

Stabilization of the aqueous phase fraction of pine wood bio-oil using zirconia-supported Fe/Cu/Pd nano-catalysts at mild conditions

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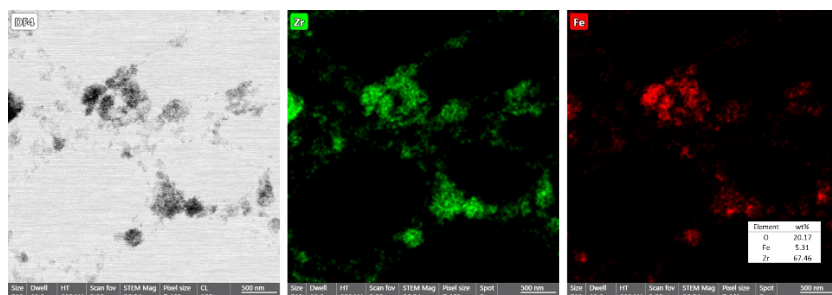


Figure S1. TEM image and elemental mapping for FeZrO₂.

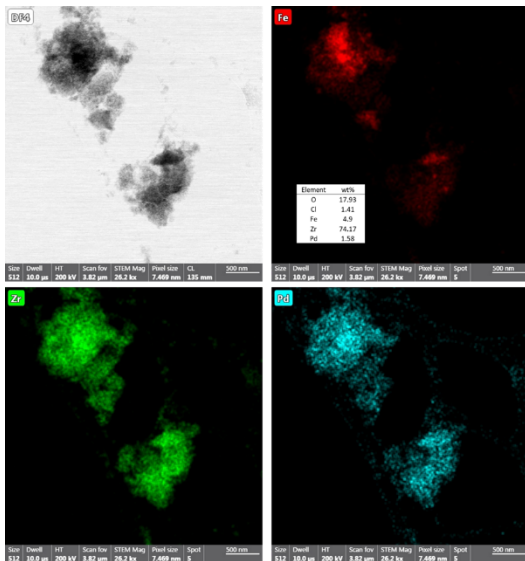
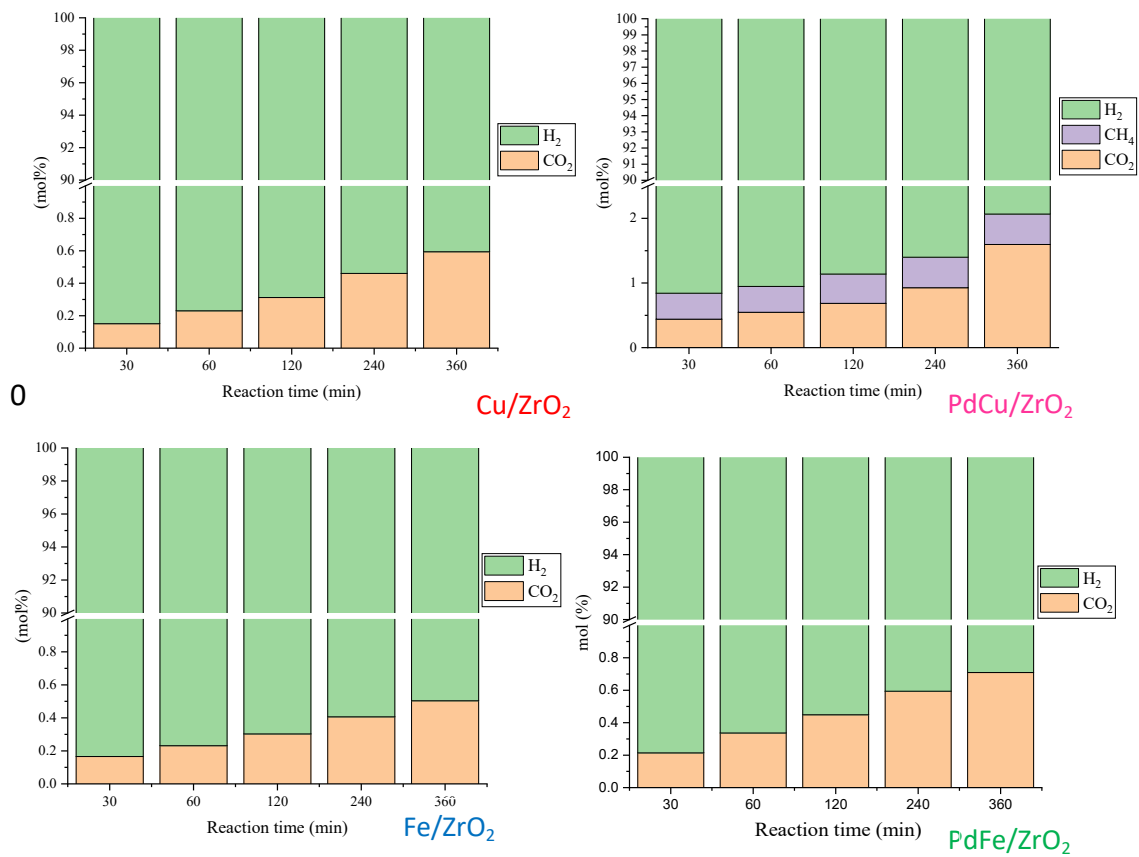


