Preparation of a Cellulase-imitated Solid Acid Catalyst With High Acid Density and Its Evaluation for Hydrolysis of Cellulose

Bo Deng  
Taiyuan University of Technology

Ya-xiong Wang  
Taiyuan University of Technology

Li Huo  
Taiyuan University of Technology

Ying Wang  
Taiyuan University of Technology

Li’e Jin (✉ lejin2003@163.com)  
Taiyuan University of Technology

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Preparation of a cellulase-imitated solid acid catalyst with high acid density and its evaluation for hydrolysis of cellulose

Bo Deng\textsuperscript{a}, Ya-xiong Wang\textsuperscript{a}, Li Huo\textsuperscript{a}, Ying Wang\textsuperscript{a}, Li’e Jin\textsuperscript{a,\*}

\textsuperscript{a,\*}Institute of Chemistry and Chemical Engineering, Taiyuan University of Technology, 030024 P.R.China.

*Corresponding author. E-mail address: lejin2003@163.com (Li’e Jin)

Abstract: In this paper, tannic acid, a polyphenolic substance rich in plants, is modified by the glutamic acid and cross-linked with formaldehyde to prepare a high acid density tannin-glutamate acid resin-based imitation enzyme solid acid catalyst (T-Glu-R), which is completely different from traditionally carbon-based solid acid synthesized by concentrated sulfuric acid and carbonized matter. The solid acid catalyst was characterized by Fourier transform infrared spectroscopy, scanning electron microscope, thermogravimetry, and X-ray photoelectron spectroscopy. The catalytic activity and cycle performance of T-Glu-R in the cellulose hydrolysis reaction were evaluated. The results show that the acid density of T-Glu-R reached 7.28 mmol/g, which is much higher than that of the highest acid density of carbon-based solid acid. Microcrystalline cellulose was hydrolyzed in distilled water at 180 °C for 2 h, the yield of total reducing sugars reached 72.15%. After four cycles of hydrolysis, the yield was only reduced by 4.32%, showing excellent cycle performance and stability. The study provides a new strategy with the synthesis of solid acid catalyst for hydrolysis of cellulose converted into platform compounds without concentrated sulfuric acid.

**Keywords:** Solid acid; Glutamic acid; Hydrolysis of cellulose; Tannic acid; catalyst

1. Introduction
The use of traditional fossil energy has brought various environmental problems, like air pollution and global warming. Fossil resources will not be able to meet the future energy needs of humanity due to their non-renewability. As the only renewable organic carbon source on Earth, biomass is regarded as the best substitute for fossil resources (Huang and Yao 2013; Zhang et al. 2016). The most valuable biomass is cellulose, which can produce glucose after depolymerization. Glucose can be fermented to ethanol or dehydrated to form platform compounds, such as 5-hydroxymethylfurfural (Arthur et al. 2006).

Cellulose is a high polymer composed of glucose units connected by β-1,4-glycosidic bonds. Numerous hydrogen bonds exist within and between cellulose molecules, bringing great difficulties to the hydrolysis of cellulose into glucose. Acids and biological enzymes are often used to hydrolyze cellulose. For example, concentrated sulfuric acid can effectively cause the swelling of and hydrolyze crystalline cellulose to form glucose by breaking the hydrogen bonds. However, many kinds of issues should be considered, such as by-products, corrosion equipment, the difficult separation of catalyst and product, and wastewater treatment. Studies have identified the main reason for the efficient hydrolysis of cellulase as the presence of binding and catalytic groups in the structure. Catalytic groups, like the carboxyl and phenolic hydroxyl groups of amino acids, are used as proton sources to attack and hydrolyze the glycosidic bond on the cellulose chain. Meanwhile, binding groups enables the cellulase and the hydroxyl group on the cellulose chain to form a hydrogen bond to shorten the distance between the cellulase and the cellulose. Cellulase can selectively hydrolyze cellulose under mild conditions. However, due to the thermal instability of cellulase, the hydrolysis rate cannot be increased by increasing the temperature, resulting in a long reaction time. Cellulase itself is expensive and difficult
to recycle, limiting its use in enzymatic hydrolysis. The above shortcomings limit the
application of liquid acid and cellulase in cellulose hydrolysis (Lanzafame et al. 2012).

