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Electronic Supplementary Information

Functionalising hydrothermal carbons for catalysis – Investigating Solid Acids in esterification reactions

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1. Solid state ^{13}C NMR characterisation of HTC-B50, HTC-B100 and HTC-B300 sample

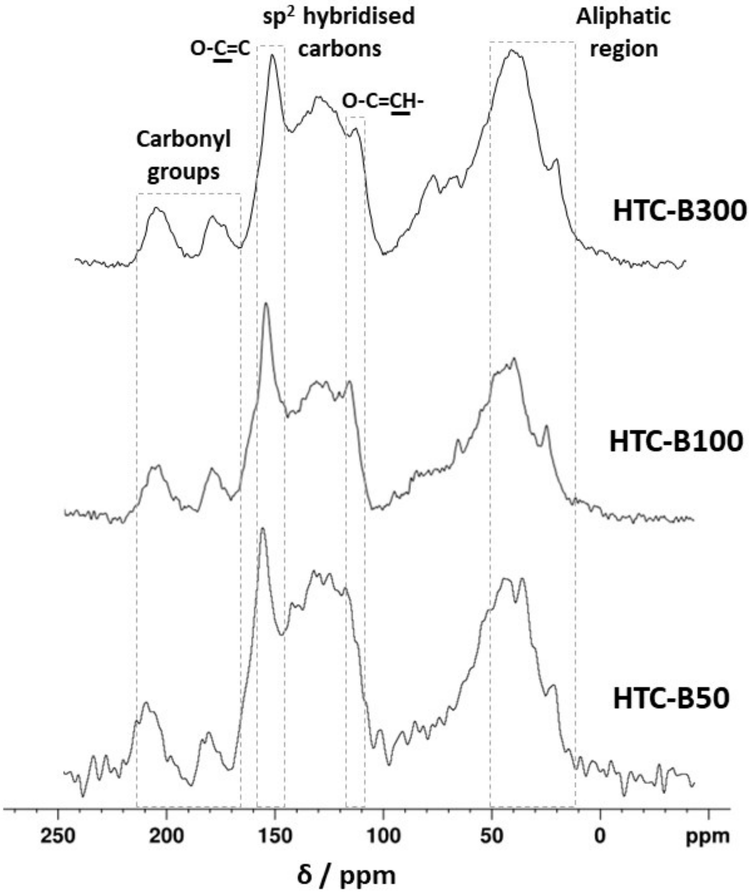

Figure S1 Solid state ^{13}C NMR spectra of borax-mediated materials HTC-B50, HTC-B100 and HTC-B300.

2. Addition of borax increases the HTC material yield by enhanced isomerization/dehydration/polymerization reactions. Consequently the amount of C increases as well

Table S1 CHNS elemental analysis of HTC materials in addition of different amounts of borax and elemental analysis of conventional HTC material (HTC-B0).

Sample name	C wt%	H wt%	O wt%
HTC-B0	59.5	5.0	35.6
HTC-B50	60.3	4.8	35.0
HTC-B100	62.2	4.8	33.0
HTC-B300	64.3	5.1	30.7

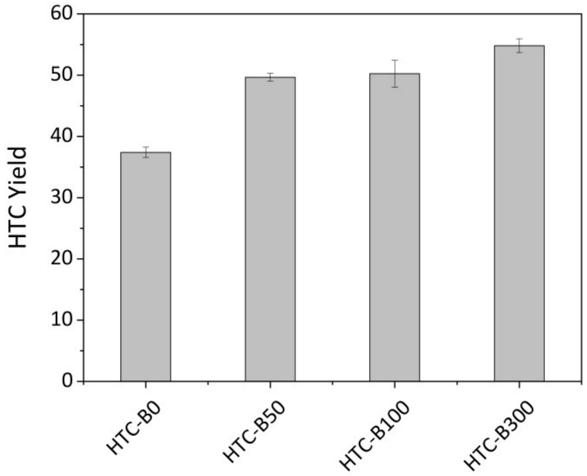

Figure S2 HTC material yield increases by addition of borax.

