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Authors: Huan Li, Qiang Deng, Hao Chen, Jing Zheng, Yao Zhong, Peixin Zhang, Jun Wang, Zheling Zeng, Shuguang Deng



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Benzenesulfonic acid functionalized hydrophobic mesoporous biochar as an efficient catalyst for the production of biofuel

Huan Li,^{a,b} Qiang Deng^{*},^{a,b,c} Hao Chen,^d, Jing Zheng,^{a,b} Yao Zhong,^{a,b} Peixin Zhang,^{a,b} Jun Wang,^{a,b} Zheling Zeng,^{a,b} Shuguang Deng^{a,b,c}

a Key Laboratory of Poyang Lake Environment and Resource Utilization, Nanchang University, Ministry of Education, Nanchang 330031, PR China

b School of Resource, Environmental and Chemical Engineering, Nanchang University, Nanchang 330031, PR China

c School for Engineering of Matter, Transport and Energy, Arizona State University, 551 E. Tyler Mall, Tempe, AZ 85287, USA

d Key Laboratory of Biomass Chemical Engineering of Ministry of Education, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, PR China

*Corresponding Author. E-mail: dengqiang@ncu.edu.cn (Qiang Deng)



Highlights

- A sulfonated biochar was prepared by sulfonation method of 4-chlorobenzenesulfonic acid.
- The sulfonated biochar have a strong hydrophobic network and acid density.
- The catalyst was highly active for the esterification reactions.
- The catalyst was active and selective for alkylation reactions.
- The catalyst was stable for five runs.

Abstract:

Catalytic esterification of fatty acid with methanol, alkylation of 4-ethylphenol with benzyl alcohol as well as 2-methylfuran with cyclopentanone are of great significant for the production of biofuels. However, the in-situ produced water decreases the acidity of catalyst and induces side reaction, leading to an unsatisfactory catalytic activity and selectivity. Herein, a novel biochar-based hydrophobic benzenesulfonic acid is prepared for the first time by one-pot sulfonation method of biochar with 4-chlorobenzenesulfonic acid. It has a large specific surface area of 100-400 m²/g, a hydrophobicity with H₂O contact angle higher than 110° and a high concentration of sulfonic acid over 1.0 mmol/g. In the esterification reaction of fatty acid with methanol for synthesis of biodiesel, it shows a higher conversion of 96.0% than sulfonic acid resin amberlyst-15 (86.7%) and traditional sulfonated biochar-SO₃H (28.0%). In the alkylation reaction of 4-ethylphenol with phenylmethanol/2-methylfuran with cyclopentanone for high-density bicyclic/monocyclic biofuel, its catalytic efficiency with target product yields are 69.4% and 70.5% respectively, which are also higher than that of amberlyst-15 (74.3%, 49.4%) and biochar-SO₃H (14.7%, 13.0%). Furthermore, the catalyst is more stable than biochar-SO₃H. The preparation of hydrophobic biochar-based sulfonic acid catalysts not only opens a new way for high-value utilization of biochar, but also provides a novel efficient catalyst in many acid-catalyzed transformation reactions that the product H₂O causes deleterious effects.

Keywords: biochar, benzenesulfonic acid, hydrophobicity-oleophilicity, esterification, alkylation,

biofuel

1. Introduction

Due to the fast depletion of petroleum resource and environmental concerns about climate change, renewable biomass is expected to become an important feedstock for the production of fuels.[1] Typically, the esterification reaction of fatty acid and methanol is widely researched for biodiesel.[2] Meanwhile, the alkylation reactions of lignocellulose-derived 2-methylfuran with cyclopentanone, 4-ethylphenol with benzyl alcohol combined with subsequent hydrodeoxygenation reaction are considered as important reactions for high-density monocyclic and bicyclic biojet fuel, which is used as a propellant of volume-limited aircraft, missile and rocket.[3-9] To date, numerous solid acidic catalysts such as heteropolyacids, sulfated metal oxides, zeolites and acid-treated clays have been used in these reactions.[10,11] It seems sulfonic acid functionalized solid catalysts (zeolite-based, organic mesoporous silicon-based, carbon-based, resin-based and metal-organic framework-based SO₃H) with strong acidity, large surface and pore size are needed for these reactions due to their great reactivity and accessibility of acidic sites.[12-16] However, the catalytic activity is still unsatisfactory, because the product H₂O is easily adsorbed on the hydrophilic SO₃H groups, and decreases even deactivates its acidity.[17-18] Moreover, these catalysts show a weak wettability with organic reactants and further prohibit the activity, because the hydrophobic weak-polar reactants are difficult to contact the active sites. More importantly, especially for the alkylation of 2-methylfuran with cyclopentanone, product H₂O incurs hydrolysis reactions of 2-methylfuran to 4-oxopentanal, which can quickly react with 2-methylfuran to generate branched product and lead to a low selectivity for the target product.[3,4]