The widely studied new type of catalyst solid acid used to catalyze the hydrolysis
of cellulose has the advantages of easy separation of products, recyclability, low
corrosion to equipment, and low cost. This catalyst solid acid can meet the needs of
catalytic reactions by adjusting the specific surface area and pore size and grafting
active functional groups, such as the acid and adsorption centers (Pang et al. 2010).
Suganuma et al. (2012) used polyvinyl chloride as a carbon source to synthesize
sulfonation catalysts to catalyze the hydrolysis of cellobiose. The absence of -OH makes
cellobiose adsorption difficult, preventing the catalyst from exhibiting high catalytic
activity, thereby resulting in a glucose yield of only 30.1%. Jiang et al. (2011) used
glucose as a carbon source to prepare a solid acid catalyst. When the degree of
carbonization is low, the catalyst retains a high -OH density and has a strong adsorption
to cellulose, and the glucose yield reaches 74%. Thus, the catalyst has a high -OH
density as the binding group, which can selectively form hydrogen bonds with the
oxygen atoms of the glycosidic bond of cellulose to produce adsorption and improve the
hydrolysis efficiency.

Fan et al. (2013) synthesized a sulfonated polymer solid acid (SPS-DVB-SO\textsubscript{3}H).
After the catalyst undergoes catalytic hydrolysis, the loss of H\textsuperscript{+} greatly reduces the acid
density of the catalyst, and the glucose yield drops from 37% to 7%. Therefore, the
catalyst must be immersed in a sulfuric acid solution for regeneration after the reaction.
Yang and Pan (2016) synthesized an enzyme-like solid acid (POP-SO\textsubscript{3}H-Cl). After four
cycles of use of the solid acid, the glucose yield dropped from 84.9% to 17.2%. The test
revealed that the density of its sulfonic acid dropped from 0.74 mmol/g to 0.16 mmol/g.
Zhang et al. (2013) treated activated carbon with low-concentration nitric acid, not only
oxidizing the lactone, ether, quinine, and other functional groups on the surface of the activated carbon to -COOH, but also dissolving the ash on the surface of the activated carbon to allow the grafting of more -SO₃H onto the activated carbon. The acid density of the catalyst increased from 1.58 mmol/g to 2.23 mmol/g, and the glucose yield increased to 62.2%. In summary, high-density acid centers are essential to cellulose hydrolysis.

Most of the above solid acids use -SO₃H as the catalytic group. However, the -SO₃⁻ formed after the sulfonic acid group releases H⁺ will be hydrolyzed and fall off in the aqueous acidic medium, causing the loss of the sulfonic acid group (Min et al. 2013). Moreover, -SO₃H will further degrade glucose at high temperatures. The concentrated sulfuric acid and the sulfonating agent chlorosulfonic acid used in the catalyst sulfonation process cause great environmental pollution and are inconsistent with the environmental friendliness of green chemistry. In the current research, co-doping, grafting, and other methods are used to introduce binding groups (Jin et al. 2020; Zhou et al. 2013). However, these groups easily leach out under high-temperature hydrolysis conditions, reducing the catalytic efficiency of the catalyst cycle.

Tannic acid (TA) is a type of polyphenol widely found in plants. Given the presence of numerous phenolic hydroxyl groups in TA, the resin prepared by crosslinking TA with formaldehyde also has many polar functional and phenolic hydroxyl groups, which can be used as binding groups for the preparation of cellulose hydrolysis catalysts. Glutamic acid is an acidic amino acid containing the -COOH group, which is present in cereal protein. To overcome the low surface acid density problem of the existing imitation enzyme solid acid catalysts, this experiment used TA as the raw material and modified it with glutamic acid to prepare tannic-glutamate (T-Glu). Then, T-Glu was crosslinked with formaldehyde to prepare a tannic glutamate phenolic resin
imitation enzyme solid acid catalyst with a binding group (-OH) and a catalytic group (-COOH). On the one hand, the T-Glu-R solid acid catalyst has a wide range of raw materials, is biodegradable, does not pollute the environment, and is easier to recycle than cellulase. On the other hand, the direct cross-linking method avoids the loss of active groups, retains the original cellulase-like active sites of TA and glutamic acid, and can effectively reduce the activation energy of the reaction. In addition, the resin-based enzyme that mimics solid acid has a certain thermal stability, which can increase the temperature appropriately, accelerate the reaction speed, and effectively hydrolyze cellulose into reducing sugars, providing a powerful means of converting cellulose to platform compounds.

