Electronic Supplementary Material (ESI) for Green Chemistry

Supporting Information

Decomposition of Biomass-derived Hexose Sugars to Levulinic Acid Using Graphene Oxide Catalysts with Brønsted Acid Sites

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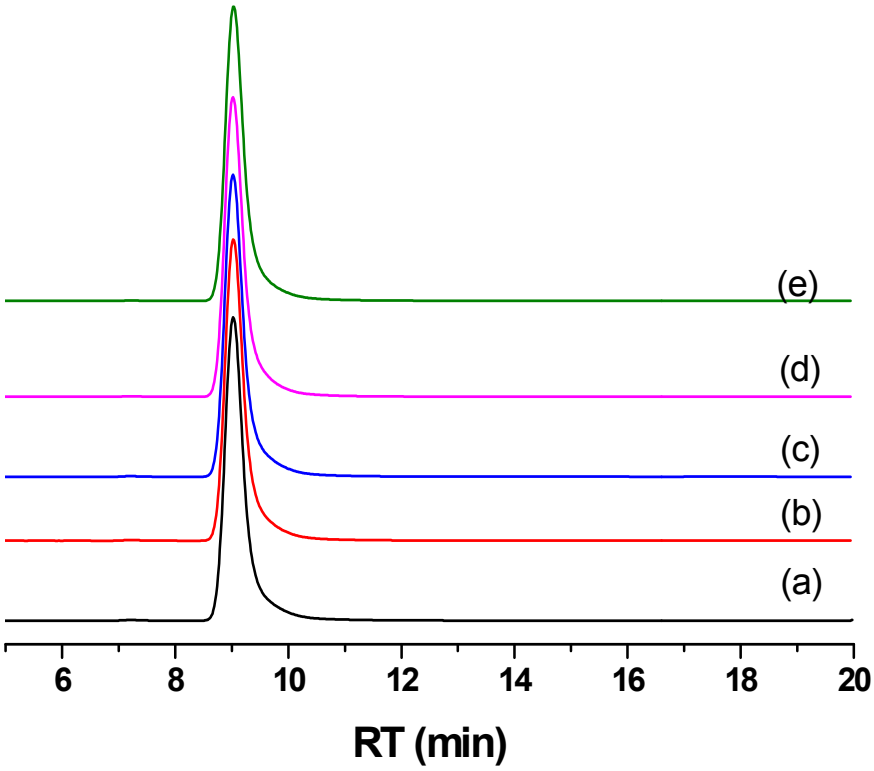


Figure S1. HPLC chromatogram (a) 5% auqeous glucose solution, (b) GO, (c) Carbon, (d) AC-SO_3H and (e) GO-SO_3H absorbed 5% glucose solution, respectively.

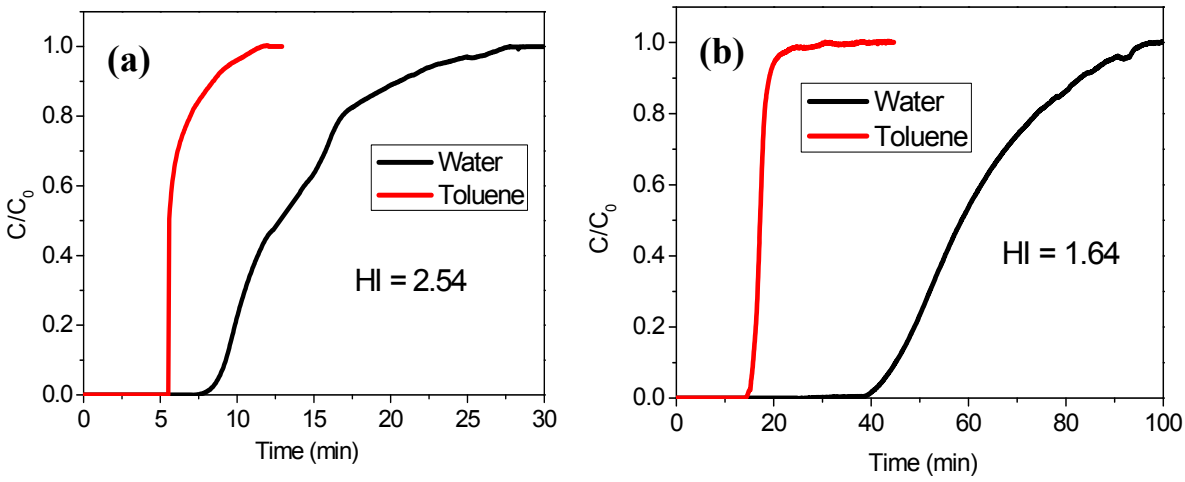


Figure S2. Breakthrough curves of equimolar water and toluene mixture in helium on (a) GO-SO_3H and (b) AC-SO_3H catalysts at 35^{o}C. Before test, catalysts were pretreated at 150 ^{o}C for 3 h with 15cc/min of helium.