The essential relationship between catalytic performance and hydrophobicity of solid acid has been well recognized.[19] Some hydrophobic mesoporous sulfonic acid functional resins have been synthesized via copolymerization of petroleum-derived monomers, and show a better catalytic performance than sulfonic acid resin amberlyst-15 for esterification and alkylation reactions.[4,20-22] However, the raw materials are high-price and unsustainable, which limits their industrial application.

Biochar is easily obtained from low-cost waste biomass and possesses a large surface area, adjustable pore size and good stability.[23] Recently, it has been widely explored for the

high-value utilization in many fields such as electrochemistry, energy storage, adsorption, and catalysis.[24-32] In the field of acid catalysis, the biochar-based acidic catalyst (B-SO₃H) is usually prepared by direct sulfonation of biochar with H₂SO₄/fuming sulfuric acid as well as quaternary ammonization of nitrogen-containing biochar with 1,3-propanesultone. Generally, these reactions are conducted under severe conditions.[33-37] Whereas, although the pristine biochar is hydrophobic, biochar-based sulfonic acidic catalyst cannot maintains its hydrophobility after grafting the hydrophilic SO₃H. Meanwhile, the chemical bond of the sulfur and the carbon material is always unstable, resulting in the leaching of SO₃H groups and low cycle performance of catalyst.[38] Very recently, our group synthesized a hydrophobic acidic biochar via diazo reduction method of biochar with amino-arenesulfonic acid. It shows a great catalytic activity, selectivity and stability for esterification, transesterification and alkylation reactions.[39] However, the synthesis process is complex, and sulfonated agent amino-arenesulfonic acids are scarce and high-price. To provide more alternatives for the industrial production in the future, a new synthesis route still need to be studied.

Herein, a novel hydrophobic benzenesulfonic acid functionalized biochar (B-PhSO₃H) is prepared via sulfonation method of biochar with 4-chlorobenzenesulfonic acid. The acid density, specific surface area and hydrophobicity are controlled by the amount of grafting groups. Compared with amberlyst-15 and B-SO₃H, it is highly active and selective in the esterification of fatty acid and methanol, alkylation of 4-ethylphenol and benzyl alcohol, as well as alkylation of 2-methylfuran and cyclopentanone. Moreover, it has a higher stability against leaching of SO₃H group than B-SO₃H. In fact, H₂O is a common byproduct in many biomass conversion reactions, such as the dehydration of glucose/fructose for 5-hydroxymethylfurfural, and traditional acid catalysts inevitably suffer from the deleterious effect of H₂O.[40-41] The hydrophobic biochar-based acidic catalyst is promising in these catalytic conversion reactions of biomass derivatives.

2. Experimental

2.1 Materials

Chlorosulfonic acid, 4-chlorobenzenesulfonic acid, sulfuric acid, aluminum chloride, dichloromethane, acetone, 4-ethylphenol and benzyl alcohol were purchased from Sinopharm

Chemical Reagent Company. Methanol, oleic acid and methyl heptadecanoate were obtained from Sigma-Aldrich Chemical Reagent Company. Potassium hydroxide, 2-methylfuran, cyclopentanone, amberlyst-15 were supplied by Shanghai Crystal Pure Reagent Company. All chemicals were used without further purification.