Table S2 CHNS elemental analysis of HTC materials in addition of different amounts of borax and elemental analysis of conventional HTC material (HTC-B0) post-carbonised at 400 °C.

Sample name	C wt%	H wt%	O wt%
HTC-B0-400	78.0	3.8	18.2
HTC-B50-400	78.8	3.9	17.3
HTC-B100-400	79.0	4.0	17.0
HTC-B300-400	89.0	2.7	8.3

3. N_2 sorption analysis of HTC material before sulfonation

Table S3 N_2 sorption data of HTC materials with different borax amount and T_c.

Sample name	S_{BET} a) [m^2/g]	V_{pore} b) [cm^3/g]	V_{micro} b) [cm^3/g]	V_{meso} b) [cm^3/g]
HTC-B0-400	295	0.17	0.17	/
HTC-B50-400	396	0.27	0.13	0.14
HTC-B100-400	395	0.27	0.12	0.15
HTC-B300-400	4.5	0.005	/	/
HTC-B100-350	201	0.25	0.01	0.24
HTC-B100-480	410	0.30	0.11	0.19
HTC-B100-550	476	0.34	0.14	0.20
HTC-B100-700	416	0.28	0.13	0.15

a)Specific surface area from BET method, b)Pore size characteristics obtained via the QSDFT model.

4. XPS analysis of HTC-B100-400 material and after sulfonation HTC-B100-400-S

The presence of bonded S-functional groups was confirmed by X-ray photoelectron spectroscopy (XPS). Survey spectrum of HTC-B100-400-S (Fig. S3) presents the appropriate S 2p (168.5 eV) spectral regions / binding energies (BE) alongside the C 1s and O 1s. By comparison, the original HTC-B100-400 does not present any BE signals in S 2p region. Elemental quantification based on these survey scans indicates atomic %s of O 19.17% (23.7 wt%), C 78.89% (71.6 wt%) and S 1.94% (4.6 wt%) for HTC-B100-400-S, and O 13.18% (3.6 wt%), C 86.82% (96.4 wt%) for HTC-B100-400. After acid treatment HTC-B100-400-S has a higher surface oxygen content demonstrating additional evidence of a successful oxidation through the introduction of $–SO_4^{2-}$, $-SO_2OH$ and $R_2S=O$ functionality. On the other hand strong sulfonation also may oxidize aliphatic CH_3/CH_2 groups to carboxylic acid groups.

Deconvolution of the C 1s core level (Fig. S4a) reveals BE associated with such functional carbon materials. The BE at 284.8 eV is assigned to C=C (sp^2 carbon) and BE at 285.8 eV are associated with C-H and C-C or sp^3 carbon. BEs at 286.6 eV are attributed to singularly bonded to oxygen (C-O-C, C-OH, etc.) and carbonyl and quinone groups at BEs at 287.8 eV. BEs at 288.8 eV are assigned to ethers and carbon bonded to oxygen through double bonds (R-HC=O, R$_2$-C=O, R-C(OH)=O, R-C(OR)=O).[1]

