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One-step preparation of carbon-based solid acid catalyst from water hyacinth leaves for esterification of oleic acid and dehydration of xylose

Jutitorn Laohapornchaiphan,[a] Christopher B. Smith,*[b] and Siwaporn Meejoo Smith*[c]

Abstract: Carbon-based solid acid catalysts were successfully obtained *via* one step hydrothermal carbonization (HTC) of water hyacinth (WH) in the presence of *p*-toluenesulfonic acid (PTSA). Increasing HTC temperatures from 180 to 240°C resulted in carbonaceous materials with increased sulfur content, and less adsorbed water. Material obtained at 220°C (WH-PTSA-220) contains the highest amount of acid sites, and promotes the highest initial rate of two transformations, methanolysis of oleic acid, and dehydration of xylose to furfural. While all PSTA treated WH catalysts gave comparable fatty acid conversions (~97%) and furfural yields (~60%) after prolonged reaction times, the WH-PTSA-240 system bearing a relatively low acid density maintains the most favorable reusability profile. Higher HTC temperatures (220-240°C) improved catalyst reusability profiles due to graphitization and hydrophobicity of the carbon surface. The catalyst systems derived herein from biomass may have potential applications in biorefining platforms, utilizing the conversion of waste biomass to chemicals.

Introduction

The shift from petroleum (*e.g.* crude oil and natural gas) to sustainably produced liquid fuels and fine chemicals from renewable carbon resources (*i.e.* biomass) requires new conversion technologies. In the case of biorefining, these technologies should be environmentally benign, and if possible utilize feedstock components to enhance sustainability metrics. Plant derived biomass typically requires depolymerization of cellulosic/lignocellulosic components into sugar monomers (*e.g.* glucose and xylose) which can be fermented to produce bio-alcohols, or catalytically converted into various carbon-based fuels and chemicals through intermediates (*e.g.* furfural, 5-hydroxymethylfurfural (HMF), and levulinic acid) by acid-catalyzed dehydration.[1] Acid catalyst systems are also important for the production of oleochemicals from free fatty acids (FFAs), including the esterification of FFA in low-quality triglyceride feedstocks (*e.g.* waste cooking oils) for biodiesel production prior to transesterification.[2]

Although liquid mineral acids (*e.g.* HCl, H_2SO_4, and H_3PO_4) are cheap and often effective for catalyzing the above processes, storage, use and transportation of these reagents is a concern due to their corrosive nature. Recovery, and re-use from homogeneous systems is difficult, and safe disposal is also a major concern impacting the environmental footprint of chemical industries. These factors give credence to the use of solid, easily separable and re-usable heterogeneous acids for the sustainable production of biofuels and chemicals.[3]

Carbon is an attractive support material for solid acid catalyst systems due to its stability, availability, and ease of functionalization.[4] Its derivation from biomass such as forest residues, weeds, and agricultural waste, allows for the catalyst preparation step to be integrated into biorefinery systems. As an example, carbon bearing strong Brønsted acid ($–SO_3H$) sites can be prepared in two steps through substrate (sugars, starch, cellulose, or lignocellulosic biomass) carbonization followed by sulfonation.[5] Solid acid catalysts prepared by this method exhibit high catalytic performance and good stability in cellulose hydrolysis,[6] dehydration of pentoses or hexoses,[7] and esterification of FFAs.[8] However, the high-temperature (≥400°C) thermal treatment required is energy intensive, with sulfonation requiring very corrosive reagents and generating a noxious waste stream.

Carbon-based solid acid materials have been prepared by one step hydrothermal carbonization (HTC) of aqueous furfural (2-furaldehyde) with hydroxyethylsulfonic acid[9] or *p*-toluenesulfonic acid (PTSA),[10] using polyvinyl alcohol as a carbon substrate,[11] or autoclaving a mixture of glucose and PTSA.[12] The former show comparable catalytic activity in esterification reactions to those of sulfuric acid, Amberlyst-15 resin and H-Y zeolite, with the glucose/PTSA system being more hydrophobic and promoting chemoselectivity towards dimethyl succinate formation from succinic acid. Moreover, this carbon-based solid acid catalyst also exhibits good performance and reusability in fructose dehydration to the platform chemical 5-hydroxymethylfurfural (5-HMF).

While the above systems allow for facile and environmentally benign preparations of SO_3H-functionalized carbonaceous materials, there are only limited reports of one-step acid catalyst preparations from cellulose or lignocellulosic biomass. Several

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previous studies have obtained bio-based catalysts from multi-step processes, involving acid or base treatment of cellulosic raw materials followed by sulfonation, although the use of multiple steps is not advantageous from an environmental standpoint.[8g, 13] In this study, water hyacinth (WH, *Eichhornia crassipes*), an invasive rapidly proliferating weed,[14] was chosen as a biomass carbon substrate due to its abundance. Biomass-derived solid acids were obtained in one step, using HTC at different temperatures (180-240°C) with PTSA. The influence of HTC temperature on physical/chemical properties, reusability profiles, and catalytic activity of these materials towards two conversions: oleic acid esterification, and dehydration of xylose to furfural (Figure 1), was subsequently examined.

