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Article

Fabrication of a solid superacid with temperature-regulated silica-isolated biochar nanosheets

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ABSTRACT

This paper reports a new strategy for the structural reconstruction of biomass carbon sulfonic acid (BCSA) to its solid superacid counterpart. In this approach, a cheap layered biomass carbon (BC) source is chemically exfoliated by cetyltrimethyl ammonium bromide and then converted to silica-isolated carbon nanosheets (CNSs) by a series of conversion steps. The state of the silica-isolated CNSs and the stacking density of their nanoparticles are regulated by the dehydration temperature. Only the highly isolated and non-crosslinked CNSs with loose particle stacking structures obtained upon dehydration at 250 °C can be turned into superacid sites (with stronger acidity than that of 100% H₂SO₄) after sulfonation. This is accompanied by the creation of abundant hierarchical slit pores with high external surface area, mainly driven by the strong hydrogen bonding interactions between the introduced sulfonic acid groups. In typical acid-catalyzed esterification, etherification, and hydrolysis reactions, the newly formed superacid exhibits superior catalytic activity and stability compared to those of common BCSA and commercial Amberlyst-15 catalysts, owing to its good structural stability, highly exposed stable superacidic sites, and abundance of mesoporous/macroporous channels with excellent mass transfer rate. This groundbreaking work not only provides a novel strategy for fabricating bio-based solid superacids, but also overcomes the drawbacks of BCSA, i.e., unsatisfactory structural stability, acidity, and porosity.

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1. Introduction

Acid catalysis is one of the key strategies for the production of industrially important chemicals [1]. Solid acids are particu-

larly attractive due to their easy separation, reductive corrosion, good recyclability, and green chemical processes [2–12]. Since their discovery in 2005, biomass carbon-derived solid sulfonic acids (BCSAs) have attracted worldwide attention as

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very promising solid acids [13–16], owing to their low cost, easy availability, and higher activity in some acid-catalyzed reactions compared to those of commercial sulfonated resins. However, a major challenge that limits their large-scale application is that the polycyclic aromatic carbon nanosheets (CNSs) composing the compact laminated structure of BCSAs suffer from partial leaching/dissolution in many condensed phases including water, and are unlikely to exhibit satisfactory long-term performances. Moreover, common BCSAs have some other intrinsic shortcomings, including unsatisfactory mass transfer efficiency, relative weakness, instability, and low exposure of acid sites [17,18].

Several effective methods, such as chemical grafting of functionalized ionic liquids [19] and thermal carbonization under catalytic activation [20–23], as well as hard [24,25] or soft [26–28] templates, have been developed to overcome the above issues. In addition, some elegant methods have also been developed, mainly focused on increasing the acid density and spatial proximity of the sulfonated polystyrene resin to enhance the strength of its sulfonic acids [29–31], as well as varying the crystallinity, topological structure, morphology, and chemical composition of the inorganic solid acids to adjust their acid strengths [32–35]. Current methods have led to great progress in improving the properties of solid acids. However, most of these methods are still strategically complex or poorly efficient, and thus achieve only limited improvements in structure, acidity, or porosity. Therefore, it is highly desirable to develop new strategies to prepare an efficient solid acid that can meet the following requirements [16,17,36–38]: i) cheap and easily available precursors, along with a simple/practical fabrication method to facilitate its potential application; ii) sufficiently strong acidity (e.g., higher than that of 100% H_2SO_4) and maximum exposure of acid sites on the external surface; iii) sufficient structural stability with abundant hierarchical pores, resulting in excellent accessibility and reusability.

Herein, we report a new structural reconstruction (SR) strategy for fabricating silica-isolated biomass carbon sulfonic acids (SIBCSAs) by using bamboo powder from forestry waste and very cheap water glass as the main raw materials. In the SR strategy, the layered bamboo carbon source was chemically exfoliated by cetyltrimethylammonium bromide (CTMA) solu-

tion to yield its individual carbon nanosheets (CNSs, representing the building units of biomass carbon, BC), highly isolated by CTMA. Then, this binary composition was further combined with an acidic silica sol to yield a ternary composition, which was in turn converted into silica-isolated CNSs (SIBCs) *via* dehydration at 250 or 350 °C and removal of CTMA. Finally, the silica-isolated CNSs were transformed into their sulfonated carbon nanosheet derivatives (SCNSs, marked as SIBCSAs) using concentrated H_2SO_4 (see Scheme 1). The structural reconstruction of the BCSAs can thus be successfully achieved using this strategy. A series of characterizations confirmed that the newly synthesized SIBCSA-1 material (obtained after dehydration at 250 °C) exhibits the representative features of efficient solid acids discussed above, and thus shows excellent catalytic performances in acid-catalyzed esterification, etherification, and hydrolysis reactions.

2. Experimental

2.1. General information and methods

All reagents were of analytical grade. Concentrated sulfuric acid, sodium silicate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$), oxalic acid, phenol, ferric chloride, ammonium nitrate, concentrated hydrochloric acid, sodium hydroxide, hexadecyl trimethyl ammonium bromide (CTMA), adipic acid, isooctanol, isobutene, methanol, hydroxypropyl cellulose, and Amberlyst-15 reagents were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Preparation of BC material

According to our patented procedure (ZL 201710129798.3), the bamboo carbon material was prepared by hydrothermal carbonization of bamboo powder. In detail, bamboo powder (6 g, main elemental composition listed in Table S1), ferric chloride (3.6 g), phenol (1.2 g), and 0.1 mL concentrated HCl were added to 10 mL of deionized water and then placed in a stainless steel (100 mL) reactor. Afterward, the stainless steel reactor was heated to 180 °C and kept at that temperature for 9 h. After carbonization, the reactor was cooled to room temperature in air and biochar was collected along with the liquid

Scheme 1. Synthetic strategy for preparing silica-isolated biochar sulfonic acid (SIBCSA) *via* structural reconstruction.

products. The obtained mixture was centrifuged and washed several times with distilled water, followed by drying at 60 °C in vacuum overnight to obtain black solid BC.

