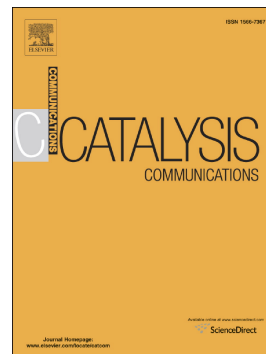# Accepted Manuscript

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Hydrothermal carbon enriched with sulfonic and carboxyl groups as an efficient solid acid catalyst for butanolysis of furfuryl alcohol

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Abstract

Carbonaceous material (GC-PTSA-AC) functionalized with both high density of SO_3H and COOH groups was prepared by one-step hydrothermal carbonization of glucose with p-toluenesulfonic acid and acrylic acid. This novel carbon could be used directly for the alcoholysis of furfuryl alcohol and n-butanol without any post-modification, and it was found to be more efficient than the monofunctional hydrothermal carbon only decorated with SO_3H or COOH groups. The reason was attributed to the larger amount of COOH groups on GC-PTSA-AC, cooperating with the SO_3H active sites to facilitate the butanolysis reaction.

Key words: Hydrothermal carbon; Solid acid; Butanolysis; Synergic effect.

1. Introduction

The efficient transformation of renewable biomass into fuels and valuable chemicals has attracted considerable interest in green chemistry [1-3]. Furfural is the hydrolysis product of hemicellulose, which can be further hydrogenated to furfuryl alcohol (FAL) over copper-based catalysts [4]. Alkyl levulinates, an important downstream derivative of FAL, has been identified by the U.S. Department of Energy as one of the top ten biorefinery candidates [5]. In particular, n-butyl levulinates (BL) is a versatile chemical with numerous applications as solvent, flavor, and plasticizer [6]. Moreover, BL has been proved to be a more promising fuel additive than ethyl levulinate, as it possesses better miscibility in diesel fuel at low temperature [7]. The acid-catalyzed alcoholysis of FAL is the common route to produce alkyl levulinates. Substitution of homogeneous acids by heterogeneous acids is recommended to avoid handling corrosion and environmental problems. To date, various solid acid catalysts including zeolites [8,9], resins [10], metal oxides [11,12], aluminosilicate [13], modified mesoporous silica [5,14], graphene [15], supported heteropoly acids [16], organic-inorganic hybrid solid acid [17], and ionic liquids [18] have been explored for the synthesis of alkyl levulinates. Nevertheless, the high cost and tedious preparation protocol are major obstacles to the wide applications of these solid acids. Recently aluminum salts were found to be cheap and efficient catalysts for catalyzing alcoholysis, but the separation of the catalysts was difficult [19,20]. Consequently, it is desirable to develop an easy-to-prepare, economical, and efficient solid acid catalyst for production of BL.

Carbonaceous solid acid catalysts, mainly derived from biomass, have gained great attention in recent years as a novel type of "green catalysts". They are generally prepared by high-temperature pyrolysis (>400 ℃) followed by sulfonation with concentrated sulfuric acid [21-23]. However, due to harsh carbonization conditions and emission of harmful gases, this synthetic route is not energy-effective and ecofriendly. In this case, more facile and environmentally benign processes for the preparation of carbonaceous materials by in-situ functionalization are essential for the catalysis. Hydrothermal carbonization provides a sustainable synthetic method using mild conditions (<250 ℃), self-generated pressures, and water as the carbonization medium [24-26]. It is well-known that the oxygenated groups have been assumed to be the active centers in many acid-catalyzed reactions [27], whereas the raw hydrothermal carbon (HTC) only possesses small quantity of carboxyl and phenolic groups, therefore, much attention has been paid to in-situ functionalization on the HTC matrix to prepare promising solid acid catalysts. For instance, Titirici et al. [24] showed that carboxyl groups could be enriched on HTC by commixing acrylic acid and glucose in the carbonization process. Wang et al. [28] and Qi et al. [29] synthesized sulfonated HTC by the hydrothermal carbonization of glucose with p-toluenesulfonic acid or sulfosalicylic acid. These modified HTCs exhibited good catalytic activities for esterification, hydrolysis and Beckmann rearrangement [28-30]. Motivated by the aforementioned ideas, we found that many research efforts have concentrated on preparing monofunctional HTCs by merely introducing sulfonic or carboxyl groups to the carbon matrix, and the interactions of different functional

groups in catalytic reactions are less discussed.

Herein, a method to synthesize bifunctional HTCs enriched with both sulfonic and carboxyl groups was presented by hydrothermal carbonization of glucose in presence of two co-monomers. This carbon was characterized and first employed to catalyze the butanolysis of FAL to produce the versatile chemical BL. The results showed that this carbonaceous solid acid displayed better activity than those of HTC only functionalized with SO_3H or COOH groups.