2.2 Catalyst preparation

Biochar was obtained from coconut shell by KOH activation. The mixture of 4.0 g coconut shell powder, 6 g KOH and 40 mL H₂O was dried at 110 °C for 3 h. Then the slurry was heated of 600 °C at a heating rate of 10 °C/min in N₂ atmosphere and kept for 1 h. The obtained solid was dispersed in 1 mol/L HCl aqueous solution at 70 °C for 1 h, followed by washing with H₂O until neutral, and drying in a vacuum oven at 90 °C for 24 h.

In a flask, 1.5 g biochar and 2.0-5.0 g 4-chlorobenzenesulfonic acid or 7.0 g chlorosulfonic acid were added into 60 mL dichloromethane at 35 °C. Subsequently, 0.5 g aluminum chloride as catalyst was added. After 12 h, the resultant solid was obtained by washing with 20 mL dichloromethane and 30 mL acetone, drying for 12 h. The benzenesulfonic acid and sulfonic acid functionalized biochar were referred to as Xwt%B-PhSO₃H and Xwt%B-SO₃H, respectively, where the X denotes the weight content of S.

As a comparison, direct sulfonation of biochar was obtained by hydrothermal method. The mixture of 1.0 g biochar, 30 mL H_2SO_4 was sealed in a 50 mL Teflon-lined autoclave, heated to 180 °C and kept for 24 h. The resultant solid were obtained by washing with H_2O and acetone until the filtrate into neutral, drying for 12 h, and referred to as Xwt%B-SO₃H.

2.3 Catalyst characterization

Fourier transform infrared (FTIR) spectra was recorded in the range of 400-4000 cm⁻¹ on a Nicolet 5700 using the KBr pellet method. The porous structure was taken by N₂ adsorption-desorption at -196 °C on ASAP 2460 surface analyzer. The specific surface area was calculated by the BET method, and pore size distribution was calculated using BJH method using the adsorption isotherm. Morphology was obtained with a JEM-2100 transmission electron microscope. The bulk composition was characterized using a CHNS elemental analyzer (Vario MICRO). X-Ray photoemission spectroscopy (XPS) data were gained by an ESCALAB 250Xi instrument equipped with a monochromatic Al anode X-ray gun. Hydrophobic and oleophilic

properties were measured by a Sindatek 100P contact angle goniometer. H_2O and cyclohexane adsorption was collected using a Hiden Intelligent gravimetric sorption analyzer (IGA-100) at 25 °C with different humidity. Before measurement, 100 mg of sample was treated for 10 h at 150 °C under vacuum, then the sample was exposed to H_2O and cyclohexane vapor at different humidity, which could be adjusted by controlling the vapor pressure. The amount of acid was determined by acid-base titration. The mixture of hydrophobic biochar-based acidic catalyst (0.2 g) and NaOH alcoholic solution(50 mL, 0.0085 M) was sealed and stirred for 2 h at room temperature, then the solids were filtered off and the filtrate was back-titrated using 0.0136 M hydrochloric acid. The amount of acid sites was calculated according to the consumed sodium hydroxide amount.

2.4 Catalytic reactions

The esterification of oleic acid and methanol was carried out in a 25 mL round bottom flask equipped with a reflux condenser and a magnetic stirrer. The mixture of 3.0 g (0.01 mol) oleic acid and 3.4 g (0.1 mmol) methanol was heated to 60 °C, and then 0.3 g catalyst was added. The reaction products were sampled periodically, and methyl hexadecanate was added as internal standard, then subsequent quantitative analyzed by Trace 1300 gas chromatograph equipped with FID detector and a TG-WAXMS capillary column (30 m \times 0.32 mm).

The alkylation of 4-ethylphenol and benzyl alcohol was carried out in a round bottom flask. The mixture of 2.70 g (25 mmol) benzyl alcohol and 6.11 g (50 mmol) 4-ethylphenol was heated to 110 °C, and then 0.1 g catalyst was added, and sampled periodically. The products were analyzed by Agilent 6890N GC/5973 MS detector and quantified by Trace 1300 gas chromatograph equipped with FID detector and a HP-5 capillary column (30 m \times 0.32 mm).