Figure S2. TEM image and elemental mapping for FePdZrO₂.



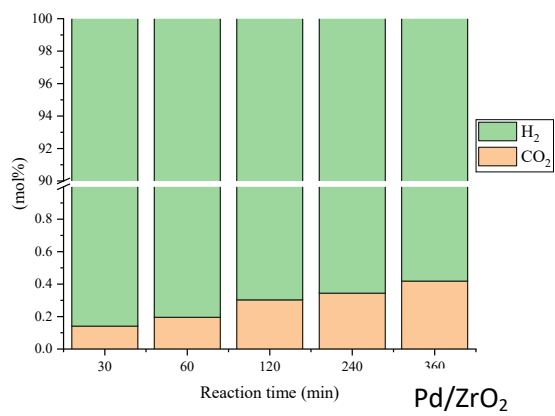
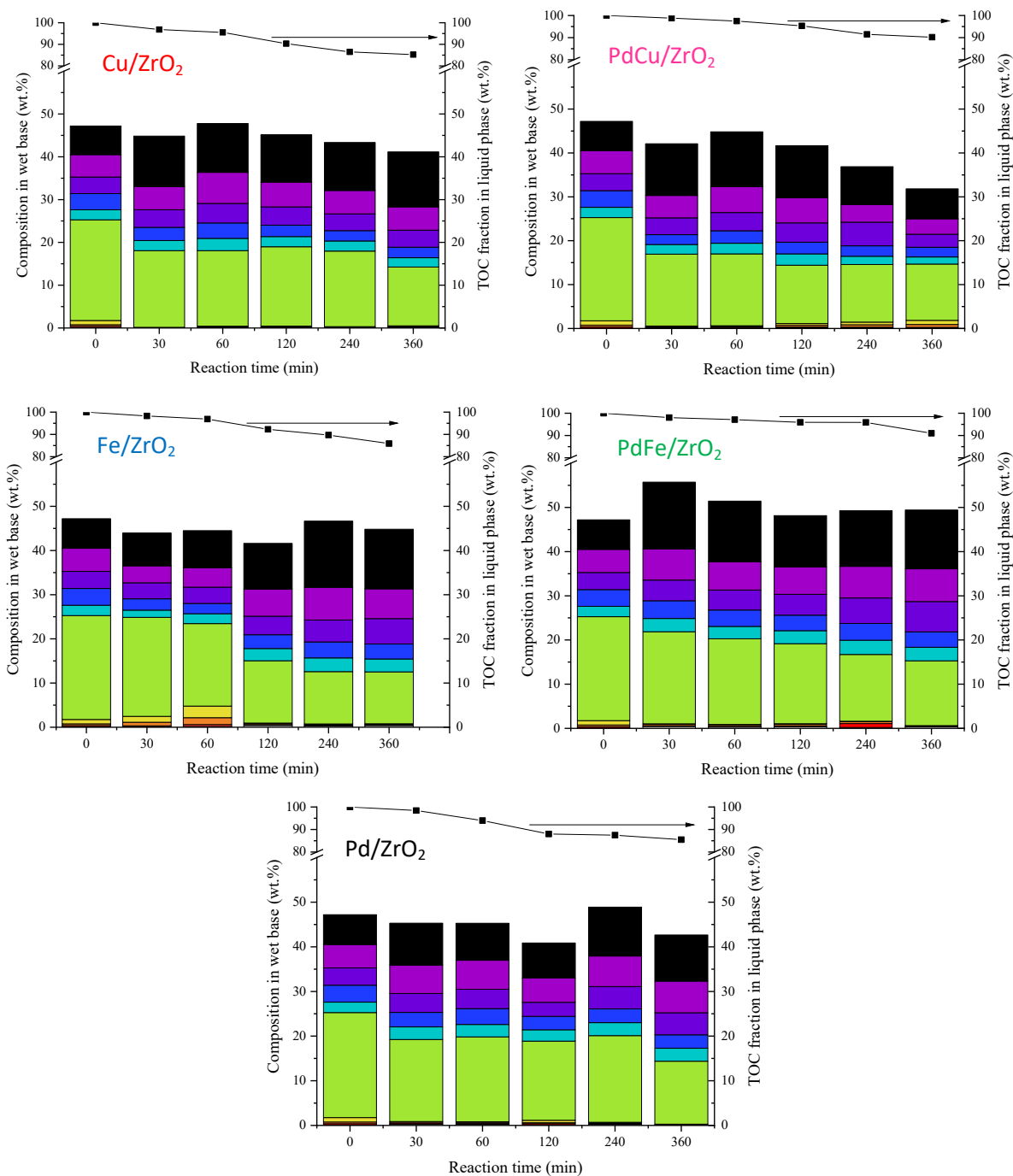