2. Experimental

2.1. Catalyst preparation

The bifunctional carbon was prepared as follows. 5 g glucose, 5 g p-toluenesulfonic acid (PTSA), and 5 g acrylic acid (AC) were dissolved in 50 mL deionized water. The mixture was placed in a stainless-steel autoclave and treated at 180 °C for one day. The resulting product was filtered, washed with water and ethanol, and dried overnight. The sample was denoted as GC-PTSA-AC. The control sample GC was prepared in the same way without adding co-monomers. As a comparison, 5 g PTSA or 5 g AC was added into the glucose solution before it was transferred to the autoclave, the following procedure was the same with that described above, and the resulting carbonaceous materials were denoted as GC-PTSA or GC-AC. Hβ zeolite (SiO_2/Al_2O_3=25) were provided by Nankai University. Amberlyst-15 resin was purchased from Sigma-Aldrich. Sulfonated active carbon was prepared according to the literature [23].

2.2. Catalyst characterization

The powder X-ray diffraction patterns were collected by PANalytical X'Pert-Pro diffractometer using Cu Kα radiation source (λ = 0.1541 nm). The SEM images were recorded by VEGA3 TESCAN scanning electron microscope. Elemental analysis was determined by Elementar vario EL b apparatus. XPS analysis was conducted with an ESCALAB 250Xi spectrometer using Al Kα X-ray source. FT-IR was recorded by a VERTEX 70 with the KBr pellet. NH_3-TPD was conducted with a Micromeritics AutoChem II 2920 Automated Catalyst Characterization System coupling with a mass spectrometry detector. The acidity densities of the carbon materials were measured by the Boehm titration method [29].

2.3. Activity test

Typically, 0.196 g FAL, 5.92 g n-butanol and 0.1 g catalyst were added into a Parr batch reactor. The reaction mixture was stirred and heated at 120 °C after introduction of N_2. The liquid sample was analyzed by HP6890 gas chromatograph equipped with a HP-INNOWAX capillary column and a flame ionization detector. The intermediates were identified by mass spectrometry coupled with gas chromatography.

3. Results and discussion

3.1. Catalyst characterization

The formation of GC-PTSA-AC catalyst involved the dehydration of glucose into the key intermediate 5-(hydroxymethyl)-2-furaldehyde) as the first step and subsequent polymerization and carbonization as a second step [24]. During this process, PTSA and AC could not only react with the intermediates to introduce SO_3H and COOH groups to the carbon matrix, but also work as acids to catalyze the

dehydration of glucose. The XRD patterns of GC-PTSA-AC and GC catalysts are

shown in Fig. 1. Both samples exhibited a broad C (002) diffraction peak at 10–30°

and a weak C (101) diffraction peak at 35–50°, which were assigned to the amorphous

carbon composed of aromatic carbon sheets oriented in a considerably random

fashion [21]. Meanwhile, GC-PTSA-AC displayed a stronger diffraction intensity,

indicating a higher aromatization degree than GC. The elemental analysis (Table S1)

also supports this view, as the carbon content increased from 62.21% to 65.64% after

modification with co-monomers. The SEM images (Fig. S1) showed that upon

hydrothermal carbonization of glucose, micrometer sized (2–4 μm) carbon spheres

with smooth surfaces were obtained. The addition of co-monomers induced a change

in the particle morphology, that is, the diameter of the carbon spheres increased to 3–5

μm and the carbon surface was no longer smooth.

The FT-IR spectra of GC-PTSA-AC and GC catalysts are shown in Fig. 2. The

distinct bands at 1043, 1173 and 1396 cm^{-1} on GC-PTSA-AC corresponded to

O=S=O stretching vibration in SO_3H groups [31], indicating SO_3H groups have been

successfully incorporated into GC-PTSA-AC due to the participation of PTSA in the

hydrothermal process. Meanwhile, both catalysts possessed the bands at 1616, 1700

and 3425 cm^{-1}, which were assigned to the stretching vibration of C=C in aromatic

carbons, C=O in COOH groups, O-H in COOH and phenolic OH groups, respectively

[31]. It is worth noting that GC-PTSA-AC had a stronger adsorption peak at 1700 cm^{-1} in comparison with GC, highlighting its higher content of COOH groups. The

quantitative results of various functional groups were summarized in Table 1. The

SO$_3$H density was calculated according to the sulfur content in the catalyst composition, since the sulfur component was only in the form of SO$_3$H groups with S$_{2p}$ binding energy of 168.7 eV (Fig. S2). The density of COOH and phenolic OH groups were determined by Boehm titration. As we can see, COOH and phenolic OH groups were generated upon hydrothermal carbonization of pure glucose without additives, but the density of COOH groups was only 0.71 mmol g^{-1}. The addition of AC or PTSA as a co-monomer to the glucose solution successfully incorporated COOH or SO$_3$H group to the carbon, leading an obvious increase in COOH content (from 0.71 to 1.28 mmol g^{-1}) or SO$_3$H content (from 0 to 0.51 mmol g^{-1}). When the two co-monomers were carbonized with glucose together, the as-prepared GC-PTSA-AC was found to possess the largest content of SO$_3$H and COOH groups at the same time. The NH$_3$-TPD result shows that GC-PTSA-AC catalyst possessed both weak and strong acid sites on the carbon surface, because two desorption peaks around 200 °C and 530 °C were observed as depicted in Fig. 3. The former resulted from the interaction of NH$_3$ with incompletely formed carbon sheets and COOH groups, and the latter was due to the desorption on SO$_3$H groups [32]. The missing peak at elevated temperature on GC catalyst indicates the participation of co-monomers in the hydrothermal process could improve the acid strength of conventional HTC.