The alkylation of 2-methylfuran with cyclopentanone was carried out in a 50 mL batch autoclave. The mixture of 17.2 g (210 mmol) 2-methylfuran, 8.8 g (105 mmol) cyclopentanone and 0.1 g catalyst was added to the autoclave, heated to 80 °C and sampled periodically. The analysis method was as same as the alkylation of 4-ethylphenol and benzyl alcohol.

Adsorption of reactants on biochar: In a flask, 0.1 g organic reactant and 0.05 g catalyst were stirred in 20 mL H₂O under reaction temperature, and sampled periodically, and the concentration

of organic residue in the aqueous solution was quantified using a U-3010 UV-vis spectrometer (Hitachi).

3. Results and Discussion

3.1 Structural characteristics of acid functionalized biochar

The amount of S corresponding to the sulfonic acid was detected by the element analysis as listed in Table 1. The result shows the biochar contains a large amount of S, which confirms that the sulfonic acid groups can be easily grafted onto the biochar. The amount of S increases with the concentration of 4-chlorobenzenesulfonic acid, reaching a maximum value of 6.33wt% when the mass ratio of 4-chlorobenzenesulfonic acid to biochar is 2.66. When the amount of 4-chlorobenzenesulfonic acid is further increased to 5 g, and the mass ratio of 4-chlorobenzenesulfonic acid to biochar is 3.33, the S content of biochar is 6.58 wt%. The S content reaches a plateau due to surface saturation.(Table S1) On the contrary, the functionalized biochar obtained without AlCl₃ has a low S amount (4.68wt%), indicating the AlCl₃ has positive effect on the grafting process via elimination of Cl anion (Scheme 1). Similarly, sulfonic acid functionalized B-SO₃H with 7.63wt% S was obtained via sulfonation with sulfuric acid is only 2.75wt%, demonstrating that the sulfonation method for via grafting sulfonic acid on biochar has a higher grafting efficiency.

FTIR spectroscopy shows the vibration bands at 827 cm⁻¹ (S-O symmetric stretching), 1006 cm⁻¹ (S-O asymmetric stretching) and 1170 cm⁻¹ (S=O symmetric stretching) were attributed to the SO₃H groups (Figure S1).[42,43] In addition, for all samples, the intensity of the strongest peak of SO₃H (1006 cm⁻¹) is linear with the S content with the intensity of 2.75wt%B-SO₃H as baseline (Figure 1). Meanwhile, the acid concentration detected by acid-base titration is equal to the value calculated by the S content, further confirming the successful grafting of SO₃H group on the biochar. The acid amount of biochar is lower than that of amberlyst-15, because of relatively low concentration of SO₃H groups.

The surface composition of sulfonated biochar is analyzed by X-ray photoelectron spectroscopy (XPS). Clearly, the signals of C 1s, O 1s, and S 2p were present in the sulfonated samples (Figure S2A,B). The C 1s spectrum includes differentiated binding energy values with

three peaks at 284.1, 284.4 and 285.0 eV (Figure S2C), which could be assigned to C-C in the major network, C-S in the sulfonic group, sp²-hybridized aromatic carbon (C=C sp²)[44]. Compared with the raw biochar, the introduction of sulfonic acid results in a large amount of C-S in 6.33wt% B-PhSO₃H. In the case of O1s, typically four bonding groups are located at 531.7 (C-O-C), 532.33 (O=C), 533 (C-OH) and 532.8 eV (O-S) (Figure S2D) [45]. Compared with the raw biochar, the peak area of the functionalized biochar increased significantly after grafting. The relative oxygen atom content of C-OH is decreased., while C-O-C is increased. It is proved that 4-chlorobenzenesulfonic acid is grafted onto the hydroxyl group of biochar via nucleophilic aromatic substitution reaction.

The N₂ adsorption-desorption isotherm (Figure 2) shows a typical type IV isotherm for all samples, confirming that the existence of mesoporous of synthesized biochar. With the increase of the grafting amount of benzenesulfonic acid groups from B to 6.33wt%B-PhSO₃H, the BET surface areas, pore volumes and pore diameters decrease from 196.8 to 112.1 m² g⁻¹, 0.30 to 0.24 cm³ g⁻¹ and 12.5 to 11.9 nm, respectively (Table 1). Although the content of S of 7.63wt%B-SO₃H is higher than that of 6.33wt%B-PhSO₃H, the surface area and pore volume are larger because the smaller sulfonic acid group occupies less channels. The TEM image of B-PhSO₃H shows that the sulfonated biochar retains a certain wormhole-like mesoporous structure (Figure 3), which is well agreed with the pore textural result obtained from the N₂ adsorption isotherms.

