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Supporting Information

Acid Functionalized Hydrochar as Heterogeneous Catalysts for Solventless Synthesis of Biofuel Precursors

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Materials characterization

X-ray diffraction (XRD) measurements were acquired by using the Rigaku Smart Lab 9 kW rotating anode X-ray diffractometer with Ni-filtered Cu K_α radiation (λ = 0.1542 nm) at 100 mA and 45 kV in 2θ range from 5° to 80° with a scan rate of 2° per min with step size of 0.02°. Raman spectroscopic measurements were performed using Horiba LabRaM high resolution instrument. The samples were irradiated using 532 nm laser excitation with 1800 grooves mm^{-1}, 10 sec acquisition time, 10% laser power and 50x objective lens. The Raman spectra was plotted using OriginPro 8.5 software. FT-IR spectra were done on a PerkinElmer Spectrum 2 spectrometer. Thermogravimetric (TGA) analyses were performed from the PerkinElmer Pyris 1 instrument, wherein the samples were heated from 25 °C to 800 °C at a heating rate of 10 °C min^{-1} under nitrogen atmosphere with a flow rate of 20 mL min^{-1}. The Brunauer-Emmett-Teller (BET) specific surface area and nitrogen adsorption-desorption isotherms of the samples were done on a Quanta chrome Autosorb-iQ-MP-XR system at 77 K. The morphology of the samples was surveyed by using a scanning electron microscope (SEM), FEI Nova SEM-450, and a transmission electron microscope (TEM), FEI Tecnai G2 20 S-twin microscope operating at 200 kV. Energy dispersive x-ray spectra (EDAX) and elemental mapping data were also acquired by using the same TEM instrument. For electron microscopic measurements, 1 mg of sample was taken in a vial along with 1 mL of ethanol. After sonication for 1 h, the suspension was drop casted on a piece of Si wafer (for SEM measurements) and on a carbon coated Cu grid (for TEM measurements). These were allowed to dry for overnight and subsequently, the SEM and TEM measurements were done under vacuum conditions. The X-ray photoelectron spectroscopy (XPS) measurements were done using Thermo Scientific NEXSA photoemission spectrometer with a micro focused X-ray spot size of 400 µm, using monochromatic Al-K_α (1486.6 eV) x-ray source and analyzed by using Avantage software. The samples were placed in the instrument in load lock chamber and waited for 5.0 x 10^{-8} mbar vacuum before entering the analysis chamber with 8.0 x 10^{-10} mbar vacuum. For the preparation of XPS samples, 5 mg of sample was taken in a vial along with 1 mL of ethanol. After sonication for 30 min, the suspension was drop casted on a piece of Si wafer. The samples were allowed to dry for few hours and subsequently, the XPS measurements was performed under vacuum conditions. For the deconvolution of different elements, the C-C peak sets at 284.8 eV for the reference. The peak fitting has been done by selecting range for each element like C 1s (280-292 eV), O 1s (528-538 eV), N 1s (392-410 eV),

S 2p (160-174 eV) and P 2p (128-138 eV). After the selection of the range for each element, the peaks were added to the graph followed by peak fitting to the best possible extent. After deconvolution, the data was exported and the plots were prepared by using OriginPro 8.5 software. The temperature-programmed desorption (TPD) measurements were carried out using BEL/CAT2 instrument fitted with TCD detector. For a typical NH_3 TPD measurements, 60 mg of sample was activated in He (30 mL min^{-1}) at 120 °C for 80 min. After cooling to the required temperature (50 °C), the pre-heated sample was saturated with NH_3 (partial pressure of 100 Torr, 10% NH_3 mixed in helium) for 1 hour. Further, the sample was flushed with helium gas stream (30 mL min^{-1}) for 1 h to remove any of the physiosorbed ammonia gas. After that, desorption of the gas was recorded and monitored by using the filament thermal conductivity detector (TCD). The temperature programmed desorption experiments were conducted in the temperature regime of 50-300 °C with a heating rate of 10 °C min^{-1}. Elemental analysis was recorded with high performance elemental analyzer for simultaneous CHNOS analyses. NMR spectra were taken from the JEOL-USA (JNMECX500) spectrometer in $CDCl_3$ taking TMS (trimethyl silane) as an internal standard. ^{1}H spectra were acquired in 500 MHz frequencies, and ^{13}C NMR spectra were acquired in 125 MHz frequencies. pH experiments were performed by using Cole Parmer pH meter. 5 mg of the sample were stirred for 4 h in 10 mL Hepes buffer of 10 mM of pH = 7.2 before taking the measurement. Deionized water (18.2 M Ω cm) used in this work was obtained from a double stage water purifier (ELGA PURELAB Option-R7).

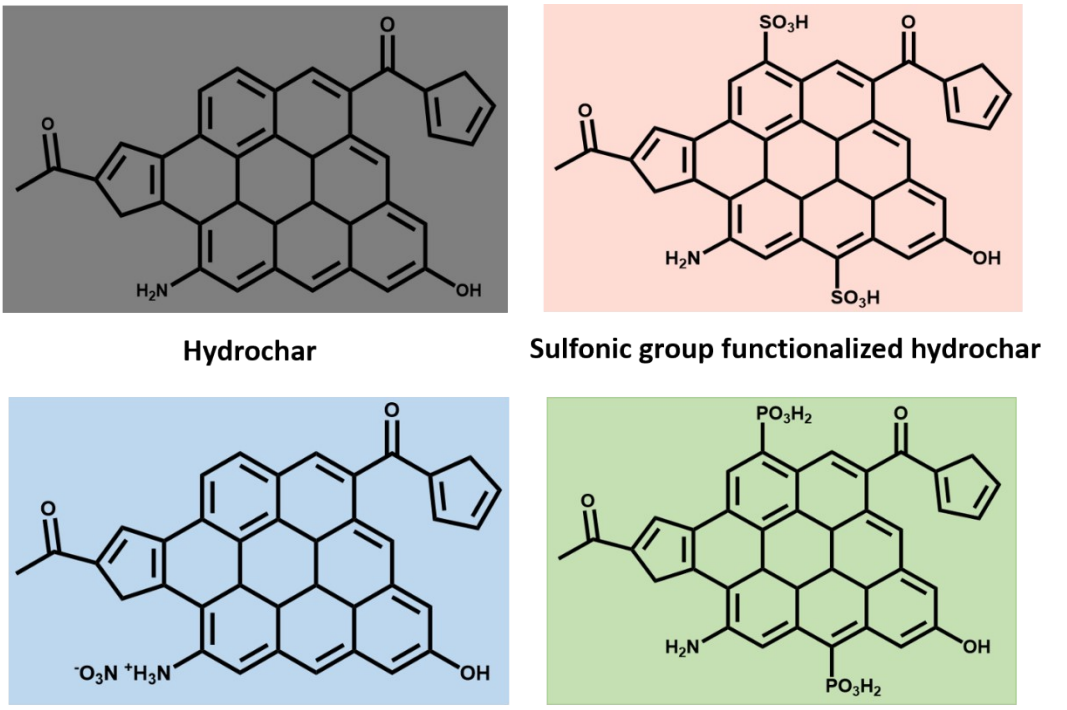

Fig. S1 Proposed molecular structures of HC, SHC, NHC and PHC.