3.2. Activity

The catalytic activities of GC-PTSA-AC as well as the control samples were evaluated for the butanolysis of FAL into BL (Scheme S1). All experiments were conducted at 120 °C for 4 h with n-butanol to FAL molar ratio of 40. 2-

butoxymethylfuran (BMF) was identified as the main intermediate according to GC-MS results, and the by-product dibutyl ether resulted from the non-productive consumption of n-butanol (Fig. S3), the phenomenon was in accordance with previous reports [14, 16]. Trace of humins derived from the polymerization of FAL was also obtained on these carbonaceous catalysts (Table S2). The reason for low humins yield was that the amount of soluble humin precusors was excluded from the amount of solid residue by washing with ethanol and a large excess of water, besides, the low concentration of FAL suppressed the humins formation. As shown in Table 2, GC and GC-AC samples exhibited negligible activity for alcoholysis, indicating that weak acidic COOH groups and phenolic OH groups on these samples could not effectively catalyze this reaction. Conversely, upon adding PTSA as co-monomer, GC-PTSA sample exhibited a good activity with 82.4% BL yield, which was owing to the increased acidity provided by SO_3H groups. A comparative test was carried out under the catalysis of PTSA, acetic acid and phenol which represents the SO_3H, COOH and OH groups on GC-PTSA, respectively. Both acetic acid and phenol were inactive, whereas PTSA exhibited near complete conversion of FAL with 75.0% yield of BL. The above results unambiguously revealed that only SO_3H groups were the intrinsic active sites for the alcoholysis. It is worth mentioning that up to 16.0% yield of humins (Table S2) was obtained in the reaction catalyzed by PTSA, decreasing the reaction temperature could suppress the formation of humins and increase the BL yield to 94.2%. However, homogeneous PTSA suffer from disadvantages such as corrosion, difficulty in the separation and acid-waste generation, leading to it

uncompetitive with respect to the carbonaceous solid acids.

In addition, compared to GC-PTSA sample, GC-PTSA-AC displayed a further increment of activity with a complete conversion of FAL and 91.0% yield of BL, even though both carbons possessed similar SO_3H densities. The consumption rate of FAL and the formation rate of BL on GC-PTSA-AC were observed to be faster than those on GC-PTSA as well (Fig. S4). This result implies that the SO_3H density was not the only factor to influence catalytic activity. As mentioned in Table 1, GC-PTSA-AC was found to possess higher density of COOH groups than GC-PTSA, suggesting that the presence of COOH groups are crucial for the conversion of FAL to BL. The hypothesis was confirmed by the adsorption test. GC-PTSA-AC exhibited stronger adsorption capacity of FAL in comparison with GC-PTSA (1.72 *v.s.* 1.08 g g^{-1}, Table S3). The phenomenon can be rationalized by the higher content of COOH groups on GC-PTSA-AC, because they can adsorb hydroxyl group of FAL through forming hydrogen bonds, thus improving the accessibility of the FAL molecules to SO_3H active sites and promoting the alcoholysis reaction. Moreover, the order of the adsorption capacity of different carbons (GC-PTSA-AC > GC-AC > GC-PTSA, Table S3) agreed with the order of their COOH density, further indicating the COOH group could improve the affinity of catalyst towards FAL. Consequently, the remarkable activity of GC-PTSA-AC was attributed to the synergic effect of SO_3H and COOH groups.

The product yield as a function of reaction time over GC-PTSA-AC is demonstrated in Fig. 4. The reactant was almost completely consumed in 1 h, whereas

only 50.0% yield of BL and 45.8% yield of BMF were formed respectively. As the reaction proceeded, the BL yield increased gradually at the same time a decrease in the BMF yield was observed. It indicates that the butanolysis of FAL occurred through the formation of BMF as intermediate which further converted to BL as the reaction progressed. Increasing the temperature or catalyst amount could facilitate the conversion of FAL and BMF to final product, the maximum yield of BL was obtained at 120 °C with 0.1 g catalyst (Fig. S5 and S6). Besides, the FAL alcoholysis with other alcohols (such as methanol, ethanol or n-propanol) over GC-PTSA-AC catalysts could also achieve satisfactory product yields (> 91.0%, Table S4), indicating its great versatility.