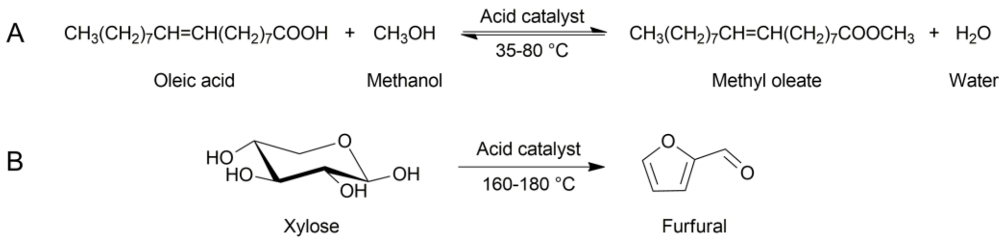

Figure 1. Acid-catalyzed reactions used to investigate the catalytic activities of the prepared carbon-based solid acids: (A) esterification of oleic acid and (B) dehydration of xylose into furfural.

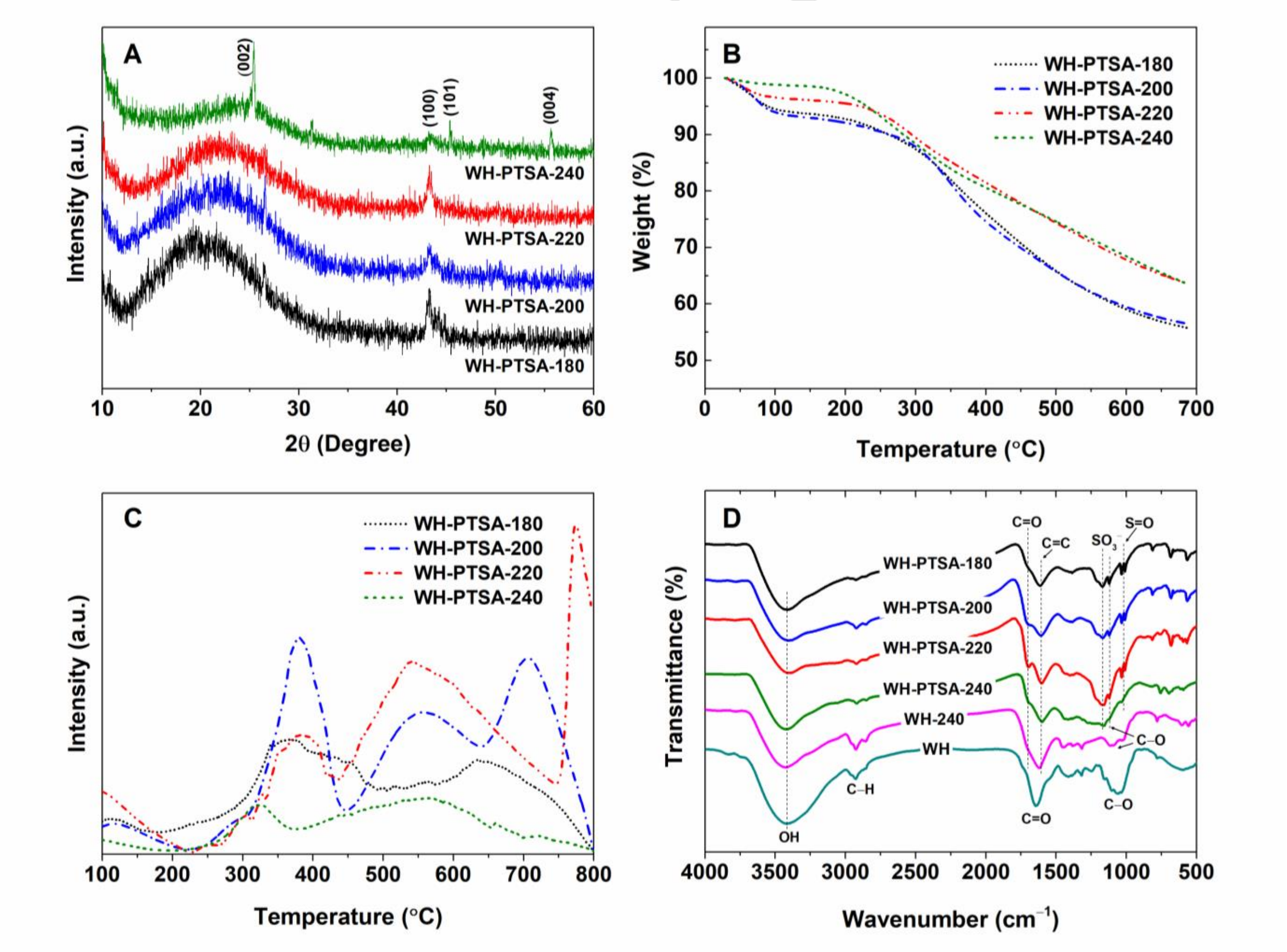

Figure 2. (A) Powder XRD patterns, (B) TGA curves, (C) NH_3-TPD spectra, and (D) FT-IR spectra of carbon-based solid acids prepared at different HTC temperatures.