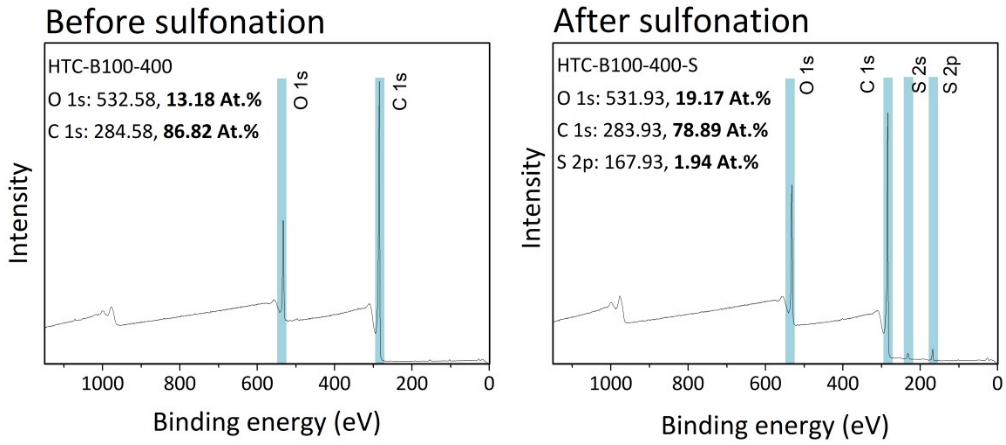

Figure S3 Survey spectra of a) HTC-B100-400 material and b) sulfonated HTC-B100-400-S.

After sulfuric acid treatment a small increase in the relative intensity of the BE = 287.8 eV is observed probably as a result of the partial oxidation process(es) during the sulfonation.[2]

The deconvolution of the O 1s photoelectron envelope for HTC-B100-400 and HTC-B100-400-S revealed four BEs, namely at 533.7, 532.7, 531.6 and 535.8 eV (Fig. S4b). The BE at 531.6 eV is assigned to –C(O)OH groups in HTC-B100-400 material, whereas after acid treatment increased intensity of this BE was observed and it could be attributed to the oxygen found in sulfonic groups (-S=O),[3] thereby successful transformation of surface oxygenated functional groups to sulfonic –SO$_3$H and sulfate SO$_4^{2-}$ groups is confirmed. The following BEs are assigned to 532.7 eV (-C=O) and 533.7 eV (C-O-H). A BE of 535.8 eV is proposed to be associated with chemisorbed H-O-H.

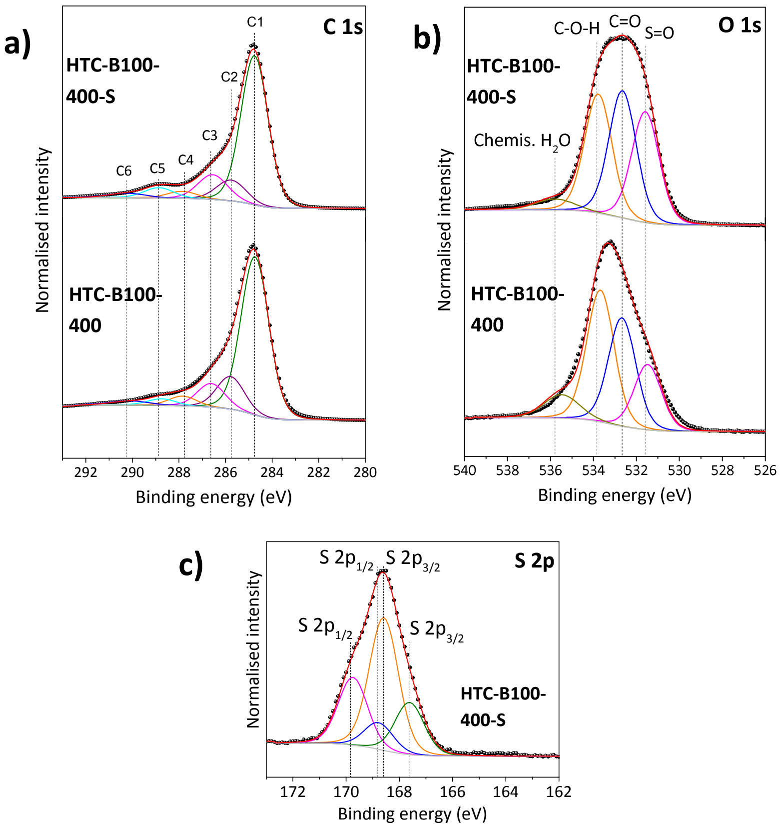

Figure S4 Narrow scans for a) C 1s, b) O 1s of HTC-B100-400 and HTC-B100-400-S and c) S 2p spectra of HTC-B100-400-S.