The catalytic performance of some typical solid acid catalysts, including Hβ zeolite, Amberlyst-15, and sulfonated active carbon, were also evaluated under the same conditions (Table S5). Hβ zeolite gave a low BL yield of 40.3%, which was likely due to its weak acidity as the maximum NH_3 desorption temperature was only 375 °C (Fig. S7). Amberlyst-15, a commercial resin with high SO_3H density (4.8 mmol g^{-1}), displayed satisfactory activity with 86.2% BL yield. Compared to Amberlyst-15, GC-PTSA-AC catalyst had lower SO_3H density, however, it displayed higher catalytic activity, further indicating that the presence of COOH groups in GC-PTSA-AC were crucial for the alcoholysis. Sulfonated active carbon displayed a moderate activity with 61.0% BL yield. This catalyst had a low SO_3H density (0.31 mmol g^{-1}) based on the elemental analysis, thereby the active sites were supposed to be insufficient to convert the FAL and BMF to final product.

3.3. Catalyst stability

The reusability of catalyst is vital to evaluate the efficiency of catalyst. Fig. 5 shows that 100.0% FAL conversion and 87.0% yield of BL were still obtained after four times cycles, indicating a good catalytic stability of GC-PTSA-AC catalyst. In order to exclude the possibility of homogeneous catalysis, the catalyst was filtered out under hot conditions and the reaction was continued with the filtrate under same conditions. The result (Fig. S8) shows that the reaction stopped when the catalyst was removed, and the reaction resumed with a similar rate after re-adding the catalyst. It proves that the leaching of SO_3H active species was negligible. FT-IR and element analysis further demonstrated that the sulfur content in the spent catalyst was almost constant (Fig. S9 and Table S6). The high stability of GC-PTSA-AC can be ascribed to the high density of COOH group on the carbon surface, as the electron-withdrawing COOH groups are supposed to increase the electron density between carbon and sulfur atoms, resulting in the tight attachment of SO_3H groups to carbon framework [33].

According to previous literatures, ionic liquid $[MIMBS]_3PW_{12}O_{40}$ could gave 88% BL yield via alcoholysis for 12 h, and the activity decreased obviously with 65% BL yield in the second run [34]. Aluminosilicate Al-TUD-1 only gave 60% BL yield at 140 °C [13]. Up to 96% yield of BL could be obtained on SO_3H/SBA-15 while the catalyst reusability was not reported [5]. Commercial α-Fe_2O_3 gave 86% yield of BL at a high temperature of 250 °C [11]. $Zn1TPA/Nb_2O_5$ was found to be an active and stable catalyst for the butanolysis, yielding 94% BL after four cycles, nevertheless, the

catalyst preparation was costly and complicated [16]. In this work, a cheap

carbonaceous catalyst GC-PTSA-AC could be prepared by one-step facile

hydrothermal carbonization of glucose and organic acids. It possessed great

advantages with respect to economy, activity and reusability.

4. Conclusion

A novel carbonaceous material enriched with abundant SO_3H and COOH groups

was synthesized via one-step hydrothermal carbonization of glucose with two organic

co-monomers (PTSA and AC) under mild conditions. The carbon exhibited good

catalytic activity and stability for butanolysis of FAL. The superior performance

resulted from the synergic effect of SO_3H and COOH groups on the carbon surface.

Because SO_3H groups played the role of active sites, and the high density of COOH

groups improved the affinity of carbonaceous material towards FAL.

Figure Captions

Fig. 1. XRD patterns of GC-PTSA-AC and GC catalysts.

Fig. 2. FT-IR spectra of GC-PTSA-AC and GC catalysts.

Fig. 3. NH_3-TPD results of GC-PTSA-AC and GC catalysts.

Fig. 4. The conversion and product yield as a function of reaction time over GC-PTSA-AC catalyst. Reaction conditions: 0.196 g FAL, 5.92 g n-butanol, 0.1 g catalyst, 120 °C.

