

ESI

Ni(II)-Oxalate on Plastic-Derived Carbon: A Green Platform for Furfural Diacetal Synthesis

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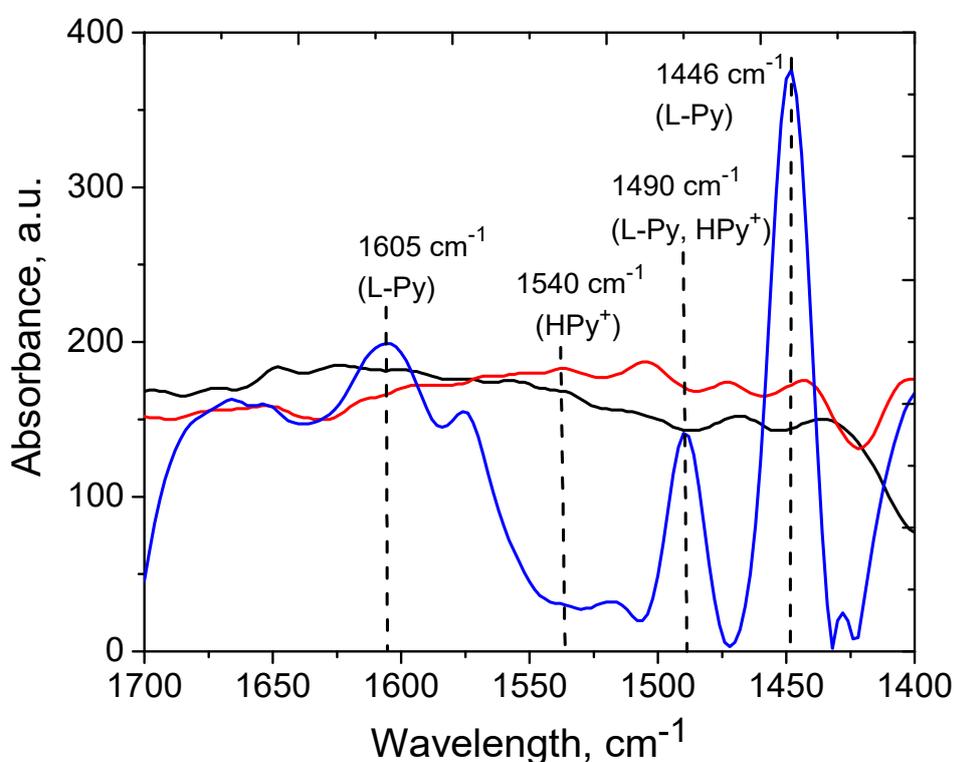


Figure S1. Py-DRIFT spectra of host (CSR, black), catalyst (2.5%NiOx@CSR, red) and NiOx (bulk, blue). HPy⁺ - Brønsted, L - Lewis and L-Py - Brønsted + Lewis acidic sites, respectively. Temperature inside of the instrument chamber was 100 °C, N₂ atmosphere.