S 2p photoelectron envelope breakdown into S 2p$_{3/2}$-S 2p$_{1/2}$ spin orbital splitting, the existence of two doublets confirming the evidence of two chemically different sulphur species: a lower energy doublet S 2p$_{3/2}$ at 168.6 eV and 167.6 eV and a higher energy doublet S 2p$_{1/2}$ at 169.7 eV and 168.8 eV. Usually a higher binding energies (BEs) between 168.5 and 169.0 eV are attributed to sulphate functionalities (–SO$_4^{2-}$)[4] whereas BEs between 167.4 and 168.5 eV are assignment to sulfonic (–SO$_3$H) groups.[1,5] In contrast, no C-SH sulphide functional groups, which are attributed to the lower BE (164.0 eV)[6], are not present in S 2p region.

Table S4 Binding energies and peak areas of C 1s core level of all catalysts and HTC-B100-400 material.

	C1 [C=C]		C2 [C-C/C-H]		C3 [C-OH/C-O]		C4 [C=O]		C5 [O-C=O]		C6 [π-π*]	
Catalyst	**B.E. (eV)**	**Peak area (%)**	**B.E. (eV)**	**Peak area (%)**	**B.E. (eV)**	**Peak area (%)**	**B.E. (eV)**	**Peak area (%)**	**B.E. (eV)**	**Peak area (%)**	**B.E. (eV)**	**Peak area (%)**
HTC-B100-350-S	284.8	65.5	285.8	10.7	286.6	12.2	287.9	0.5	288.7	10.1	290.3	1.0
HTC-B100-400	284.7		285.8	70.5	286.6	17.9	287.8	5.6	288.7	3.6	290.0	2.0
HTC-B100-400-S	284.8	67.0	285.8	10.0	286.6	12.0	287.9	3.4	288.8	4.9	290.3	2.6
HTC-B100-550-S	284.8	74.6	285.8	6.7	286.6	9.3	287.9	1.8	288.8	5.5	290.3	2.1
HTC-B100-700-S	284.8	71.7	285.8	5.2	286.6	10.7	287.8	-	288.7	12.4	-	-

HTC-B0-400-S	284.7	67.4	285.8	13.6	286.6	9.9	287.8	4.1	288.7	2.6	290.0	2.4

Table S5 Full-width at half-maximum (FWHM) values of C 1s core level spectra.

	C1 [C=C]		C2 [C-C/C-H]		C3 [C-OH/C-O]		C4 [C=O]		C5 [O-C=O]		C6 [π-π*]	
Catalyst	**B.E. (eV)**	**FWHM**	**B.E. (eV)**	**FWHM**	**B.E. (eV)**	**FWHM**	**B.E. (eV)**	**FWHM**	**B.E. (eV)**	**FWHM**	**B.E. (eV)**	**FWHM**
HTC-B100-350-S	284.8	1.40	285.8	1.40	286.6	1.40	287.9	1.40	288.7	1.40	290.3	1.80
HTC-B100-400	284.7	1.40	285.8	1.50	286.6	1.50	287.8	1.50	288.7	1.50	290.0	1.90
HTC-B100-400-S	284.8	1.40	285.8	1.50	286.6	1.50	287.9	1.50	288.8	1.50	290.3	1.90
HTC-B100-550-S	284.8	1.30	285.8	1.40	286.6	1.40	287.9	1.40	288.8	1.40	290.3	1.80
HTC-B100-700-S	284.8	1.30	285.8	1.30	286.6	1.30	287.8	1.30	288.7	1.30	-	-
HTC-B0-400-S	284.7	1.40	285.8	1.40	286.6	1.40	287.8	1.40	288.7	1.40	290.0	1.90

Table S6 Binding energies (B.E.) and peak areas of O 1s core level of all catalysts and HTC-B100-400 material.