Results and Discussion

Properties of carbonaceous materials

Chemical and thermal properties. PXRD data indicate that WH-PTSA materials consist of amorphous carbon comprised of disordered graphitic carbon sheets, as indicated by the broad and weak diffraction peaks at 2θ~10-30° and 40-50° (Figure 2A), which correspond to the diffraction of C(002), C(100), and C(101) planes in graphitic carbon.[15] Increases in HTC temperature from 180°C to 220°C result in marginal shifting of the broad C(002) peak center to a higher angle, a consequence of greater degree of carbonization and structural rigidity.[8g] Further temperature increases (240°C) result in C(002) peak sharpening and additional shifting to higher angle, although some broadening related to an amorphous or turbostratic carbon framework is still evident.[16] Diffraction peaks due to C(101) and C(004) are more noticeable at this temperature, consistent with graphitization of the carbon framework.[15b, 17]

Carbon-based materials prepared by one-step HTC of WH in the presence of PTSA possess different morphologies, depending on preparation temperature (see Supporting Information). Materials prepared at 180 and 200°C (WH-PTSA-180 and WH-PTSA-200, respectively) appear as microscale (~200 µm) structures having flat surfaces interspersed with cracks and large cavities. Higher preparation temperatures (220 and 240°C) result in smaller particles, with WH-PTSA-220 exhibiting a range of size distributions (~5-50 µm) and shapes. Samples prepared at 240°C (WH-PTSA-240) exist as tightly packed aggregates of small irregular shard-like (~1-40 µm) particles, although the formation of carbon spheres (~0.2-10 µm diameter) is now clearly noticeable, a feature seen previously in products derived from corncob HTC.[8g]. The formation mechanism of WH-carbon based catalysts can be explained based on that proposed for conversion of starch to acidic carbon based materials.[9, 18] During hydrothermal treatment, cellulose degradation takes place through hydrolysis followed by carbonization (aromatization) processes, producing hydrochar. Including PTSA in the treatment creates defect sites on the treated biomass resulting in surface functionalized hydrochar (acidic carbon based material). At higher HTC temperatures, cellulose breakdown occurs more effectively, resulting in the formation of tightly packed aggregates of small irregular shard-like particles, and carbon spheres. All samples exhibit similar, low BET surface areas and micro/mesoporous structure (Supporting Information), as determined by N_2 desorption/adsorption isotherms.

Solid acid materials prepared at various HTC temperatures show variations in elemental composition, water content, and acid properties. As shown in Table 1, sulfur content is greatly enhanced at higher preparation temperatures (220°C, 240°C), at the expense of carbon, hydrogen and oxygen. Decreases in H/C molar ratio as the temperature is increased may be attributed to the formation of cross-links between polycyclic aromatic carbon sheets.[19] Both H/C and O/C ratios for WH-PTSA-240 are significantly lower than those of materials prepared at lower temperatures; these data are consistent with XRD results indicating greater levels of carbonization at this temperature.

Thermogravimetric analysis (Figure 2B) indicates that higher preparation temperatures results in material having lower overall water content. Weight loss due to removal of water (between 30-200°C, Table 1)[8a] is most pronounced in WH-PTSA-180 and WH-PTSA-200 (approximately 6 wt. %), while markedly lower for higher preparation temperatures (WH-PTSA-240, ~1 wt.%). The TGA results indicating low water content in WH-PTSA materials derived at high HTC temperatures is consistent with XRD results indicating carbon framework graphitization, resulting in a more hydrophobic character. In these systems, further assessments of the hydrophobicity is not possible through the use of contact angle measurements, as these materials are utilized in powder form to ensure efficient sorption and chemical processes at the catalyst surface. Pelletization, as is required for contact angle measurements, may give erroneous results as the measured values may not be representative of the powdered material. Indeed, recent reports[20] provide strong evidence that contact angle values are highly dependent on compression pressure.

Acid properties of WH-PTSA materials. Increases in sulfur content with HTC temperature for WH-PTSA materials do not correlate with total acid density, as shown by titration results in Table 1. WH-PTSA-220, while having markedly higher S content than material prepared at lower temperatures, shows negligible difference in acid density in comparison to these materials. In contrast, WH-PTSA-240, with highest S content, has significantly lower numbers of acid sites suggesting that some sulfur containing groups are not responsible for acid behavior. It is likely in WH-PTSA-220 that titrable oxygen-containing functionalities (*e.g.* carboxylic, phenolic groups), abundant in biomass, also contribute to the total acidity of these materials.[21]

Table 1. Elemental compositions (carbon, hydrogen, sulfur, and oxygen), water content, and total acid density of carbonaceous materials prepared at different temperatures.

Sample	C[a] (wt.%)	H[a] (wt.%)	S[a] (wt.%)	O[b] (wt.%)	H/C molar ratio	O/C molar ratio	Water[c] (wt.%)	Total acid density[d] (mmol g^{-1})	O$_{1s}$[e] (atomic%)	S$_{2p}$[e] (atomic%)
WH-240	60.02	5.45	0.74	29.87	1.09	0.37	0.95	1.5±0.1	n.d.	n.d.
WH-PTSA-180	60.52	4.65	4.70	28.40	0.92	0.35	6.26	3.1±0.5	15.86	1.16
WH-PTSA-200	58.81	4.01	4.52	30.55	0.82	0.39	6.97	3.1±0.5	14.31	1.91
WH-PTSA-220	52.51	3.25	16.07	26.57	0.74	0.38	3.83	3.2±0.6	14.48	5.19
WH-PTSA-240	51.21	2.38	27.49	18.05	0.56	0.26	1.20	2.1±0.5	9.67	7.44

[a] C, H, and S contents were determined by CHNS analysis. [b] O content was calculated from CHNS results; %O = 100−(%C+%H+%N+%S). [c] As obtained from TGA analysis. [d] Total acid density was determined by acid-base back titration. [e] From XPS measurements. n.d. = not determined.