3.2 Hydrophobicity and oleophilicity of acid functionalized biochar

Figure 4 shows the contact angles of H_2O on various samples. Amberlyst-15 with the contact angles 31° shows very weak hydrophobicity because of large amount of hydrophilic SO₃H groups. The contact angle of H_2O on pristine biochar is 132°. However, the direct grafting of SO₃H destroys the hydrophobicity, and 2.75wt%B-SO₃H and 7.63wt%B-SO₃H show contact angles of 75° and 49°, respectively. This is consistent with the fact that the higher the sulfur content, the worse hydrophobicity. Fortunately, the hydrophobicity of biochar can be well retained by the introduction of hydrophobic benzenesulfonic acid because of it have long carbon chain. For the B-PhSO₃H, the contact angle only slightly decreases from 128° to 114° with the increasing amount of benzenesulfonic acid.

The adsorption properties of H₂O and nonpolar cyclohexane over different samples was

further measured (Figure 5). Agreed with the results of contact angle, the 6.33wt%B-PhSO₃H shows only 29.8% of the adsorption capacity of H₂O, much lower than that of amberlyst-15 (60.5%), 2.75wt%B-SO₃H (47.5%) and 7.63wt%B-SO₃H (41.4%). Conversely, a strong hydrophobicity means an excellent oleophilicity, and the order of adsorption capacity of cyclohexane is 6.33wt%B-PhSO₃H (31.7%) > 2.75wt%B-SO₃H (14.7%) > 7.63wt%B-SO₃H (12.4%) > amberlyst-15 (10.9%) (Figure 3B). These results indicate that hydrophobic biochar easily adsorbs the weak-polar reactants whereas repulses H₂O.

3.3 Esterification of oleic acid with methanol

Figure S3 shows the kinetics curves in esterification of oleic acid with methanol over 6.33wt% B-PhSO₃H, 7.63wt%B-SO₃H and amberlyst-15. Although it has the lowest acid density, 6.33wt%B-PhSO₃H shows a conversion merit of 93.0% than 86.7% for amberlyst-15 and 65.7% for 7.63wt%B-SO₃H after 10 h of reaction time due to better wettability of reactants and hydrophobicity of product H₂O. Obviously, the turnover number (TON) and turnover frequency (TOF) values are calculated based on the low conversion because of plenty reactants. Obviously, 6.33wt%B-PhSO₃H shows a higher TOF value (17.0 h⁻¹) than that of B-SO₃H (2.5 h⁻¹) and amberlyst-15 (2.6 h⁻¹) (Table S2). All B-PhSO₃H samples show more efficient activity than that of B-SO₃H (Figure 6). Meanwhile, the catalytic activity of B-PhSO₃H increases with the amount of benezesulfonic acid group, because more acidic sites could enhance the catalytic activity. However, further increase of benezesulfonic acid group will decrease the activity because the surface area decreases. As a result, there is an optimal sulfur content, and 5.46wt%B-phSO₃H shows the best performance with the yield of 96.0% for esterification after 10 h.

3.4 Alkylation of 4-ethylphenol with benzyl alcohol

The alkylation of 4-ethylphenol with benzyl alcohol produces H_2O and mono-alkylated products (2-benzyl-4-ethylphenol and 3-benzyl-4-ethylphenol), which have a great potential in production of high-density biocyclic hydrocarbon biofuel. Besides the main reaction, some di-alkylated by-products (2,6-dibenzyl-4-ethylphenol, 2,5-dibenzyl-4-ethylphenol and 3,5-dibenzyl-4-ethylphenol) can also be formed during the reaction. It is worth mentioning that di-alkylated products can generate the tricyclic alkane after hydrodeoxygenation, which have a high freezing point and viscosity, and is not suitable for the utilization as jet fuel. Figure S4 shows