Figure S3. Gas products composition at different reaction time of LTMP hydrogenation at 100 °C and 50 bar.



FigureS4. Products distribution at different reaction time of LTMP hydrogenation at 100 °C and 50 bar for a) PdCu/ZrO₂ and b) PdFe/ZrO₂ catalysts. ■ catechols, ■ phenolics, ■ ketones/alcohols, ■ levoglucosan, ■ guaiacols, ■ acids, ■ alkanes, ■ aromatics, ■ cyclohexenes, ■ naphthalenes

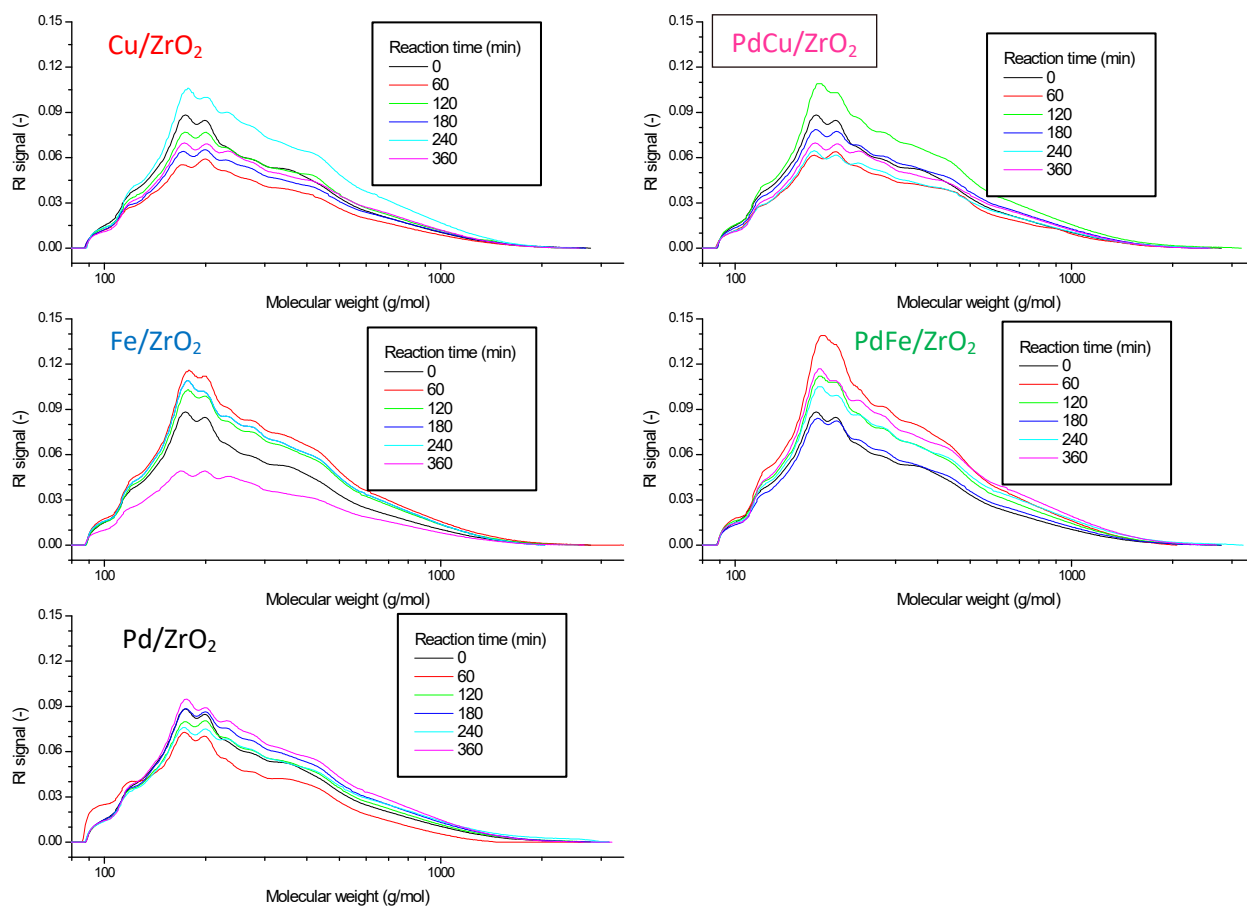


Figure S5. Molecular weight distribution (in dry base) for at different reaction time of LTMP hydrogenation at 100 °C and 50 bar