Temperature-programmed desorption of ammonia (NH_3-TPD) provides more details on acid behavior, with acid strength in solid acids being related to the desorption temperature. Higher NH_3-desorption temperatures infer stronger acidity, with relative quantities of acid sites being ascertained through integration of NH_3-TPD curve peak area.[13b] As seen in Figure 2C, prepared solid acids contain several types of moderate to strong Brønsted acid sites (*e.g.* $–SO_3H$, $–SO_4H$), as indicated by NH_3 desorption above 300°C, and weak acid sites (*e.g.* –COOH, phenol) as indicated by lower (40-250°C) temperature desorption.[12b, 13b, 22] Through comparison of peak areas obtained from equal weights of each material, results indicate that WH-PTSA-220 contains the highest number of moderate to strong acid sites (7.4% greater peak area above 300°C) than for WH-PTSA-200, followed by other materials in the order WH-PTSA-180 > WH-PTSA-240. A further desorption peak above 750°C in WH-PTSA-220 may indicate the presence of even higher strength acid sites.

FT-IR spectra of raw WH leaves before hydrothermal treatment (WH), material prepared from HTC of WH at 240°C without PTSA (WH-240), and WH-PTSA solid acids are shown in Figure 2D. All spectra contain OH stretching vibrations (3000-3700 cm^{-1}) indicative of water content, or phenolic/carboxylic functional groups, however from comparison of WH and WH-PTSA the intensity of this vibration decreases slightly on hydrothermal treatment. Vibrations due to C-O stretching in WH (~950-1350 cm^{-1}) are still observable after HTC (WH-240), although these are of very low intensity in WH-PTSA. This would indicate that such weakly acidic residues are retained in WH-PTSA materials, consistent with titration and NH_3-TPD results. Addition of PTSA followed by HTC results in shifting of the C=O stretch in WH (1650 cm^{-1}) to higher frequency (1700 cm^{-1}) in conjunction with the appearance of a new C=C vibration at 1620 cm^{-1}; both of these result from dehydration, and aromatization, during HTC.[18] Most notably, new resonances at 1034 cm^{-1} and 1160 cm^{-1} in WH-PTSA spectra are evident arising from the presence of sulfonic acid/sulfonate groups.[8g, 12a, 23]

X-ray photoelectron spectroscopy (XPS) allows further probing of the nature of WH-PTSA acid sites. XPS survey spectra (Figure 3A) confirm that the surface of solid acids is comprised primarily of carbon, oxygen, sulfur, and nitrogen. Oxygen to carbon ratio (O/C) trends are consistent with those obtained from elemental analysis, indicating greater carbonization levels with temperature. Increases in surface S content with HTC temperature are consistent with CHNS analysis (Table 1). The high resolution spectrum of C 1s region in WH-PTSA (Supporting Information) indicates surface carbon to be mainly in a non-oxidized, or aromatic state (CH_x, C–C, C=C, ~285 eV), although higher HTC temperatures result in more contribution from sulfur and oxygen-bound carbon atoms (*e.g.* C–S, C–O, C=O, O–C=O),[24] having higher binding energies. From XPS C1s measurements, the peak corresponding to C-S is suggestive of sulfonic/sulfonate group grafting to the WH support. This finding is consistent with results obtained by Liu *et. al.* [25], who report SO_3H group binding to a biomass carbon substrate. WH-PTSA-220 exhibits the highest portion of carbon bound to sulfur or oxygen atoms. Furthermore, S 2p spectra (Figure 3B) suggest that the surface sulfur atoms in samples prepared at 180-200°C are predominantly in oxidized forms, as indicated by the peaks in region B.[8c, 24a, 26] On the contrary, region C belonging to the C–S–C structure, [24a, 26] or thiol (–SH) groups,[22, 27] becomes the main contributor to the S 2p peak at higher (220-240°C) HTC temperatures. This indicates that the acidity of WH-PTSA-220 is likely due to several factors: a large number of acid sites, the presence of oxy-acid groups (*e.g.* carboxylic), some oxidized sulfur groups contributing from region C, as well as additional but unknown species at higher binding energy (region A), as noted at high NH_3 desorption temperatures (Figure 2C). The low acidity of WH-PTSA-240 is thus likely to be a consequence of S being predominately in non-acidic (*e.g.* C-S-C) forms, and may likely be involved in cross-linking of graphitic carbon sheets.[19]

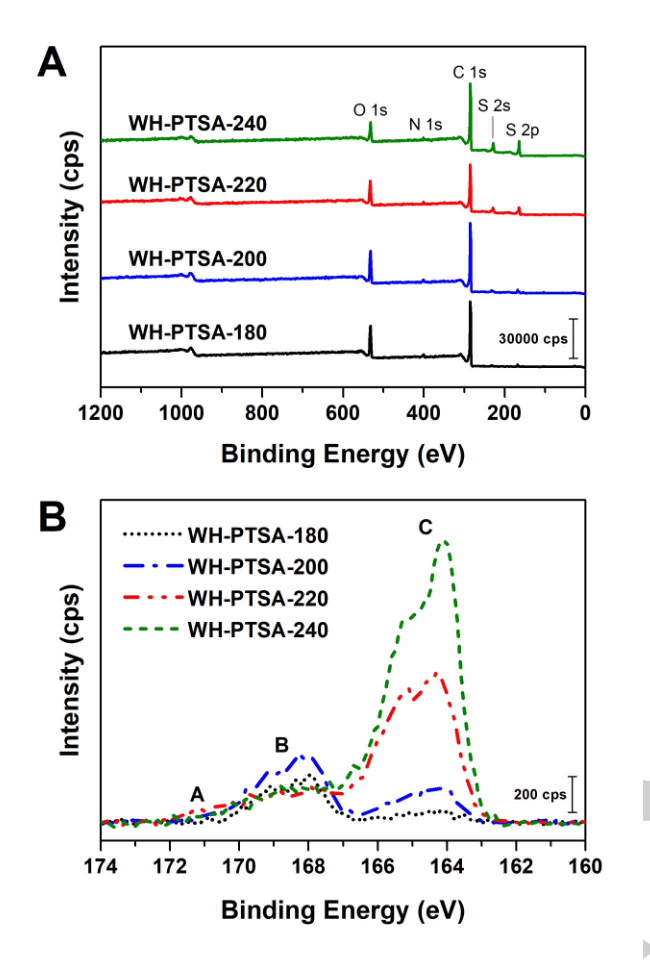

Figure 3. (A) XPS survey spectra and (B) S 2p spectra of carbon-based solid acids prepared at different HTC temperatures.