Fig. 5. Stability test of GC-PTSA-AC catalyst. Reaction conditions: 0.196 g FAL, 5.92 g n-butanol, 0.1 g catalyst, 120 °C.
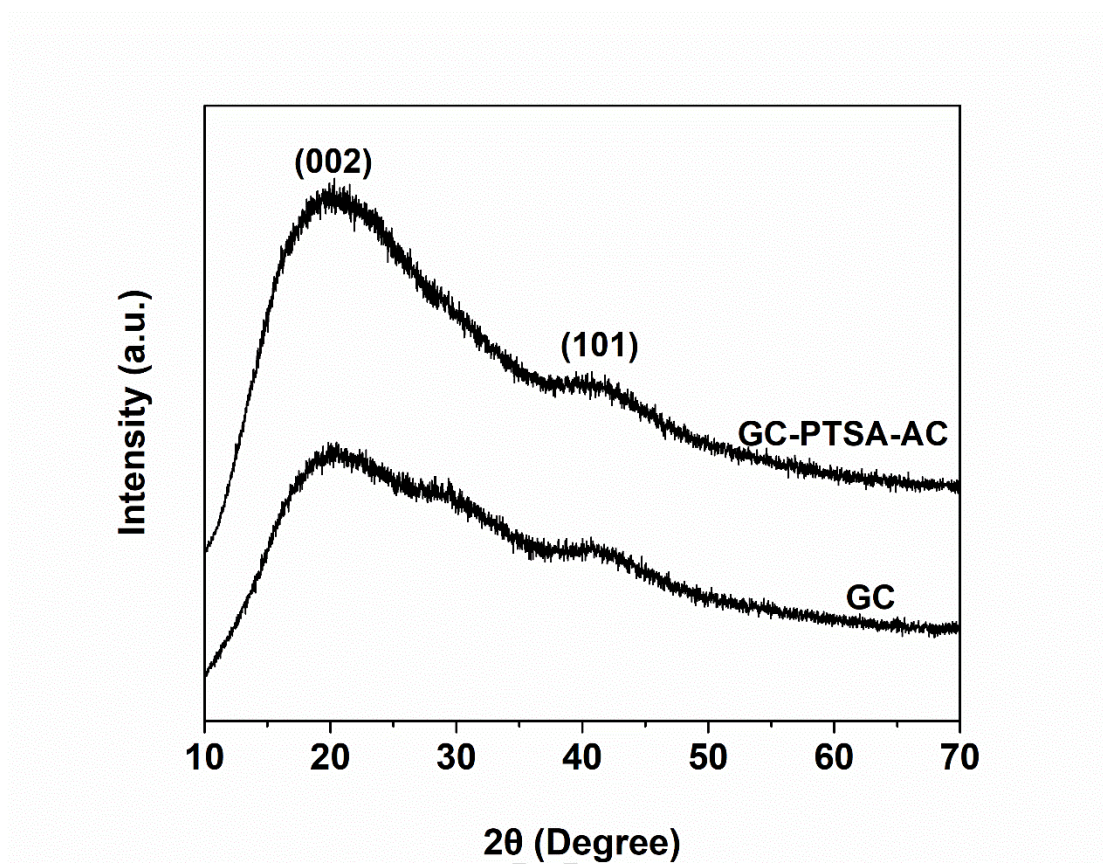