the time-dependent product distribution over 6.33wt%B-PhSO₃H, 7.63wt%B-SO₃H and amberlyst-15. It reveals that 6.33wt%B-PhSO₃H with better hydrophobicity-oleophilicity possesses activity merit compared with 7.63wt%B-SO₃H (89.6% vs. 37.7%). B-PhSO₃H shows a higher TOF value (68.7 h⁻¹) than that of B-SO₃H (34.9 h⁻¹) (Table S2). All B-PhSO₃H samples and amberlyst-15 showed higher activity than B-SO₃H (Figure 7). For all the B-PhSO₃H series samples, the catalytic activity increases with the amount of benezesulfonic acid group owing to the higher acid density and stable hydrophobicity-oleophilicity, whereas the selectivity of mono-alkylated product decreases slightly due to the generation of di-alkylated products. As a result, 6.63wt%B-PhSO₃H with the conversion of benzyl alcohol 89.6% and selectivity for mono-alkylated products 77.5%, shows the highest yield of mono-alkylated 69.4% in the reaction.

To further elucidate the influence of the hydrophobicity-oleophilicity, the adsorption kinetic of benzyl alcohol from H₂O over various catalysts is studied under 110 °C (Figure S5). Figure 8 shows adsorption quickly reaches equilibrium over all catalysts, and the adsorption quality of benzyl alcohol (6.33wt%B-PhSO₃H > 7.63wt%B-SO₃H > amberlyst-15) is consistent with the order of hydrophobicity-oleophilicity. It means that the organic reactants are easily adsorbed on B-PhSO₃H under the reaction conditions, and subsequent transformation will occur.

3.5 Alkylation of 2-methylfuran with cyclopentanone

As mentioned above, apart from the alkylation product FCF and intermediate FC, trimerized product FFF is also formed through hydrolysis of 2-methylfuran (Figure 9A). Figure S6 shows the time-dependent product distribution over 6.33wt%B-PhSO₃H, 7.63wt%B-SO₃H and amberlyst-15. 6.33wt%B-PhSO₃H shows two merits on conversion and selectivity compared with 7.63wt%B-SO₃H. First, the conversion of 2-methylfuran increases from 39.0 to 83.5% because the better oleophilicity exposes more active sites to the reactants in 6.33wt%B-PhSO₃H, although its total acid concentration and surface area is lower than 7.63wt%B-SO₃H. Second, the selectivity of FFF decreases from 24.0 to 7.5% due to the hydrophobicity inhibits the hydrolysis reaction of 2-methylfuran. Although amberlyst-15 has the highest activity with conversion of 2-methylfuran 95.0%, the selectivity for FCF is only 52.6%. B-PhSO₃H shows a higher TOF value (33.4 h⁻¹) than that of B-SO₃H (13.4 h⁻¹) and amberlyst-15 (17.9 h⁻¹) (Table S2). Meanwhile, PhSO₃H functionalized biochar with the high hydrophobicity has high selectivity for FCF, because the

formation of side product FFF is mostly suppresse. For the samples of B-PhSO₃H, owing to the higher acid density and better hydrophobicity-oleophilicity, both of the activity and selectivity are increased with the amount of sulfonic acid group (Figure 9B). At last, it is found that 6.63wt%B-PhSO₃H with the conversion of reactants 83.5%, selectivity for FCF 84.4% and yield of FCF 70.5% shows the best catalytic performance in the reaction.

3.6 Catalyst stability and recycling

The recycling of these catalysts is further evaluated in the esterification reaction. The catalyst is centrifuged after the reaction, washed by acetone, dried overnight, and then used for the next run. As shown in Figure 10, after 5 cycles, 6.33wt%B-PhSO₃H only shows a slightly decrease activity from 93.0% to 86.1%, whereas 7.63wt%B-SO₃H decreased from 65.7% to 44.7%. It should be attributed to S content of 6.33wt%B-PhSO₃H slightly decrease to 6.02wt%, and 7.63wt%B-SO₃H is decrease to 4.63wt%. The acid-base titration test results of 6.33wt%B-PhSO₃H and 7.63wt% B-SO₃H were 1.76 mmol g⁻¹ and 1.36 mmol g⁻¹, respectively (Table S3). This result shows the organic sulfonic acid is more difficult to be leached out of biochar and organic sulfonic acid functionalized biochar is more stable. It can be used as a highly efficient and stable catalyst.

