

Electronic Supplementary Information

One pot conversion of glucose to ethyl levulinate over a porous hydrothermal acid catalyst in green solvents

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1. HTC-400-S catalyst synthesis details

0.1 g of borax ($\geq 99\%$ $\text{Na}_2\text{B}_4\text{O}_7$) was dissolved in 15 mL distilled water with 6.5 g of D-glucose ($\geq 99.5\%$ $\text{C}_6\text{H}_{12}\text{O}_6$) in a high purity borosilicate glass autoclave insert. This was then placed in a Teflon-lined autoclave and heated to $180\text{ }^\circ\text{C}$ for 8 h. The obtained HTC solid products were washed by immersion firstly with H_2O and then with ethanol (3 x 100 mL for one day). Materials were dried under vacuum oven overnight at $80\text{ }^\circ\text{C}$ and then thermally carbonized at $400\text{ }^\circ\text{C}$ under N_2 atmosphere for 5 h. HTC-B-400 material was treated with conc. 98 % w/w H_2SO_4 (1 g HTC-400 material/10 mL H_2SO_4) at $80\text{ }^\circ\text{C}$ under an N_2 atmosphere for 4 h. The material was subsequently washed with triple distilled deionized water until the washings were neutral. The acid-functionalized carbons (denoted as HTC-400-S) were then conditioned firstly in boiling toluene ($150\text{ }^\circ\text{C}$, 4 h) and water ($100\text{ }^\circ\text{C}$, 3 h) using a Soxhlet extraction setup. This was performed to remove any physisorbed sulphate or sulfuric acid. Following conditioning materials were dried under vacuum overnight at $80\text{ }^\circ\text{C}$. In comparison HTC-S catalyst was synthesized without addition of structure directive agent sodium borate and without post-thermal treatment. The sulphonation procedure was performed under the same reaction conditions as HTC-400-S.

The amount of acid groups on the HTC-400-S were initially determined through back titration. The material was stirred at room temperature for 24 h in NaOH (aq) (0.03 M, 25 mL) and then titrated with HCl (aq) (0.02 M) until endpoint ($\text{pH} = 7$).

2. N_2 sorption analysis of HTC-400-S catalyst

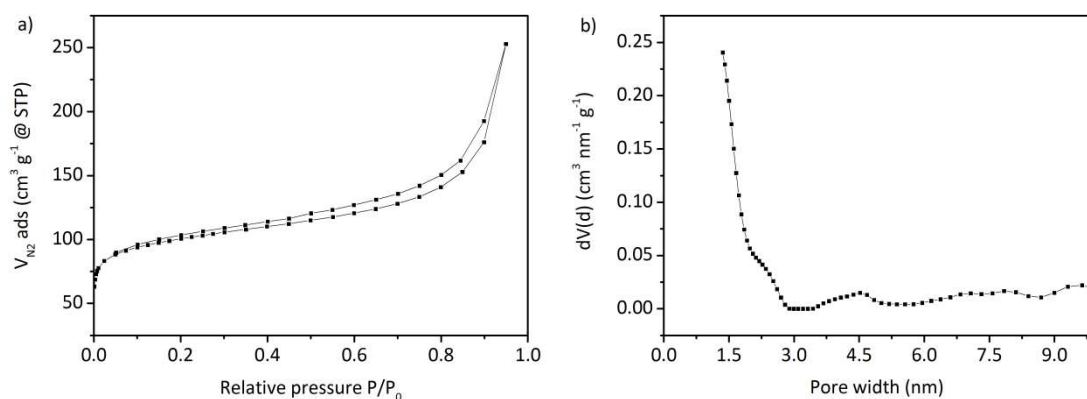


Figure S1 a) N_2 adsorption-desorption isotherms and b) pore size distribution for a HTC-400-S determined by QSDFT model.

Table S1 N₂ sorption and CHNS elemental analysis of fresh and spent HTC-400-S after 4th catalytic cycles (as investigated in different solvents). Results of leached S in the product solution after 1st catalytic cycle in different solvents analysed by CHNS analysis and ICP-OES.