2. Materials and methods

2.1 Materials

The chemical reagents, including TA, glutamic acid, 3,5-dinitrosalicylic acid (DNS), formaldehyde, natrium bicarbonate (NaHCO₃), hydrochloric acid (HCl, 37%), sodium hydroxide (NaOH), nickel nitrate (Ni(NO₃)₂), and hydrogen peroxide (H₂O₂), were purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents were of analytical grade and directly used without further purification. Microcrystalline cellulose (MCC) was purchased from Shandong Ehua Pharmaceutical Co., Ltd.

2.2 Preparation of T-Glu-R solid acid catalyst

First, TA was modified with glutamic acid. According to the 1:3 molar ratio of TA to glutamic acid, 4 g of TA and 1.05 g of glutamic acid were dissolved in 100 mL of distilled water. Then, the pH was adjusted to 1.5 with 37% HCl, and the solution was heated in a water bath at 60 °C for 5 h. After adjusting the pH to 6.8 by the isoelectric point method, the product appeared as a precipitate (Aelenei et al. 2009; Badawi et al. 2017). Then, the precipitate was washed with distilled water, centrifuged, and dried to
obtain T-Glu. Subsequently, 4 g of T-Glu, 3 mL of formaldehyde, 2 mL of HCl, and 20 mL of distilled water were added to a 100-mL Teflon-lined stainless-steel autoclave and reacted hydrothermally at 120 °C for 12 h to obtain a brown resin, which was washed to the solution is neutral. The product was ground and passed through a 100-mesh sieve to obtain a resin-based solid acid catalyst, which was named T-Glu-R. The preparation’s reaction equation is shown in Fig. 1.

![Reaction equation for preparing T-Glu and T-Glu-R.](image)

Fig. 1 Reaction equation for preparing T-Glu and T-Glu-R.

2.3 Determination of acid density of T-Glu-R solid acid catalyst

According to the literature, the densities of the total acid, the carboxyl group, and the phenolic hydroxyl group on the surface of the prepared catalyst were measured by the Boehm back titration method (Zhang et al. 2013). First, 0.1 g of catalyst was added to a 30 mL, 0.05 mol/L NaOH aqueous solution. The solution was sonicated at room temperature for 60 min and then centrifuged. Using phenolphthalein as an indicator, the filtrate was titrated with a 0.05 mol/L HCl aqueous solution, and the total acid density ($C_T$) was calculated according to Formula (1). Finally, 0.1 g of the catalyst was added to a 30 mL, 0.01 mol/L NaHCO$_3$ aqueous solution. The solution was sonicated at room temperature for 60 min and centrifuged. Using BroMo Green-Methyl Red TS as an indicator, the filtrate was titrated with a 0.01 mol/L HCl aqueous solution, and the carboxyl group density ($C_{COOH}$) on the catalyst surface was calculated according to...
Formula (2), and the phenolic hydroxyl group ($C_{OH}$) density was calculated according to Formula (3).

\[
C_T = \frac{100 \text{ mmol/L} \times 0.03 \text{ L} - 100 \text{ mmol/L} \times V_{HCl}}{0.1 \text{ g}}
\]  
(1)

\[
C_{COOH} = \frac{100 \text{ mmol/L} \times 0.03 \text{ L} - 100 \text{ mmol/L} \times V_{HCl}}{0.1 \text{ g}}
\]  
(2)

\[
C_{OH} = C_T - C_{COOH}
\]  
(3)