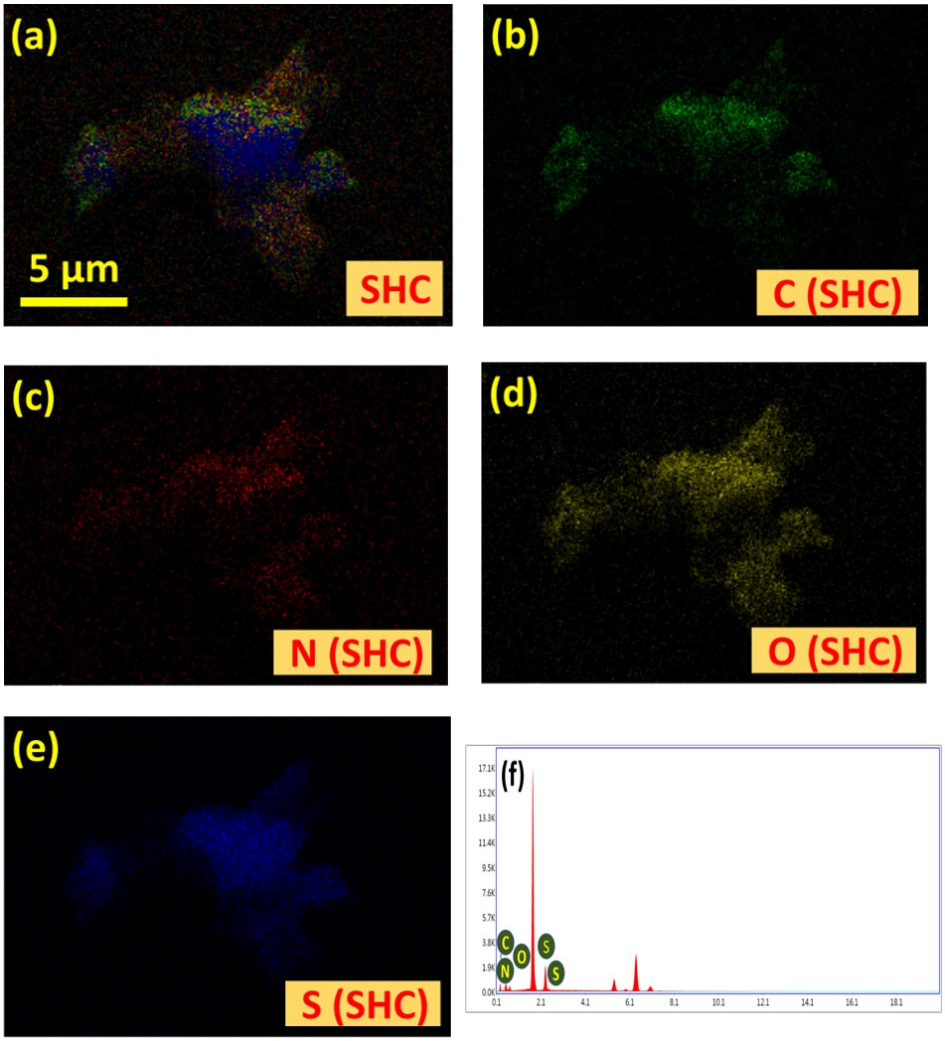

Fig. S2 (a-e) Elemental mapping and (f) EDAX of SHC.

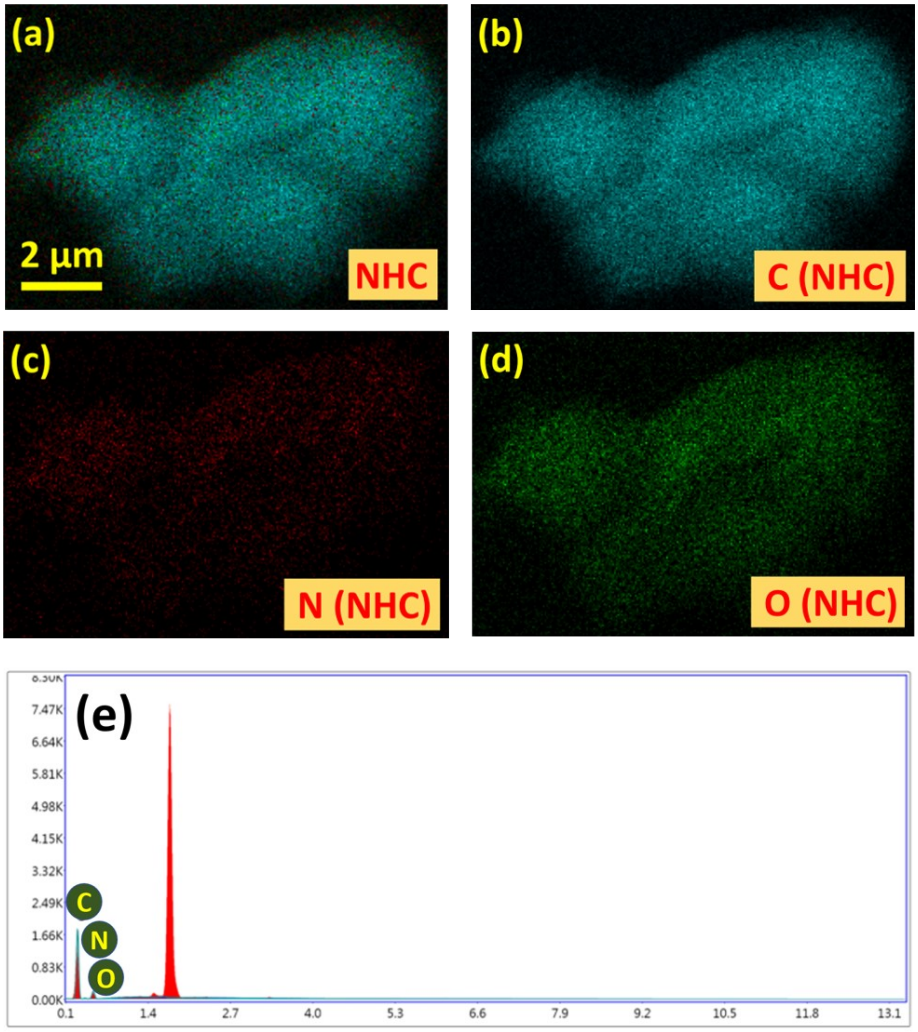

Fig. S3 (a-d) Elemental mapping and (e) EDAX of NHC.