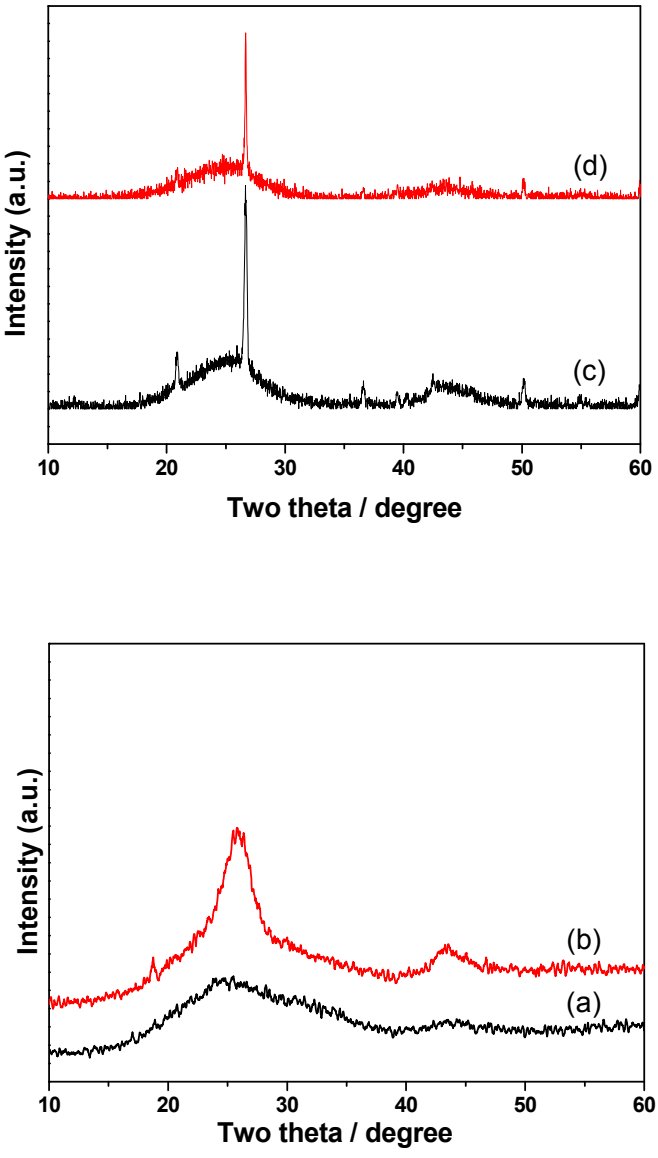


Figure S3. X-ray diffraction patterns of (a) Graphene oxide (GO), (b) SO_3H functionalized graphene oxide (GO-SO_3H), (c) activated carbon (AC) and (d) SO_3H functionalized activated carbon (AC-SO_3H), respectively.

