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1 Preparation of a cellulase-imitated solid acid catalyst with high acid 2 density and its evaluation for hydrolysis of cellulose

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7
8 **Abstract:** In this paper, tannic acid, a polyphenolic substance rich in plants, is modified
9 by the glutamic acid and cross-linked with formaldehyde to prepare a high acid density
10 tannin-glutamate acid resin-based imitation enzyme solid acid catalyst (T-Glu-R), which
11 is completely different from traditionally carbon-based solid acid synthesized by
12 concentrated sulfuric acid and carbonized matter. The solid acid catalyst was
13 characterized by Fourier transform infrared spectroscopy, scanning electron microscope,
14 thermogravimetry, and X-ray photoelectron spectroscopy. The catalytic activity and
15 cycle performance of T-Glu-R in the cellulose hydrolysis reaction were evaluated. The
16 results show that the acid density of T-Glu-R reached 7.28 mmol/g, which is much
17 higher than that of the highest acid density of carbon-based solid acid. Microcrystalline
18 cellulose was hydrolyzed in distilled water at 180 °C for 2 h, the yield of total reducing
19 sugars reached 72.15%. After four cycles of hydrolysis, the yield was only reduced by
20 4.32%, showing excellent cycle performance and stability. The study provides a new
21 strategy with the synthesis of solid acid catalyst for hydrolysis of cellulose converted
22 into platform compounds without concentrated sulfuric acid.

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

24 1. Introduction

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

33 Cellulose is a high polymer composed of glucose units connected by β -1,4-
34 glycosidic bonds. Numerous hydrogen bonds exist within and between cellulose
35 molecules, bringing great difficulties to the hydrolysis of cellulose into glucose. Acids
36 and biological enzymes are often used to hydrolyze cellulose. For example,
37 concentrated sulfuric acid can effectively cause the swelling of and hydrolyze
38 crystalline cellulose to form glucose by breaking the hydrogen bonds. However, many
39 kinds of issues should be considered, such as by-products, corrosion equipment, the
40 difficult separation of catalyst and product, and wastewater treatment. Studies have
41 identified the main reason for the efficient hydrolysis of cellulase as the presence of
42 binding and catalytic groups in the structure. Catalytic groups, like the carboxyl and
43 phenolic hydroxyl groups of amino acids, are used as proton sources to attack and
44 hydrolyze the glycosidic bond on the cellulose chain. Meanwhile, binding groups
45 enables the cellulase and the hydroxyl group on the cellulose chain to form a hydrogen
46 bond to shorten the distance between the cellulase and the cellulose. Cellulase can
47 selectively hydrolyze cellulose under mild conditions. However, due to the thermal
48 instability of cellulase, the hydrolysis rate cannot be increased by increasing the
49 temperature, resulting in a long reaction time. Cellulase itself is expensive and difficult

50 to recycle, limiting its use in enzymatic hydrolysis. The above shortcomings limit the
51 application of liquid acid and cellulase in cellulose hydrolysis (Lanzafame et al. 2012).

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

67 Fan et al. (2013) synthesized a sulfonated polymer solid acid (SPS-DVB-SO₃H).
68 After the catalyst undergoes catalytic hydrolysis, the loss of H⁺ greatly reduces the acid
69 density of the catalyst, and the glucose yield drops from 37% to 7%. Therefore, the
70 catalyst must be immersed in a sulfuric acid solution for regeneration after the reaction.
71 Yang and Pan (2016) synthesized an enzyme-like solid acid (POP-SO₃H-Cl). After four
72 cycles of use of the solid acid, the glucose yield dropped from 84.9% to 17.2%. The test
73 revealed that the density of its sulfonic acid dropped from 0.74 mmol/g to 0.16 mmol/g.
74 Zhang et al. (2013) treated activated carbon with low-concentration nitric acid, not only

75 oxidizing the lactone, ether, quinine, and other functional groups on the surface of the
76 activated carbon to -COOH, but also dissolving the ash on the surface of the activated
77 carbon to allow the grafting of more -SO₃H onto the activated carbon. The acid density
78 of the catalyst increased from 1.58 mmol/g to 2.23 mmol/g, and the glucose yield
79 increased to 62.2%. In summary, high-density acid centers are essential to cellulose
80 hydrolysis.

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

91 Tannic acid (TA) is a type of polyphenol widely found in plants. Given the
92 presence of numerous phenolic hydroxyl groups in TA, the resin prepared by cross-
93 linking TA with formaldehyde also has many polar functional and phenolic hydroxyl
94 groups, which can be used as binding groups for the preparation of cellulose hydrolysis
95 catalysts. Glutamic acid is an acidic amino acid containing the -COOH group, which is
96 present in cereal protein. To overcome the low surface acid density problem of the
97 existing imitation enzyme solid acid catalysts, this experiment used TA as the raw
98 material and modified it with glutamic acid to prepare tannic-glutamate (T-Glu). Then,
99 T-Glu was crosslinked with formaldehyde to prepare a tannic glutamate phenolic resin

100 (T-Glu-R) imitation enzyme solid acid catalyst with a binding group (-OH) and a
101 catalytic group (-COOH). On the one hand, the T-Glu-R solid acid catalyst has a wide
102 range of raw materials, is biodegradable, does not pollute the environment, and is easier
103 to recycle than cellulase. On the other hand, the direct cross-linking method avoids the
104 loss of active groups, retains the original cellulase-like active sites of TA and glutamic
105 acid, and can effectively reduce the activation energy of the reaction. In addition, the
106 resin-based enzyme that mimics solid acid has a certain thermal stability, which can
107 increase the temperature appropriately, accelerate the reaction speed, and effectively
108 hydrolyze cellulose into reducing sugars, providing a powerful means of converting
109 cellulose to platform compounds.