2.3. Synthesis of acidic silica sol

A 0.5 mol/L acidic silica sol (pH 3.5–4.0) was synthesized by adding 12 mL of 1 mol/L Na_2SiO_3 solution to 10 mL of 2 mol/L oxalic acid solution dropwise, at 35 °C, and with magnetic stirring. The particle size distribution of the 0.5 mol/L silica sol was measured by a Nano ZS90 dynamic light scattering instrument with a HeNe laser ($\lambda = 633 \text{ nm}$). The light source (75 mW) and the obtained results are shown in Fig. S1. The average particle size measured for the 0.5 mol/L silica sol was about 17 nm.

2.4. Synthesis of conventional biomass carbon sulfonic acid

The BC material (3 g) was sulfonated with 30 mL concentrated H_2SO_4 at 100 °C for 3 h (solid/liquid = 1:10 g/mL). After reaction, the sulfonated precipitate was filtered, repeatedly washed with distilled water until free from SO_4^{2-} ions (as detected by Ba^{2+} ions), and dried at 60 °C in vacuum overnight, yielding BCSA. The contents of OH, COOH, and SO_3H groups in BCSA were measured *via* chemical titration [39].

2.5. Synthesis of silica-isolated BCSA

First, the BC material (2 g) was treated with NaOH (1.2 g) in 12 mL distilled water; the treatment was carried out in a three-necked flask at 100 °C for 12 h. After treatment, the mixture was cooled to 60 °C and its pH value was adjusted to 8.5 with 6 mol/L HCl. Afterward, the reaction mixture was treated with CTMA (1.38 g) at 60 °C for 6 h with vigorous stirring. After treatment, the precipitate was filtered, washed three times with distilled water, and dried in vacuum at 60 °C overnight to yield 3.26 g of a binary mixture denoted as CTMA-BC.

Then, 2 g CTMA-BC and 10 mL distilled water were mixed at 50 °C for 0.5 h in a three-necked flask with vigorous stirring. A 22 mL aliquot of the 0.5 mol/L acidic silica sol was slowly added dropwise to the above mixture. After reacting at 50 °C for 3 h, the resulting precipitate was filtered, washed three times with distilled water, and dried under vacuum at 60 °C overnight, to yield 2.90 g of a ternary mixture denoted as $(\text{H}_4\text{SiO}_4)_n$ -CTMA-BC. In the following step, the above mixed solid was heated to 250 or 350 °C in a tube furnace, through temperature programming with a heating rate of 1 °C/min under N_2 atmosphere, followed by dehydration for 5 h at the selected temperature. After cooling the furnace to 25 °C, the dehydrated black solid was treated with a 3 mol/L aqueous solution of ammonium nitrate (solid/liquid = 1:30 g/mL) under magnetic stirring at 100 °C for 3 h. The precipitate was filtered, washed three times with distilled water, and dried under vacuum at 60 °C overnight, to yield 1.14–1.00 g of silica-isolated BC solid; the SIBC samples dehydrated at 250 at 350 °C were labeled SIBC-1 and SIBC-2, respectively. Finally, the SIBC solid was converted to its sulfonated derivative through the same

sulfonation conditions applied in the synthesis of BCSA (the corresponding samples were denoted as SIBCSA-1 and SIBCSA-2). The SiO_2 content of the materials was measured by a high-temperature combustion treatment at 950 °C for 9 h in air. The OH, COOH, and SO_3H densities of the materials were measured *via* chemical titration [39].

2.6. Characterizations

Fourier transform infrared (FT-IR) spectra of the samples in the 400–4000 cm^{-1} region were recorded on a Nicolet Avatar 370 spectrometer using KBr pellets. Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) images were obtained on a JEM-2100F instrument equipped with a high-angle annular dark field (HAADF) detector and an Oxford energy-dispersive X-ray spectroscopy (EDS) detector under an accelerating voltage of 220 kV. ^{13}C , ^{29}Si , and trimethylphosphine oxide (TMPO)-adsorbed ^{31}P magic-angle spinning (MAS) solid NMR spectra (Bruker AVANCE III 500 Hz) were measured on a Varian Infinity-typuls-400 spectrometer equipped with a 4 mm double-resonance MAS probe at a 10 kHz spinning rate. The corresponding measurement conditions and procedures are described in our recent publication [40]. The Brunauer-Emmett-Teller (BET) specific surface area, pore volume, and Barrett-Joyner-Halenda (BJH) pore size distribution of the samples were measured on a Micromeritics ASAP 2400 low-temperature N_2 adsorption apparatus after evacuation of the sample at 150 °C. Thermogravimetric analysis (TGA) of the samples was performed on a NETZSCH-STA 409PC instrument at a 20 °C·min $^{-1}$ heating rate under N_2 flow (10 mL/min).

2.7. Detailed procedures of acid-catalyzed reactions

The etherification of isobutene to methyl *tert*-butyl ether (MTBE) in methanol, the esterification of adipic acid to diisooctyl adipate (DOA) with isooctanol, and the hydrolysis of hydroxypropyl cellulose to reducing sugars (RSs) were employed to evaluate the catalytic performances of the present solid acids. The corresponding procedures are described in the following sections.