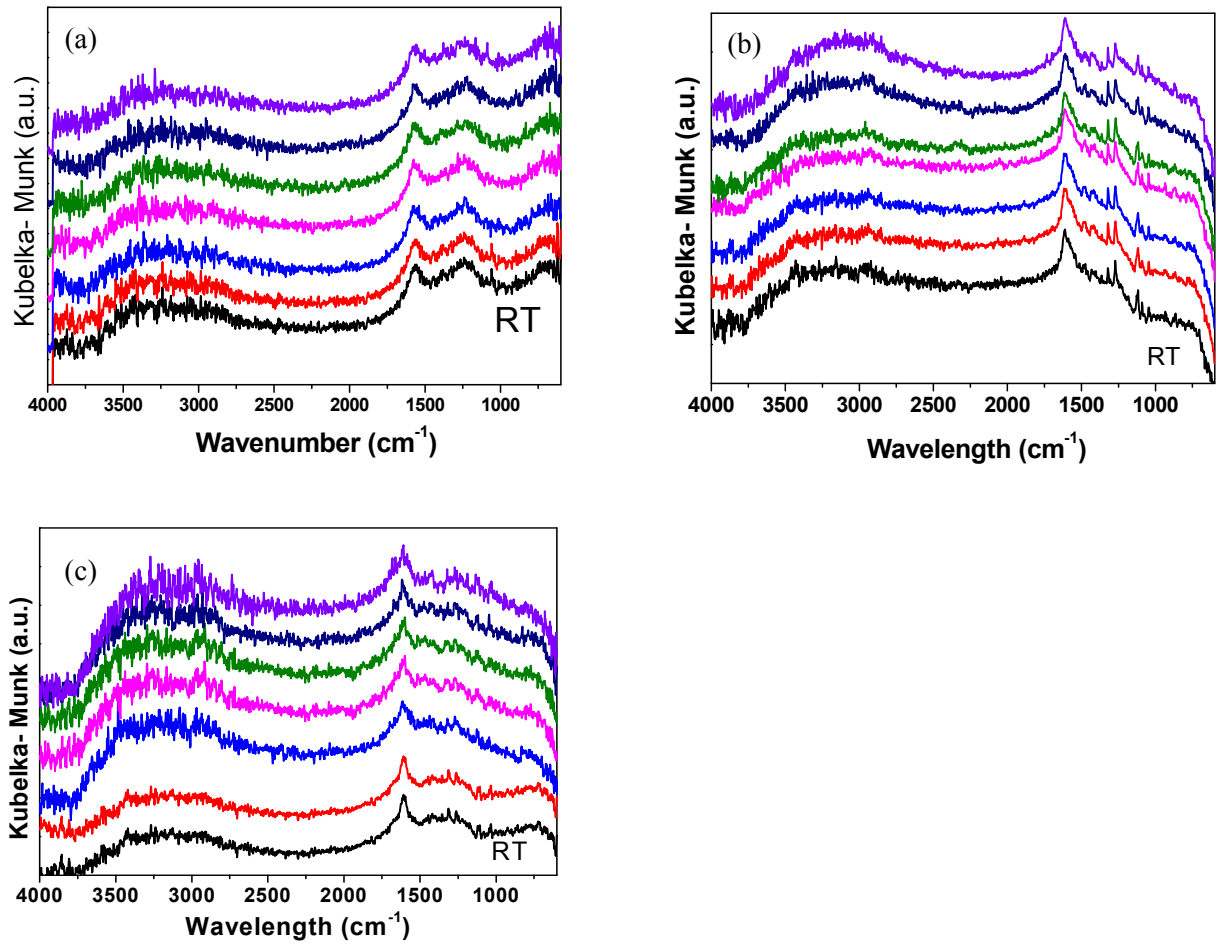


Figure S4. Diffuse Reflectance(DR) FT-IR spectra of (a) Graphene oxide (GO), (b) SO_3H functionalized graphene oxide (GO-SO_3H) and (c) SO_3H functionalized activated carbon (AC-SO_3H), respectively. The DR FT-IR analysis was performed with 500 scans and a resolution of 4cm^{-1} . The spectra were presented by Kuelka-Munk funciton. Spectra was obtained with 50^oC interval from second to top lines in (a), (b) and (c)..