Catalyst	S content ^{a)} (wt.%)	C content ^{a)} (wt.%)	S _{BET} ^{b)} (m ² /g)	V _{micro} ^{c)} (cm ³ /g)	V _{meso} ^{c)} (cm ³ /g)	Leached S in product solution ^{d)} (wt.%)
Fresh HTC-400-S	3.6	60.8	506	0.15	0.27	/
Spent HTC-400-S in EtOH ^{e)}	0.7	71.0	207	0.01	0.16	0.9
Spent HTC-400-S in EtOH/GVL ^{e)}	1.1	69.6	185	0.06	0.20	0.1
Spent HTC-400-S in EtOH/GLY ^{e)}	1.0	71.2	188	0.01	0.19	0.2

^{a)} Sulphur and carbon content determined by CHNS elemental analysis, ^{b)} Specific surface area from BET method, ^{c)} Pore size characteristics obtained via the QSDFT model, ^{d)} Sulphur content in the product mixture after 1st catalytic cycle determined by ICP-OES and CHNS analysis, ^{e)} Spent HTC-400-S was after each cycle washed with boiling acetone for 2 h and dried at 80 °C for 12 h.

3. XPS of HTC-400-S catalyst

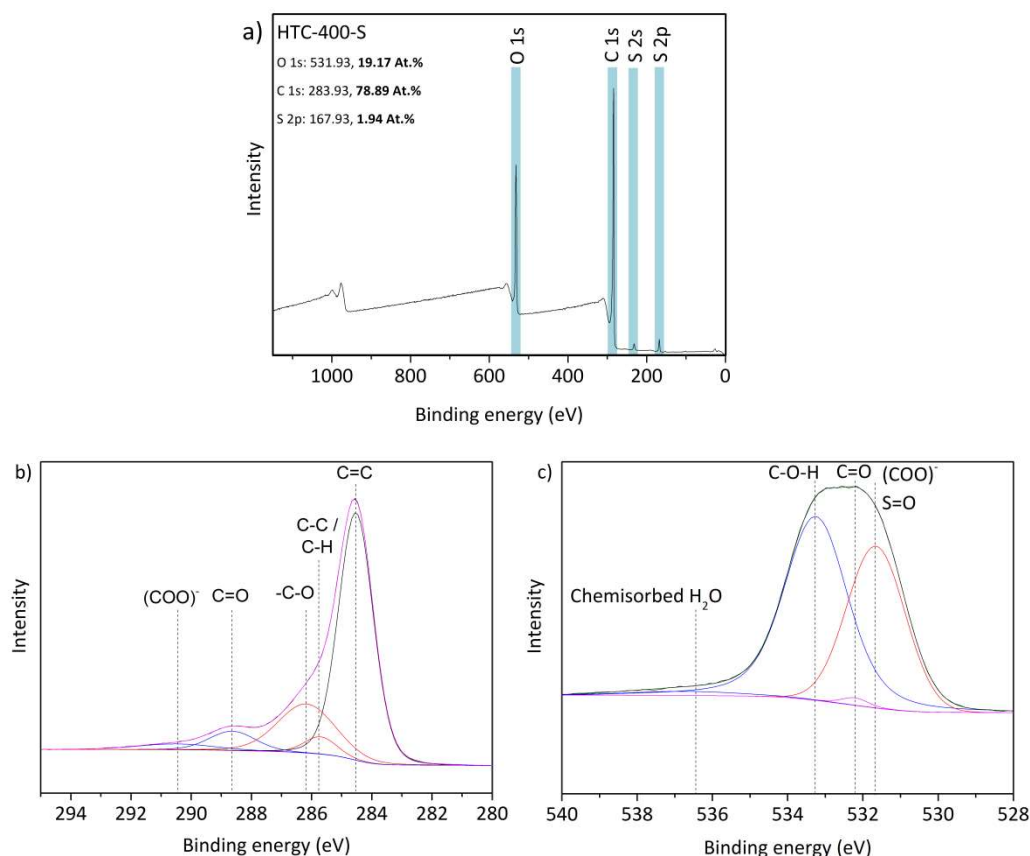


Figure S2 a) Survey photoelectron spectra of HTC-400-S; Core level spectra of b) C1s, and c) O1s for HTC-400-S.