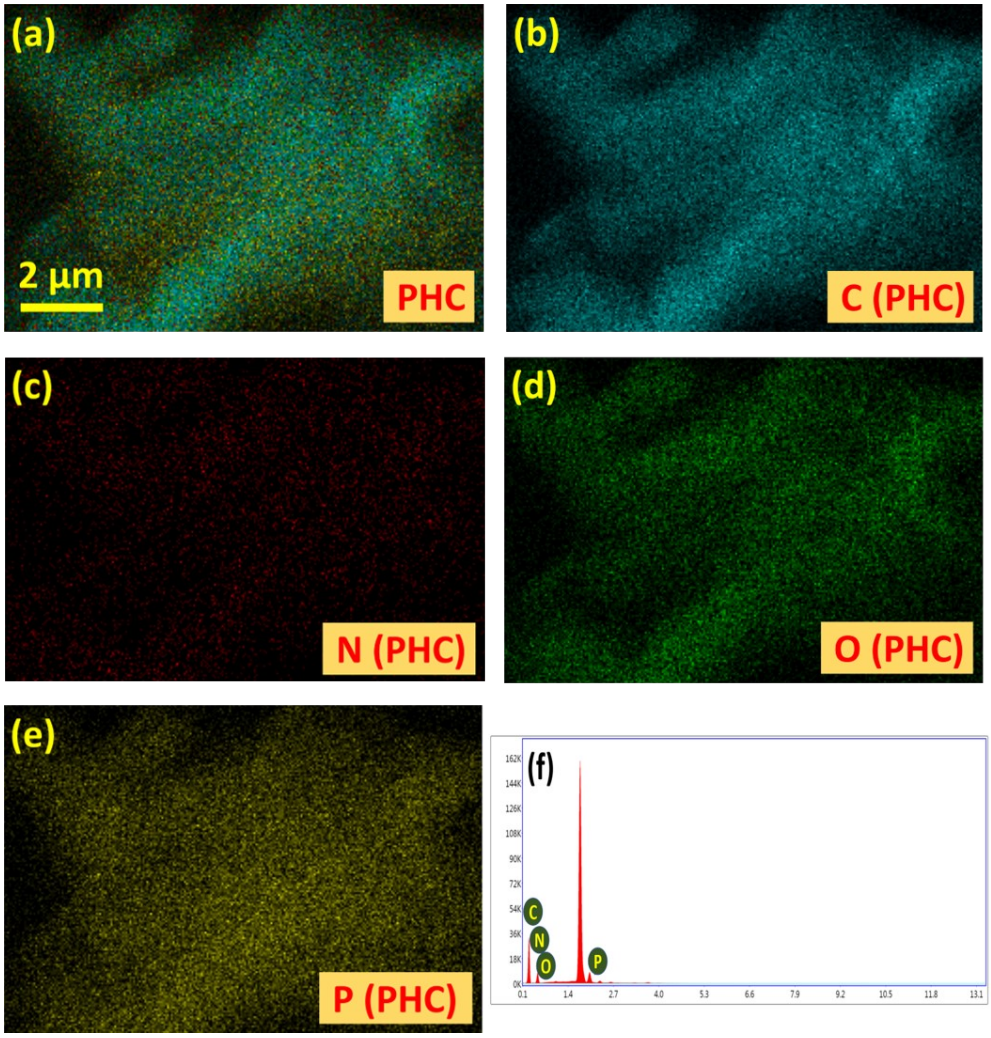

Fig. S4 (a-e) Elemental mapping and (f) EDAX of PHC.

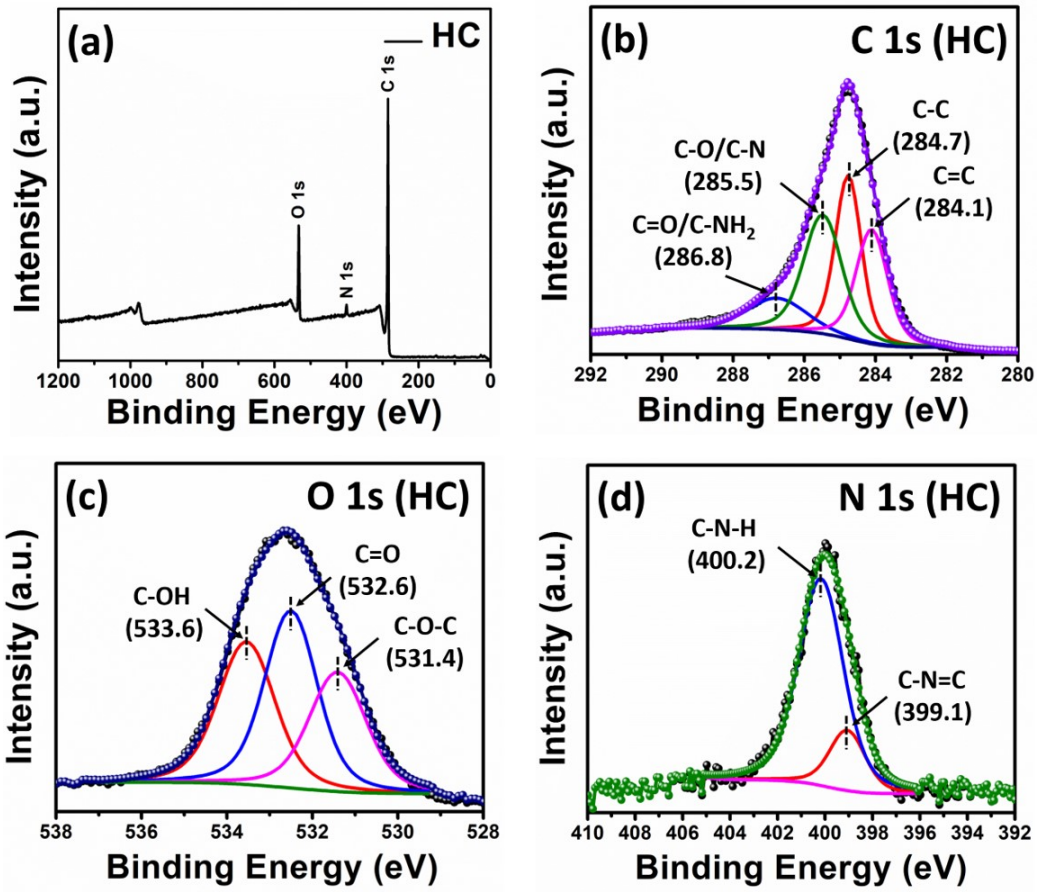

Fig. S5 XPS plots of HC (a) survey spectrum, (b) C 1s, (c) O 1s and (d) N 1s.