Catalytic activity in esterification of oleic acid

Reaction parameter screening. As WH-PTSA-240 was expected to be least catalytically active of the series due to its lower acidity it was selected for reaction parameter screening for the esterification of oleic acid. The results of these experiments appear in the Supporting Information. For a catalyst loading of 7 wt.% and 1:20 oleic acid to methanol molar ratio, esterification proved sluggish at 35°C, reaching only 40% conversion after 10 h. Higher reaction temperatures (65-80°C) greatly enhanced conversion, as could be expected through increased reaction rates.[28] At 65°C, 96% conversion of oleic acid was achieved in 5 h, with near quantitative conversion after 3 h at 80°C. For practical purposes, being the boiling point of methanol, 65°C was selected as the basis for other parameter screening tests. Increasing the amounts of methanol or catalyst loading resulted in higher conversions, however, at a methanol molar ratio of 1:20, only slight increases in the conversion resulted from higher (10 wt.%) catalyst loadings. Halving the amount of methanol (1:10 molar ratio) dramatically reduces conversion levels (approx. 70% after 5 hours), such that a 7 wt.% catalyst loading and 1:20 oleic acid to methanol ratio provides optimal performance for esterification using WH-PTSA-240.

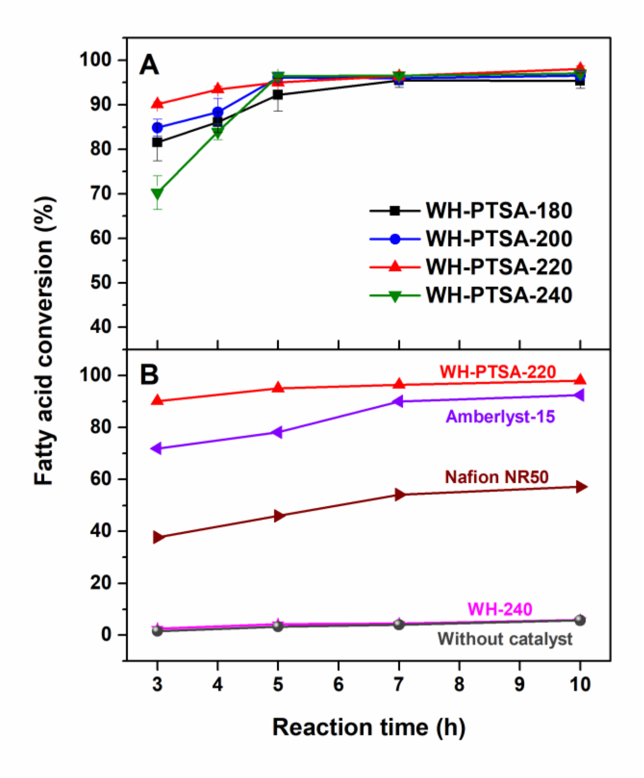

Figure 4. Conversion of oleic acid to methyl oleate using (A) carbon-based solid acids prepared at different HTC temperatures and (B) a comparison of conversions using commercial acid catalysts and WH solid acids. Reaction temperature was 65°C, oleic acid/methanol molar ratio was 1:20, catalyst loading 7 wt.% with respect to oleic acid.

Catalytic activity of other WH-PTSA solid acids. As illustrated in Figure 4, and utilizing the parameters derived from screening above, solid acids prepared at lower HTC temperatures show higher activity in esterification of oleic acid than WH-PTSA-240. This is most apparent after 3-4 h reaction time, with conversions correlating with the amount and strength of acid sites as given by NH_3-desorption results (Figure 2C). WH-PTSA-220, having the highest amount of moderate to strong acid sites, is most active, with WH-PTSA-240 being least active to esterification. The more graphitized, cross-linked structure of the WH-PTSA-240 catalyst might also contribute to its lower activity, potentially by limiting accessibility of the reactants to the active sites.

The esterification of oleic acid using WH-PTSA-220 versus commercially available sulfonated ion-exchange resins and the control (WH-240) highlights its superior catalytic activity (Figure 4B). WH-240 bearing weakly acidic –OH and –COOH groups is catalytically inactive, conversion rates being comparable to those in the absence of catalyst. The activity of the WH-PTSA-220 system emphasises the importance of the active sulfur acid

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sites in the catalytic process, although the hydrophobicity of carbon-based catalysts may contribute to their superior performance, facilitating adsorption of long-chained fatty acids and thus preventing adsorption of water produced in the esterification process leading to potential active site poisoning.[8e, 29]

Catalytic activity in dehydration of xylose

Effects of reaction temperature and catalyst loading on xylose dehydration to furfural were studied in GVL using WH-PTSA-240, the lowest acidity system. Increases in reaction temperature or catalyst loading resulted in higher furfural yields, although optimal catalyst loadings and reaction temperatures were 2 wt.% with respect to GVL and 170°C after 3 h, respectively (Supporting Information). Further increases in reaction temperature, catalyst loading, or reaction time led to lower yields of furfural, possibly due to degradation or condensation of the product to form insoluble humins[7b] as suggested by the formation of dark solid products on the wall of the reaction vessel.