X-ray photoelectron spectroscopy (XPS) measurements were performed using a ThermoScientific K-Alpha⁺ X-ray Photoelectron Spectrometer. All samples were analyzed using a microfocused, monochromated AlK_α X-ray source (1486.68 eV; 400 μm spot size). The analyzer had a pass energy of 200 eV (survey), and 50 eV (high resolution spectra), respectively. To prevent any localized charge buildup during analysis the K-Alpha⁺ charge compensation system was employed at all measurements. The samples were mounted on conductive carbon tape and the resulting spectra

analysed using the CasaXPS software (v.2.3.19). The binding energies were calibrated by taking the adventitious C1s binding energy (284.8 eV) as a reference.

Analysis of the C1s and O1s photoelectron core states revealed BEs associated with C(O)OH groups (Fig. S6b, c). BEs in the C1s core state at 286.2 eV corresponds to C-OH, 288.6 eV and 290.5 eV are associated with carbon atoms bonded through double bonds (R-HC=O, R₂-C=O, R-C(OH)=O, R-C(OR)=O) to oxygen. O1s core state with a binding energy of 531.3 eV is corresponding to chemical state of oxygen in sulfonic groups (-S=O).¹ Higher BEs are assigned to 532.0 eV (-C=O) and 532 eV (C-O-H).

4. Acid-catalysed conversion of glucose to EL - Reaction and product analysis details

As an exemplary description of the catalyst testing experiment set-up, 50 mL sealed stainless steel batch autoclave reactor (with a glass insert) was charged with 0.5 g (2.4 wt.%) glucose, 20.0 g EtOH and 0.1 g (0.5 wt.%) HTC-400-S. Testing in different solvent systems was performed in EtOH/GVL or EtOH/GLY mass ratio of 1.86. After reaction completion, the reactor was quickly cooled to RT in a water bath before opening.

Analysis of the recovered product solution was performed with an Agilent gas chromatograph (GC) 7890A equipped with an FID detector, and DB-5ms capillary column (30.0 m × 250.0 μm × 0.5 μm) using Helium as carrier gas. 0.4 μL of the sample solution was injected into the GC injector port, which was set at 250 °C and the detector temperature was 275 °C. The GC oven was programmed with the increasing starting temperature from 60 to 240 °C with a 10 C/min ramp rate. Commercially available standards were used for calibration and to identify the corresponding products in the gas chromatograph.

EL and side products were confirmed by Agilent gas chromatograph (GC) 7890A coupled with mass spectrometry (GC-MS) and DB-5ms capillary column (30.0 m × 250.0 μm × 0.5 μm). 0.4 μL of the sample was injected to the inlet at 280 °C. The oven program started at 35 °C with 6 min holding time and was heated with 10 °C/min to 180 °C with holding time of 5 min. Split ratio was set to 15:1 and detector temperature was 250 °C.

Glucose was detected by high performance liquid chromatography (HPLC) using a Hewlett Packard Series 1100 HPLC. The HPLC was coupled to an Alltech 3300 Evaporative Light Scattering detector (ELSD). Separation was performed on an Agilent Zorbax NH₂ column of 250 mm length, internal diameter of 4.6 mm and particle size of 5 μm. The injection volume was 10 μL and the flow rate was 1 mL/min with a total run time of 15 minutes. A mobile phase of acetonitrile:water = 75:25 was used and the column oven temperature was kept at 30 °C. Standard of glucose was used to generate a standard curve for quantification.