Table S1 Atomic percentage of various elements from XPS for HC, NHC, SHC and PHC.

Catalyst	C (%)	O (%)	N (%)	S (%)	P (%)
HC	58.39	38.48	3.13	-	-
NHC	65.08	29.45	5.47	-	-
SHC	53.40	33.73	3.21	9.65	-
PHC	68.94	26.16	1.64	-	3.26

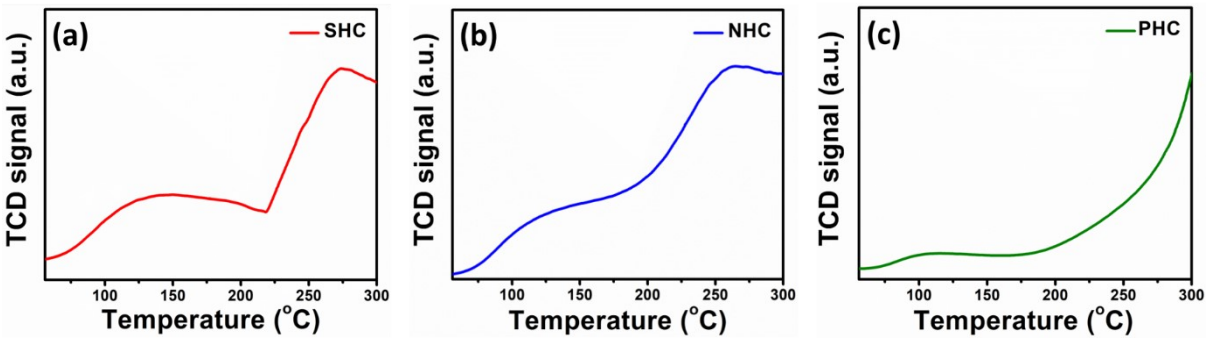

Fig. S6 NH_3 TPD spectra of (a) SHC, (b) NHC and (c) PHC.

Table S2 pH values of HC, SHC, NHC and PHC.

Catalyst	pH value
HC	7.27
SHC	6.84
NHC	7.06
PHC	7.17

Table S3 Elemental analysis from CHNOS technique of HC, NHC, SHC and PHC.

Catalyst	C (%)	H (%)	N (%)	O (%)	S (%)
HC	69.950	5.303	2.220	19.879	0.071
NHC	49.290	4.270	5.690	39.492	0
SHC	42.320	4.877	1.100	38.911	8.365
PHC	42.860	5.931	1.540	41.937	0.219

Product yield calculation

The product was isolated through column chromatography and the mass yield was calculated by using the following formula.

$$\text{Yield (\%)} = [\text{Actual yield (in mg)} / \text{Theoretical yield (in mg)}] * 100$$

Herein, Theoretical yield = Molecular weight of product * mmol of starting material

(Theoretical yield is the 100 % yield)

Green metrics calculations

Green chemistry metrics calculations were described the environment friendliness and sustainability of any chemical reaction. The various green metrics parameters have been used for HAA reaction to compare the catalytic process with SHC, NHC and PHC catalyst. The calculation method for various green metrics parameters is given below.

1) Atom economy or AE

AE (%) = {[Mol wt. of product] / [Sum of mol wt. of reactants]} * 100

For HAA reaction, AE (%) = [Molecular weight of BMFM] / Mol. wt. of FAL + 2* Mol wt. of 2-MF

(In one HAA reaction, 1 molecule of FAL and 2 molecules of 2-MF are used to form one molecule of BMFM)

2) Environmental factor or E-factor

E = [Total mass of waste] / [Mass of final product]

Mass of waste = Total mass of reactant – Total mass of product

3) Solvent intensity or SI

SI = [Mass of solvents] / [Mass of product]

4) Mass intensity or MI

MI = [Total mass in process] / [Mass of product]

5) Process mass intensity or PMI

PMI = [Total mass in process (incl. solvent)] / [Mass of product]

6) Reaction mass efficiency or RME

RME (%) = [Mass of product] / [Total mass of reactants] * 100

7) Mass productivity or MP

MP (%) = [Mass of product] / [Total mass (incl. solvents)] * 100

8) Carbon economy or CE

CE (%) = [Carbon in product] / [Total carbon in reactant] * 100

= {[Number of moles of product*Number of C in product] / [Number of moles of reactant*Number of C in reactant]} * 100