110 **2. Materials and methods**

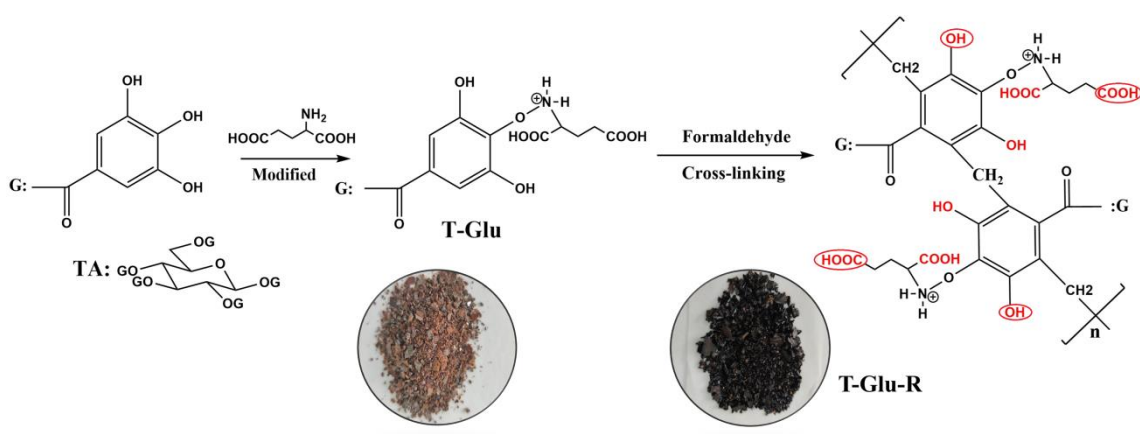
111 2.1 Materials

112 The chemical reagents, including TA, glutamic acid, 3,5-dinitrosalicylic acid
113 (DNS), formaldehyde, sodium bicarbonate (NaHCO_3), hydrochloric acid (HCl, 37%),
114 sodium hydroxide (NaOH), nickel nitrate ($\text{Ni}(\text{NO}_3)_2$), and hydrogen peroxide (H_2O_2),
115 were purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents were of
116 analytical grade and directly used without further purification. Microcrystalline
117 cellulose (MCC) was purchased from Shandong Ehua Pharmaceutical Co., Ltd.

118 2.2 Preparation of T-Glu-R solid acid catalyst

119 First, TA was modified with glutamic acid. According to the 1:3 molar ratio of TA
120 to glutamic acid, 4 g of TA and 1.05 g of glutamic acid were dissolved in 100 mL of
121 distilled water. Then, the pH was adjusted to 1.5 with 37% HCl, and the solution was
122 heated in a water bath at 60 °C for 5 h. After adjusting the pH to 6.8 by the isoelectric
123 point method, the product appeared as a precipitate (Aelenei et al. [2009](#); Badawi et al.
124 [2017](#)). Then, the precipitate was washed with distilled water, centrifuged, and dried to

125 obtain T-Glu. Subsequently, 4 g of T-Glu, 3 mL of formaldehyde, 2 mL of HCl, and 20
 126 mL of distilled water were added to a 100-mL Teflon-lined stainless-steel autoclave and
 127 reacted hydrothermally at 120 °C for 12 h to obtain a brown resin, which was washed to
 128 the solution is neutral. The product was ground and passed through a 100-mesh sieve to
 129 obtain a resin-based solid acid catalyst, which was named T-Glu-R. The preparation's
 130 reaction equation is shown in Fig. 1.



131

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

133 2.3 Determination of acid density of T-Glu-R solid acid catalyst

134 According to the literature, the densities of the total acid, the carboxyl group, and
 135 the phenolic hydroxyl group on the surface of the prepared catalyst were measured by
 136 the Boehm back titration method (Zhang et al. 2013). First, 0.1 g of catalyst was added
 137 to a 30 mL, 0.05 mol/L NaOH aqueous solution. The solution was sonicated at room
 138 temperature for 60 min and then centrifuged. Using phenolphthalein as an indicator, the
 139 filtrate was titrated with a 0.05 mol/L HCl aqueous solution, and the total acid density
 140 (C_T) was calculated according to Formula (1). Finally, 0.1 g of the catalyst was added to
 141 a 30 mL, 0.01 mol/L NaHCO₃ aqueous solution. The solution was sonicated at room
 142 temperature for 60 min and centrifuged. Using BroMo Green-Methyl Red TS as an
 143 indicator, the filtrate was titrated with a 0.01 mol/L HCl aqueous solution, and the
 144 carboxyl group density (C_{COOH}) on the catalyst surface was calculated according to