Table S1. GC-MS compounds

N	Compound	N	Compound	N	Compound
1	(3-Methyl-oxiran-2-yl)-methanol	36	2- Hydroxy octanoic acid	71	Acetic acid
2	(S)-(+)-1,2-Propanediol	37	2-Hydroxy-3,5-dimethylcyclopent-2-en-1-one	72	Acetic acid, decyl ester
3	(S)-(+)-2',3'-Dideoxyribonolactone	38	2-Isobutoxyethyl acetate	73	Ethanol, 2-(pentyloxy)-, acetate
4	1-(2-Ethoxyphenyl)acetone	39	2-Pentanone, 5-(acetyloxy)-	74	Ethanol, 2-(vinyloxy)-
5	1,2-Benzenediol	40	2-Pentenoic acid	75	Ethanone, 1-(2-furanyl)-
6	1,2-Cyclopentanediol, trans-	41	2-Propanone, 1,3-dihydroxy-	76	Ethanone, 1-(4-hydroxy- 3-methoxyphenyl)-
7	1,2-Dimethoxy-4-n-propylbenzene	42	2-Propanone, 1-hydroxy-	77	Ethanone, 1-oxiranyl-
8	1,2-Epoxy- 3-propylacetate	43	2-Propenoic acid, 2-methyl-, ethyl ester	78	Ethene, ethoxy-
9	1,2-Ethanediol	44	3,3-Dimethyl- 2, 4-pentanedione	79	Ethyl alcohol
10	1,2-Ethanediol, monoacetate	45	3,3-Dimethyl- 2-pentanone	80	Ethyl ether
11	1,2-Propanediol, 3-methoxy-	46	3,4-Altrosan	81	Ethyl hydrogenoxalate
12	1,3,6-Trioxocane	47	3,4-Anhydro- d-galactosan	82	Eugenol
13	1,3-Butanediol, diacetate	48	3,4-Dihydroxy- 5-methyl-dihydrofuran- 2-one	83	Formaldehyde
14	1,3-Dioxane, 4-methyl-	49	3,5-dimethyl-2(5H)-furanone	84	Formic acid
15	1,3-Dioxane-4,6-dione, 2,2-dimethyl-	50	3,6-Dimethylperhydro-1,3-oxazine	85	Formic acid, 1-methyl ethyl ester
16	1,3-Dioxepane, 2-methyl-2-propyl-	51	3,7-Benzofurandiyl, 2,3-dihydro-2,2-dimethyl-	86	Formic acid, ethenyl ester
17	1,3-Dioxolane, 2,4,5-trimethyl-	52	3-Butene-1, 2-diol	87	Furan
18	1,3-Dioxolane, 2-methyl-	53	3-Butenoic acid	88	Furan, tetrahydro-
19	1,4- Butanediol	54	3-Cyclobutene-1 ,2-dione, 3,4-dihydroxy-	89	Furfural
20	1,4- Diacetoxy butane	55	3-Cyclohexen-1-carboxaldehyde, 3-methyl-	90	Furyl hydroxyl methyl ketone
21	1,4:3,6-Dianhydro-a-d-glucopyranose	56	3-Heptanol, 2-methyl-	91	Galacto-heptulose
22	1,4-Benzenediol, 2-methyl-	57	3-Hexanone	92	Galactosan triacetate
23	1,4-Butanediol, diacetate	58	3-Mercaptohexyl hexanoate	93	Glycidol
24	1,4-Dioxane, 2-ethyl-5-methyl-	59	3-Pentanol	94	Guanidineacetic acid
25	1,4-Pentadiene	60	4-Methyl- 2-tert-octylphenol	95	Hexane, 2,3,5- trimethyl-
26	1,4-Pentanediol	61	4-Methyl- 5H-furan- 2-one	96	Hexanoic acid
27	1,6-Anhydro- b-D-glucopyranose (levoglucosan)	62	5- Hydroxy methyl dihydrofuran- 2-one	97	Hexanoic acid, 3-hydroxy -5-methyl-, methylester
28	1-Hepten- 4-ol	63	5,9-Dodecadien-2-one, 6,10-dimethyl	98	Hexanoic acid, 5-oxo-, ethyl ester
29	1-Heptene	64	5-Hydroxymethyl-dihydrofuran-2-one	99	Homovanillyl alcohol
30	1-Hydroxy- 2-butanone	65	5-Methylfurfural	100	Hydroquinone
31	1-Hydroxy- 2-pentanone	66	6,6,7-Trimethyl- octane- 2,5-dione	101	Hydroxymethylfurfural
32	1-Pentanol, 2,3-dimethyl-	67	6-Dodecanone	102	Isocrotonic acid
33	1-Propanol	68	7-Decen-2-one	103	L-Mannose, 6-deoxy-
34	1-Propanol, 2-methyl-	69	Acetaldehyde	104	Maltol
35	1-Propene, 3-methoxy- 2-methyl-	70	Acetaldehyde, hydroxy-	105	Methyl a d-rhamnopyranoside