Conversion of glucose was calculated using the Eq. (1), where C_{G,0} and C_{G,1} are the initial mol concentrations of glucose and moles of converted glucose, respectively.

$$\text{Glucose conversion (mol. \%)} = C_{G,1}/C_{G,0} \times 100 \% \quad (1)$$

a) In EtOH

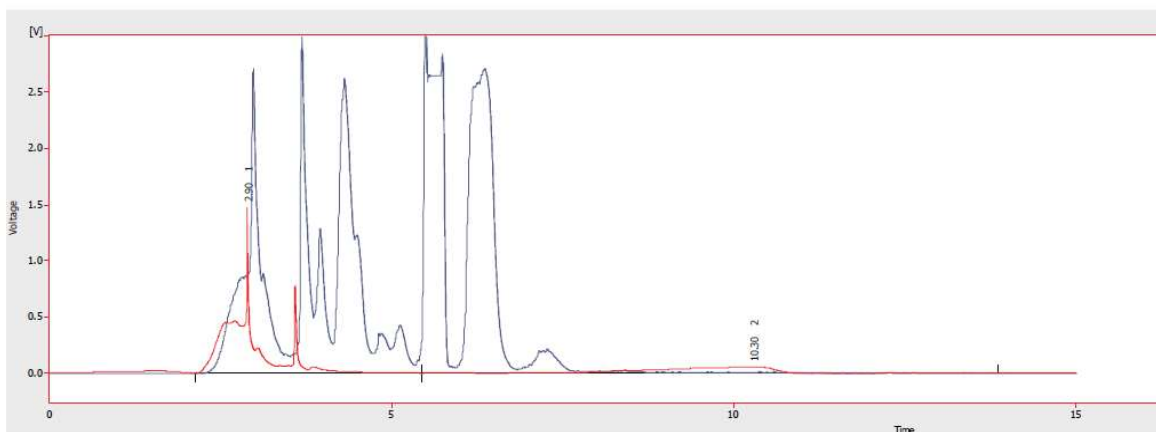
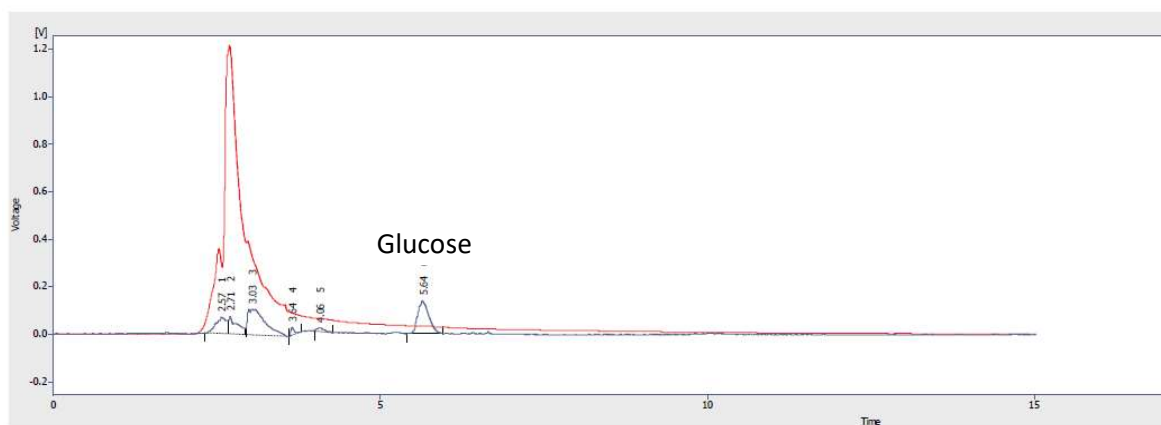
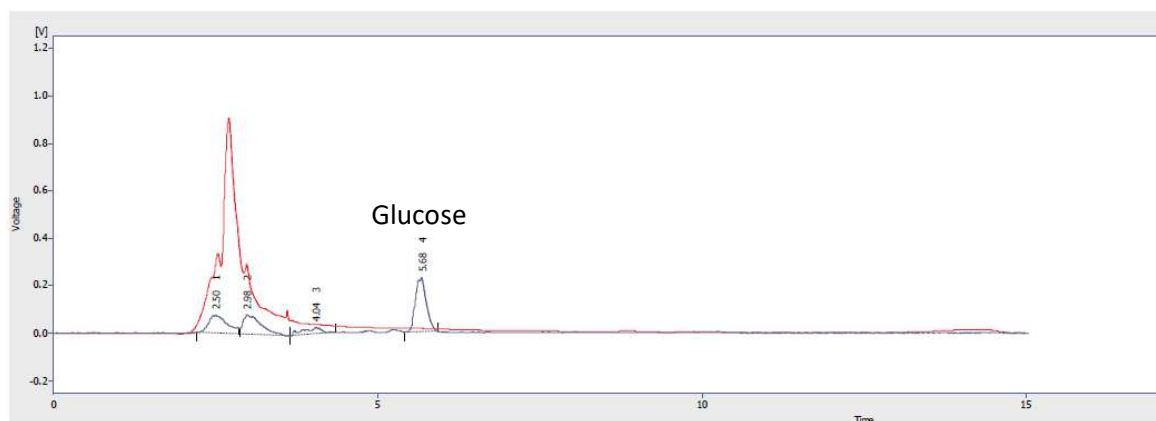