2.4 Characterization of T-Glu-R solid acid catalyst

The changes in the structure of the catalyst were investigated by Fourier transform–infrared spectroscopy (FTIR, BRUKER TENSOR 27). The spectra were recorded from 400 cm\(^{-1}\) to 4000 cm\(^{-1}\) with a 4 cm\(^{-1}\) resolution. Approximately 1 mg of the sample was mixed with 80 mg of spectroscopy-grade KBr, and the mixture was pressed in a standard device. The morphology of the catalyst was analyzed by field-emission scanning electron microscopy (FE-SEM, Hitachi, S-3000N) working at 5 kV. Thermal gravimetry (TG) was adopted to analyze the thermal behavior of the catalyst using a thermal gravimetric analyzer (WCT-2D) from 50 °C to a final temperature of 800 °C with a heating rate of 10 °C/min under N\(_2\) flow (40 mL/min). The X-ray photoelectron spectra (XPS) of the catalyst were recorded using a Thermo Fisher ESCALAB 250xi spectrometer with Al K\(\alpha\) radiation (1486.6 eV). The binding energies were calculated with respect to C1s at 284.8 eV with a precision of ±0.05 eV.

2.5 Cellulose pretreatment

The pretreatment of cellulose before hydrolysis can reduce its crystallinity and improve hydrolysis efficiency (Syafitika and Matsumura 2018; Kumar and Sharma 2017). Studies on the pretreatment of cellulose have shown that some organic solvents can dissolve cellulose, like phosphoric acid (Zhang et al. 2006). After adding the dissolved cellulose to the reverse solvent, the cellulose is precipitated and regenerated.
During this process, the crystalline form of cellulose is transformed, and the hydrogen bonds between molecules are broken and rearranged, reducing the crystallinity of cellulose and increasing the pores (Yuan et al. 2017). Metal ions are often used to promote hydrolysis to pretreat cellulose because the empty orbitals of metal ions can combine with the lone pair of electrons on the β-1,4 glycosidic bond oxygen atom of cellulose (Li et al. 2015), thereby activating the carbon-oxygen bond, which is conducive to cellulose hydrolysis. In this experiment (Li et al. 2018), pretreated cellulose was obtained by combining ultrasonic wave, metal ion, and oxidation methods. In the typical pretreatment process, 5 g of MCC, 200 mL of 0.15 wt% nickel ion solution, and 0.5 mL of H₂O₂ were added into a flask and sonicated at 75 °C for 2 h. Then, the solid was separated and washed with distilled water. The dried sample was labelled pretreated cellulose.

2.6 Hydrolysis of cellulose

Typically, 0.2 g of T-Glu-R, 0.1 g of pretreated cellulose, and 30 mL of distilled water were added into a 100-mL Teflon-lined stainless-steel autoclave and heated to 180 °C for 2 h. After the reaction, the mixture was separated by filtration. The total reducing sugar (TRS) yield was analyzed by the DNS method (Mission et al. 2017). A mixture containing 1 mL of hydrolysate, 1 mL of DNS, and 3mL of distilled water was heated at 100 °C for 5 min and then cooled to room temperature. The absorbance of the mixture was measured using a TU-1901 spectrophotometer at 540 nm. The TRS concentration was quantified based on a standard curve obtained with glucose. The TRS yield is calculated as follows:

\[ TRS(\%) = \frac{C_{TRS} \times V}{M_{Cellulose}} \times 100\%, \]  

where \( C_{TRS} \) is the concentration of the reducing sugar in the hydrolysate (mg/mL), \( M_{Cellulose} \) is the initial cellulose mass (mg), and \( V \) is the volume of the hydrolysate (mL).
At the end of the reaction, the unreacted cellulose and the solid acid catalyst were filtered. Afterward, it was washed with distilled water and dried at 100 °C. The separated catalyst was used in the cyclic hydrolysis experiment.