2.7.1. Etherification reaction procedure

The liquid-phase etherification reaction for the synthesis of MTBE was carried out in a stainless steel autoclave (YZ-MR-100 ML). In a typical experiment, 2.7 mol methanol and 0.4 g catalyst were added to the autoclave simultaneously. Then, the sealed reactor was pressurized to 1.5 MPa with N_2 and 0.18 mol isobutene was introduced in the pressurized reactor. The reaction mixture was heated to 65 °C and kept at this temperature for 2 h, with vigorous magnetic stirring. After reaction, the mixture was separated by centrifugation and the etherified MTBE product in the filtrate was analyzed on a Shimadzu GC-2010Plus instrument equipped with an SE-54 quartz capillary column (30 m $\times$ 0.32 mm $\times$ 0.25 μm) and a flame ionization detector (FID), using cyclopentanone as an internal standard. The temperatures of both injector and detector were

Table 1

Silica content, acid group density, and porosity parameters of investigated samples.

Sample	SiO ₂ (wt.%)	Acid group density (mmol/g)			Porosity parameters			
		COOH	OH	SO ₃ H	S _{BET} (m ² /g)	S _{t-plot} ^a (m ² /g)	P _V (cm ³ /g)	D (nm)
BC	0.34	0.37	1.62	—	—	—	—	—
BCSA	0.45	0.43	1.86	3.46	—	—	—	—
Amberlyst-15	—	—	—	5.00	42.5	—	0.40	28.8
SIBC-1	30.96	0.14	0.52	—	98 (6 ^b)	92	0.34	13.9
SIBCSA-1	32.11	0.70	0.95	1.57	218	211	0.38	6.5
SIBC-2	35.21	0.28	0.25	—	159 (36 ^b)	123	0.38	9.5
SIBCSA-2	36.06	0.18	0.76	1.19	285 (136 ^b)	149	0.50	4.4

^a *t*-plot external surface areas. ^b The values in brackets indicate the *t*-plot micropore surface areas.

set to 250 °C, while the column temperature was increased from 35 °C (maintained for 4 min) to 100 °C at 50 °C/min and maintained for 3 min at 100 °C. The separated catalyst was thoroughly washed with petroleum ether, dried under vacuum at 60 °C overnight, and then reused in the next recycling run.

2.7.2. Esterification reaction procedure

In a typical procedure, 750 mmol isooctanol, 300 mmol adipic acid, and 0.5% catalyst (defined as mmol SO₃H/mmol adipic acid × 100%) were mixed in a three-necked glass reactor equipped with a water segregator and a condenser under magnetic stirring. The mixture was stirred at 125 °C and a sample was collected every 10 min. After reaction, the catalyst was filtered and the residual adipic acid in the filtrate was measured according to the Chinese standard GB/T1668-2008; the yield of DOA was then calculated based on the consumption of adipic acid. The used catalyst was thoroughly washed with ethanol and distilled water, dried under vacuum at 60 °C overnight, and then reused in the next recycling run. The kinetic experiments illustrated in Fig. S2 were performed under the following conditions: 600 mmol isooctanol, 150 mmol adipic acid, and 0.2% catalyst at 125 °C (or 115 °C), with sample collection every 10 min.

2.7.3. Hydrolysis reaction procedure

All hydroxypropyl cellulose hydrolysis experiments were carried out in a stainless steel microautoclave (YZ-MR-100 ML). The detailed procedure is as follows: first, 0.4 g hydroxypropyl cellulose, 0.2 g catalyst, and 25 mL deionized water were simultaneously added to the autoclave, and the sealed reactor was maintained at 140 °C for 3 h. After the autoclave was cooled down to room temperature, the reaction mixture was centrifuged to separate the solid catalyst. Thereafter, the yield of the liquid RS products was measured by the dinitrosalicylic acid (DNS) method.

To evaluate the activity of the catalysts in the three reactions discussed above, the turnover frequency (TOF) was estimated as the molar amount of converted substrate per mole of effective acid sites (–SO₃H), per unit time (min^{−1} or h^{−1}).

3. Results and discussion

3.1. Characterization

Table 1 shows that the acidity of BCSA originates from its hydroxyl (OH), carboxyl (COOH), and sulfonic acid (SO₃H) groups, whose contents are 1.86, 0.43, and 3.46 mmol/g, respectively. In addition, the material contains 0.45 wt.% silica originating from the raw bamboo material. Compared to BCSA, the acidic group content of the two SIBCSA materials decreases to some extent, owing to the dilution effect of the introduced silica. Notably, the BC, SIBC-1, and SIBC-2 precursors generally have lower silica, COOH, and (especially) OH contents than their corresponding sulfonated materials (BCSA, SIBCSA-1, and SIBCSA-2), indicating that carbonization, carboxylation, and especially hydroxylation of these precursors occur simultaneously during sulfonation by dehydration and oxidation of H₂SO₄. Table 1 also shows that increasing the dehydration temperature of the SIBC precursor from 250 to 350 °C causes the silica content of its sulfonated SIBCSA counterpart to increase from 30.96 wt.% to 35.21 wt.% and the SO₃H density to decrease from 1.57 to 1.19 mmol/g. These changes can be attributed to an increase in the degree of carbonization.