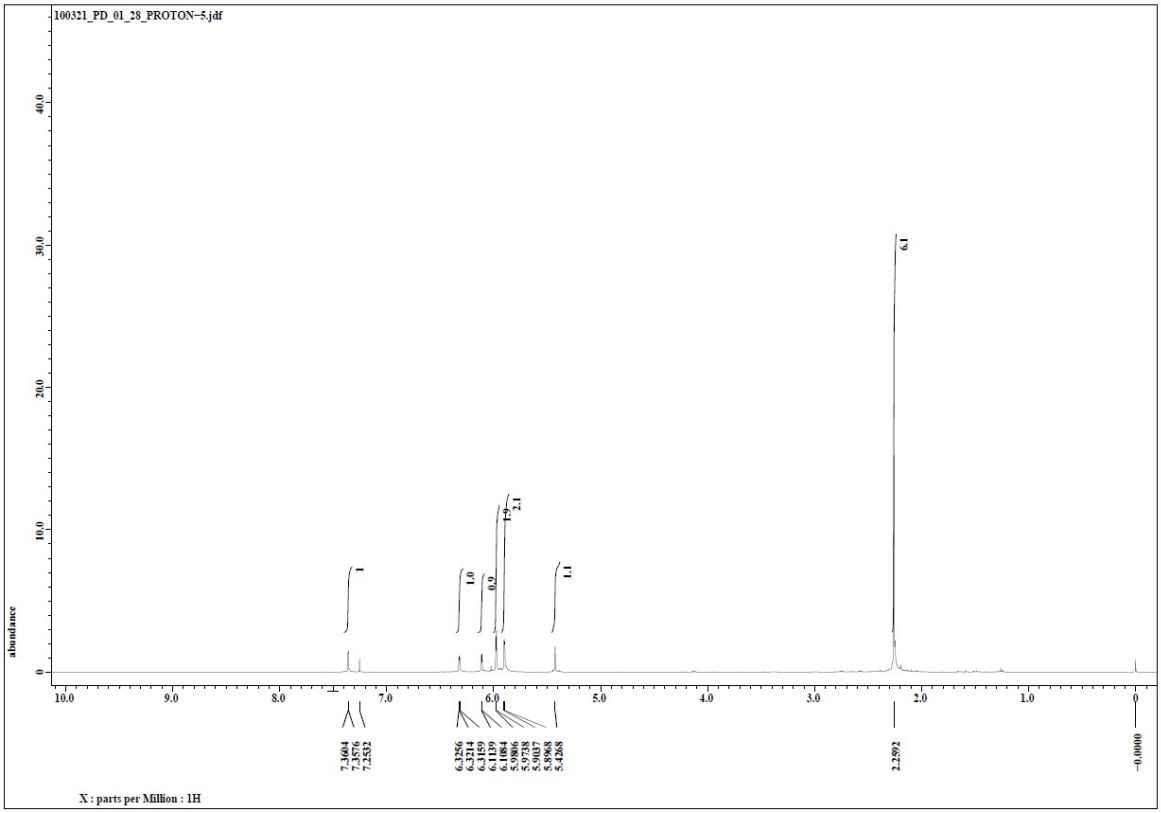

Fig. S7 ^{1}H NMR spectrum of 5,5'-(furan-2-ylmethylene)bis(2-methylfuran) [$CDCl_3$, 500 MHz].

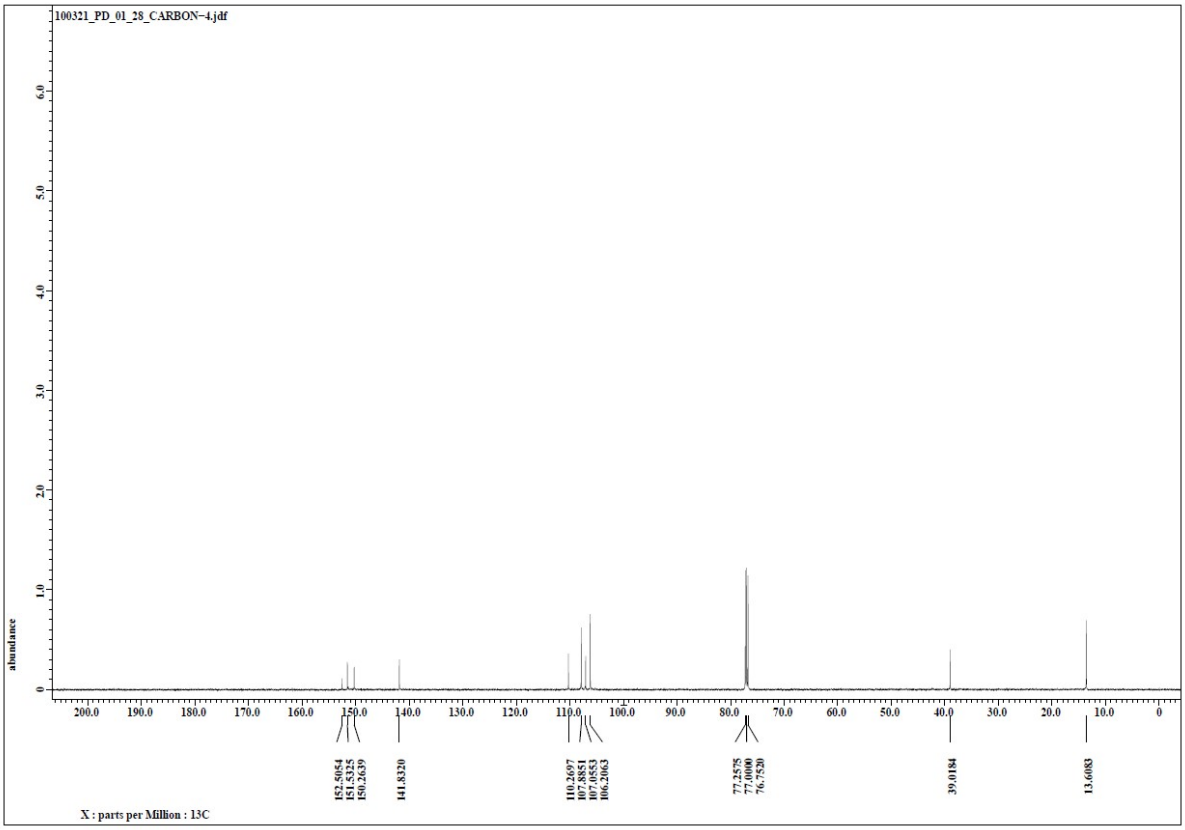

Fig. S8 ^{13}C NMR spectrum of 5,5'-(furan-2-ylmethylene)bis(2-methylfuran) [$CDCl_3$, 125 MHz].