Catalytic activities of all WH solid acids in xylose dehydration using the parameters derived above are shown in Figure 5A. As in esterification, higher acidity solid acids (*e.g.* WH-PTSA-220) provide greater product yields at short reaction times, with WH-PTSA-240 being least active. However, furfural yields of approximately 60% can be obtained after 2 h, regardless of the difference in acid density or acid strength among the prepared solid acid catalysts. WH-240 alone proved inactive to promoting dehydration (Figure 5B). Notably, only furfural was observed by HPLC under conditions of UV detection. The HPLC chromatogram (277 nm) showed a single peak attributed to furfural (see Supporting Information). Nevertheless, with a 70% furfural yield and >95% conversion of xylose, there is the possibility of other concurrent reactions occurring, perhaps generating UV inactive by-products. Further investigation to identify possible by-products using other techniques (such as high resolution HPLC-MS) is required.

The most active WH solid acid (WH-PTSA-220) compares favourably in terms of catalyst activity with other heterogeneous acid catalyst systems (Figure 5B). Commercially available solid catalysts with strong acid sites (Amberlyst-15, Nafion NR50) are most active after 30 min; rapid decreases in furfural yields after this time may result from the heat-sensitivity of Amberlyst-15 resin,[30] or potential poisoning of surface active sites in Nafion NR50, a material which contains the majority of its active sites within the polymer interior.[31] In contrast, WH-PTSA-220 exhibits more consistent performance, with furfural yields in excess of 50% over 4 h. In addition to acidity the presence of –OH and –COOH groups may facilitate xylose adsorption through hydrogen-bonding in WH-PTSA-220, resulting in enhanced catalytic performance.[6a, 12b]

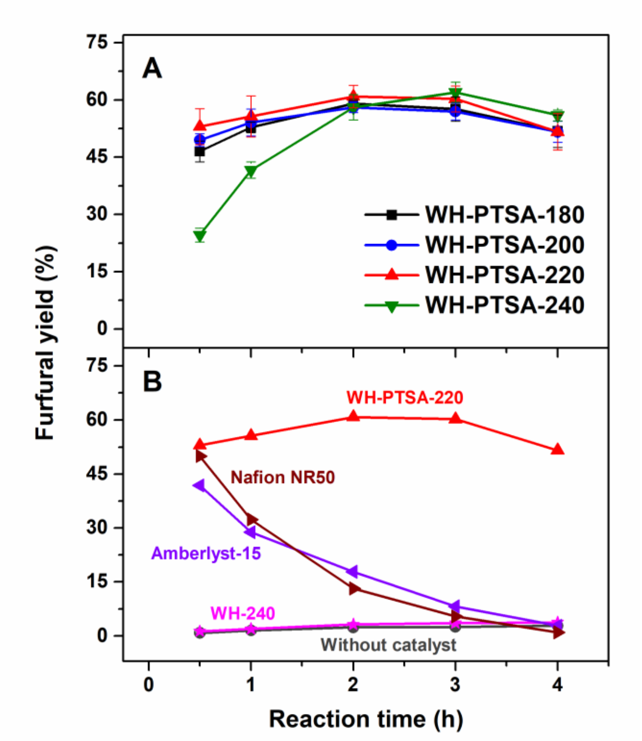

Figure 5. Furfural yields obtained in GVL over (A) carbon-based solid acids prepared at different HTC temperatures and (B) using different heterogeneous acid catalysts in comparison with WH materials. (Reaction temperature 170°C, catalyst loading 2 wt.% with respect to GVL).

The catalytic activity in terms of furfural yield obtained using WH-PTSA-220 is comparable to that of magnetic porous carbon-based solid acids prepared from sawdust (61% within 6 h in DMSO at 150°C), but lower than sulfonated carbon prepared by a two-step procedure from D-glucose (~70% within 20 min in GVL at 175°C)[7b] and calcined co-polymerized PTSA/paraformaldehyde (~80% within 10 min in GVL at 170°C).[23] However, the catalysts reported here are prepared in a single step from an abundant biomass substrate, with the benefit that the use of corrosives, and high energy consumption processes (pyrolysis, calcination), are avoided.

Solid acid catalyst reusability profiles

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Catalyst stability with prolonged use is a necessary requirement in practical applications. As shown in Figure 6, solid acid prepared at 240°C (WH-PTSA-240) exhibits the most favorable reusability profile in both esterification and dehydration processes, with 86% oleic acid conversion and 57% furfural yields obtained after eight consecutive reaction cycles. Although higher HTC temperatures result in lower acidity material the more graphitic, hydrophobic nature of WH-PTSA-240 relative to other WH solid acids may alleviate active site poisoning through water adsorption over time. SEM images of fresh and reused WH-PTSA-240 reveal little change in morphology.