3. Results and discussion

3.1 Characterization of T-Glu-R solid acid catalyst

3.1.1 FT-IR

The infrared spectra of TA, T-Glu, and T-Glu-R are shown in Fig. 2. The figure shows a stretching vibration peak of -OH around 3400 cm\(^{-1}\), indicating that TA, T-Glu, and T-Glu-R contain phenolic hydroxyl groups. In the T-Glu spectrum, 1310, 1715, and 2976 cm\(^{-1}\) are the stretching vibration peaks of C-N, carboxyl C=O, and N-H (Erdem et al. 2013; Zhao et al. 2011), respectively. A new infrared absorption band appeared at 1542 cm\(^{-1}\), confirming the formation of the O-NH\(_2^+\) bond. The reaction between TA and glutamic acid formed between the amino and phenolic hydroxyl groups indicates the successful preparation of T-Glu. The characteristic peak of T-Glu-R is more obvious at 1380 cm\(^{-1}\), which is the characteristic peak of -CH\(_2^-\) (Shi et al. 2019), indicating the existence of many methylene groups in T-Glu-R and the successful cross-linking of formaldehyde with T-Glu.

![Fig. 2 FTIR spectra of T-Glu-R (a: TA, b: T-Glu, c: T-Glu-R).](image_url)
3.1.2 FE-SEM Analyses

Fig. 3 presents a scanning electron micrograph of the catalyst. The solid acid catalyst has a rough surface and pores, exhibiting an obvious porous structure. A resin network structure forms when formaldehyde cross-links with T-Glu, thereby forming a porous structure. Therefore, this structure is highly conducive to the contact of the prepared resin-based solid acid with the reactants, which can expose more effective groups on the surface of the catalyst, provide sufficient catalytic reaction sites, and increase the collision frequency between the catalyst and the cellulose. Consequently, the catalytic performance of the catalyst is improved (Onda et al. 2009; Akiyama et al. 2011).

![SEM images of T-Glu-R (a:×100, b:×1000).](image)

3.1.3 TG Analyses

The thermal behavior of the solid acid catalyst is shown in Fig. 4. The thermogravimetric curve indicates that the percentage of mass retention gradually decreases as the temperature increases. The temperature increased from 100 °C to 200 °C, and the weight of the catalyst was reduced by 1.7%. The weight loss may be caused by the evaporation of water adsorbed on the sample (Hu et al. 2016). The respective temperatures at 5% and 10% weight loss (T$_{5\%}$ and T$_{10\%}$) were 254 °C and 307 °C, indicating that when the temperature was below 254 °C, the catalyst did not
change significantly when cellulose was hydrolyzed. T-Glu-R performance was relatively stable. At 420 °C, the maximum weight loss rate was reached. At this time, the mass retention percentage was 66%. This phenomenon may be attributed to the decomposition of -OH and -COOH groups at high temperatures. When the temperature continued to rise, the rate of weight loss began to decrease, and the rate of weight loss approached zero at 800 °C. The mass retention percentage at 800 °C indicates the good thermal stability of T-Glu-R.

**Fig. 4** TG curves spectra of T-Glu-R (a:TG, b:DTG).

3.1.4 XPS Analyses

X-ray photoelectron spectroscopy was used to analyze the surface chemical composition of T-Glu-R. Fig. 5a shows the full scan spectrum of the catalyst, the surface of the solid acid catalyst contains three elements, namely, C, O, and N. The typical N 1s peak appeared at 401.7 eV (Xu et al. 2016), confirming that glutamic acid successfully modified TA and has the unique amino group of glutamic acid. The C 1s spectra for T-Glu-R can be resolved into four peaks centered at 284.79, 285.7, 286.26, and 288.48 eV, which can be respectively assigned to C=C, C-N, C-O, and C=O. Moreover, the O 1s spectra can also be resolved into three peaks centered at 531.5 and 533.3 eV, which are most likely related to C=O and C-O (Chen et al. 2017; Pan et al. 2017; Xu et al. 2016).
2017), respectively. Meanwhile, the XPS results show that the solid acid catalyst surface contains active groups, such as -OH, -COOH, and -NH$_2$.