	C-OH		**C=O**		**S=O or C(O)OH**		**Chemisorbed H_2O**	
Catalyst	**B.E. (eV)**	**Peak area (%)**	**B.E. (eV)**	**Peak area (%)**	**B.E. (eV)**	**Peak area (%)**	**B.E. (eV)**	**Peak area (%)**
HTC-B100-350-S	533.6	34.2	532.7	23.9	531.8	39.0	535.3	3.2
HTC-B100-400	533.7	39.6	532.7	29.2	531.5	24.0	535.4	7.1
HTC-B100-400-S	533.7	32.0	532.7	34.1	531.6	29.8	535.8	4.1
HTC-B100-550-S	533.8	37.8	532.5	38.3	531.6	22.1	535.7	1.9
HTC-B100-700-S	533.6	6.8	532.8	35.2	531.7	57.9	-	-
HTC-B0-400-S	533.8	32.6	532.7	33.8	531.5	26.8	535.4	6.6

Table S7 Full-width at half-maximum (FWHM) values of O 1s core level spectra.

	C-OH		**C=O**		**S=O or C(O)OH**		**Chemisorbed H_2O**	
Catalyst	**B.E. (eV)**	**FWHM**	**B.E. (eV)**	**FWHM**	**B.E. (eV)**	**FWHM**	**B.E. (eV)**	**FWHM**
HTC-B100-350-S	533.6	1.50	532.7	1.50	531.8	1.50	535.3	2.10
HTC-B100-400	533.7	1.50	532.7	1.50	531.5	1.50	535.4	2.10
HTC-B100-400-S	533.7	1.50	532.7	1.50	531.6	1.50	535.8	1.60
HTC-B100-550-S	533.8	1.50	532.5	1.50	531.6	1.50	535.7	2.10
HTC-B100-700-S	533.6	1.40	532.8	1.40	531.7	1.40	-	-
HTC-B0-400-S	533.8	1.50	532.7	1.50	531.5	1.50	535.4	2.10

Table S8 Binding energies (B.E.) and peak areas of S 2p core level of sulfonated catalysts.

	S $2p_{3/2}$				S $2p_{1/2}$			
Catalyst	B.E. (eV)	Peak area (%)	B.E. (eV)	Peak area (%)	B.E. (eV)	Peak area (%)	B.E. (eV)	Peak area (%)
HTC-B100-350-S	168.7	34.1	167.8	32.1	169.9	17.5	168.9	16.4
HTC-B100-400-S	168.6	47.5	167.6	18.7	169.7	24.3	168.8	9.5
HTC-B100-550-S	168.7	36.5	167.5	29.7	169.9	18.7	168.6	15.2
HTC-B0-400-S	168.7	43.8	167.7	22.4	169.8	22.4	168.9	11.4

Table S9 Full-width at half-maximum (FWHM) values of S $2p_{3/2}$ and S $2p_{1/2}$ core level spectra for sulfonated catalysts.

	S $2p_{3/2}$				S $2p_{1/2}$			
Catalyst	B.E. (eV)	FWHM	B.E. (eV)	FWHM	B.E. (eV)	FWHM	B.E. (eV)	FWHM
HTC-B100-350-S	168.7	1.30	167.8	1.30	169.9	1.30	168.9	1.30
HTC-B100-400-S	168.6	1.30	167.6	1.30	169.7	1.30	168.8	1.30
HTC-B100-550-S	168.7	1.40	167.5	1.40	169.9	1.40	168.6	1.40
HTC-B0-400-S	168.7	1.40	167.7	1.40	169.8	1.40	168.9	1.40