145 Formula (2), and the phenolic hydroxyl group (C_{OH}) density was calculated according to
146 Formula (3).

$$147 \quad C_T = \frac{100 \text{ mmol/L} \times 0.03 \text{ L} - 100 \text{ mmol/L} \times V_{HCl}}{0.1 \text{ g}} \quad (1)$$

$$148 \quad C_{COOH} = \frac{100 \text{ mmol/L} \times 0.03 \text{ L} - 100 \text{ mmol/L} \times V_{HCl}}{0.1 \text{ g}} \quad (2)$$

$$149 \quad C_{OH} = C_T - C_{COOH} \quad (3)$$

150 2.4 Characterization of T-Glu-R solid acid catalyst

151 The changes in the structure of the catalyst were investigated by Fourier
152 transform–infrared spectroscopy (FTIR, BRUKER TENSOR 27). The spectra were
153 recorded from 400 cm^{-1} to 4000 cm^{-1} with a 4 cm^{-1} resolution. Approximately 1 mg of
154 the sample was mixed with 80 mg of spectroscopy-grade KBr, and the mixture was
155 pressed in a standard device. The morphology of the catalyst was analyzed by field-
156 emission scanning electron microscopy (FE-SEM, Hitachi, S-3000N) working at 5 kV.
157 Thermal gravimetry (TG) was adopted to analyze the thermal behavior of the catalyst
158 using a thermal gravimetric analyzer (WCT-2D) from $50 \text{ }^\circ\text{C}$ to a final temperature of
159 $800 \text{ }^\circ\text{C}$ with a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ under N_2 flow ($40 \text{ mL}/\text{min}$). The X-ray
160 photoelectron spectra (XPS) of the catalyst were recorded using a Thermo Fisher
161 ESCALAB 250xi spectrometer with Al $K\alpha$ radiation (1486.6 eV). The binding energies
162 were calculated with respect to C1s at 284.8 eV with a precision of $\pm 0.05 \text{ eV}$.

163 2.5 Cellulose pretreatment

164 The pretreatment of cellulose before hydrolysis can reduce its crystallinity and
165 improve hydrolysis efficiency (Syafrika and Matsumura 2018; Kumar and Sharma
166 2017). Studies on the pretreatment of cellulose have shown that some organic solvents
167 can dissolve cellulose, like phosphoric acid (Zhang et al. 2006). After adding the
168 dissolved cellulose to the reverse solvent, the cellulose is precipitated and regenerated.

169 During this process, the crystalline form of cellulose is transformed, and the hydrogen
170 bonds between molecules are broken and rearranged, reducing the crystallinity of
171 cellulose and increasing the pores (Yuan et al. 2017). Metal ions are often used to
172 promote hydrolysis to pretreat cellulose because the empty orbitals of metal ions can
173 combine with the lone pair of electrons on the β -1,4 glycosidic bond oxygen atom of
174 cellulose (Li et al. 2015), thereby activating the carbon-oxygen bond, which is
175 conducive to cellulose hydrolysis. In this experiment (Li et al. 2018), pretreated
176 cellulose was obtained by combining ultrasonic wave, metal ion, and oxidation methods.
177 In the typical pretreatment process, 5 g of MCC, 200 mL of 0.15 wt% nickel ion
178 solution, and 0.5 mL of H₂O₂ were added into a flask and sonicated at 75 °C for 2 h.
179 Then, the solid was separated and washed with distilled water. The dried sample was
180 labelled pretreated cellulose.

181 2.6 Hydrolysis of cellulose

182 Typically, 0.2 g of T-Glu-R, 0.1 g of pretreated cellulose, and 30 mL of distilled
183 water were added into a 100-mL Teflon-lined stainless-steel autoclave and heated to
184 180 °C for 2 h. After the reaction, the mixture was separated by filtration. The total
185 reducing sugar (TRS) yield was analyzed by the DNS method (Mission et al. 2017). A
186 mixture containing 1 mL of hydrolysate, 1 mL of DNS, and 3mL of distilled water was
187 heated at 100 °C for 5 min and then cooled to room temperature. The absorbance of the
188 mixture was measured using a TU-1901 spectrophotometer at 540 nm. The TRS
189 concentration was quantified based on a standard curve obtained with glucose. The TRS
190 yield is calculated as follows:

$$191 \quad TRS(\%) = \frac{C_{TRS} \times V}{M_{Cellulose}} \times 100\%, \quad (4)$$

192 where C_{TRS} is the concentration of the reducing sugar in the hydrolysate (mg/mL),
193 $M_{cellulose}$ is the initial cellulose mass (mg), and V is the volume of the hydrolysate (mL).

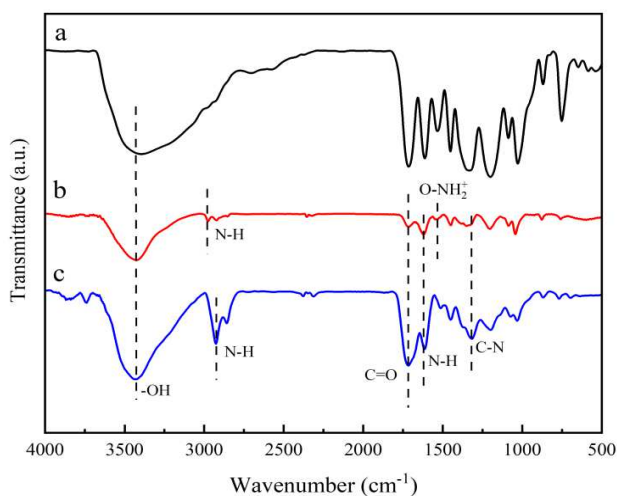
194 At the end of the reaction, the unreacted cellulose and the solid acid catalyst were
195 filtered. Afterward, it was washed with distilled water and dried at 100 °C. The
196 separated catalyst was used in the cyclic hydrolysis experiment.