Figure S3 HPLC analysis of glucose conversion to EL in a) EtOH, b) EtOH/GVL and c) EtOH/GLY as a solvent after 1 h reaction time at 200 °C. Detection of glucose in solvent mixture EtOH/GLY was not possible due to the co-eluting components.

The EL yield (in mol.%) from glucose was calculated using Eq. (2), where C_G and C_{EL} are the initial molar concentrations of glucose and obtained mole concentration of EL, respectively.

$$EL \text{ yield (mol. \%)} = C_{EL}/C_G \times 100 \%$$

(2)

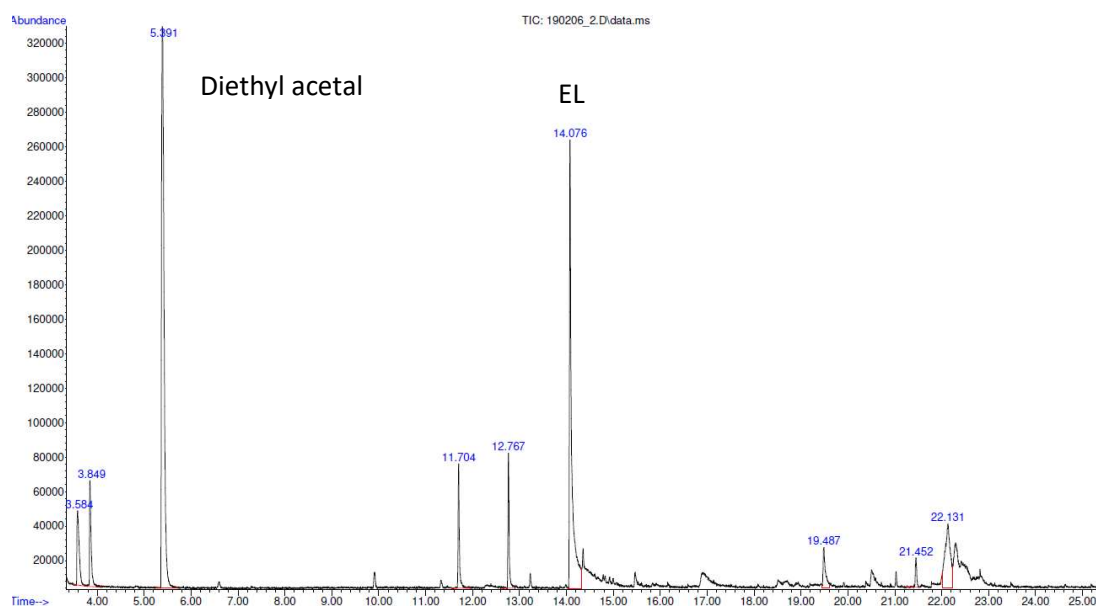


Figure S4 GC chromatogram of the reaction mixture obtained from the catalytic conversion of glucose by HTC-400-S in EtOH at 200 °C and 12 h.