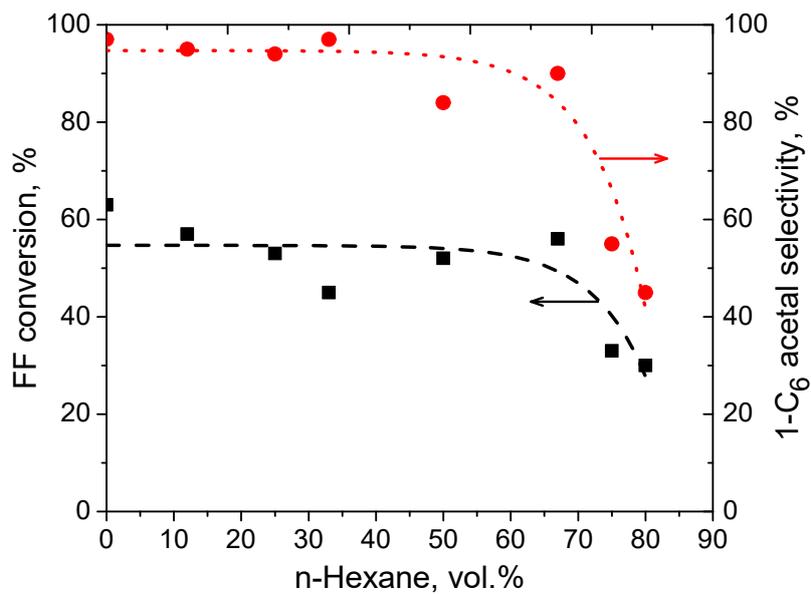


Figure S2. Impact of co-solvent (n-Hexane) additives on the performance of FF acetalization with 1-Hexanol. *Reaction conditions:* 2.5%NiOx@CSR (50 mg), reaction volume 2 ml, 170 °C, 1 h.

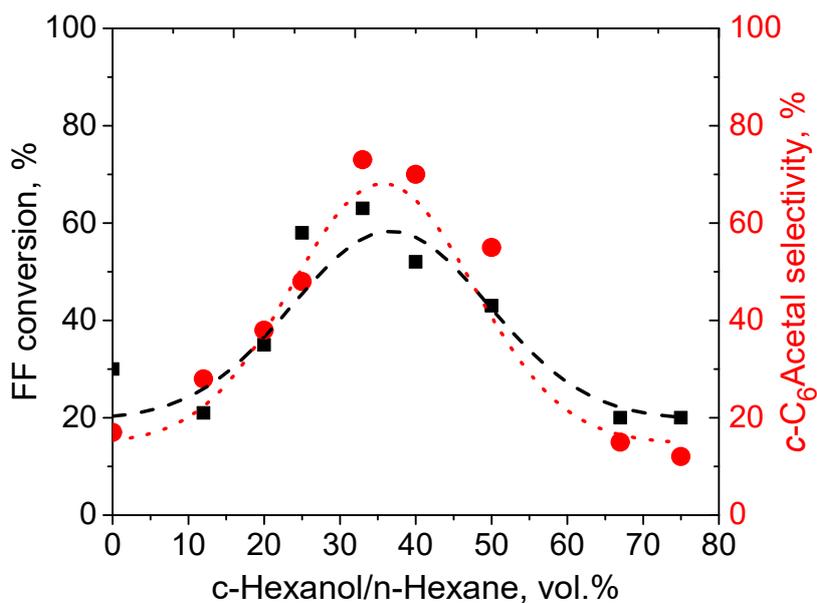


Figure S3. Impact of co-solvent (n-Hexane) additives on the performance of FF acetalization with *c*-Hexanol. *Reaction conditions:* 2.5%NiOx@CSR (50 mg), reaction volume 2 ml, 150 °C, 1 h.

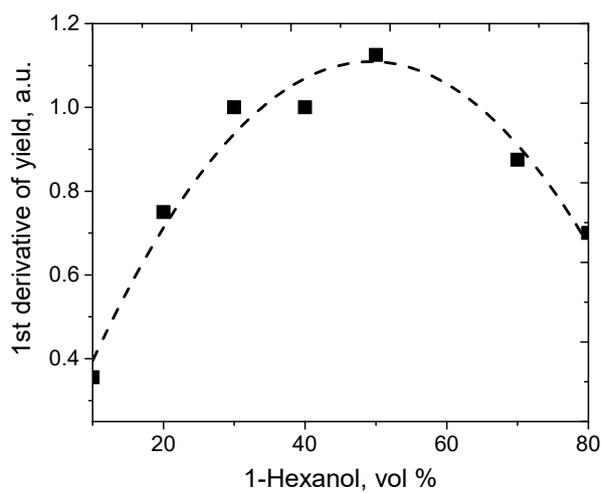


Figure S4. Impact of 1-Hexanol additives on 1st derivative (rate) of yield changing during of FF acetalization with c-Hexanol, 150 °C, 1 h.