197 3. Results and discussion

198 3.1 Characterization of T-Glu-R solid acid catalyst

199 3.1.1 FT-IR

200 The infrared spectra of TA, T-Glu, and T-Glu-R are shown in Fig. 2. The figure
201 shows a stretching vibration peak of -OH around 3400 cm^{-1} , indicating that TA, T-Glu,
202 and T-Glu-R contain phenolic hydroxyl groups. In the T-Glu spectrum, 1310, 1715, and
203 2976 cm^{-1} are the stretching vibration peaks of C-N, carboxyl C=O, and N-H (Erdem et
204 al. 2013; Zhao et al. 2011), respectively. A new infrared absorption band appeared at
205 1542 cm^{-1} , confirming the formation of the O-NH₂⁺ bond. The reaction between TA and
206 glutamic acid formed between the amino and phenolic hydroxyl groups indicates the
207 successful preparation of T-Glu. The characteristic peak of T-Glu-R is more obvious at
208 1380 cm^{-1} , which is the characteristic peak of -CH₂- (Shi et al. 2019), indicating the
209 existence of many methylene groups in T-Glu-R and the successful cross-linking of
210 formaldehyde with T-Glu.



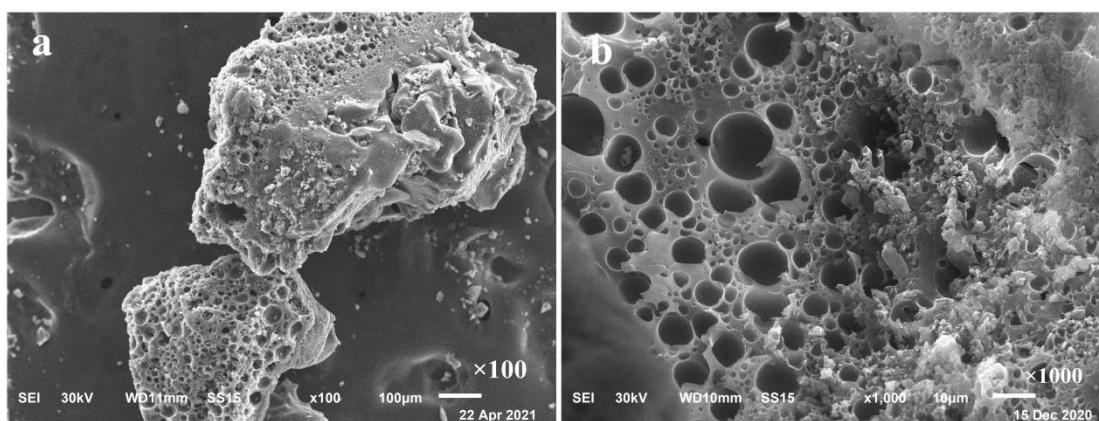
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212

Fig. 2 FTIR spectra of T-Glu-R (a: TA, b: T-Glu, c: T-Glu-R).

213 3.1.2 FE-SEM Analyses

214 Fig. 3 presents a scanning electron micrograph of the catalyst. The solid acid
215 catalyst has a rough surface and pores, exhibiting an obvious porous structure. A resin
216 network structure forms when formaldehyde cross-links with T-Glu, thereby forming a
217 porous structure. Therefore, this structure is highly conducive to the contact of the
218 prepared resin-based solid acid with the reactants, which can expose more effective
219 groups on the surface of the catalyst, provide sufficient catalytic reaction sites, and
220 increase the collision frequency between the catalyst and the cellulose. Consequently,
221 the catalytic performance of the catalyst is improved (Onda et al. 2009; Akiyama et al.
222 2011).

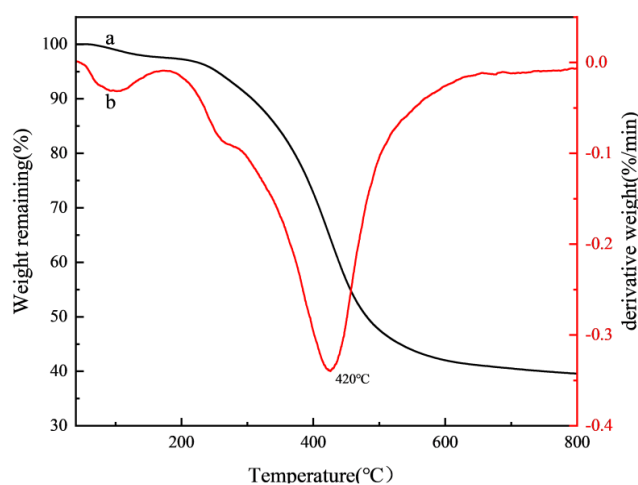


224 **Fig. 3** SEM images of T-Glu-R (a:×100, b:×1000).

225 3.1.3 TG Analyses

226 The thermal behavior of the solid acid catalyst is shown in Fig. 4. The
227 thermogravimetric curve indicates that the percentage of mass retention gradually
228 decreases as the temperature increases. The temperature increased from 100 °C to
229 200 °C, and the weight of the catalyst was reduced by 1.7%. The weight loss may be
230 caused by the evaporation of water adsorbed on the sample (Hu et al. 2016). The
231 respective temperatures at 5% and 10% weight loss ($T_{5\%}$ and $T_{10\%}$) were 254 °C and
232 307 °C, indicating that when the temperature was below 254 °C, the catalyst did not

233 change significantly when cellulose was hydrolyzed. T-Glu-R performance was
234 relatively stable. At 420 °C, the maximum weight loss rate was reached. At this time,
235 the mass retention percentage was 66%. This phenomenon may be attributed to the
236 decomposition of -OH and -COOH groups at high temperatures. When the temperature
237 continued to rise, the rate of weight loss began to decrease, and the rate of weight loss
238 approached zero at 800 °C. The mass retention percentage at 800 °C indicates the good
239 thermal stability of T-Glu-R.