4. Conclusions

In this work, a novel hydrophobic biochar-based benzenesulfnic acid was synthesized via simple sulfonation method of biochar with 4-chlorobenzenesulfonic acid. With the grafting amount of benzenesulfoic acid, they maintain the hydrophobicity of biochar and avoid the deterious effect of H₂O produced in-situ in many reactions. In the esterification of fatty acid and methanol for biodiesel, the catalyst has higher catalytic activity and better recyclability than amberlyst-15 and 2.75wt%B-SO₃H. Meanwhile, it also shows higher activity and selectivity in the alkylation reaction of 4-ethylphenol and benzyl alcohol as well as 2-methylfuran with cyclopentanone for high-density biofuel. This work not only provides an efficient way to produce biofuel, but also shows a novel high-value utilization route for biochar.

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Scheme 1. Sulfonation method of biochar with benzenesulfonic acid.



Figure 1. Relation peak area of S-O band at 1006 cm⁻¹ with sulfur content and acidity density in functionalized biochar.



Figure 2. (a,c) N₂ adsorption isotherms and (b,d) pore size distribution of functionalized biochar.



Figure 3. TEM micrographs of (a,b) biochar, (c,d) 7.63wt%B-SO₃H and (e, f) 6.33wt%B-PhSO₃H.



Figure 4. hydrophobic contact angle test of H_2O on functionalized biochar.







(a) Main reaction



Figure 7. The reaction pathway scheme (a) and catalytic performance of functionalized biochar (b) in the alkylation of 4-ethylphenol with phenyl methanol. Reaction conditions: 2.70 g phenyl methanol, 6.11 g 4-ethylphenol, 0.1 g catalyst, temperature 110 °C, time 2 h.



Figure 8. Adsorption kinetics of benzyl alcohol over amberlyst-15, 7.63wt%B-SO₃H and 6.33wt%B-PhSO₃H. Adsorption conditions: 0.1 g benzyl alcohol, 0.05 g catalyst, 20ml H₂O, temperature 110 °C.







Figure 10. The recycle performance of functionalized biochar in the esterification. Reaction conditions: 3.4 g methanol, 3.0 g oleic acid, 0.3 g catalyst, temperature 60 °C, time 10 h.

Samples	reactant	SBET	V _{total}	Sulfur	Acid density	Contact angle
	$(g g^{-1})$	$(m^2 g^{-1})$	$(cm^3 g^{-1})$	(wt%)	(mmol g ⁻¹)	of H ₂ O (°)
Biochar	0	927.1	0.89	0.63	0.06 (0.19)	132
2.75wt%B-SO ₃ H	48	757.9	0.71	2.75	0.67 (0.80)	75
7.63wt%B-SO ₃ H	4.66	349.2	0.34	7.63	2.34 (2.38)	49
4.30wt%B-PhSO ₃ H	1.33	196.8	0.30	4.30	1.26 (1.34)	128
4.54wt%B-PhSO ₃ H	1.66	191.8	0.26	4.54	1.39 (1.42)	122
4.68wt%B-PhSO ₃ H ^b	2.66	253.4	0.34	4.68	1.41 (1.46)	120
4.83wt%B-PhSO ₃ H	2	182.2	0.23	4.83	1.50 (1.51)	121
5.46wt%B-PhSO ₃ H	2.33	139.0	0.24	5.46	1.70 (1.71)	116
6.33wt%B-PhSO ₃ H	2.66	112.1	0.24	6.33	1.91 (1.98)	114
amberlyst-15	-	45	0.31	13.43	4.11 (4.14)	49

Table 1. Physicochemical properties of functionalized biochar.

a Detected by titration, in brackets data are calculated according to the amount of functional group.

b the functionalized biochar is obtained without AlCl₃ in the synthesis conditions.