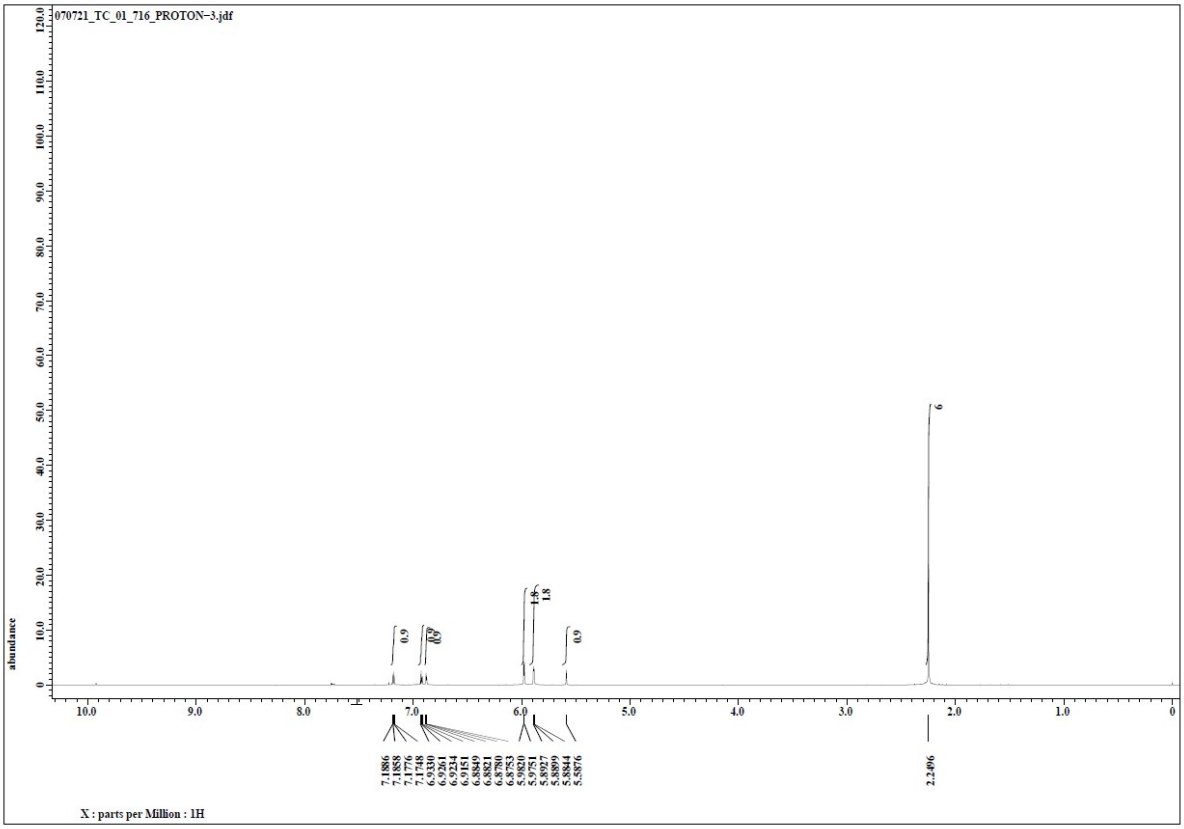

Fig. S9 ^{1}H NMR spectrum of 5,5'-(thiophen-2-ylmethylene)bis(2-methylfuran) [$CDCl_3$, 500 MHz].

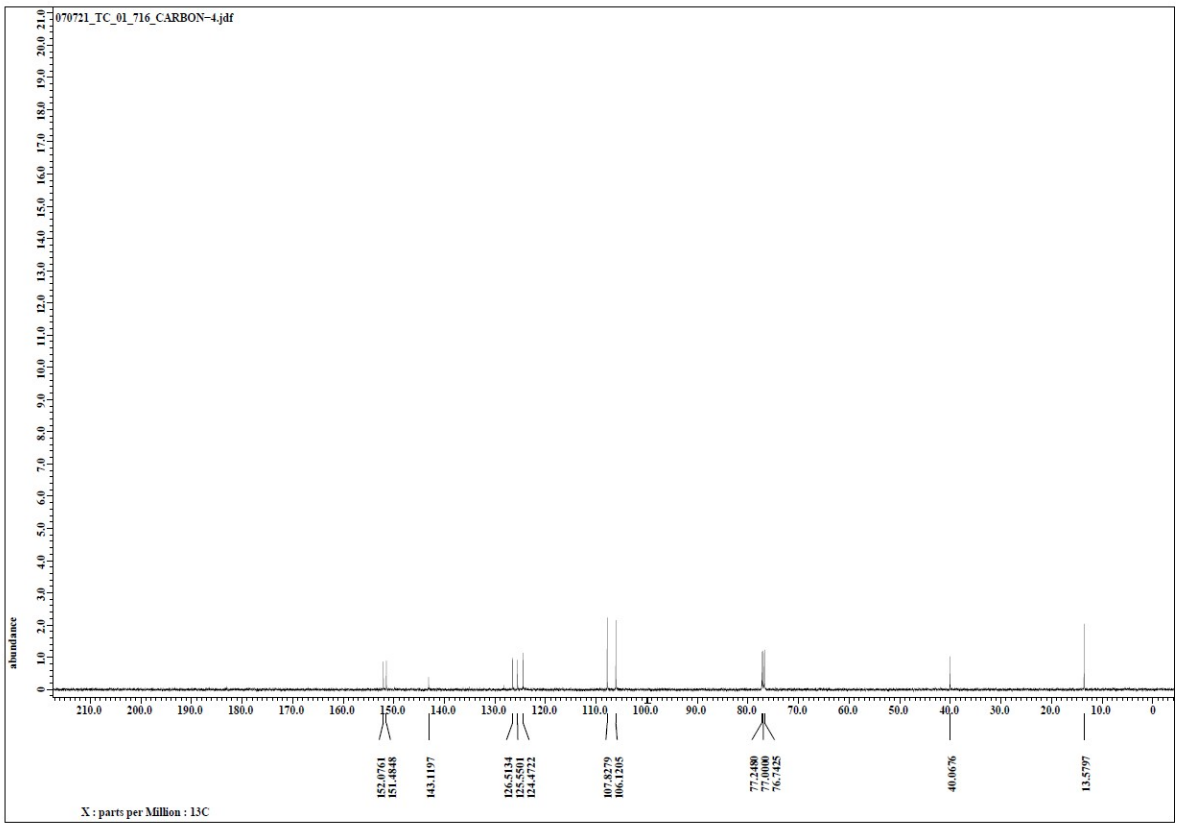

Fig. S10 ^{13}C NMR spectrum of 5,5'-(thiophen-2-ylmethylene) bis(2-methylfuran) [$CDCl_3$, 125 MHz].