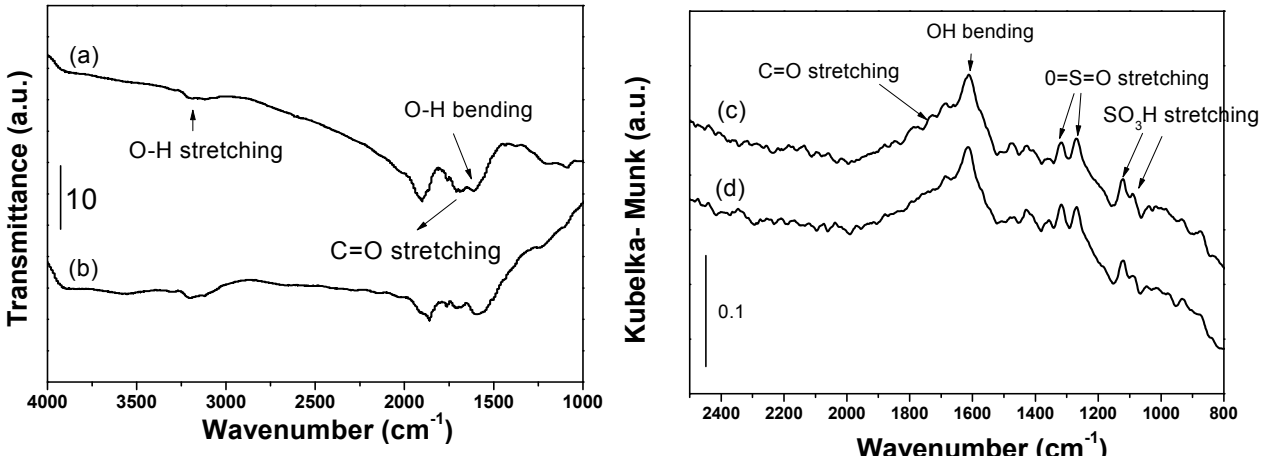


Figure S5. Tranmittance and Diffuse Reflectance(DR) FT-IR spectra of (a) and (c) as-synthesized SO_3H functionalized graphene oxide (GO-SO_3H), and (b) and (d) thermally treated SO_3H functionalized graphene oxide (GO-SO_3H) at 300 ^oC for 12 h, respecitvely. The DR FT-IR analysis was performed with 500 scans and a resolution of 4 cm^{-1} . The spectra were presented by Kuelka-Munk funciton.

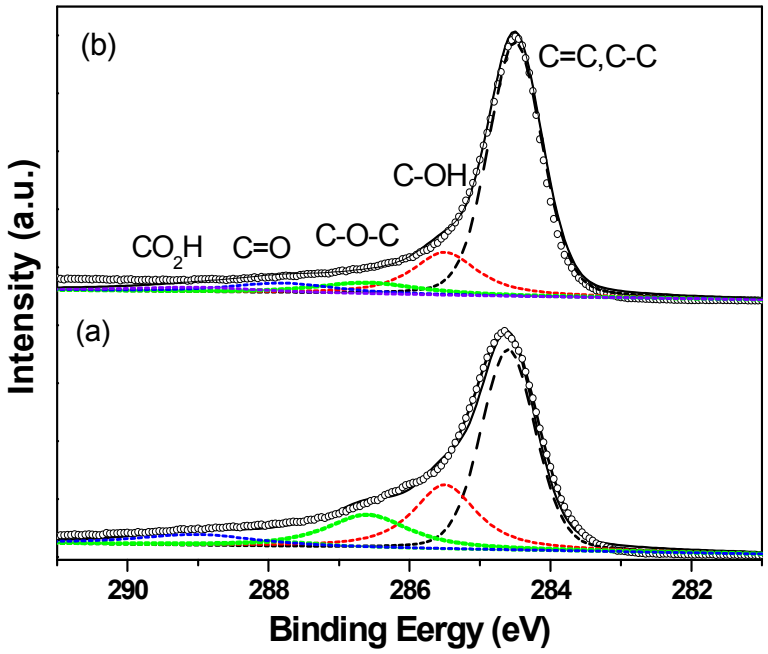


Figure S6. XPS profile of the C1s region of: (a) GO and (b) GO-SO_3H. The XPS peaks were fitted to Voigt functions, after performing a linear background subtraction (XPSPEAK Version 4.1). Color segmented lines indicate the contributions from various funcational groups obtained by deconvolution.