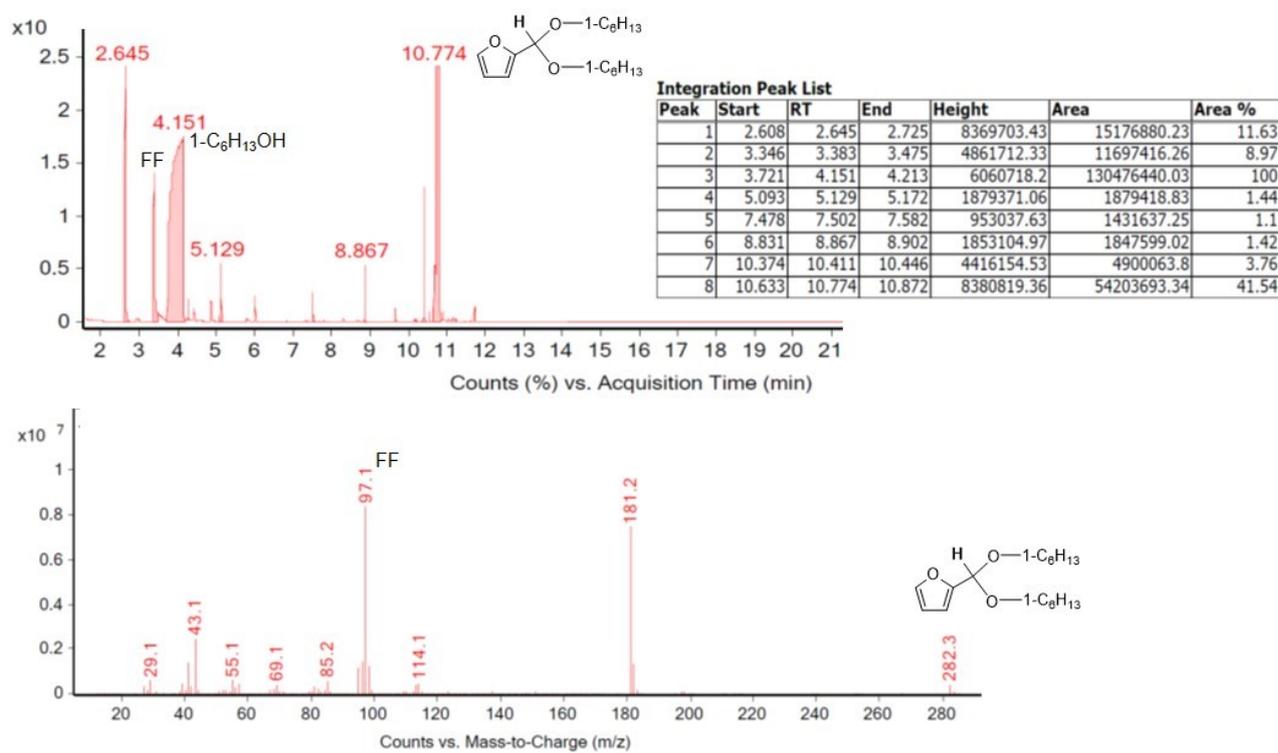


Figure S5. GC-MS spectra of the reaction mixture after acetalization of FF with 1-Hexanol. Reaction conditions: FF (0.5 M) in 1-Hexanol medium (2.0 ml), 170 °C/1h, magnetic stirring.