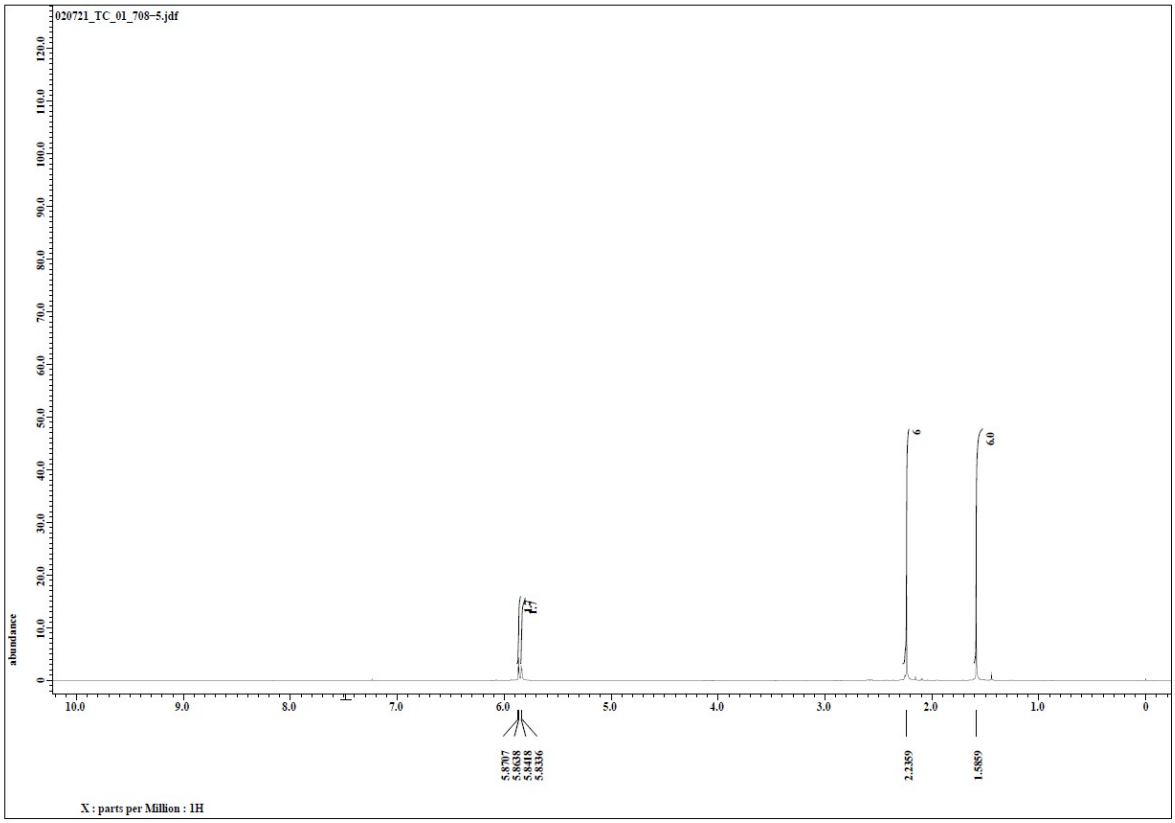

Fig. S11 ^{1}H NMR spectrum of 5,5’-(propane-2,2-diyl)bis(2-methylfuran) [$CDCl_3$, 500 MHz].

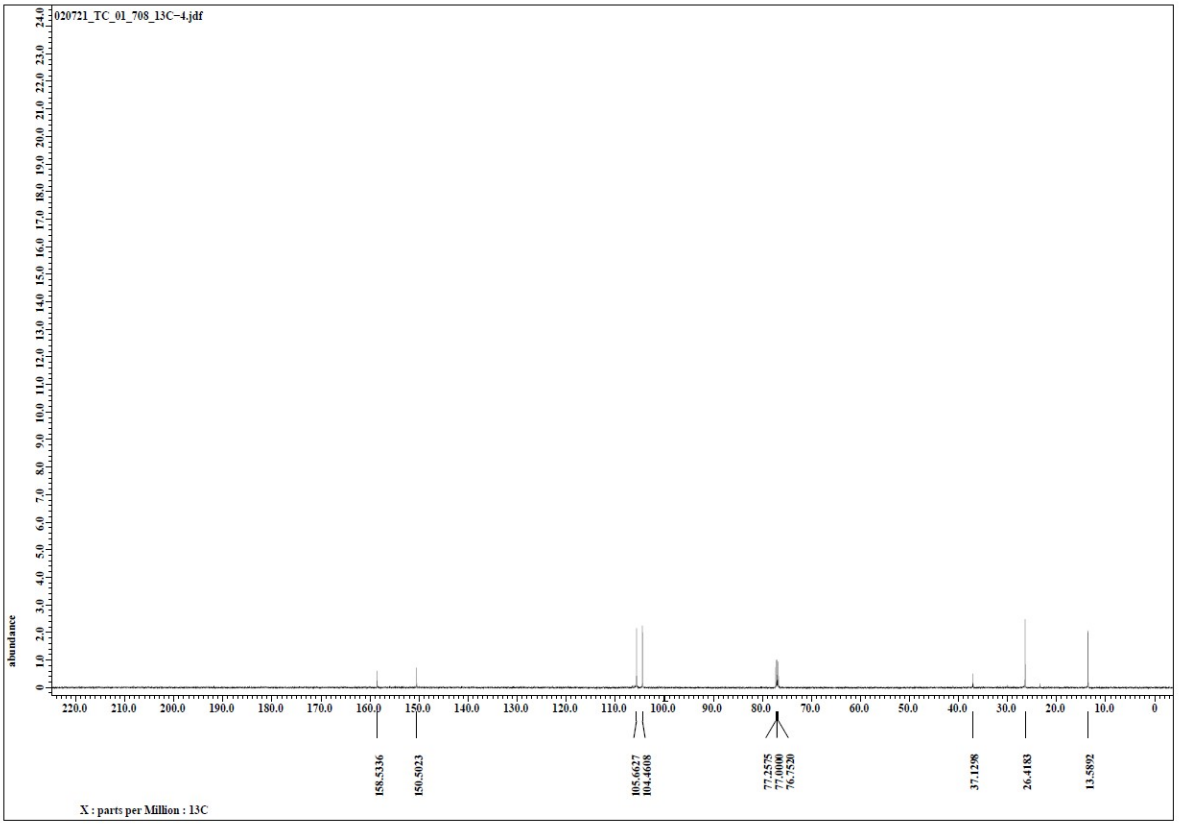

Fig. S12 ^{13}C NMR spectrum of 5,5'-(propane-2,2-diyl)bis(2-methylfuran) [$CDCl_3$, 125 MHz].