The morphologies of SIBCSA-1 and of some of its precursors were observed by TEM, and the obtained images are shown in Figure 1. The parent BC material (Fig. 1a) exhibits a large block-like shape and a compact layered structure characteristic in its side. In addition, small amounts of nanoparticles (with a diameter of *ca.* 5–8 nm) form loose aggregates on the sample edge, likely implying that the layered BC material is formed through the compact aggregation of these nanoparticles *via*

Fig. 1. TEM morphology of (a) BC, (b) CTMA-BC, (c) SIBC-1, (d) SIBC-2, (e) SIBCSA-1, and (f) Na⁺-exchanged SIBCSA-1 samples.

strong hydrogen bonding (HB) interactions between their surface polar OH and COOH groups [29–31]. The TEM image of CTMA-BC in Fig. 1b shows that the sample is composed of fully dispersed nanoparticles of 10–50 nm size, likely reflecting the highly isolated state of the BC nanosheets exfoliated by CTMA. Such binary composition was treated with the acidic silica sol to yield its ternary counterpart, which further transforms into the SIBC-1 sample after 250 °C dehydration and removal of CTMA. SIBC-1 exhibits disordered and loose aggregates of particles of about 12 nm size (Fig. 1c); these particles do not show significant difference in chromatic aberration, indicating that the majority of the CNS and silica components have been uniformly dispersed into each other. In sharp contrast, the control sample SIBC-2 obtained upon 350 °C dehydration displays a very similar layered structure to the parent BC material (Fig. 1d), suggesting that the high dehydration temperature likely drives the silica-isolated CNSs to reunite. After SIBC-1 is eventually converted to its sulfonated counterpart (SIBCSA-1) using H₂SO₄, the original loose aggregates turn into layered ones (Fig. 1e), probably induced by the strong hydrogen bond interactions among the introduced sulfonic groups. This conclusion is supported by the observation that when the sulfonic protons of SIBCSA-1 are exchanged with an NaCl solution under ultrasonication, the obtained SO₃Na-exchanged sample (Fig. 1f) fully recovers its nanoparticle aggregate structure, similar to that of SIBC-1. In contrast, the layered morphology of BCSA hardly changes after being converted into the SO₃Na-exchanged sample (see Figs. S3a and S3b), indicating that, unlike SIBCSA-1, BCSA does not exhibit strong hydrogen bond interactions among the SO₃H groups.

The combination of STEM and EDS techniques is a powerful tool for determining the composition and distribution of elements at the micro-interface of materials on a near-nanometer scale [41,42], and is thus applied to study the present solid acids. Figures 2a–2c display overlaid elemental mappings of BCSA, SIBCSA-1, and SIBCSA-2 (the individual element mappings, corresponding HAADF-STEM images, and EDS spectra are also shown in Fig. 2). The C, S, and O atoms exhibit a fairly uniform distribution in the overlaid elemental mapping of BCSA (Fig. 2a), reflecting the homogeneous distribution of the COOH, OH, and SO₃H groups. The content of SO₃H groups in BCSA, calculated from the EDS composition analysis (Fig. 2d), is *ca.* 1.36 mmol/g, which accounts for only 39% of the amount measured by chemical analysis (3.46 mmol/g). This indicates that the SO₃H groups of BCSA have a low degree of exposure, due to their incorporation in the dense layers of BCSA. The distributions of C and Si atoms are fairly uniform in most areas of the overlaid elemental mapping of SIBCSA-1, but significantly inhomogeneous in the bottom (marked as 1) and especially left (marked as 2) regions of Fig. 2b, which present carbon enrichment and silicon depletion. This indicates that SIBCSA-1 has at least two kinds of sulfonated carbon nanosheets found in either high or low silica-isolated states, with the high isolated state being clearly predominant. Based on EDS elemental analysis, the content of surface SO₃H groups is estimated to be 1.15 mmol/g (Fig. 2e), which accounts for *ca.* 73% of the total amount of SO₃H groups (1.57 mmol/g) measured by chemical

analysis. This suggests that silica isolation can significantly improve the exposure of the SO₃H groups. Notably, the distributions of C and Si atoms are fairly inhomogeneous in most areas of the overlaid elemental mapping of SIBCSA-2, denoting carbon enrichment and silicon depletion features (Fig. 2c) that correspond to the high carbon (53.7%) and low Si (15.9%) contents observed in the EDS analysis (Fig. 2f). Moreover, the content of surface SO₃H groups calculated from the EDS elemental analysis is 1.88 mmol/g, which is significantly higher than the actual content (1.19 mmol/g) measured by chemical analysis. This indicates that thermal migration of the isolated CNSs to the silica surface can take place easily under deep dehydration conditions.

The thermal decomposition behavior of the three solid acids was investigated by the TGA technique, and the differential thermogravimetry (DTG) curves are shown in Fig. 3a (the corresponding TGA curves are shown in Fig. S4). The DTG curve of BCSA displays two main weight loss peaks in the 50–350 °C range. The first peak at 134 °C (9.4% weight loss in the DTG curve) can be assigned to evaporation of the adsorbed water molecules located between the inner layers of BCSA. Another strong peak at 258 °C (23.7% weight loss) can be attributed to the decomposition process of SO₃H groups [19]. The two SIBCSA materials exhibit similar TGA/DTG thermal decomposition behaviors to those described above; however, the weight loss peak corresponding to adsorbed water is weaker and shifted to low temperatures in SIBCSA-1 (7.72% weight loss at 122 °C) and especially SIBCSA-2 (4.94% weight loss at 106 °C), indicating that the water adsorption capacity of these two materials is reduced, likely due to the low density of sulfonic acid groups. In addition, the deep dehydration process contributes to decrease the hydrophilicity of SIBCSA-2. Another weight loss peak corresponding to the SO₃H groups in the DTG curve of SIBCSA-1 also becomes weaker and broader (with a weight loss of *ca.* 13.11%), and is shifted by 24 °C toward high temperatures. On the other hand, this peak appears at 254 °C with *ca.* 11.69% weight loss for SIBCSA-2, corresponding to a slight shift toward low temperatures compared to that of BCSA. In generally, the thermal stability and acidity of sulfonated materials can be improved by increasing the density and spatial proximity of their SO₃H groups [29–31], and in particular by introducing halogen substituents on the polyaromatic ring [43–46]. This is mainly because the C-S bonds can be strengthened by increasing the delocalization of the negative charges of the sulfonate group toward the aromatic ring *via* the HB interactions of the SO₃H groups [29–31] and the electron-withdrawing effect of the halogen substituent [43–46]. The enhanced thermal stability of SIBCSA-1 suggests the existence of strong HB interactions between its SO₃H groups, probably created by the migration and rearrangement of its high silica-isolated CNSs with a loose stacking particle structure during sulfonation. However, BCSA and SIBCSA-2 lack these strong HB interactions between their SO₃H groups, because both the BC and SIBC-2 precursors possess a densely layered structure that hinders the migration and rearrangement of their CNSs during sulfonation, in agreement with the above TEM results.