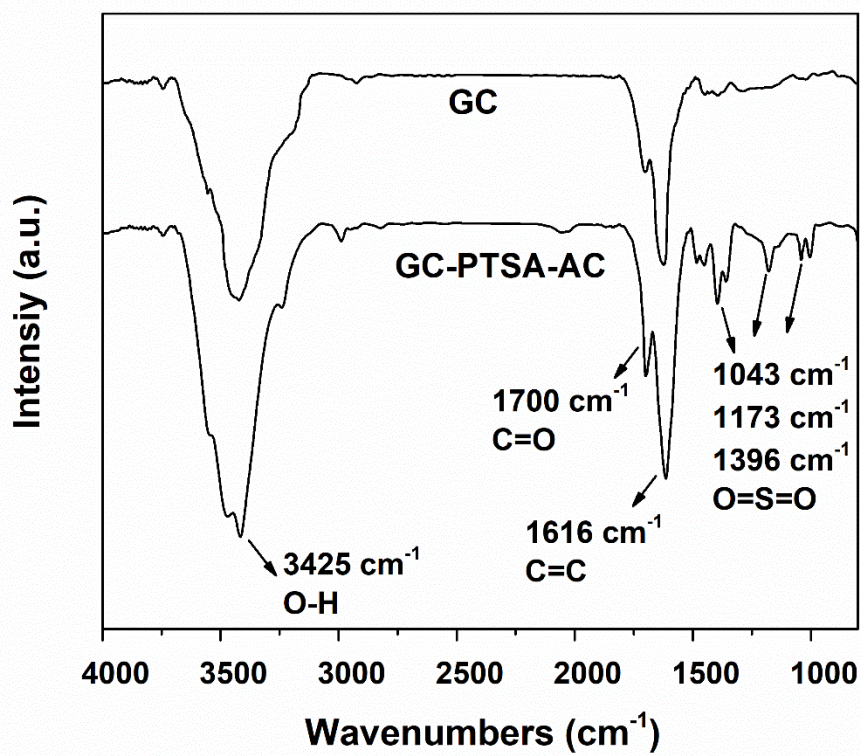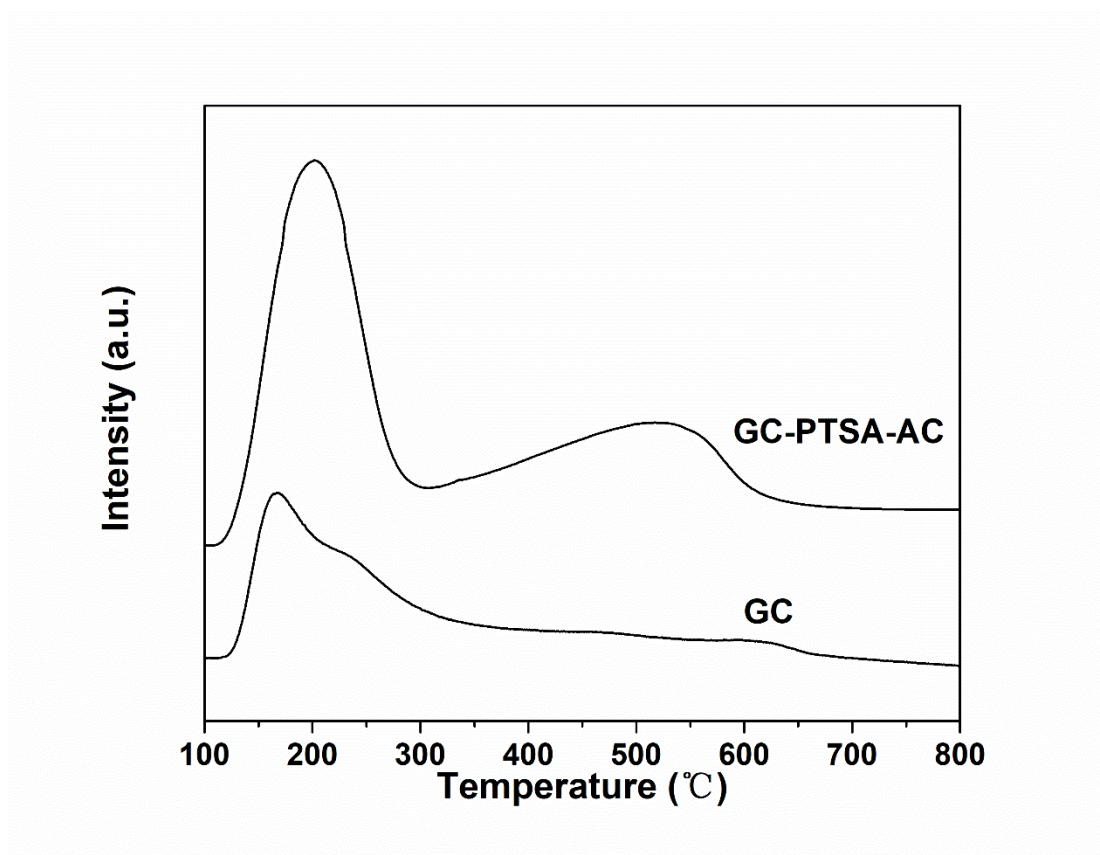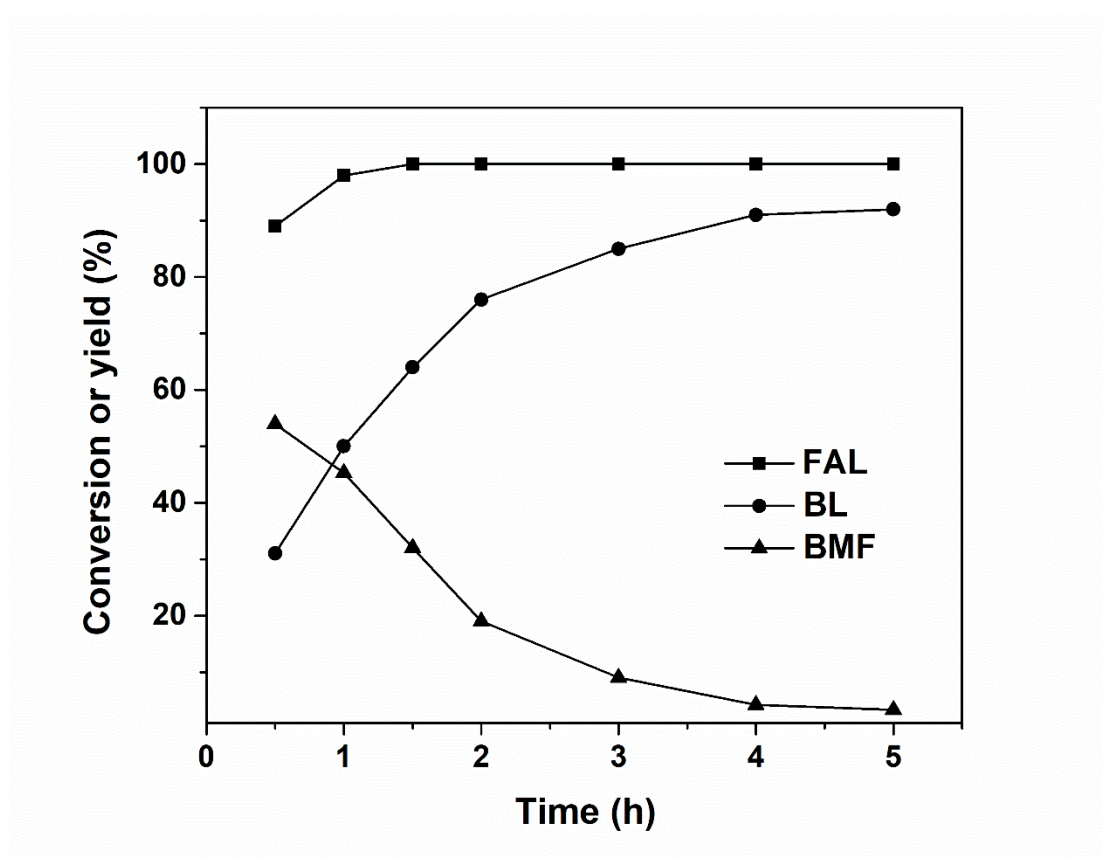
Fig. 1