![XPS spectra of T-Glu-R solid acid catalyst](image)

**Fig. 5** XPS spectra of T-Glu-R solid acid catalyst (a: full spectra, b: C 1s spectra, c: O 1s spectra).

3.2 Analysis of the surface acid density of T-Glu-R solid acid

The surface acid density of T-Glu-R under different preparation conditions was measured according to the experimental method in Section 1.2.2, and the results are shown in Fig. 6. The influence of different temperatures on the acid density of the prepared catalyst is shown in Fig. 6a. The figure indicates that when the molar ratio of TA to T-Glu was 1:3, the reaction time was 12 h, the total acid, phenolic hydroxyl, and carboxyl group densities increased from 100 °C to 120 °C, and the maximum densities were 7.12, 5.84, and 1.28 mmol/g, respectively. The surface acid density of acid T-Glu-
R decreased slightly and remained unchanged with the increase of temperature, indicating that the high-temperature hydrothermal synthesis conditions had little effect on the structure of T-Glu-R.

The influence of different times on the acid density of the prepared catalyst is shown in Fig. 6b. When the temperature was 120 °C and the molar ratio of TA to T-Glu was 1:3, the total acid, phenolic hydroxyl, and carboxyl group densities were the highest at 12 h, namely, 7.23, 5.91, and 1.32 mmol/g, respectively. The amount of acid on the surface of the resin solid acid no longer changed with the increase of time, probably due to the increase of steric hindrance between the functional groups and absence of reaction.

The influence of the molar ratio of TA to Glu on the acid density of the catalyst is shown in Fig. 6c. The carboxyl group density rose rapidly with the molar ratio from 1:1 to 1:3. With the further increase of the molar ratio, the carboxyl group density tended to be stable, which may be attributed to the saturation of the reaction between the phenolic hydroxyl group on the TA and the glutamic acid.

The total acid, phenolic hydroxyl, and carboxyl group densities of the catalyst prepared under 120 °C for 12 h and at the molar ratio of TA to Glu of 1:3 were the highest, namely, 7.28, 5.55, and 1.73 mmol/g, respectively.
Fig. 6 Influence of reaction temperature (a), time (b), and the molar ratio (c) of TA and T-Glu on catalyst acid density.

Table 1 shows a comparison of the acid density of solid acid and the TRS yield in the literature. Compared with other catalysts, T-Glu-R solid acid has the highest surface acid density of 7.28 mmol/g, and the catalytic efficiency is also the highest (72.15%). The surface hydroxyl content of T-Glu-R (5.55 mmol/g) is much higher than those of other catalysts because the raw material TA is rich in phenolic hydroxyl groups, which can provide more adsorption sites in the cellulose hydrolysis reaction. -COOH as the acid center (1.73 mmol/g) dissociates H⁺ in water to attack the oxygen atom on the glycosidic bond to rapidly protonate it, breaking the cellulose glycosidic bond and thereby depolymerizing the cellulose. -COOH can also form hydrogen bonds with the -
OH of cellulose, improving the efficiency of the hydrolysis reaction of cellulose. The schematic of the active site of T-Glu-R is shown in Fig. 1.

**Table 1** Comparison of acid density of solid acid and TRS yield in the literatures.

| Solid acid                  | C_{Total acid} (mmol/g) | C_{SO3H} (mmol/g) | C_{COOH} (mmol/g) | C_{OH} (mmol/g) | TRS/% | References          |
|-----------------------------|------------------------|-------------------|-------------------|----------------|-------|---------------------|
| CMC-SO3H                    | 1.82                   | 0.73              | 1.09^a            |               | 44.4  | Hu et al. (2016)   |
| Amberlyst-15                | 4.70                   | 4.7               | -                 | -             | 29.5  | Tyufekchiev et al. (2018) |
| carbon material (CH_{0.62}O_{0.54}S_{0.05}) | 4.3                   | 1.9               | 0.4               | 2.0           | 68    | Suganuma et al. (2008) |
| LPC-SO3H                    | 3.52                   | 0.88              | 0.96              | 1.68          | 50.8  | Zhu et al. (2017)   |
| SLC-SO3H                    | 2.4                    | 0.85              | 0.59              | 0.96          | 41.1  | Erdem et al. (2013) |
| T-Glu-R                     | 7.28                   | -                 | 1.73              | 5.55          | 72.15 | This work           |
| T-Glu-R^b                   | 7.03                   | -                 | 1.65              | 5.38          | 67.83 | This work           |

^a:C_{COOH} and –OH.  ^b: After four times run.