The porosity largely determines the activity of a heterogeneous catalyst. The porosity of SIBCSA-1 and SIBCSA-2, as well as that of the SIBC-1 and SIBC-2 precursors, was measured by low-temperature N_2 adsorption-desorption experiments. Compared to the nonporous nature of BCSA [47], the N_2 adsorption-desorption isotherms in Fig. 3b show that SIBCSA-1 presents typical type-IV isotherms with a hysteresis loop in the P/P_0 range of 0.6–0.95, indicating characteristic interlayer

slit-like pores [48]. The BJH pore distribution curve of SIBCSA-1 displayed in the inset of Fig. 3b shows a bimodal pore distribution, with most of the mesopores located in the 2–15 nm range and a certain amount of large pores with diameter greater than 100 nm. Similar to SIBCSA-1, SIBCSA-2 also shows type-IV isotherms with a hysteresis loop in the P/P_0 range of 0.5–0.9 (Fig. 3c); however, its bimodal BJH pore distribution is much less defined than that of SIBCSA-1. This indicates that mesopores

Fig. 2. Characterization of the catalysts. Overlaid elemental mappings of (a) BCSA, (b) SIBCSA-1, and (c) SIBCSA-2. EDS analysis of (d) BCSA, (e) SIBCSA-1, and (f) SIBCSA-2. Individual elemental mappings of (g) C, (h) Si, and (i) O, along with (j) the corresponding STEM-HAADF image of BCSA. Individual elemental mappings of (k) C, (l) Si, and (m) O, along with (n) the corresponding STEM-HAADF image of SIBCSA-1. Individual elemental mappings of (o) C, (p) Si, and (q) O, along with (r) the corresponding STEM-HAADF image of SIBCSA-2.

Fig. 3. (a) DTG curves of BCSA, SIBCSA-1, and SIBCSA-2. Adsorption-desorption isotherms and BJH pore distribution of SIBCSA-1 (b) and SIBCSA-2 (c) (d) ^{31}P , (e) ^{13}C , and (f) ^{29}Si solid-state MAS NMR spectra of BCSA, SIBCSA-1, and SIBCSA-2.

are present in significantly lower amounts than macropores in the SIBCSA-2 structure, which also contains an appreciable amount of micropores smaller than 2 nm (see the BJH curve in the inset of Fig. 3c). Figure S5 shows that SIBC-1 and SIBC-2 exhibit similar N_2 adsorption-desorption isotherms and BJH pore distributions to the sulfonated samples. Table 1 shows that the BET and t-plot external surface areas (S_{BET} and $S_{\text{t-plot}}$, m^2/g), average pore size (D , nm), and porous volume (V_p , cm^3/g) of SIBC-1 are 98, 92, 13.9, and 0.34, respectively. Compared to SIBC-1, the S_{BET} , $S_{\text{t-plot}}$, and V_p values of SIBC-2 increase to some extent, but its D value markedly decreases to 9.5 nm, along with an increase in its microporous surface area (36 m^2/g). These results indicate that increasing the dehydration temperature promotes the formation of the dense stacking pores and the partial cross-linking pores of the silica-isolated CNS nanoparticles, in agreement with the above TEM results. After sulfonation of the two precursors, their porosity is significantly improved, leading to marked increases in the V_p and especially S_{BET} values, accompanied by a significant decrease in the D values, indicating that the sulfonation process can trigger aggregation of the silica-isolated CNS particles to generate more abundant and smaller slit-like interlayer pores. Notably, SIBCSA-1 exhibits a clearly superior pore distribution compared to that of its precursor, and is entirely composed of slit-like pores with a high external surface area of 211 m^2/g , suggesting that the creation of interlayer slit-like pores is mainly driven by the strong hydrogen bonding interactions between the introduced sulfonic acid groups. On the other hand, SIBCSA-2 possesses a much larger microporous surface area of 135 m^2/g , which accounts for almost half of the total BET surface area of 285 m^2/g . This indicates that the cross-linking between the CNSs that migrate to silica surface

can be significantly accelerated under the action of H_2SO_4 , thus forming abundant micropores, which are the main contributors to the significantly enhanced porosity of SIBCSA-2.