Fig. 2

Fig. 3

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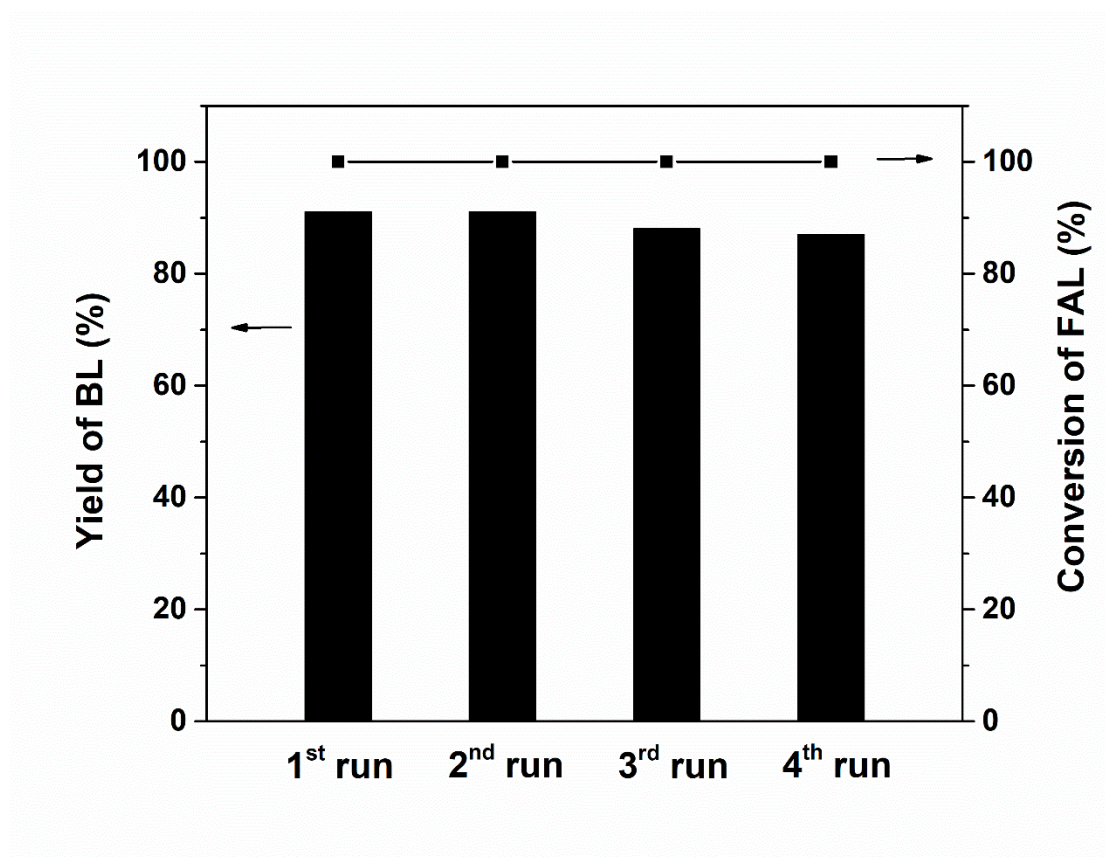
Fig. 5

Table 1. Acidity distributions of different carbonaceous materials.

Samples	S content[a] (wt %)	SO$_3$H density (mmol g^{-1})	COOH density[b] (mmol g^{-1})	Ar-OH density[c] (mmol g^{-1})	Total acid density[d] (mmol g^{-1})
GC	-	-	0.71	1.15	1.86
GC-AC	-	-	1.28	1.17	2.45
GC-PTSA	1.66	0.51	0.80	1.20	2.51
GC-PTSA-AC	1.68	0.53	1.33	1.18	3.04

[a] Based on elemental analysis.

[b] Obtained by subtracting concentration of sulfonic groups from titration results with NaHCO$_3$.

[c] Obtained by subtracting titration results using NaHCO$_3$ from titration results of NaOH.

[d] Obtained by titration with NaOH.

Table 2. Catalytic performance of FAL alcoholysis to BL over different catalysts[a].

Entry	Catalyst	Conversion (%)	Yield (%)	
			BL	BMF
1	GC	5.2	0	0.8
2	GC-AC	6.0	0	1.7
3	GC-PTSA	94.5	82.4	8.0
4	GC-PTSA-AC	100.0	91.0	4.2
5	PTSA	100.0	75.0 / 94.2[b]	3.6 / 1.5[b]

[a] Reaction conditions: 0.196 g FAL, 5.92 g n-butanol, 0.1 g catayst, 120 °C, 4 h.

[b] 80 °C.

References

[1] M.J. Climent, A. Corma, S. Iborra, Green Chem. 16 (2014) 516-547.

[2] R.A. Sheldon, Green Chem. 16 (2014) 950-963.

[3] D.M. Alonso, J.Q. Bond, J.A. Dumesic, Green Chem. 12 (2010) 1493-1513.

[4] L. Jean-Paul, v.d.H. Evert, v.B. Jeroen, P. Richard, ChemSusChem 5 (2012) 150-166.