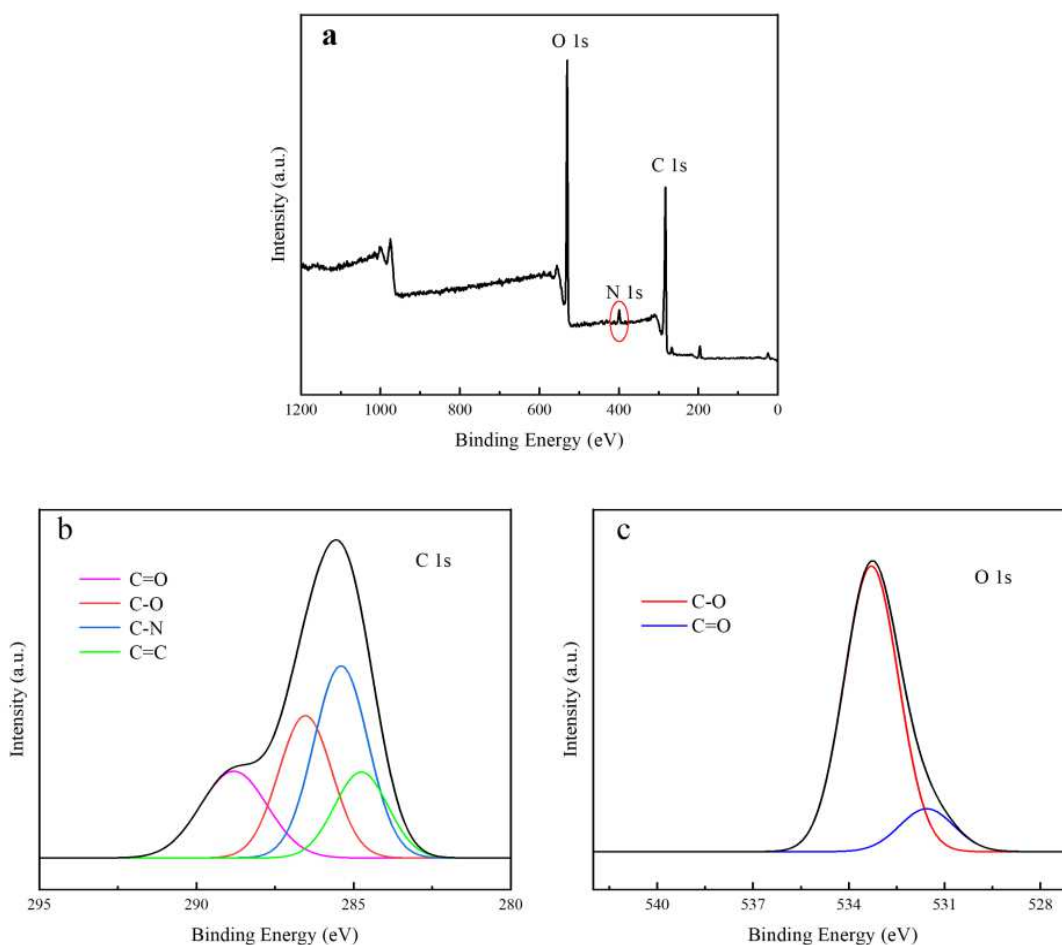
240

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

242 3.1.4 XPS Analyses

243 X-ray photoelectron spectroscopy was used to analyze the surface chemical
244 composition of T-Glu-R. Fig. 5a shows the full scan spectrum of the catalyst, the
245 surface of the solid acid catalyst contains three elements, namely, C, O, and N. The
246 typical N 1s peak appeared at 401.7 eV (Xu et al. 2016), confirming that glutamic acid
247 successfully modified TA and has the unique amino group of glutamic acid. The C 1s
248 spectra for T-Glu-R can be resolved into four peaks centered at 284.79, 285.7, 286.26,
249 and 288.48 eV, which can be respectively assigned to C=C, C-N, C-O, and C=O.
250 Moreover, the O 1s spectra can also be resolved into three peaks centered at 531.5 and
251 533.3 eV, which are most likely related to C=O and C-O (Chen et al. 2017; Pan et al.

252 2017), respectively. Meanwhile, the XPS results show that the solid acid catalyst
253 surface contains active groups, such as -OH, -COOH, and -NH₂.



254

255 **Fig. 5** XPS spectra of T-Glu-R solid acid catalyst (a: full spectra, b: C 1s spectra, c: O
256 1s spectra).

