range of 20–80 degrees. The cellulose hydrolysis yield increased slowly at temperatures from 20 to 50 degrees and a relatively fast increase in the yield was obtained in the temperature range of 50 to 70 degrees, and leveled off to 80 degrees. The temperature for cellulose hydrolysis was much lower than the hydrothermal treatments, suggesting a possible development of a low-temperature process for cellulose hydrolysis. Figure 7c further shows the effect of the solid–liquid ratio on cellulose hydrolysis. Water as a mass transfer medium and reactant simultaneously affected the hydrolysis efficiency. Therefore, there existed the best condition of a liquid–solid...

Figure 5. Scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) analyses of the prepared sample with P element distribution; SEM scale: (a) 1 μm and (c) 10 μm; (b) different element content diagrams; and (d) distribution map of the P element.

Figure 6. Thermal stability test of the prepared catalyst.
ratio of 40 mL/g to give a high glucose yield over 3%. The low value meant that less water was not sufficient as a reactant for the hydrolysis reaction. The high value meant too much water to reduce the probability of reaction contact surfaces and inhibit the efficiency of hydrolysis. As to the effect of catalyst dosage to cellulose, as shown in Figure 7d, clearly the glucose yield increased steadily with an increase in catalyst dosage and reached over 6% at 9:1. Further increase in the catalyst dosage did not give further yield increase and the value leveled off.

In summary, the optimized conditions for hydrolysis were listed as: a hydrolysis time of 20 h; a hydrolysis temperature of 70 degrees; a solid–liquid ratio of 40 mL/g; and a catalyst dosage ratio of 9:1. At this time, the glucose yield reached 6.85%. Although detailed investigations are required to cover other possible products and evaluate reasonable application as well as further enhancement in catalyzing glucose production, the H₃PO₄-based catalyst prepared by mechanical ball-milling exhibited a significant performance in the catalytic effect to work at a very low temperature. At the same time, the cycling test of the catalyst was performed. The recovery of the catalyst was only by means of filtration. The results showed that it was affected by the dissolution of the active components and retained its catalytic efficiency of 82% after three times.

With the aid of mechanical force from high-energy ball-milling, changes in the crystal structure of kaolinite increases its particle size and reactive contact surface as the consequence of mechanical activation-promoted dissociation of protons of H₃PO₄ and its interaction with kaolinite. Active groups inside the sample were developed including a binding group that acted on cellulose glycosidic bonds, and active hydrogen directly participated in catalysis. As illustrated in Figure 8, it combines with water molecules to form hydronium ions, acts on \(\beta\)-1,4 glycosidic bonds, and forms an unstable oxygen-binding tetravalent structure, so that the oxygen bond is broken to generate two \(-OH\), while releasing hydrogen ions to complete the catalysis. As the most easily conquered site in the cellulose long chain, active hydrogen -H₂PO₄ was believed to act on the amorphous region of cellulose and catalyze its chain-breaking to form glucose monomers. The hydrolysis results could be simplified as reaction eq 3. As the hydrolysis...
temperature increases, the active hydrogen in the solid acid acts more actively on the active site of cellulose. On the other hand, the acid-active components of the solid acid also begin to dissolve in small amounts. This phenomenon indicates that the kaolinite-based H₃PO₄ solid acid may not be suitable for high temperature operation. It did realize the obvious promotion of the hydrolysis and conversion of cellulose under mild conditions, the preparation of solid acid for mechanochemical means, and even at room temperature. Low-temperature hydrolysis of fibers offers greater possibilities. Since the yield of glucose was not high enough, further research studies are under planning to raise the efficiency of the prepared catalyst through increasing acid dosage or mixed use of different types of acids.

\[(\text{C}_6\text{H}_{10}\text{O}_5)_n + n\text{H}_2\text{O} \xrightarrow{\text{Al}_2\text{Si}_3\text{O}_9(\text{OH})_2 \cdot \text{H}_3\text{PO}_4} n\text{C}_6\text{H}_2\text{O}_6\] (3)

### 3. CONCLUSIONS

The successful loading of H₃PO₄ to enhance the acidic sites of kaolinite showed considerable efficiency in catalytic hydrolysis of cellulose, confirming that the mechanochemical route is not only easy and economical but also efficient for the synthesis of the H₃PO₄-based solid catalyst. With conditions optimized as 343 K for 20 h, low catalytic load (9:1), and a liquid–solid ratio of 40 mL/g, the saccharification rate of cellulose reached 6.85%, especially 83% of the catalytic activity was retained after being recycled three times. This research opened up a novel approach for the preparation of solid acid catalysts, and provided more possibilities for the low-temperature hydrolysis of cellulosic biomass.

### 4. MATERIALS AND METHODS

#### 4.1. Materials

Glucose (Maclin; 99 wt %;A.R.), cellulose (Maclin; 99 wt %;A.R.), kaolinite (C.P; Jiangxi, China), H₃PO₄ (Maclin; ≥85 wt %;A.R.), salicylic acid (Maclin; 99.5 wt %;A.R.), 1,2-propanediol (Maclin; 99 wt %;A.R.), and sodium hydroxide (Maclin; 95 wt %;A.R) were obtained and used directly without purification.

#### 4.2. Catalyst Preparation

Mixtures of kaolinite and H₃PO₄ were milled in a planetary ball-mill (Pulverisette-7, Fritsch, Germany), with two stainless-steel milling pots (45 cm³ inner volume each) and 7 steel balls (Ø15 mm). Kaolinite (4 g) and H₃PO₄ at a mass ratio of 5, 10, 15, and 20% were prepared and subjected to ball-milling for 2 h at different spinning speeds.