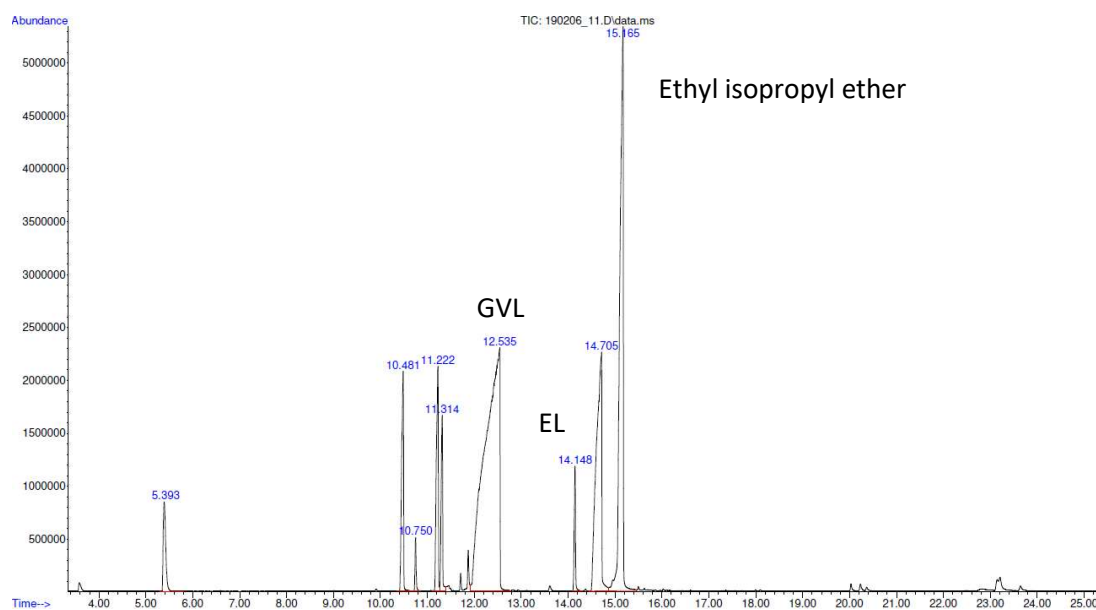


Figure S5 GC chromatogram of the reaction mixture obtained from the catalytic conversion of glucose by HTC-400-S in EtOH/GVL solvent mixture at 200 °C and 12 h.