TMPO-adsorbed ^{31}P MAS NMR spectroscopy was used to evaluate the acidity of the three solid acids. As shown in Fig. 3d, BCSA only exhibits one ^{31}P NMR peak at 83.0 ppm attributed to the SO_3H groups [49], and no ^{31}P NMR signal for the weak acidic groups appears in its spectrum. This may imply that these weak acidic groups are not accessible to the probing TMPO molecules, owing to an obstruction of their extended HB network. In contrast, SIBCSA-1 and SIBCSA-2 clearly display the ^{31}P NMR peak corresponding to the weak acid sites at 54.4 and 50.9 ppm, which are shifted by about 6 and 2 ppm, respectively, to low field compared to the peak position reported in literature [40]. This indicates that the accessibility and strength of the weak acid sites of SIBCSA-2 and especially SIBCSA-1 are improved, likely due to the breakage of the hydrogen bonding network upon silica isolation. In addition, SIBCSA-1 displays two ^{31}P NMR peaks in the 80–91 ppm range, indicating the presence of two types of SO_3H groups with different acidities. According to its peak area, the peak at 83.0 ppm (similar to that of BCSA) accounts for about 42.5% of the total sulfonic acid content, which likely corresponds to the carbon-rich and silicon-depleted region in Fig. 2b. The other peak at 90.4 ppm is clearly shifted to low field, indicating the presence of superacid sites stronger than 100% sulfuric acid [50] in SIBCSA-1. The corresponding peak area accounts for *ca.* 57.5% of the total peak area of the SO_3H groups, which approximately matches the region with uniform silicon and carbon distribution in Fig. 2b. In contrast, SIBCSA-2 only exhibits a ^{31}P NMR peak at 79.1 ppm attributable to the SO_3H groups, which corresponds to the carbon-rich and silicon-depleted features of its elemental map-

ping, indicating that this material has acidity similar to that of BCSA. These findings further confirm that only those SCNSs completely isolated by silica can exhibit superacidity through the strong HB interactions developed *via* the SO₃H groups, in line with the above TEM and TGA results. The solid-state ¹³C and ²⁹Si MAS NMR spectra provide insight into the surface species of BCSA, SIBCSA-1, and SIBCSA-2. As shown in Figure 3e, the ¹³C MAS NMR spectrum of BCSA exhibits two intense and broad signals at 126 and 117 ppm attributed to polycyclic aromatic carbons [17,51]; this is different from the spectra of highly cross-linked BCSA materials [17,51], which display only one symmetric peak at 130 ppm. In addition, the two broad signals at *ca.* 154 and 195 ppm may be assigned to phenolic OH and COOH groups, respectively. The signals of the OH and especially COOH groups are split, implying that BCSA contains two kinds of polycyclic aromatic carbons with a different cross-linking degree or arrangement type, which leads to different environments surrounding its OH and especially COOH groups. In sharp contrast, the ¹³C peak of the SO₃H groups at 143 ppm [31] is hardly noticeable for the parent BCSA, in agreement with previous reports [17,51]. No clear ¹³C NMR signals for the sp³ carbons at 0–40 ppm are observed in Fig. 3e, indicating that most of the sp³ carbons in the cellulose molecules of the bamboo material have been converted to the corresponding aromatic sp² carbons after the hydrothermal carbonization treatment. The above-mentioned signals are not split in the ¹³C NMR spectra of the two SIBCSA materials, but the signal of their polycyclic aromatic carbons shows a slight shift to low field (curves 2 and 3 in Fig. 3e), indicating that the silica-induced isolation results in the polycyclic aromatic carbons having uniform structure and chemical environment. In the solid-state ²⁹Si MAS NMR spectra of the two SIBCSA materials (Fig. 3f), the two peaks at around 104 (Q₃) and 114 (Q₄) ppm can be assigned to surface silanol groups, i.e., [(SiO)₃Si-OH] and [(SiO)₄Si] units, respectively [52,53].

The results of the above characterizations strongly suggest that SIBCSA-1, as a cheap solid acid, possesses high thermal stability and highly exposed superacid sites, as well as abundant mesoporous/macroporous channels with excellent mass transfer rate. Therefore, this novel acidic material is expected to show excellent performance in acid-catalyzed reactions. Three important typical acid-catalyzed reactions were then carried out to test the catalytic performance of SIBCSA-1, which was compared to those of the parent BCSA, control SIBCSA-2, and commercial Amberlyst-15 samples.

3.2. Acid catalysis reactions

The etherification of isobutylene with methanol is an important acid-catalyzed reaction used to produce the common gasoline additive MTBE. Table 2 shows a comparison of the data obtained for this reaction using the present solid acid catalysts in a batch reactor. SIBCSA-1 exhibits the highest activity among the four solid catalysts, giving an 88.7% MTBE yield after reacting at 65 °C for 2 h, along with a TOF up to 127 h⁻¹, which is more than two times higher than those obtained with the two reference catalysts Amberlyst-15 and BCSA. However, the SIBCSA-2 sample only gives a MTBE yield of *ca.* 14.0% under the same conditions, owing to the severe self-polymerization of isobutylene in its micropores. Figure 4a shows the results obtained for the above reaction using SIBCSA-1 and the two reference catalysts under different reaction temperatures. The superior activity of SIBCSA-1 is further enhanced when the reaction temperature is reduced to 55 and especially 45 °C. For example, its TOF can still reach 87 h⁻¹ at 45 °C, which is three and seven times higher than the corresponding values of BCSA and Amberlyst-15, respectively. This fully supports the suggestion that the superacidity of SIBCSA-1 can lead to an excellent low-temperature activity [54]. Figure 4b further shows that SIBCSA-1 can achieve a MTBE yield above 84% after being reused four times, and no dissolution of its SCNSs into the reaction solution occurs during the recycling runs (Fig. S6a). In sharp contrast, leaching of the catalyst in the reaction solution is observed in the recycling runs of Amberlyst-15 and especially BCSA, with a resulting obvious decrease in the MTBE yield of these two catalysts.