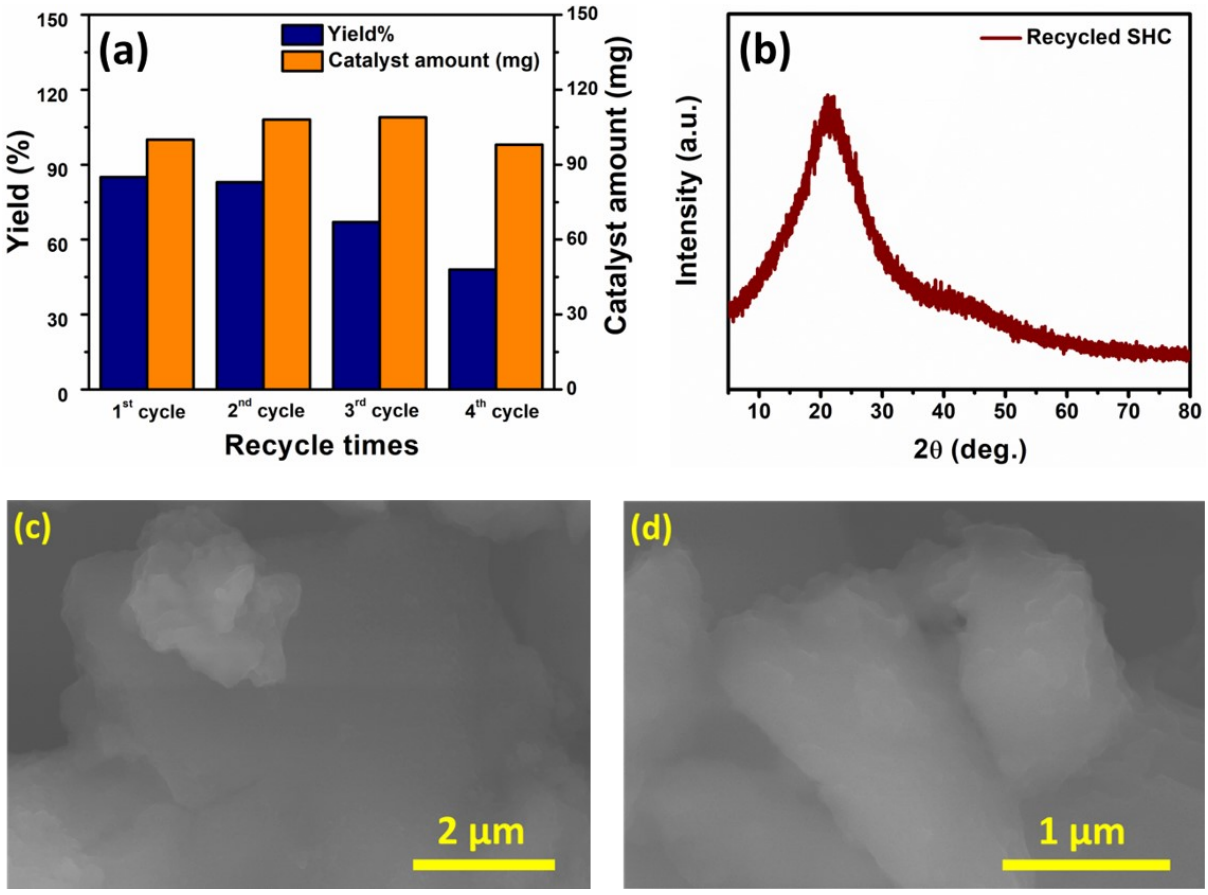

Fig. S13 (a) Recyclability study with SHC catalyst, (b) XRD pattern of recycled SHC catalyst and (c, d) SEM images of recycled SHC catalyst.

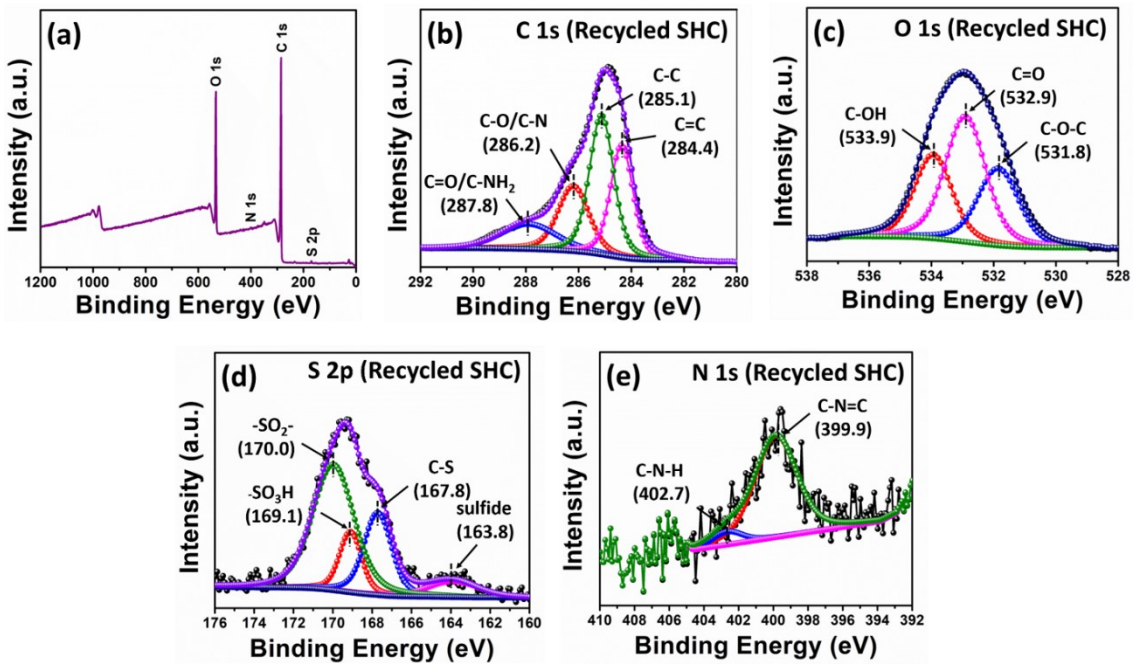

Fig. S14 XPS plots of (a) survey spectra of recycled SHC, (b) C 1s (recycled SHC), (c) O 1s (recycled SHC), (d) S 2p (recycled SHC) and (e) N 1s (recycled SHC).

Table S3 Atomic percentage of various elements from XPS for recycled SHC.

Sl. No.	Elements	Atomic Percentage
1	C	77.21
2	O	21.23
3	N	1.09
4	S	0.48

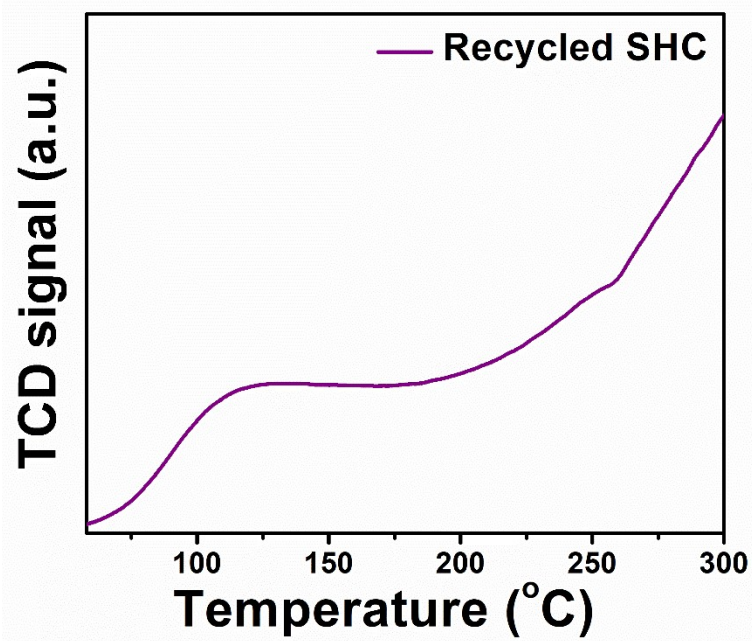

Fig. S15 NH_3 TPD spectra of recycled SHC.