257 3.2 Analysis of the surface acid density of T-Glu-R solid acid

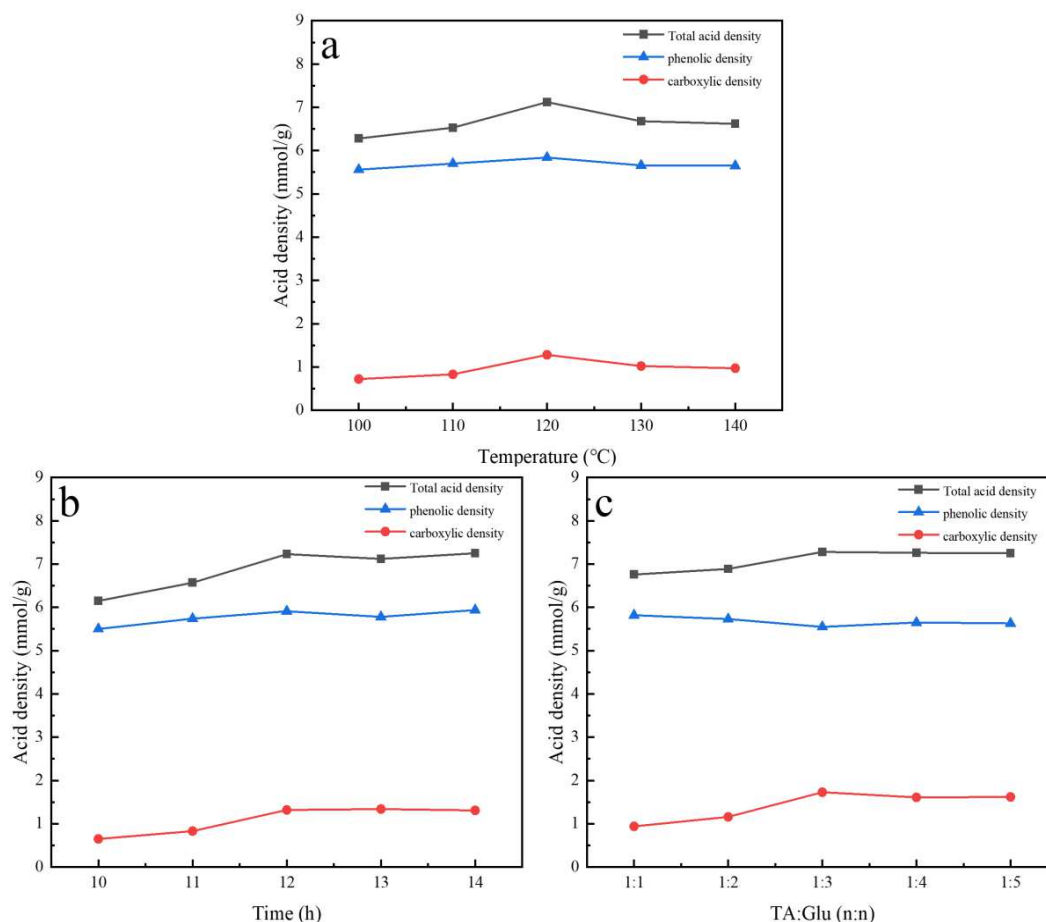
258 The surface acid density of T-Glu-R under different preparation conditions was
259 measured according to the experimental method in Section 1.2.2, and the results are
260 shown in Fig. 6. The influence of different temperatures on the acid density of the
261 prepared catalyst is shown in Fig. 6a. The figure indicates that when the molar ratio of
262 TA to T-Glu was 1:3, the reaction time was 12 h, the total acid, phenolic hydroxyl, and
263 carboxyl group densities increased from 100 °C to 120 °C, and the maximum densities
264 were 7.12, 5.84, and 1.28 mmol/g, respectively. The surface acid density of acid T-Glu-

265 R decreased slightly and remained unchanged with the increase of temperature,
266 indicating that the high-temperature hydrothermal synthesis conditions had little effect
267 on the structure of T-Glu-R.

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

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

280 The total acid, phenolic hydroxyl, and carboxyl group densities of the catalyst
281 prepared under 120 °C for 12 h and at the molar ratio of TA to Glu of 1:3 were the
282 highest, namely, 7.28, 5.55, and 1.73 mmol/g, respectively.



283

284 **Fig. 6** Influence of reaction temperature (a), time (b), and the molar ratio (c) of TA and
 285 T-Glu on catalyst acid density.

286

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

295 OH of cellulose, improving the efficiency of the hydrolysis reaction of cellulose. The
 296 schematic of the active site of T-Glu-R is shown in Fig. 1.

297 **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-SO ₃ H	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-SO ₃ H	3.52	0.88	0.96	1.68	50.8	Zhu et al. (2017)
SLC-SO ₃ H	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

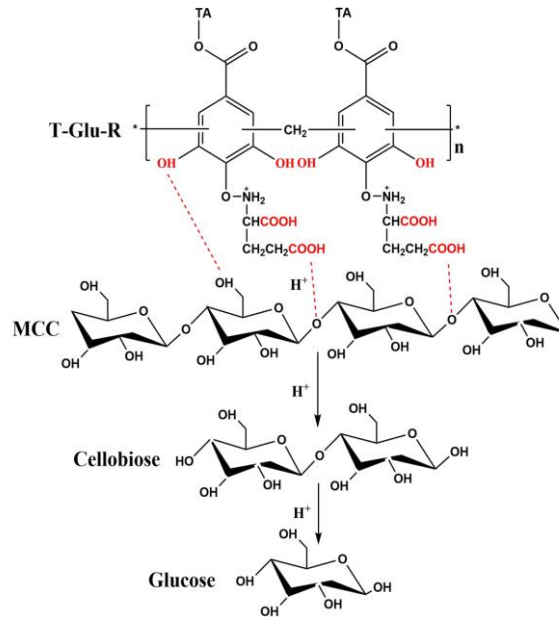
298 a: C-COOH and -OH. b: After four times run.