5. Addition of borax increases the HTC material yield by enhanced isomerization/dehydration/polymerization reactions

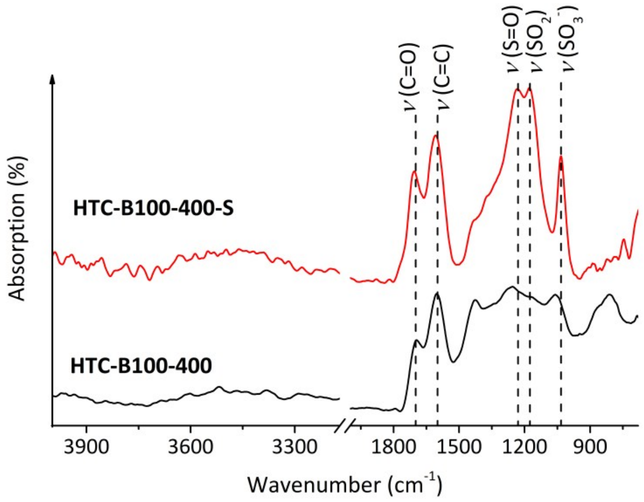

Figure S5 FT-IR spectrum of the HTC-B100-400 sample and HTC-B100-400-S sample after treatment with H_2SO_4.

6. SEM analysis of HTC before and after sulfonation

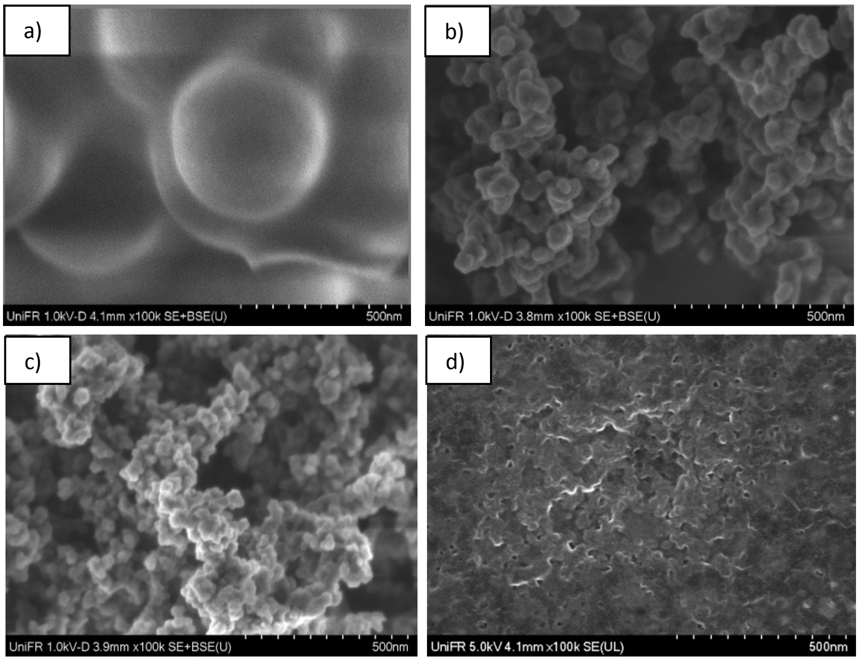

Figure S6 SEM images of a) HTC-B0-400, b) HTC-B50-400 c) HTC-B100-400 and d) HTC-B300-400 material.