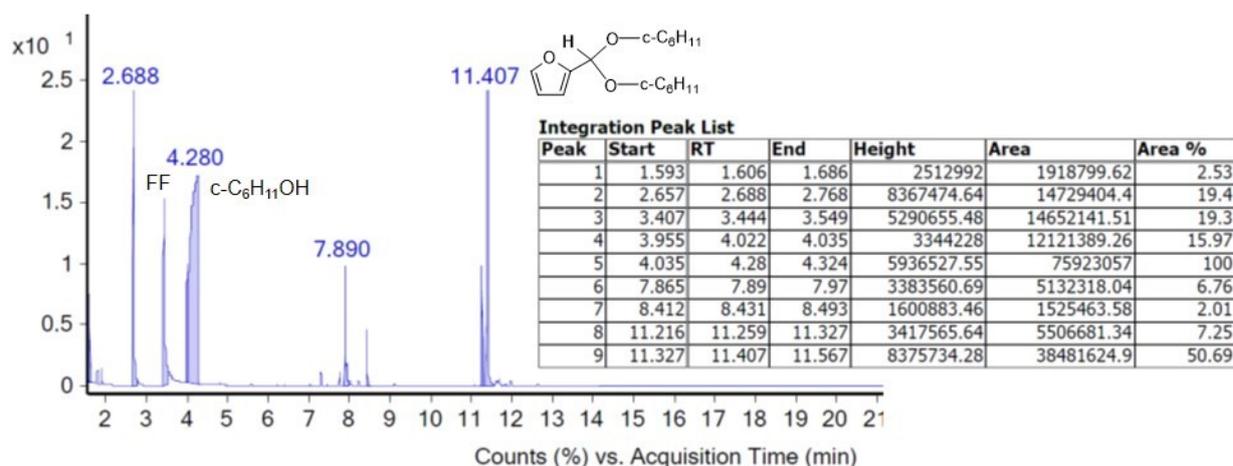


Figure S6. GC-MS spectra of the reaction mixture after acetalization of FF with c-Hexanol. *Reaction conditions:* FF (0.5 M) in c-Hexanol medium (2.0 ml), 170 °C/1h, magnetic stirring.