299

300 3.3 T-Glu-R solid acid hydrolysis of cellulose capacity

301 3.3.1 Mechanism of T-Glu-R solid acid catalyst for hydrolysis of cellulose

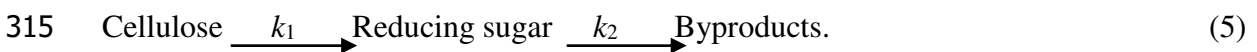
302 The large number of phenolic hydroxyl groups in the T-Glu-R solid acid catalyst
 303 has a similar effect to the binding group of cellulase, which can form hydrogen bonds
 304 with cellulose, thereby shortening the distance with cellulose and playing a binding role.
 305 The carboxyl group can cut the glycosidic bond of the cellulose chain, which acts
 306 similarly as the catalytic group of cellulase. Fig. 7 presents a schematic of the
 307 hydrolysis of cellulose with the T-Glu-R solid acid catalyst.



308

309 **Fig. 7** T-Glu-R solid acid catalyst hydrolysis mechanism diagram of cellulose.

310 To better understand the mechanism of cellulose hydrolysis catalyzed by solid acid
 311 catalysts, the hydrolysis kinetics was analyzed. Cellulose was first hydrolyzed by a
 312 catalyst to generate reducing sugars, and then the reducing sugars were further
 313 decomposed into other by-products (Kobayashi et al. 2011). The hydrolysis process is a
 314 continuous first-order reaction. The hydrolysis kinetic model is as follows:



316 k_1 and k_2 represent the rate constants of the cellulose hydrolysis reaction and the
 317 reducing sugar decomposition, respectively.

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

320
$$\frac{dC_c}{dt} = -k_1 C_c \quad (6)$$

321
$$\frac{dC_r}{dt} = k_1 C_c - k_2 C_r \quad (7)$$

322 where C_c and C_r respectively represent the concentrations of cellulose and reducing
 323 sugar. After solving Formula (6), the cellulose concentration can be obtained and
 324 expressed by Formula (8):

325 $C_c = C_0 \exp(-k_1 t)$ (8)

326 where C_0 represents the initial cellulose concentration.

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

328 Formula (9):

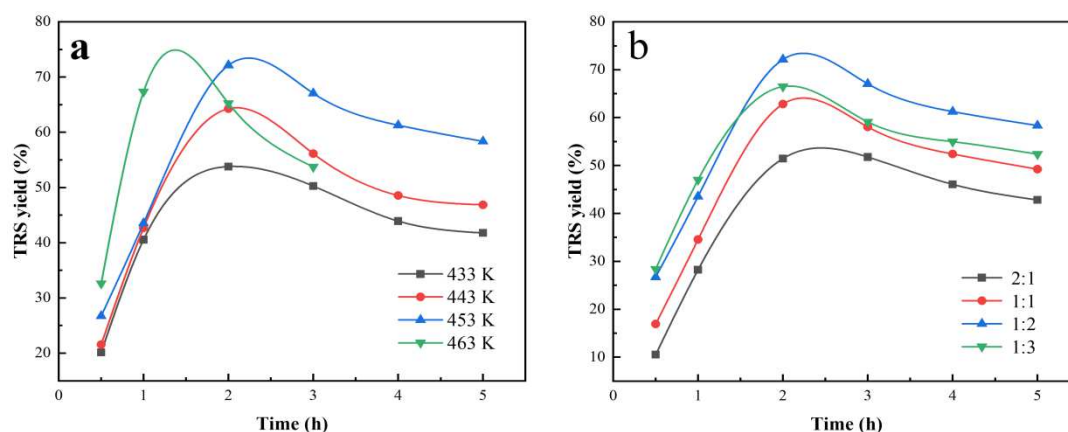
329
$$C_r = \frac{C_0 k_1 (e^{-k_1 t} - e^{-k_2 t})}{k_2 - k_1}$$
 (9)

330 The apparent activation energy required for the reaction is calculated by Arrhenius

331 Formula (10).

332 $\ln k = \ln A - E_a / RT$ (10)

333 The mass ratio of fixed microcrystalline cellulose to catalyst is 1:2 (g/g). The effect
334 of temperature on the yield of hydrolyzed cellulose TRS was studied, and the results are
335 shown in Fig. 8a. When the hydrolysis temperature was 160 °C, 170 °C, 180 °C, and
336 190 °C, the TRS first increased and then decreased with the increase of time. When the
337 hydrolysis temperature was 180°C and the hydrolysis time was 2 h, the TRS yield
338 reached 72.15%. Under optimal hydrolysis temperature and time, the influence of the
339 amount of catalyst on the experimental results is shown in Fig. 8b. The TRS yield
340 showed increased first and then decreased with the increase of the amount of catalyst.
341 When the amount of catalyst was 0.3 g, the TRS yield was 66.48%. The presence of
342 excess catalyst might not only accelerate the hydrolysis of cellulose into sugars but also
343 cause further hydrolysis of reducing sugars into small molecular compounds, such as 5-
344 hydroxymethylfurfural and furfural (Shen et al. 2018).



345

346 **Fig. 8** Effects of temperature and catalyst dosage on TRS yield of hydrolysis for MCC.

347 Reaction conditions: (a) 0.1 g of MCC, 0.2 g of T-Glu-R, and 30 mL of H₂O, (b) 0.1 g

348

of MCC, 30mL of H₂O, 180°C, 2 h.