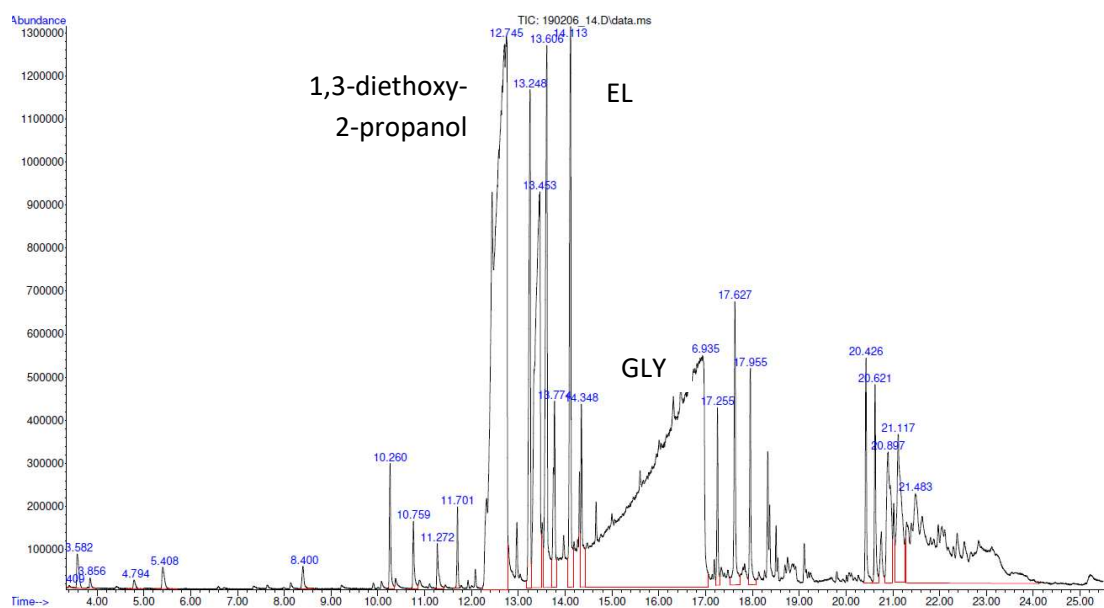


Table S2 Synthesis of ethyl levulinate (EL) from fructose and glucose with metal oxides and sulfonated carbonaceous catalysts in comparison to HTC-400-S catalyst and its non-porous version HTC-S catalyst.

Catalyst	BET (m ² /g)	Active sites (mmol/g)	Reaction conditions	Cat. based on glucose/fructose (wt.%)	EL yield (mol.%)	Stability	Reference
TiO ₂ -SO ₃ H nanoparticles	238	0.3	Glucose, MeOH, 175 °C, 1 h	56	61	Reported for fructose conversion: 80-70 mol.% after 5 cycles	2
SO ₄ ²⁻ /ZrO ₂	122	0.6	Glucose, EtOH, 200 °C, 3h	50	30	Stable in 5 cycles	3
SZ/SBA-15	367	0.4	Glucose, EtOH, 140 °C, 24 h	50	25	Stable in 3 cycles	4
SO ₄ ²⁻ /ZrO ₂	179	1.2	Glucose, EtOH, 140 °C, 24 h	30	13	Reported for fructose conversion: 56-53 mol.% after 3 cycles	5
ZrY6 (zirconia zeolite)	656	1.0	Glucose, MeOH, 180 °C, 3 h	60	68	Stable in 5 cycles	6
AC-Fe-SO ₃ H	9	4.0	Glucose, EtOH, 200 °C, 3h	50	19	Reported for fructose conversion: 58-46.1 mol.% after 5 cycles	7
Poly(p-styrenesulfonic acid)-grafted carbon nanotubes	Not reported	2.9	Fructose, EtOH, 120 °C, 24h	40	84	Reported for fructose conversion 84-69 mol.% after 5 cycles	8
SO ₃ H-SBA-15-PS (post-synthetic grafting SBA 15)	589	0.8	Glucose, EtOH, 140 °C, 24 h	30	0	Reported for fructose conversion: 56-53 mol.% after 3 cycles	5
C/SBA (ordered mesoporous silica + toluenesulfonic acid)	238	1.9	Fructose, EtOH+H ₂ O, 140 °C, 6 h	17	16	Reported for fructose conversion 16-8 mol.% after 1 cycle	9
C/MCF (mesostructurecell. foam + toluenesulfonic acid)	198	2.3	Fructose, EtOH+H ₂ O, 140 °C, 6 h	17	11	Reported for fructose conversion 11 -8 mol.% after 1 cycle	9
Fe ₃ O ₄ @C-SO ₃ H	30	1.4	Glucose, EtOH, 120 °C, 12 h	79	13	Reported for fructose conversion to 5-ethoxymethylfurfural: 67.8-58.4 mol.% in 6 cycles	10
Ar-SO ₃ H-SBA-15 (arenesulfonic mesostructured silica)	712	0.9	Fructose, EtOH+8.3 vol.% DMSO, 116 °C, 24h	82	38	Reduced activity probably due to the humin after 4 cycles	11
HTC-400-S	506	2.6	Glucose/Fructose, EtOH+GLY (13:7 v ratio), 200 °C, 6 h	20	37/45	Reduced activity after 4 cycles: 37-16 mol.%	
HTC-S	44	2.9	Glucose/Fructose, EtOH+GLY (13:7 v ratio), 200 °C, 6 h	20	28/36	Deactivated after 1 run	