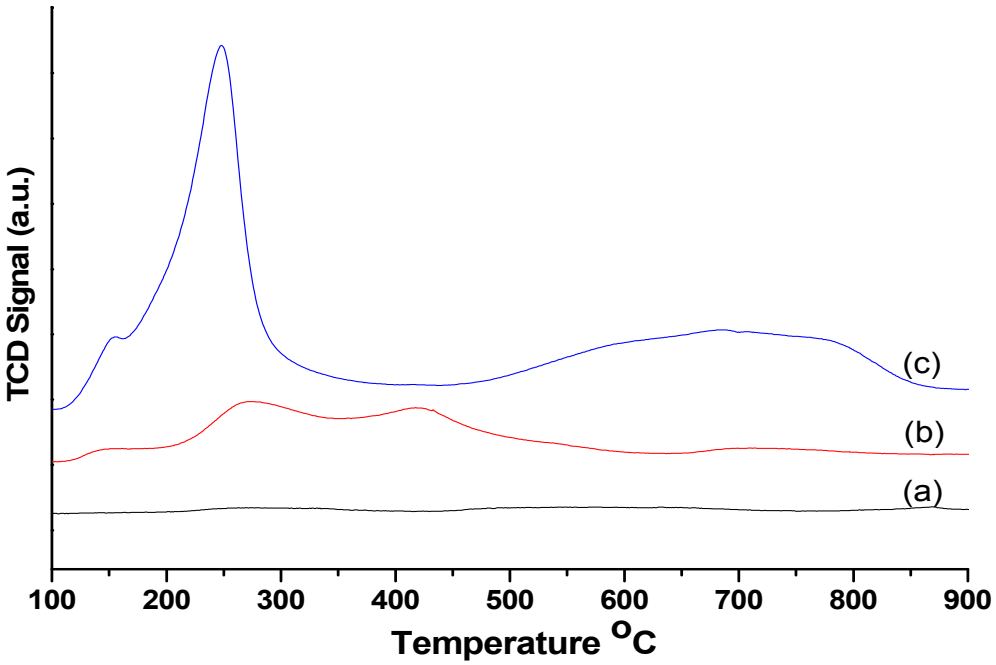


Figure S7. NH_3-TPD(temperature programmed desorption) of (a) GO, (b) GO-SO_3H and (b) AC-SO_3H.

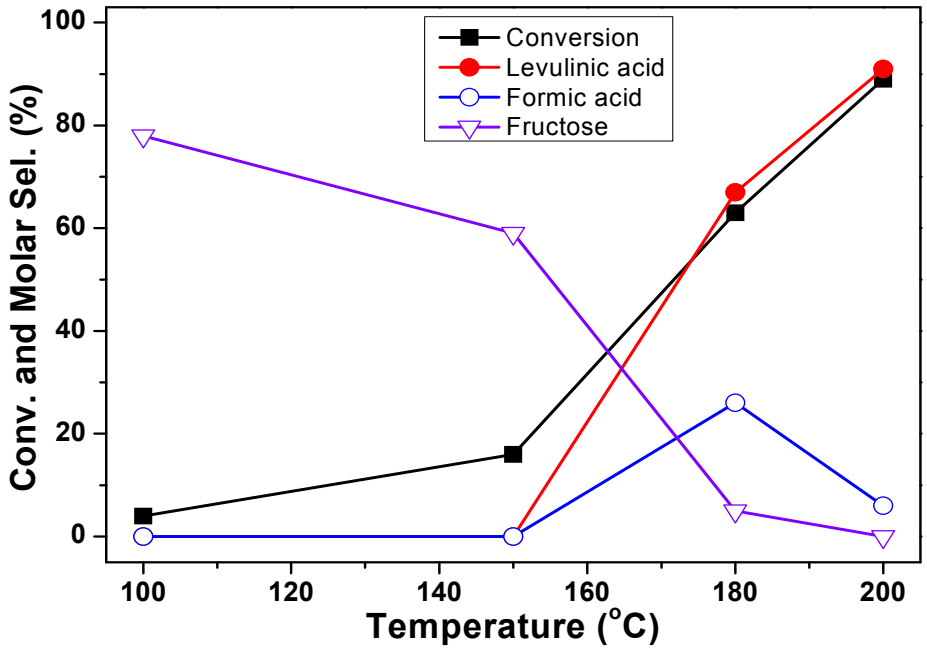


Figure S8. Effect of temperature on the activity of GO-SO_3H for glucose decomposition**.** Reaction conditions: Catalyst 0.5 g, glucose 30 g in 200 ml distilled water, reaction time of 2 h.