Since the obtained carbon-based catalysts are nonporous and have very low BET surface areas (< 7 m^2/g) compared with other catalyst systems used for esterification of oleic acid and dehydration of xylose[8i], surface area and pore volume contributions to catalytic activity in these materials should be low. FT-IR spectra of the WH solid acids after five consecutive esterification/dehydration cycles (Supporting Information) show several differences on comparison with those of freshly prepared material. Covering of the surface by reaction products, as indicated by greater intensity C-H stretching vibrations in spent catalysts, is expected to lead to further reduced surface area, pore diameter, and pore volume, as indicated through prior work by D'Agostino and co-workers.[32]

The deactivation or reduced catalytic performance of WH-PTSA catalysts on prolonged use can be explained based on FTIR data, as the result of active site contamination and some leaching of acidic sulfonate/sulfonic species. Decreases in $-SO_3H$ vibration intensities (1034 cm^{-1} and 1160 cm^{-1}) relative to fresh WH solid acids (Figure 2D) suggest leaching of, or gradual poisoning of, these sites by water, with hydration of the catalyst surface being evident through enhanced broadening of the O–H stretching vibration in reused catalyst materials. Furthermore, NH_3-TPD analysis (Supporting Information) confirmed reduced amounts of weak- and moderate-to-strong acid sites in spent catalyst material, in good agreement with IR data. Regeneration of spent catalysts can be carried out by re-sulfonation, although calcination is not appropriate as high-temperature treatment can result in decomposition of sulfonate/sulfonic groups, as addressed previously.[8a, 33]

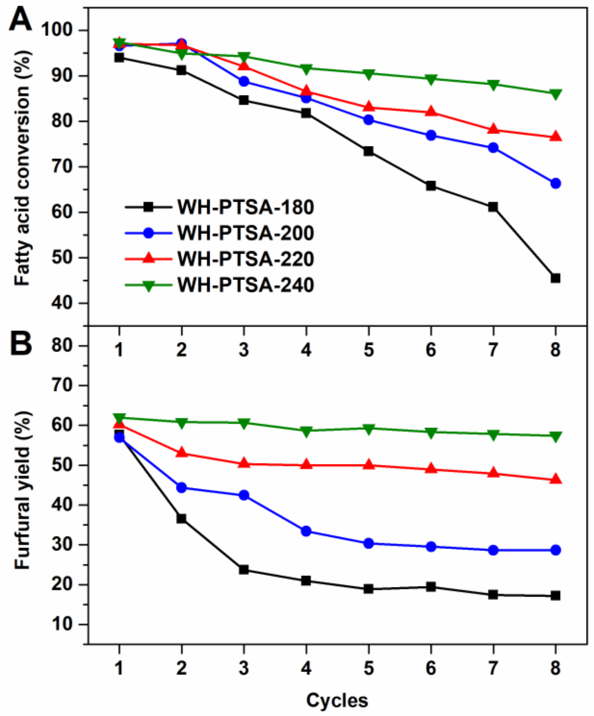

Figure 6. Reusability of carbon-based solid acid catalysts in (A) esterification of oleic acid with methanol (reaction temperature 65°C, time 7 h/cycle, catalyst 7 wt.%, oleic acid/methanol molar ratio 1:20), and (B) dehydration of xylose (reaction temperature 170°C, time 3 h/cycle, catalyst 2 wt.% based on GVL).

Conclusions

Carbon-based solid acid catalysts for esterification of oleic acid, and dehydration of xylose to furfural were prepared in a single step from HTC of readily obtainable water hyacinth biomass. The temperature of the hydrothermal treatment has a profound influence on the morphology, chemical composition, acid property, catalytic activity, stability and reusability of the obtained materials. The solid acid with highest acid density (WH-PTSA-220) exhibits highest catalytic activity, although material prepared at higher temperature (WH-PTSA-240) has a more favorable reusability profile due to enhanced graphitization and hydrophobicity. The robustness, high performance and facile preparation of these materials from an under-utilized biomass resource augur well for further studies expanding the scope of these materials to other acid-catalyzed transformations, with potential for integration of such materials in biorefining.

Experimental Section

Materials

p-Toluenesulfonic acid (AR, Carlo Erba), D-xylose (AR, Loba Chemie), γ-valerolactone (≥98%, Sigma Aldrich), oleic acid (Panreac Applichem), methanol (AR, Burdick & Jackson), ethanol (AR, RCI Labscan), Amberlyst-15 H^+ form (Sigma Aldrich), Nafion NR50 (Sigma Aldrich), sodium hydroxide pellets (AR, Merck), barium chloride dihydrate (AR, Merck), and hydrochloric acid (AR, Carlo Erba) were used as received without further purification.

Fresh WH was collected from Maha Sawat canal in Nakhon Pathom, Thailand. After collection, the biomass was washed with large quantity of tap water to remove dirt and insects. After sun-drying for 1-2 days, leaf material was oven-dried at 105°C for 12 h. The dried leaves were powdered using a stainless steel high-speed grinder, and then sieved to pass through a household sifter (~40 mesh).

One-step preparation of carbon-based solid acid catalysts

A modified methodology to that utilized for furfural-derived materials[9] was employed for the one step HTC of ground dried WH biomass and

PTSA. For this, 6.0 g of PTSA was dissolved in 20 mL of deionized water, and the solution transferred to a 70 mL Teflon-lined stainless steel autoclave containing 3.0 g of ground dried WH leaves. The autoclave reactor was then heated in an oven at either 180, 200, 220, or 240°C for 10 h. After being allowed to cool to room temperature, the reactor was opened and the resulting brown-to-black solid product was collected by vacuum filtration and washed with hot deionized water until no sulfate was detectable in the filtrate (using barium chloride solution). After drying at 120°C overnight, the material was ground to a powder using a mortar and pestle. A series of materials (WH-PTSA-*T*) were obtained, where *T* denotes the hydrothermal temperature used. Carbonaceous material from biomass alone without addition of PTSA was prepared at 240°C (denoted as WH-240) as a control.