3.3 T-Glu-R solid acid hydrolysis of cellulose capacity

3.3.1 Mechanism of T-Glu-R solid acid catalyst for hydrolysis of cellulose

The large number of phenolic hydroxyl groups in the T-Glu-R solid acid catalyst has a similar effect to the binding group of cellulase, which can form hydrogen bonds with cellulose, thereby shortening the distance with cellulose and playing a binding role. The carboxyl group can cut the glycosidic bond of the cellulose chain, which acts similarly as the catalytic group of cellulase. Fig. 7 presents a schematic of the hydrolysis of cellulose with the T-Glu-R solid acid catalyst.
To better understand the mechanism of cellulose hydrolysis catalyzed by solid acid catalysts, the hydrolysis kinetics was analyzed. Cellulose was first hydrolyzed by a catalyst to generate reducing sugars, and then the reducing sugars were further decomposed into other by-products (Kobayashi et al. 2011). The hydrolysis process is a continuous first-order reaction. The hydrolysis kinetic model is as follows:

\[
\text{Cellulose} \xrightarrow{k_1} \text{Reducing sugar} \xrightarrow{k_2} \text{Byproducts}. \tag{5}
\]

\(k_1\) and \(k_2\) represent the rate constants of the cellulose hydrolysis reaction and the reducing sugar decomposition, respectively.

According to Formula (5), the cellulose hydrolysis reaction rate equation can be expressed by Formulas (6) and (7):

\[
\frac{dC_c}{dt} = -k_1 C_c \tag{6}
\]

\[
\frac{dC_r}{dt} = k_1 C_c - k_2 C_r \tag{7}
\]

where \(C_c\) and \(C_r\) respectively represent the concentrations of cellulose and reducing sugar. After solving Formula (6), the cellulose concentration can be obtained and expressed by Formula (8):
where $C_0$ represents the initial cellulose concentration.

Combining Formulas (7) and (8), the total reducing sugar concentration is expressed by Formula (9):

$$C_r = \frac{C_0 k_1 (e^{-k_1 t} - e^{-k_2 t})}{k_2 - k_1}.$$  \hspace{1cm} (9)

The apparent activation energy required for the reaction is calculated by Arrhenius Formula (10).

$$\ln k = \ln A - \frac{E_a}{RT}.$$  \hspace{1cm} (10)

The mass ratio of fixed microcrystalline cellulose to catalyst is 1:2 (g/g). The effect of temperature on the yield of hydrolyzed cellulose TRS was studied, and the results are shown in Fig. 8a. When the hydrolysis temperature was 160 °C, 170 °C, 180 °C, and 190 °C, the TRS first increased and then decreased with the increase of time. When the hydrolysis temperature was 180°C and the hydrolysis time was 2 h, the TRS yield reached 72.15%. Under optimal hydrolysis temperature and time, the influence of the amount of catalyst on the experimental results is shown in Fig. 8b. The TRS yield showed increased first and then decreased with the increase of the amount of catalyst. When the amount of catalyst was 0.3 g, the TRS yield was 66.48%. The presence of excess catalyst might not only accelerate the hydrolysis of cellulose into sugars but also cause further hydrolysis of reducing sugars into small molecular compounds, such as 5-hydroxymethylfurfural and furfural (Shen et al. 2018).
Fig. 8 Effects of temperature and catalyst dosage on TRS yield of hydrolysis for MCC.

Reaction conditions: (a) 0.1 g of MCC, 0.2 g of T-Glu-R, and 30 mL of H$_2$O, (b) 0.1 g of MCC, 30 mL of H$_2$O, 180°C, 2 h.