#### 4.3. Catalyst Characterization

SEM-EDS were used to test the content and distribution of elements on the surface of the H₃PO₄-based solid catalyst samples. FT-IR (Nicolet 6700, Thermo, Thermo Electron Scientific Instruments Corp, Madison, WI) was used to determine the surface groups and valence bonds at a 500~4000 cm⁻¹ wavelength range. An X-ray diffractometer (Rigaku, Japan, D/MAX-IIIA) was used to analyze its crystal structure and composition with a diffraction angle 20 range from 5°~70° using a Cu target X-ray radiation source. The solid acid catalyst samples prepared by ball-milling were continuously stirred in pure water, and a pH meter (METTLER TOLEDO, Switzerland, FE28-Standard) was used to measure the pH, which to some extent characterized the acid load or not. At the same time, the residue after being passed through a 0.45 mm membrane filter was dried at room temperature and sealed for 24 h, and the weight of the residue was calculated to characterize the dissolution rate of the catalyst.

#### 4.4. Catalytic Hydrolysis of Cellulose

Microcrystalline cellulose (0.5 g) and appropriate amounts of pure water and the sample prepared by ball-milling were put into a 250 mL Erlenmeyer flask on a magnetic stirring water bath. Parameters of hydrolysis time, hydrolysis temperature, rotation speed, and solid–liquid ratio reaction conditions were examined for hydrolysis experiments. After filtering through pure water, the product filtrate was collected and analyzed qualitatively and quantitatively. All degradation products passed through a 0.45 mm membrane filter. The theoretical components of the filter residue include cellulose, catalyst, and impurities. Therefore, the filter residue is cleaned with pure water and filtered with copper–ammonia solution. The experiment of catalyst reuse was carried out three times under the same hydrolysis condition.

The 3,5-dinitrosalicylic acid (DNS) method is known for high stability and accuracy for measuring the hydrolysis glucose from cellulose polysaccharide. The UV absorption spectrophotometry-salicylic acid colorimetry method was used for qualitative and quantitative analysis of hydrolyses at a wavelength of 540 nm. The calculation of the glucose yield and was based on the following formula:

\[
\text{Glucose yield(%) = } \frac{\text{weight of Glucose produced}}{\text{weight of starting cellulose}} \times 100\%
\]

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REFERENCES

(1) Cantero, D. A.; Sánchez Tapia, Á.; Bermejo, M. D.; Cocero, M. J. Pressure and temperature effect on cellulose hydrolysis in pressurized water. Chem. Eng. J. 2015, 276, 145–154.

(2) Wu, Q.; Liu, S.; Xie, C.; Yu, H.; Liu, Y.; Yu, S.; Huang, L. Ni-promoted mesoporous carbon obtained from hydrothermal carbonization of cellulose and their catalytic hydrogenation activity study. J. Mater. Sci. 2018, 53, 7900–7910.

(3) Zhao, B.; Hu, S.; Gong, D.; Li, H. New advances on hydrolysis of cellulose to glucose by solid acid. Huagong Jinzhan 2017, 36, 555–567.

(4) Qi, X.; Yan, L.; Shen, F.; Qiu, M. Mechanochemical-assisted hydrolysis of pretreated rice straw into glucose and xylose in water by weakly acidic solid catalyst. Bioresour. Technol. 2019, 273, 687–691.

(5) Clark, J. H. Solid Acids for Green Chemistry. Acc. Chem. Res. 2002, 35, 791–797.

(6) Rinaldi, R.; Palkovits, F.; Schüth Angew. Solid acids are shown to be effective catalysts for breaking down cellulose, a potentially renewable chemical feedstock. Nat. Chem. 2008.

(7) Huang, Y.-B.; Fu, Y. Hydrolysis of cellulose to glucose by solid acid catalysts. Green Chem. 2013, 15, 1095–1111.

(8) Akiyama, G.; Matsuda, R.; Sato, H.; Takata, M.; Kitagawa, S. Cellulose Hydrolysis by a New Porous Coordination Polymer Decorated with Sulfonic Acid Functional Groups. Adv. Mater. 2011, 23, 3294–3297.

(9) Zhong, R.; Sels, B. F. Sulfonated mesoporous carbon and silica-carbon nanocomposites for biomass conversion. Appl. Catal., B 2018, 236, 518–545.

(10) Ma’rifah, Y. N.; Nata, I.; Wijayanti, H.; Mirwan, A.; Irawan, C.; Putra, M. D.; Hidetaka, K. One-step Synthesis to Enhance the Acidity of a Biocarbon-based Sulfonated Solid Acid Catalyst. Int. J. Plast. Technol. 2019, 10, 512–520.

(11) Pang, J.; Wang, A.; Zheng, M.; Zhang, T. Hydrolysis of cellulose into glucose over carbons sulfonated at elevated temperatures. Chem. Commun. 2010, 46, 6935.

(12) Takagaki, A.; Tagusagawa, C.; Domen, K. Glucose production from saccharides using layered transition metal oxide and exfoliated halloysite-polyurethane composites. Results Phys. 2018, 9, 33–38.

(13) Zhang, Q.; Solihin; Saito, F. Mechanochemical Synthesis of Slow-Release Fertilizers through Incorporation of Alumina Composition into Potassium/Ammonium Phosphates. J. Am. Ceram. Soc. 2009, 92, 3070–3073.

(14) Ogasawara, Y.; Itagaki, S.; Yamaguchi, K.; Mizuno, N. Dense catalysts for breaking down cellulose, a potentially hydrolysis residue derived solid acid under microwave irradiation. Green Chem. 2012, 14, 2162–2167.