Characterization of carbonaceous materials

Morphological investigations of prepared carbonaceous materials utilized SEM imaging (JEOL JSM-6480LV). Samples were coated with gold prior to imaging, and examined using 1000x magnification and with 15 kV accelerating voltage.

Powder X-ray diffraction (XRD) analysis was carried out on a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation (λ 1.54 Å) operating at 40 kV and 35 mA, 2θ range 10°-60°, with a step size of 0.02° and at 2 s/step.

Weight percentages of carbon, hydrogen, nitrogen, and sulfur (elemental composition) for all samples were determined using a CHNS analyzer (LECO CHN628 equipped with Sulfur Add-On Module).

Total acidity of carbon materials was determined by acid-base back titration[12b]. For this, 0.05 g of sample was added to 20 mL of 0.01 M sodium hydroxide solution. After shaking at 25°C for 24 h, the supernatant solution was titrated with 0.01 M hydrochloric acid to end-point using phenolphthalein as indicator.

Quantification of acid sites in material samples utilized NH_3 temperature-programmed desorption (NH_3-TPD) performed on a chemisorption analyzer (Microtrac BELCAT-B) equipped with a thermal conductivity detector (TCD). Prior to analysis, samples were heated at 150°C under helium gas flow (50 $mL{\cdot}min^{-1}$) for 60 min. The temperature was subsequently decreased to 50°C and NH_3 was introduced under helium flow (30 $mL{\cdot}min^{-1}$) for 30 min. Following this, physically adsorbed NH_3 was removed by rapid helium gas flow (50 $mL{\cdot}min^{-1}$) for 15 min. The NH_3-TPD desorption was then performed over 50-800°C (heating rate 10°C$\cdot min^{-1}$). Identical sample weights were used for each measurement to allow comparisons of intensity differences in acid site regions.

Surface functionalization of materials was probed using Fourier transform infrared (FT-IR), with spectra recorded as KBr discs over the range 400-4000 cm^{-1} using a PerkinElmer Spectrum GX spectrophotometer.

X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Axis Ultra DLD instrument equipped with a 150W monochromatic Al Kα source.

Thermogravimetric analysis (TGA) measurements were performed on a TA Instruments 2960 SDT V3.0F analyzer under N_2 flow, with heating rate of 10°C$\cdot min^{-1}$ from 30-700°C.

Surface area and porosity of carbon-based solid acids were studied by N_2 adsorption/desorption isotherms carried out on a Quantachrome Autosorb iQ gas sorption analyzer at -196°C. Specific surface areas were determined from the Brunauer-Emmett-Teller (BET) plot with pore volume and pore size distribution calculated using Barrett-Joyner-Halenda (BJH) analysis.

Esterification of oleic acid

Esterifications were carried out in a 100 mL glass (Ace) pressure tube using 3.0 g of oleic acid, solid acid catalyst (5-10 wt.% with respect to oleic acid) and methanol (10-20:1 molar ratio with respect to oleic acid). After closing the tube reactions were conducted at a specific temperature (35°C, 65°C, or 80°C) for a fixed time period (3-10 h). Once the reaction was deemed complete the tube was cooled to room temperature, opened, and the mixture transferred to a conical centrifuge tube for centrifugation at 3000 rpm for 20 min to separate, and collect, the used catalyst. For reusability tests, used catalyst sedimented in the centrifuge tube was washed with 20 mL of methanol, transferred to a clean Ace tube, and dried at 105°C overnight prior to exposure to fresh oleic acid and methanol under the same reaction conditions.

Conversion of oleic acid to methyl oleate (representative of ester yield) was determined from changes in acid value through titration,[30] and was calculated as follows:

$$\% \text{ Conversion} = [(AV_O - AV_S)/AV_O] \times 100 \quad (1)$$

where AV_O and AV_S are the acid values of oleic acid (before esterification) and sample (after esterification), respectively.

Dehydration of xylose to furfural

Dehydration experiments were carried out in a 10 mL Pyrex glass tube with screw cap kept at constant temperature (160°C, 170°C, or 180°C) with magnetic stirring. Typically, 40 mg of xylose, 2.0 g of solvent (γ-valerolactone, GVL), and catalyst (1-3 wt.% with respect to GVL) were placed in the tube, the tube was closed, and the reaction mixture was heated for a specific reaction time (30 min-4 h). After cooling to room temperature the used catalyst was separated by centrifugation, and washed with 20 mL of deionized water. For reusability testing the catalyst was dried at 120°C overnight before exposure to fresh reagents under the same reaction conditions.

The amount of furfural in the liquid reaction mixture was quantified by HPLC (Waters 2695 system, Nova-Pak C18 column, Waters 2487 UV detector) with detection at 277 nm, using 0.1% acetic acid (v/v) in acetonitrile as mobile phase. Furfural yields were calculated using equation (2).

$$\text{Furfural yield (\%)} = (\text{furfural content (g)}/\text{initial wt xylose (g)}) \times 100 \quad (2)$$

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Keywords: carbon-based solid acid catalyst • hydrothermal carbonization • biomass • esterification • dehydration

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FULL PAPER

Carbon-based solid acid catalysts for esterification of oleic acid, and dehydration of xylose to furfural were prepared in a single step from hydrothermal carbonization of abundant water hyacinth biomass.

Jutitorn Laohapornchaiphan, Christopher B. Smith, Siwaporn Meejoo Smith**

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One-step preparation of carbon-based solid acid catalyst from water hyacinth leaves for esterification of oleic acid and dehydration of xylose