The kinetic analysis of hydrolyzed cellulose was carried out at different temperatures according to Formula (9). The kinetic fitting results are shown in Table 2 and Fig. 9. Figure 9 indicates that as the reaction temperature increased, both $k_1$ and $k_2$ showed an increasing trend, indicating that increasing the temperature promotes the hydrolysis of MCC and the decomposition of reducing sugars. The calculation by Formula (6) shows that the apparent activation energy required for the hydrolysis of MCC and the decomposition of reducing sugar by T-Glu-R are 70.9 and 61.87 kJ/mol, respectively. The values are much lower than the apparent activation energy (170 kJ/mol) required for the sulfuric acid hydrolysis of MCC and near the apparent activation energy (3–50 kJ/mol) for the cellulase hydrolysis of MCC (Li and Pan 2012). The T-Glu-R catalyst has a high density of central phenolic hydroxyl groups (5.55 mmol/g), which can form hydrogen bonds with the oxygen atoms of the cellulose glycosidic bond to adsorb the cellulose on the surface of the catalyst. However, it cannot form hydrogen bonds with glucose to cause adsorption. The selective adsorption of cellulose and glucose by the catalyst avoids further acid-catalyzed reaction of glucose, which is beneficial to improving the selectivity of glucose. -COOH can also form hydrogen
bonds with -OH on cellulose, which improves the reaction efficiency of cellulose hydrolysis. In addition, the carboxyl group also serves as a catalytic group, which greatly improves the reducing sugars yield of hydrolyzed cellulose. The -COOH and -OH functional groups are hydrophilic, not only facilitating the uniform distribution of the catalyst in water but also the entry of oligosaccharides into the catalyst (Shimizu and Satsuma 2011). The synergistic effect of these two functional groups effectively reduces the apparent activation energy required for MCC hydrolysis.

**Table 2** Kinetic parameters for hydrolysis of cellulose and decomposition of reducing sugar with T-Glu-R as a catalyst.

| Temperature(K) | $k_1$(h$^{-1}$) | $k_2$(h$^{-1}$) |
|---------------|----------------|----------------|
| 433           | 0.409          | 0.197          |
| 443           | 0.545          | 0.303          |
| 453           | 0.984          | 0.466          |
| 463           | 1.379          | 0.583          |

**Fig. 9** Arrhenius plot of cellulose hydrolysis with T-Glu-R catalyst.

3.3.2 Study on cyclic performance of catalyst

The recyclability of the catalyst plays an important role in practical applications. The hydrolysis performance of the catalyst after three recoveries is shown in Fig. 10. The TRS yield gradually decreases as the recycling iteration increases. After four recoveries, the TRS decreased by 4.32%. In addition, the amount of acid on the surface of the catalyst recovered each time was measured, and the results are shown in
supplementary material. After recycling the solid acid four times, the total acid content and carboxyl groups on the surface of the solid acid catalyst were 7.03 and 1.65 mmol/g, respectively, indicating respective decreases of 0.25 and 0.08 mmol/g from before the first catalysis. This result indicates that the structure of the solid acid catalyst is stable, the active groups on the surface do not easily fall off, and it has excellent recyclability.

![Graph](image)

**Fig. 10** Cellulose hydrolysis by recycled T-Glu-R (note: 0.1 g of MCC, 30mL of H₂O, 180°C, 2 h).

### 4. Conclusions

The polyphenolic substance of tannic acid was the raw material and modified with glutamic acid. A resin rich in phenolic hydroxyl and carboxyl groups was successfully synthesized through cross-linking reaction, showing strong solid acid properties, and its acid density reached 7.28 mmol/g. Compared with carbon-based solid acid acidified by sulfuric acid, the acid density increases 1-1.5 times. As a catalyst, the resin contains both the hydroxyl group that forms a hydrogen bond with cellulose and the catalytic group carboxyl group, which has the structural characteristics of an imitation enzyme catalyst. The solid acid catalyst catalyzes the hydrolysis of cellulose, and the total reducing sugar yield is 72.15%. After four cycles, the acid density can still reach 7.03 mmol/g, and the total reducing sugar yield is 67.83%. The catalyst avoids the use of sulfonating agents such as concentrated sulfuric acid and chlorosulfonic acid that have a
serious impact on the environment and equipment. This research provides a new route
for the synthesis of solid acid, which has potential market application value.

Conflicts of interest

The authors declare no conflicts of interest.

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