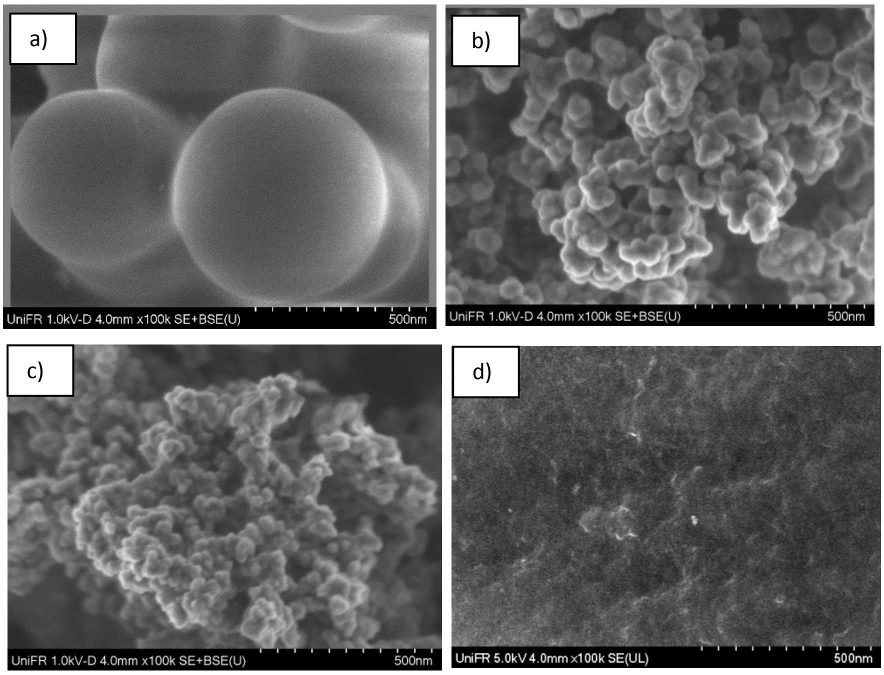

Figure S7 SEM images of a) HTC-B0-400-S, b) HTC-B50-400-S, c) HTC-B100-400-S and d) HTC-B300-400-S catalysts.

7. Dispersion of HTC-B100-400 and HTC-B100-400-S in water

Figure S8 Dispersion of HTC-B100-400 in water before (left) and after (right) sulfonation (HTC-B100-400-S). Both materials were dispersed into water through sonification. The mixtures were kept statically for about 1 h before taking the digital picture.

8. Pore size distribution and N_2 adsorption-desorption isotherms for different HTC materials after sulfonation.

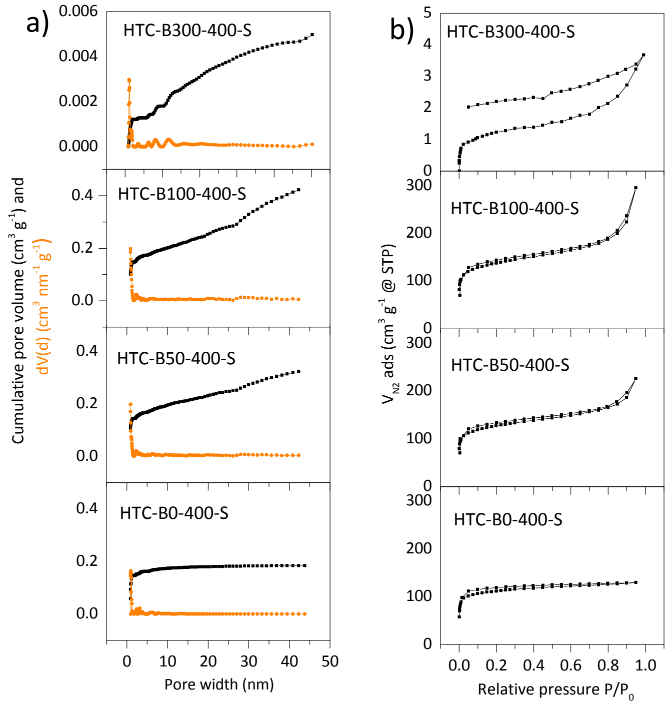

Figure S9 a) Pore size distribution and cumulative pore volume, b) N_2 adsorption –desorption isotherms for different sulfonated HTC materials.