The hydrolysis of cellulose is another acid-catalyzed key reaction for the production of biomass-derived chemicals. The hydrolysis of hydroxypropyl cellulose in water was performed to test the catalytic performance of the present solid acids. As shown in Table 2, all four solid acids exhibit significant activities in this reaction, yielding reducing sugars (52%–82% yield) as the main products, along with a small amount of 5-hydroxymethylfurfural (HMF, 0.2%–3.7% yield). SIBCSA-1 exhibits a high catalytic activity, providing the highest (82.4%) RSs yield among the solid acids. Moreover, its TOF increases to 6.56 h⁻¹, which is 2- and 4-fold higher than the TOFs obtained using BCSA and Amberlyst-15, respectively. Notably, SIBCSA-2 shows a slightly higher TOF (6.7 h⁻¹) than SIBCSA-1 in this hydrolysis, which may due to its high proportion of macropores that facilitate the diffusion of the soluble macromolecular sub-

Table 2

Reaction data for the etherification of isobutylene with methanol and hydrolysis of hydroxypropyl cellulose over the three investigated sulfonic acid solids ^a.

Catalyst	SO ₃ H/ (mmol·g ⁻¹)	Etherification		Hydrolysis ^b			Esterification ^c	
		MTBE yield/%	TOF/h ⁻¹	RSs/%	HMF/%	TOF/h ⁻¹	DOA yield/%	TOF/h ⁻¹
SIBCSA-1	1.57	88.7	127.1	82.4	3.71	6.52	92.2	184.4
SIBCSA-2	1.19	14.0	26.5	63.9	1.46	6.70	79.9	159.8
BCSA	3.46	62.1	40.4	58.5	2.49	2.13	76.2	152.4
Amberlyst-15	5.01	76.0	34.1	52.4	0.16	1.31	65.7	131.4

^a Turnover frequency (TOF) was calculated based on the yield of products (mmol)/(catalyst amount × its SO₃H density (mmol) × time (h)); ^b RSs and HMF indicated reducing sugars and 5-hydroxy-methylfurfural; ^c 0.5% catalyst (defined as (SO₃H amount (mmol)/adipic acid amount (mmol)) × 100%) at 125 °C for 1 h.

Fig. 4. Catalytic performance of the three solid acids. (a) Temperature dependence of MTBE yield (the corresponding TOF values are indicated above each bar) from etherification. (b) Repeatability of catalysts in esterification reaction. (c) Time-dependence of DOA yield from esterification. (d) Repeatability of catalysts in etherification reaction.

strate toward its strong acid sites. Moreover, the two SIBCSA catalysts show a good structural stability and their sulfonated SCNs are hardly dissolved into the water medium even at a reaction temperature of 140 °C (Fig. S6b). On the contrary, Amberlyst-15 and especially BCSA are unstable under these hydrothermal reaction conditions, and exfoliation and dissolution of both structural units in water can occur, resulting in the two corresponding hydrolysis solutions showing an orange-yellow and orange color, respectively (Fig. S6b). Esterification of adipic acid with isooctanol can produce DOA, a good cold-resistant plasticizer that has been largely used in industry. As shown in Table 2, SIBCSA-1 exhibits an excellent activity, affording the highest TOF of 184.4 h⁻¹ after 1 h. Figure 4c further shows that SIBCSA-1 exhibits a high catalytic rate in the early stages of esterification, and its DOA yield at 1 h increases up to 92.2%, which is approximately equivalent to the yields obtained for the two reference catalysts at 2 h. Fitting an irreversible second-order power model [55] to the esterification curves obtained using a low catalyst dosage (0.2%) in Fig. S2 and Table S2 reveals that SIBCSA-1 has a higher apparent rate constant (0.0442 L·mol⁻¹·min⁻¹) than BCSA (0.0376 L·mol⁻¹·min⁻¹) and especially Amberlyst-15 (0.0074 L·mol⁻¹·min⁻¹). The estimated apparent activation energy for the SIBCSA-1-catalyzed reaction at 125 and 115 °C is 85 kJ/mol, which is slightly lower than that (95 kJ·mol⁻¹) previously reported for the heteropoly acid-catalyzed homogeneous reaction [56]. Figure 4d further shows that SIBCSA-1 has superior repeatability compared to those of the two reference catalysts. The reaction catalyzed by the SIBCSA-1 catalyst after four re-

uses still produces a colorless DOA liquid with excellent yield (above 97%). In contrast, after being reused four times, BCSA and Amberlyst-15 show a DOA yield loss of 7.1% and 9.8%, respectively, and the color of the DOA liquid shown in Fig. S6c is light yellow (Amberlyst-15) or orange (BCSA).

In addition, the comparison of the data in Table S3 shows that SIBCSA-1 has a much higher activity than 98% H₂SO₄ in the three conversion reactions discussed above. The superior catalytic activity of SIBCSA-1 in these reactions is likely due to its abundant hierarchical pores, high external surface area, and highly exposed superacid sites, which accelerate the diffusion and conversion of reactants on its strong acid sites. Equally importantly, silica isolation imparts excellent structural stability to SIBCSA-1 via its chemical and hydrogen bonding interactions with the SCNs: the FT-IR spectrum of SIBCSA-1 in Fig. S7 confirms the presence of such chemical bond interactions. In contrast, the two reference catalysts are deactivated to varying degrees in the recycling runs, due to their unstable structures. Notably, the data in Tables S4–S6 show that the SO₃H groups of SIBCSA-1 are not easily lost in the three conversions compared to those in the reference catalysts, due again to the strong hydrogen bonding interactions. In addition, the TGA results of the recovered catalysts after etherification (Figs. S8–S10 and Tables S4–S6) show that SIBCSA-1 exhibits outstanding advantages in reducing the deposition of isobutylene polymers (ca. 3 wt.%) on its acid sites compared to those of Amberlyst-15 (as high as ca. 25 wt.%). This is likely due to its hydrophilicity, and in particular to the unique role played by the adsorbed water on its surface in limiting the self-polymerization

Fig. 5. Proposed formation process of hydrogen bond networks for the non-exfoliated (a) and exfoliated (b) BC nanosheets before and after sulfonation.

of isobutylene [57].