349

The kinetic analysis of hydrolyzed cellulose was carried out at different

350

temperatures according to Formula (9). The kinetic fitting results are shown in Table 2

351

and Fig. 9. Figure 9 indicates that as the reaction temperature increased, both k_1 and k_2

352

showed an increasing trend, indicating that increasing the temperature promotes the

353

hydrolysis of MCC and the decomposition of reducing sugars. The calculation by

354

Formula (6) shows that the apparent activation energy required for the hydrolysis of

355

MCC and the decomposition of reducing sugar by T-Glu-R are 70.9 and 61.87 kJ/mol,

356

respectively. The values are much lower than the apparent activation energy (170 kJ

357

/mol) required for the sulfuric acid hydrolysis of MCC and near the apparent activation

358

energy (3–50 kJ /mol) for the cellulase hydrolysis of MCC (Li and Pan 2012). The T-

359

Glu-R catalyst has a high density of central phenolic hydroxyl groups (5.55 mmol/g),

360

which can form hydrogen bonds with the oxygen atoms of the cellulose glycosidic bond

361

to adsorb the cellulose on the surface of the catalyst. However, it cannot form hydrogen

362

bonds with glucose to cause adsorption. The selective adsorption of cellulose and

363

glucose by the catalyst avoids further acid-catalyzed reaction of glucose, which is

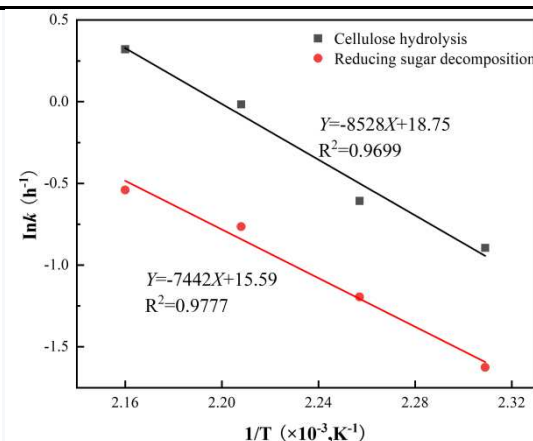
364

beneficial to improving the selectivity of glucose. -COOH can also form hydrogen

365 bonds with -OH on cellulose, which improves the reaction efficiency of cellulose
 366 hydrolysis. In addition, the carboxyl group also serves as a catalytic group, which
 367 greatly improves the reducing sugars yield of hydrolyzed cellulose. The -COOH and -
 368 OH functional groups are hydrophilic, not only facilitating the uniform distribution of
 369 the catalyst in water but also the entry of oligosaccharides into the catalyst (Shimizu and
 370 Satsuma 2011). The synergistic effect of these two functional groups effectively reduces
 371 the apparent activation energy required for MCC hydrolysis.

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

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



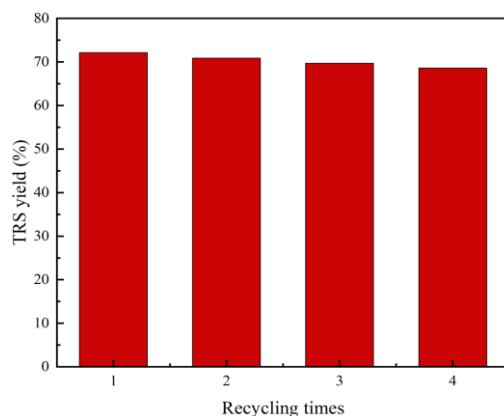
374

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

376 3.3.2 Study on cyclic performance of catalyst

377 The recyclability of the catalyst plays an important role in practical applications.
 378 The hydrolysis performance of the catalyst after three recoveries is shown in Fig. 10.
 379 The TRS yield gradually decreases as the recycling iteration increases. After four
 380 recoveries, the TRS decreased by 4.32%. In addition, the amount of acid on the surface
 381 of the catalyst recovered each time was measured, and the results are shown in

382 supplementary material. After recycling the solid acid four times, the total acid content
383 and carboxyl groups on the surface of the solid acid catalyst were 7.03 and 1.65 mmol/g,
384 respectively, indicating respective decreases of 0.25 and 0.08 mmol/g from before the
385 first catalysis. This result indicates that the structure of the solid acid catalyst is stable,
386 the active groups on the surface do not easily fall off, and it has excellent recyclability.



387

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

390 4. Conclusions

391 The polyphenolic substance of tannic acid was the raw material and modified with
392 glutamic acid. A resin rich in phenolic hydroxyl and carboxyl groups was successfully
393 synthesized through cross-linking reaction, showing strong solid acid properties, and its
394 acid density reached 7.28 mmol/g. Compared with carbon-based solid acid acidified by
395 sulfuric acid, the acid density increases 1-1.5 times. As a catalyst, the resin contains
396 both the hydroxyl group that forms a hydrogen bond with cellulose and the catalytic
397 group carboxyl group, which has the structural characteristics of an imitation enzyme
398 catalyst. The solid acid catalyst catalyzes the hydrolysis of cellulose, and the total
399 reducing sugar yield is 72.15%. After four cycles, the acid density can still reach 7.03
400 mmol/g, and the total reducing sugar yield is 67.83%. The catalyst avoids the use of
401 sulfonating agents such as concentrated sulfuric acid and chlorosulfonic acid that have a

402 serious impact on the environment and equipment. This research provides a new route
403 for the synthesis of solid acid, which has potential market application value.

404 **Conflicts of interest**

405 The authors declare no conflicts of interest.

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