5. SEM images of fresh and spent HTC-400-S catalyst

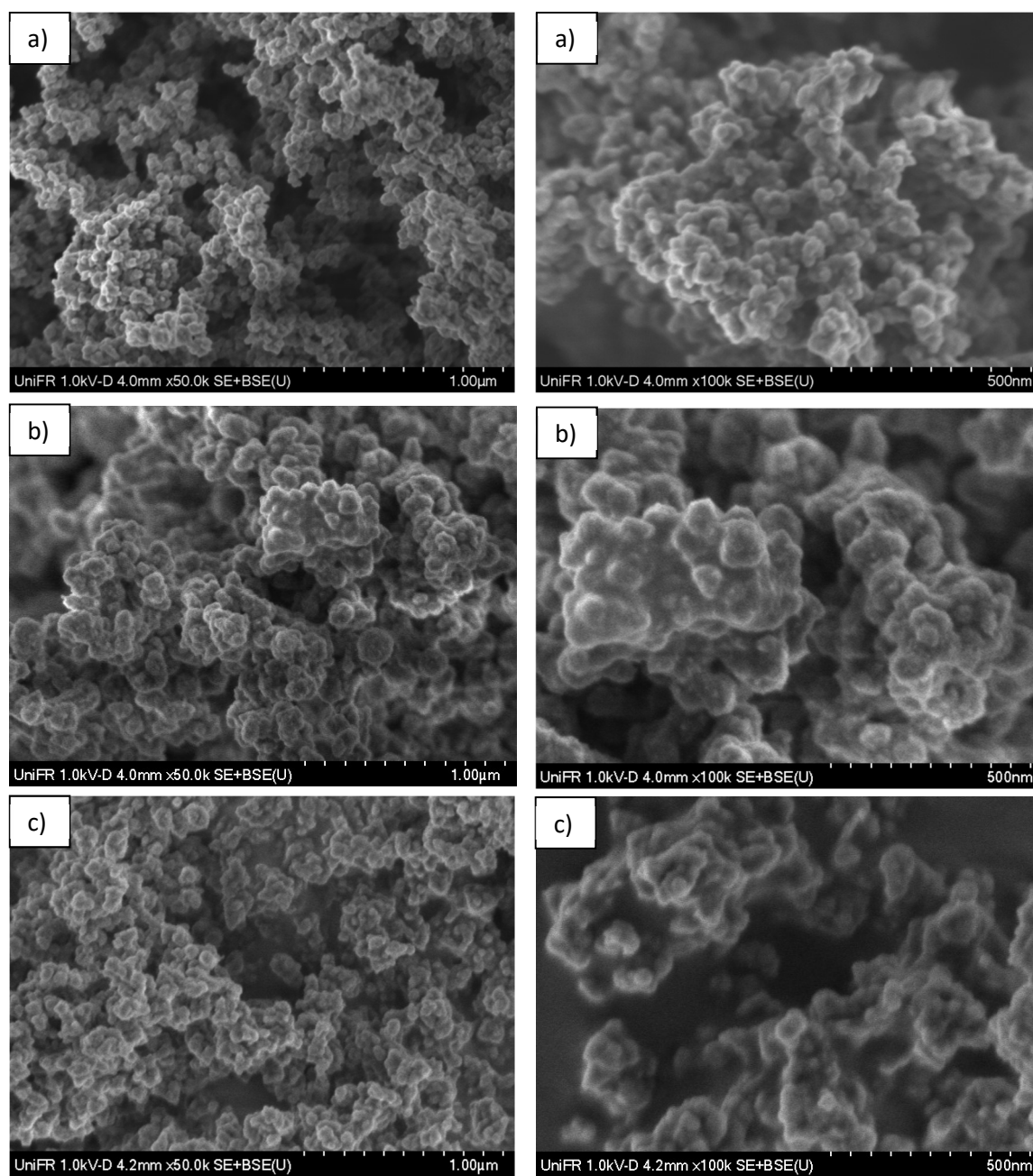


Figure S8 SEM of a) fresh HTC-400-S, b) spent HTC-400-S in EtOH and c) spent HTC-400-S in EtOH/GVL mixture.

References

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