9. Esterification with different molar ratios of acetic acid and ethanol.

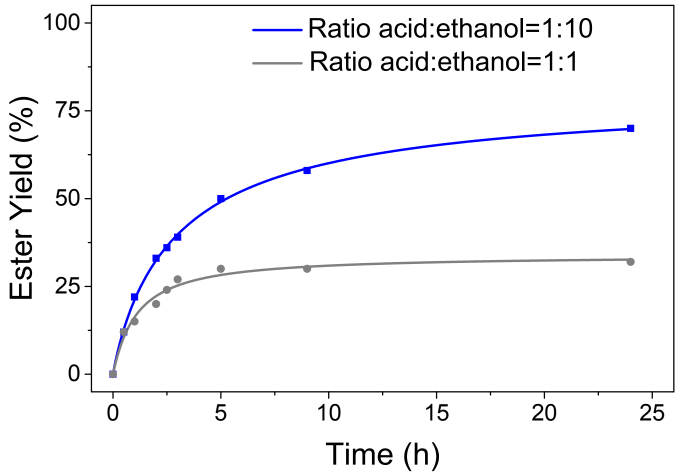

Figure S10 Comparison of esterification reaction with molar ratio of acetic acid:EtOH=1:10 and acetic acid:EtOH=1:1

1. SEM analysis of the spent catalyst after 5 catalytic cycles

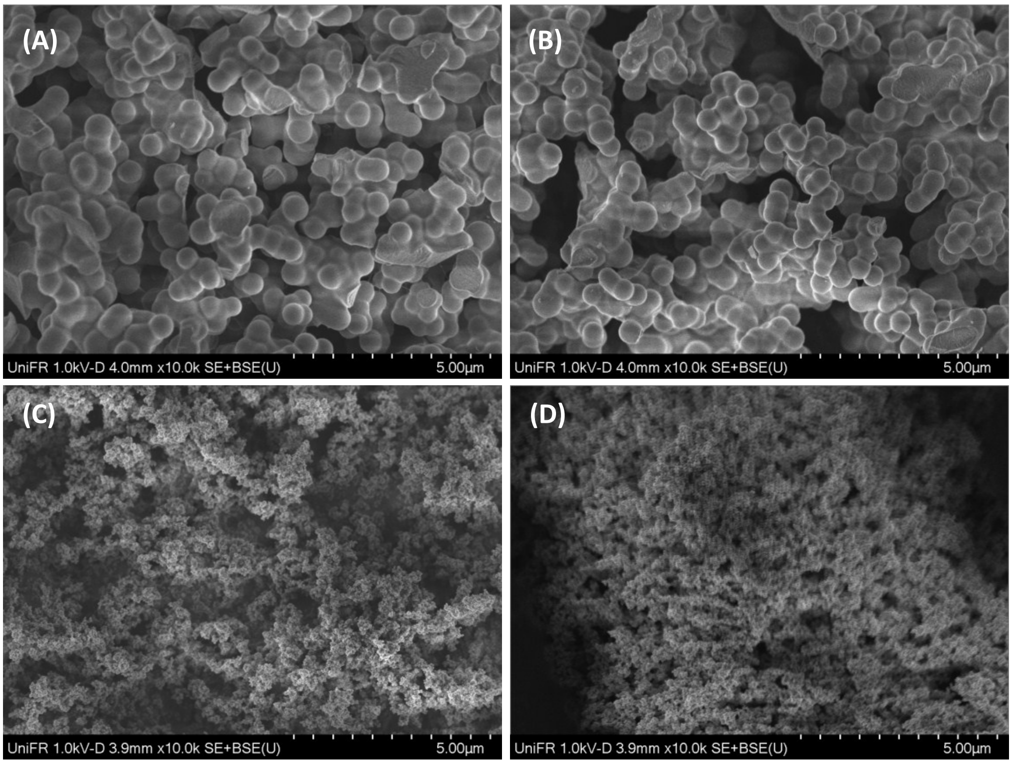

Figure S11 SEM images of HTC-B0-400-S catalyst a) fresh and b) spent in esterification of PA and HTC-B100-400-S catalyst c) fresh and d) spent in esterification of PA.

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