[5] P. Demma Carà, R. Ciriminna, N.R. Shiju, G. Rothenberg, M. Pagliaro, ChemSusChem 7 (2014) 835-840.

[6] A. Démolis, N. Essayem, F. Rataboul, ACS Sustain. Chem. Eng. 2 (2014) 1338-1352.

[7] E. Christensen, A. Williams, S. Paul, S. Burton, R.L. McCormick, Energ. Fuel. 25 (2011) 5422-5428.

[8] M. Paniagua, J.A. Melero, J. Iglesias, G. Morales, B. Hernández, C. López-Aguado, Appl. Catal. A Gen. 537 (2017) 74-82.

[9] X. Kong, X. Zhang, C. Han, C. Li, L. Yu, J. Liu, Mol. Catal. 443 (2017) 186–192.

[10] G.M. Gonzalez Maldonado, R.S. Assary, J.A. Dumesic, L.A. Curtiss, Energy Environ. Sci. 5 (2012) 8990-8997.

[11] D. Ren, J. Fu, L. Li, Y. Liu, F. Jin,Z. Huo, RSC Adv. 6 (2016) 22174-22178.

[12] M.S. Tiwari, A.B. Gawade, G.D. Yadav, Green Chem. 19 (2017) 963-976.

[13] P. Neves, M. M. Antunes, P. A. Russo, J. P. Abrantes, S. Lima, A. Fernandes, M. Pillinger, S. M. Rocha, M. F. Ribeiro, A. A. Valente, Green Chem. 15 (2013) 3367-3376.

[14] S.S. Enumula, K.S. Koppadi, V.R.B. Gurram, D.R. Burri, S.R.R. Kamaraju, Sustain. Energ. Fuel.1 (2017) 644–651.

[15] S. Zhu, C. Chen, Y. Xue, J. Wu, J. Wang, W. Fan, ChemCatChem 6 (2014) 3080-3083.

[16] B.S. Rao, P.K. Kumari, D. Dhanalakshmi, N. Lingaiah, Mol. Catal. 427 (2017) 80-86.

[17] D. Song, S. An, Y. Sun, Y. Guo, J. Catal. 333 (2016) 184-199.

[18] G. Wang, Z. Zhang, L. Song, Green Chem. 16 (2014) 1436-1443.

[19] L. Peng, X. Gao, K. Chen, Fuel 160 (2015) 123-131.

[20] Y. Huang, T. Yang, M. Zhou, H. Pan, Y. Fu, Green Chem. 18 (2016) 1516–1523.

[21] M. Okamura, A. Takagaki, M. Toda, J.N. Kondo, K. Domen, T. Tatsumi, M. Hara, S. Hayashi, Chem. Mater. 18 (2006) 3039-3045.

[22] K. Ngaosuwan, J.G. Goodwin Jr, P. Prasertdham, Renew. Energ. 86 (2016) 262-269.

[23] J. Yang, G. Li, L. Zhang, S. Zhang, Catalysts 8 (2018) 14-25.

[24] R. Demir Cakan, N. Baccile, M. Antonietti, M. M. Titirici, Chem. Mater. 21 (2009) 484-490.

[25] H. Ma, J. Li, W. Liu, B. Cheng, X. Cao, J. Mao, S. Zhu, J. Agr. Food Chem. 62 (2014) 5345-5353.

[26] P. Wataniyakul, P. Boonnoun, A.T. Quitain, T. Kida, N. Laosiripojana, A. Shotipruk, Ind. Crop. Prod. 117 (2018) 286-294.

[27] D.S. Su, S. Perathoner, G. Centi, Chem. Rev. 113 (2013) 5782-5816.

[28] B. Zhang, J. Ren, X. Liu, Y. Guo, Y. Guo, G. Lu, Y. Wang, Catal. Commun. 11 (2010) 629-632.

[29] X. Qi, Y. Lian, L. Yan, R.L. Smith, Catal. Commun. 57 (2014) 50-54.

[30] W. Guodong, W. Bolun, W. Congxin, W. Jia, T. Zhijian, S. Robert, S.D. Sheng, Angew. Chem., Int. Ed. 56 (2017) 600-604.

[31] F.A. Dawodu, O. Ayodele, J. Xin, S. Zhang, D. Yan, Appl. Energ. 114 (2014) 819-826.

[32] I.M. Lokman, U. Rashid, Y.H. Taufiqyap, R. Yunus, Renew. Energ. 81 (2015) 347-354.

[33] M. Kitano, D. Yamaguchi, S. Suganuma, K. Nakajima, H. Kato, S. Hayashi, M. Hara, Langmuir 25 (2009) 5068-5075.

[34] Z. Zhang, K. Dong, Z. Zhao, ChemSusChem 4 (2011) 112–118.

Highlights

- A novel carbon catalyst possessed both high density of SO_3H and COOH groups.

- It exhibited good activity and stability for butanolysis of furfuryl alcohol.

- COOH groups cooperated with SO_3H active sites to facilitate the reaction.