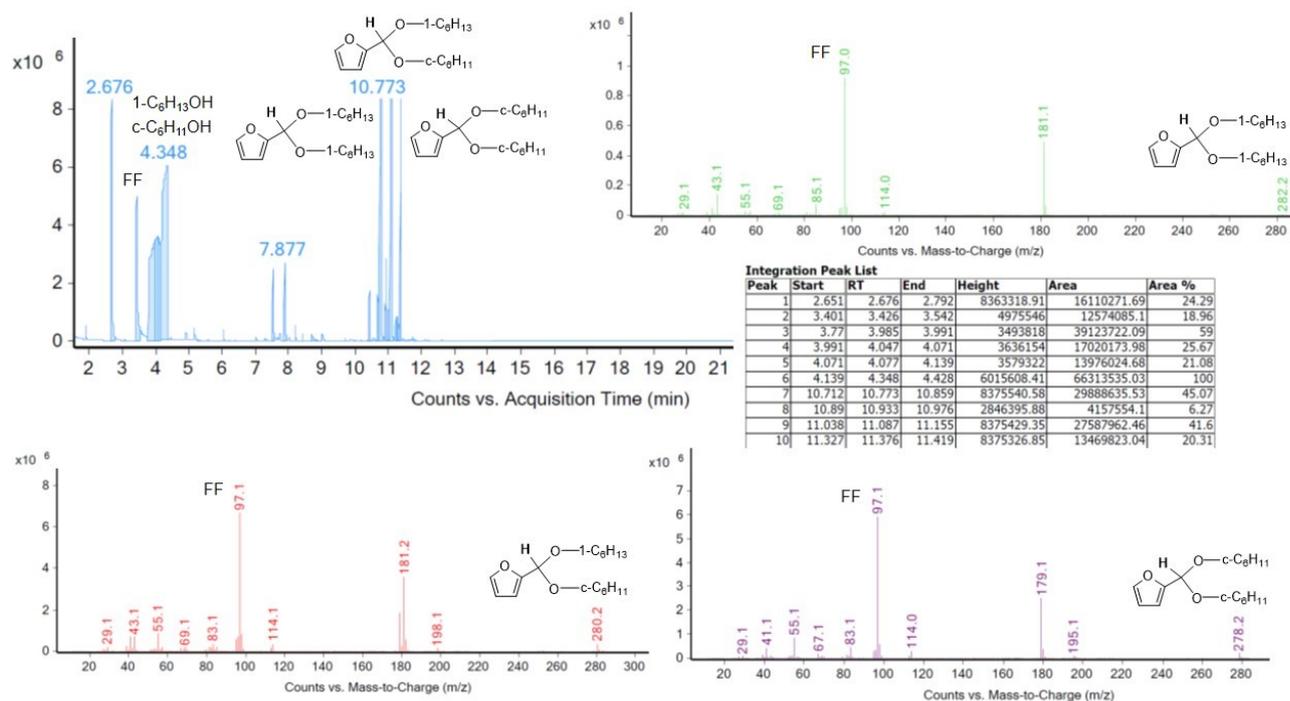


Figure S7. GC-MS spectra of the reaction mixture after acetalization of FF with c-Hexanol + 1-Hexanol 1/1 (by volume). *Reaction conditions:* FF (0.5 M) in c-Hexanol + 1-Hexanol medium (2.0 ml), 170 °C/1h, magnetic stirring.

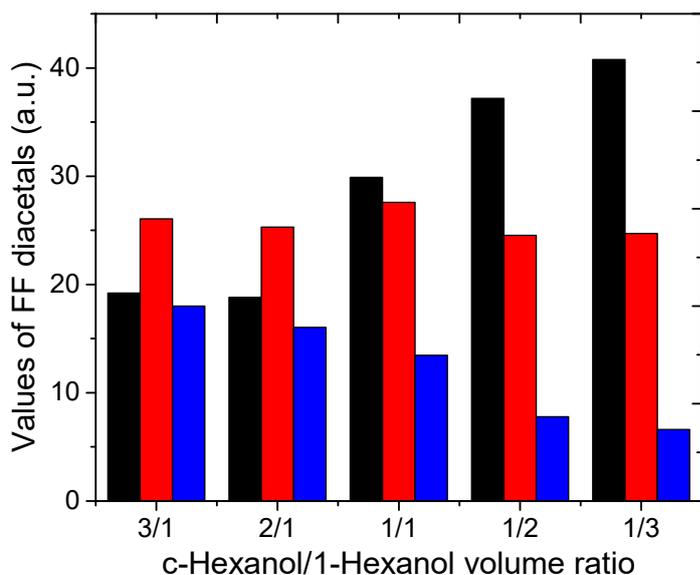


Figure S8. The relationships between the reaction mixture composition and c-Hexanol/1-Hexanol initial ratio. Black, red and blue rectangles chart furfuryl 1-Hexyl acetal, hibride furfuryl c-Hexyl+1-Hexyl acetal and furfuryl c-Hexyl acetal relative values, respectively.

Entry	Material	Alcohol	t, °C	Time, h	^d C, % mol	^d S, % mol	TON
1	CSR	1-Hexanol	170	1	2	50	10
2		1-Hexanol	130	1	26	68	45
3		1-Hexanol	150	1	39	72	80
4		1-Hexanol	170	1	64	98	100
5		1-Hexanol	190	1	69	70	95
6	2.5%NiOx@CSR	1-Hexanol	170	0.5	38	98	70
7		1-Hexanol	170	2	66	80	105
8		^b 1-Hexanol	170	1	30	96	60
9		^c 1-Hexanol	170	1	72	95	90
10		c-Hexanol	170	1	30	33	60
11	^f 2.5%NiOx@CSR AR	1-Hexanol	170	1	46	92	70
12		c-Hexanol	170	1	22	30	40
13	^g NiOx	1-Hexanol	170	1	32	90	65