Table S1. Relative contents of surface functional groups of GO, AC, GO-SO_3H, and AC-SO_3H from C1S XPS

Samples	Bond	Position (eV)	Area	Area (%)
GO-SO_3H	C=C,C-C	284.5	45951	65
	C-OH,	285.5	12052	24
	COC	286.6	5225	
	C=O,	287.8	4677	11
	CO_2H	289	2716	
GO	C=C,C-C	284.6	36672	50
	C-OH	285.5	17488	40
	COC	286.6	11831	
	C=O	287.7	1778	10
	CO_2H	289.0	5831	
Samples	**Bond**	**Position (eV)**	**Area**	**Area (%)**
AC-SO_3H	C=C,C-C	284.4	20634.0	61
	C-S, C-OH	285.4	5365.4	27
	COC	286.6	3873.4	
	C=O	287.8	2108.7	11
	CO_2H	289.0	1774.4	
AC	C=C,C-C	284.1	20950	64
	C-OH	285.4	3431	21
	COC	286.6	3274	
	C=O	287.8	2892	15
	CO_2H	289.0	1947	

Table S2. Elemental analysis (EA) results of C, H, O, S in catalysts

Materials	C mmol/g	H mmol/g	O mmol/g	S mmol/g	C/O Ratio
GO-SO_3H	80	7.92	10.57	1.17	7.56
AC- SO_3H	61.86	15.55	19.96	2.50	3.10
GO	90.49	4.14	6.16	0	14.12

Table S3. Amount of functional group density from titration and elemental analysis (EA)

Materials	Functional group density from titration				S density from EA mmol/g
	Total functional group density mmol /g	-OH density mmol /g	-COOH density mmol /g	$-SO_3H$ and sulfate densities mmol /g	
GO	1.84	1.02	0.82	-	-
GO-SO_3H	2.70	0.40	0.60	1.60	1.20
Carbon	2.14	1.80	0.30	-	-
AC-SO_3H	5.80	1.50	0.24	3.96	2.50
[a]GO-SO_3H	2.77	0.55	0.66	1.56	1.20

a.Catalyst pretreated at 300 ^{o}C in N_2.

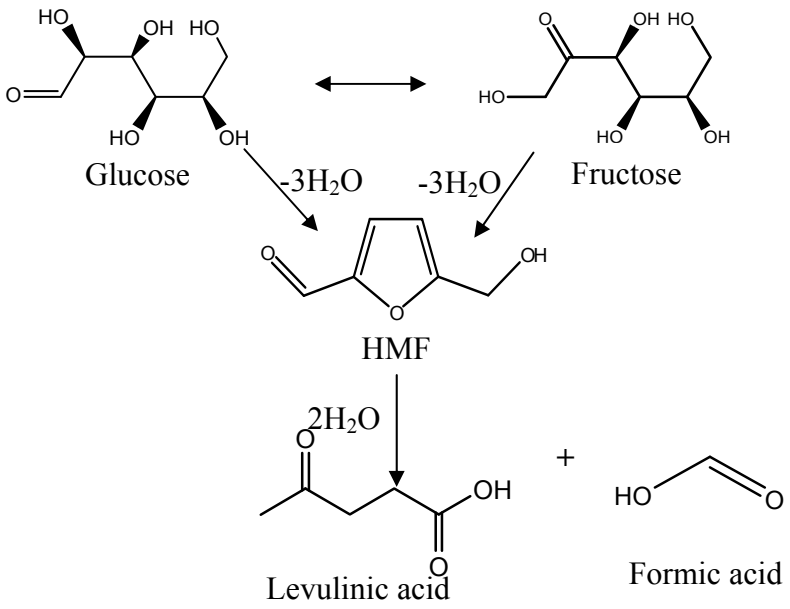
Figurer S4. Regeneration of GO-SO_3H catalyst for glucose hydrolysis.

Material	Recycle	Conv. %	Selectivities (%)			S mmol/g (EA)	TON
			LA	FA	Fructose		
GO-SO_3H	1	89	88	8	0	1.20	124
	2	86	81	11	6	1.12	128
	3	83	76	12	10	1.09	127
	4	78	71	14	14	0.89	146
	5	72	63	19	17	0.81	148

Table S5. Cellulose and fructose hydrolysis by GO-SO_3H

Catalyst	Feed stocks	pressure bar	Molar Yield (%)		
			LA	FA	Glucose
GO-SO_3H	Cellulose	16	23	10	36

Reaction conditions: Catalyst 0.5 g, alfa cellulose 10 gm in 200 ml distilled water used , Auto generated pressure has been given in above table, reaction time of 2 hrs.



Scheme S1. The proposed reaction pathway of formation of levulinic and formic acids from hexoses decomposition.