3.3. Fabrication mechanism of biochar-based superacid

The results of the above characterizations indicate that the non-exfoliated CNSs of the BC material spontaneously rearrange into a layered structure, mainly induced by the HB interactions among their weak acidic groups. These stable CNSs are unlikely to rearrange during their sulfonation, due to the restricting effect of their super hydrogen bonding networks (SHBNs). Therefore, the non-exfoliated SCNNs of BCSA hardly show superacidity, owing to the lack of strong hydrogen bonding interactions among their SO_3H groups (Figure 5a). In contrast, the exfoliated CNSs of SIBC-1 may become partially mobile (owing to the breakage of their SHBNs) and undergo a specific rearrangement in the confined space of the silica surface hydroxyls during sulfonation (Fig. 5b). Such rearrangement, whose details are still unclear at present, is likely to induce the SO_3H groups of SIBCSA-1 to reconstruct the strong local hydrogen bonding network (LHBN) confined by the surface hydroxyls of silica by increasing their spatial proximity [30,45], thus leading to the generation of superacid sites over SIBCSA-1. It should be noted that if the highly isolated state of the CNSs is lost upon their re-aggregation under deep hydration at 350°C , the above SO_3H -dominated rearrangement will hardly occur, owing to their substantial cross-linking upon sulfonation. As a result, SIBCSA-2 (like BCSA) is not able to develop a LHBN among its SO_3H groups, thus losing its superacidity.

4. Conclusions

A biomass carbon-derived solid superacid suitable for diverse acid-catalyzed reactions has been successfully fabricated by a silica isolation method. The catalyst exhibits the following advantages: 1) in addition to requiring very cheap and readily available raw materials, its fabrication involves simple and practical procedures, which are easy to implement in potential large-scale applications; 2) the catalyst overcomes the intrinsic drawbacks of biochar-derived solid sulfonic acids, as a result of its structural and chemical stabilities under hydrothermal or solvothermal reaction conditions; 3) its acidity is stronger than that of 100% H_2SO_4 ; more importantly, its abundant meso- and macroporous channels, high external surface area, and highly exposed superacid sites enable its extensive application to the acid catalysis of substrates with different polarities and molecular sizes. The favorable properties of the present renewable solid superacid are expected to prompt further applications in other biorefinery and industrially important reactions.

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Graphical Abstract

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Fabrication of a solid superacid with temperature-regulated silica-isolated biochar nanosheets

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A newly fabricated silica-isolated biochar sulfonic acid exhibits abundant hierarchical pores along with stable and fully exposed superacid sites, thus showing significant advantages in acid catalysis reactions compared to those of common BCSA and commercial Amberlyst-15 catalysts.

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温度调控二氧化硅隔离生物质碳纳米片构建固体超强酸

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摘要: 随着现代化学工业的发展, 能源短缺和环境污染成为当下所面临的两大严峻问题. 酸催化是化学工业中生产各种燃料和化学品的关键转化技术之一, 发展基于固体酸的高效、环境友好催化转化技术在当代绿色化工领域中占有十分重要的地位. 其中基于资源丰富和可再生的生物质衍生的固体碳磺酸(BCSAs)因其价廉易得、在一些重要的酸催化反应中显示出比商业化磺酸树脂更优的性能而成为当前催化研究领域的热点之一. 然而, 传统的BCSAs存在不稳定的致密层状结构及相对低的酸强度、酸位可接近性和传质效率等天然缺陷, 制约了这类价廉易得的固体酸在工业上的广泛应用. 本论文以综合解决BCSAs的这些缺陷为目标, 开展其结构重组工程(SRE)策略研究. 该SRE策略使用廉价的竹粉和水玻璃为主要原料, 竹粉首先通过水热催化炭化法转化为层状生物质碳(BC), 然后将BC材料先后用十六烷基三甲基溴化铵化学剥离、酸性硅溶胶插入、再脱水转化为二氧化硅隔离的碳纳米片, 最后用浓硫酸磺化生成硅胶隔离的生物质碳磺酸.

TEM、STEM-EDS、BET、TGA和TMPO吸附³¹P MAS NMR表征结果表明, 改变脱水温度可以调控硅胶隔离碳纳米片与其纳米粒子堆积状态, 在250 °C脱水条件下获得了具有松散颗粒堆积结构的二氧化硅高度隔离且非交联的碳纳米片, 经磺化引入的磺酸基具有明显增强的热稳定性(其热分解温度比BCSA的高出23 °C)和强于100%硫酸的超强酸性(90.4 ppm³¹P化学位移), 并构建了丰富的分级狭缝孔(外表面积达211 m²/g, 呈双孔分布), 其驱动力主要来源于引入的磺酸基之间的强氢键相互作用. 将构建的生物质固体超强酸应用于典型的酸催化己二酸与异辛醇酯化、异丁烯与甲醇醚化和羟丙基纤维素水解反应中, 与普通生物质碳磺酸和商用Amberlyst-15相比, 其催化活性和稳定性(重复使用性)具有突出优势. 这归因于生物质固体超强酸具有优异的结构稳定性、高度暴露的超强酸性位以及丰富的介孔-大孔双通道. 本文不仅为构建生物碳基固体超强酸提供了一种新的结构重组策略, 而且克服了普通生物质碳磺酸在应用中存在结构稳定性差、酸强度和孔隙率不理想的缺陷.

关键词: 生物质转化; 生物质碳磺酸; 二氧化硅隔离; 固体超强酸; 酸催化

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