Table S1. Acetalization of FF in C6 alcohols under MW irradiation.^a

^aCatalyst load 50 mg, 0.5 M FF, 1.9 mL alcohol, total volume of reactants 2 ml, batch reactor (MW Pyrex tube Ø1 cm × 10 cm), magnetic stirring. ^b, ^cCatalyst load 25 and 75 mg, respectively. ^dC and ^dS indicate FF conversion and process selectivity, respectively. ^fCatalyst regenerated after reaction. ^gIn case of bulky NiOx exploration, the catalyst load was 2.5 mg that corresponded to the content of metal in 50 mg of 2.5%NiOx@CSR.

Table S2. Acetalization of aldehydes with different alcohols.

Catalyst	Aldehyde/ alcohol	t, °C	τ , h	Acidity, $\mu\text{mol/g}$	Process output					Ref.
					Products	C, %	S, %	Y, %	TON	
2.5%NiOx@CSR ^a	FF/1-C6OH; FF/ c-C6OH	170	1	40	C6 acetals	70-75	95-98	≥ 70	60- 140 ^b	This study
5%FeOx@silica; 5%CoOx@silica ^a	FF/C1OH - 1-C8OH	170	1	26-43	C1-C4 acetals; C5-C8 hemiacetal	45-80	75-80	45-65	40-80 ^c	21
AC-SO ₃ ^d , GO-SO ₃ ^e	PhCHO/ Ethylene glycol	95	3	0.5-0.9	Benzylidene acetal (cyclic)	85-95	n/d	n/d	n/d	42
HCl	PhCHO/ MeOH	20	24	n/d	Benzylidene acetal	-	-	97	≈ 100	10
Cs-Keggin HPA ^f	PhCHO/ MeOH	25	2	500- 1000	Benzylidene acetal +Benzoic acid	80-85	95- 100	80-85	≈ 300	43
3%Ru@carbon nano tubes	PhCHO/ Ethylene glycol	90	8	30-50	Benzylidene acetal	65	99	63	≈ 400	18; 44
Zr,Ce- alumosilicate	FF/Glycerol	80	1	300-500	FF dioxolane	95- 100	>80	>80	10-15	34
Porphyrin/ <i>h</i> ν	FF/1-C5OH	25	24	0.78 (<i>H</i> ₀) ^g	C5 acetal	-	-	92	≈ 70	45
5%PdIr@C	FF/ <i>i</i> -PrOH	35	1	160-350	<i>i</i> -C3 acetal	-	85-90	-	30(tof)	46
FeCl ₃ or CoCl ₂	FF/MeOH; <i>i</i> -PrOH	25	2	n/d	C1 acetal; <i>i</i> -C3 acetal	94; 3	97; 5	91; ≤ 1	50 5	47
3%Ni@TiO ₂	FF/ <i>i</i> -PrOH, H ₂ or N ₂	150, 30 at	2	n/d	FF alcohol; <i>i</i> -C3 acetal	40 2	95 2	38 ≤ 1	≈ 30 2	48
1%Pd@SiO ₂	FF/EtOH; H ₂	120, 3 at	2	100- 1000	C2 acetal+FF alcohol	90	90	80	≈ 250	49
APAI (Al- phosphate)	FF/EtOH	25	0.5	80-100	C2 acetal	85	80	≈ 70	15	50

^aCatalyst load 50 mg, 0.5 M FF, 1.9 mL alcohol, total volume of reactants 2 ml; C, S, Y – conversion, selectivity and yield, %, respectively; ^bhigher TON relates to 1-Hexanol, lower to c-Hexanol; ^chigher TON relates to C1-C4 alcohol, lower - to C5-C8 ones; ^dAC - activated carbon; ^eGO - graphene oxide; ^fKeggin HPA – Keggin heteropolyacids; ^g*H*₀ – Hammett acidity; n/d – not determined;