Continued

N	Compound	N	Compound	N	Compound
106	Methyl formate	142	2H-Pyran, tetrahydro- 2-methyl-	177	Ethanol, 2-(2,3-butadienyloxy)-
107	Methyl propionate	143	2H-Pyran-2-one	179	n-Butyl ether
108	Montanol	144	Acetic acid, methyl ester	180	n-Capric acid isopropyl
109	2(3H)-Furanone, 5-ethylidihydro-	145	Acetone	181	n-Propyl acetate
110	2(3H)-Furanone, dihydro- 4-hydroxy-	146	Benzaldehyde, 2-hydroxy- 3-methoxy- (Vanillin)	182	Octane, 2,6,6 -trimethyl-
111	2(5H)-Furanone	147	Benzaldehyde, 4-hydroxy-	183	Octanoic Acid
112	2(5H)-Furanone, 5-methyl-	148	Benzene acetaldehyde, 2-methoxy-	184	Oxalic acid, ethyl propyl ester
113	2,2-Dimethyl pentyl cyclohexane carboxylate	149	Benzene acetic acid, 4-hydroxy- 3-methoxy-	185	Oxirane, (ethoxymethyl)-
114	2,3-Anhydro-d-galactosan	150	Benzeneacetic acid, 4-hydroxy-3-methoxy-, methyl ester	186	Oxirane, 2,3- dimethyl-
115	2,3-Anhydro-d-mannosan	151	Butanal	187	Oxirane, 3-hydroxypropyl-
116	2,3-Dihydrofuran	152	Butanal, 2-methyl-	188	Pentanal
117	2,3-O-Acetonemannosan	153	Butanal, 3-hydroxy-	189	Pentanoic acid
118	2,4-Diacetoxypentane	154	Butanal,2-ethyl-	190	Pentanoic acid, 2-methyl-4-oxo-, ethyl ester
119	2,5-Furandione, 3-methyl-	155	Butane, 1-methoxy-	191	Pentanoic acid,4-oxo-, butyl ester
120	2,5-Furandione, dihydro-3-methylene-	156	Butanedial	192	Phenol, 2,4-dimethyl-
121	2,5-Hexanedione	157	Butanedioic	193	Phenol, 2-methoxy- 4-methyl-
122	2-Acetylamino-3-hydroxy-propionic acid	158	Butanoic acid	194	Phenol, 2-methoxy- 6-(1-propenyl)-
123	2-Butanone, 4-hydroxy-	159	Butanoic acid, methylester	195	Phenol, 2-methoxy-1
124	2-Butenal, 2-methyl-	160	Butylated Hydroxy toluene	196	Phenol, 2-methoxy-4-methyl-
125	2-Butene-1, 4-diol	161	Butyrolactone	197	Phenol, 2-methoxy-4-propyl-
126	2-Butenoic acid, 2-methoxy-3-methyl-, methyl ester	162	Carbonicacid, isobutyl isohexyl ester	198	Phenol, 2-methyl-
127	2-Cyclopenten- 1-one	163	Crotonic acid	199	Phenol, 3-ethyl-
128	2-Cyclopenten- 1-one, 2-methyl-	164	Cyclobutane, methyl-	200	Phenol, 5-methoxy-2,3-dimethyl-
129	2-Cyclopenten- 1-one, 3-ethyl- 2-hydroxy-	165	Cyclobutanol	201	Propanal
130	2-Cyclopenten-1-one, 2-hydroxy-	166	Cyclobutanone, 2-methyl- 4-hydroxy-	202	Propanal, 2,3-dihydroxy-
131	2-Cyclopenten-1-one, 2-hydroxy-3,4 -dimethyl-	167	Cyclohexan- 1,4,5-triol -3-one -1-carboxylic acid	203	Propane, 1-methoxy-2-methyl-
132	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	168	Cyclohexane, ethyl-	204	Propane, 2-(ethenyloxy)-
133	2-Cyclopenten-1-one, 3-(acetyloxy)	169	Cyclohexanol,2-methyl-	205	Propanoic acid
134	2-Deoxy-D-glucose	170	Cyclohexanone, 4-hydroxy-	206	Propanoic acid, 2-methyl-, 1-methylethyl ester
135	2-Ethoxyethyl acetate	171	Cyclopentane, 1,1-dimethyl-	207	Propanoic acid, 3-hydroxy-, methyl ester
136	2-Furancarboxaldehyde, 5-(hydroxymethyl)-	172	Cyclopropyl carbinol	208	Styracitol
137	2-Furancarboxaldehyde, 5-methyl-	173	D-Erythro -Pentose, 2-deoxy-	209	Succinic anhydride
138	2-Furancarboxylic acid	174	D-Glucose, 6-O-a -D-galactopyranosyl-	210	trans-5 -Methyl- 2-isopropyl- 2-hexen
139	2-Furanmethanol, tetrahydro-	178	Ethanol, 2-(2-butoxyethoxy)-, acetate	211	Vanillin
140	2-Hexanone, 4-methyl-	175	d-Glycero -d-galacto -heptose		
141	2-Hexene, 2,5-dimethyl-	176	dl-Glyceraldehyde		

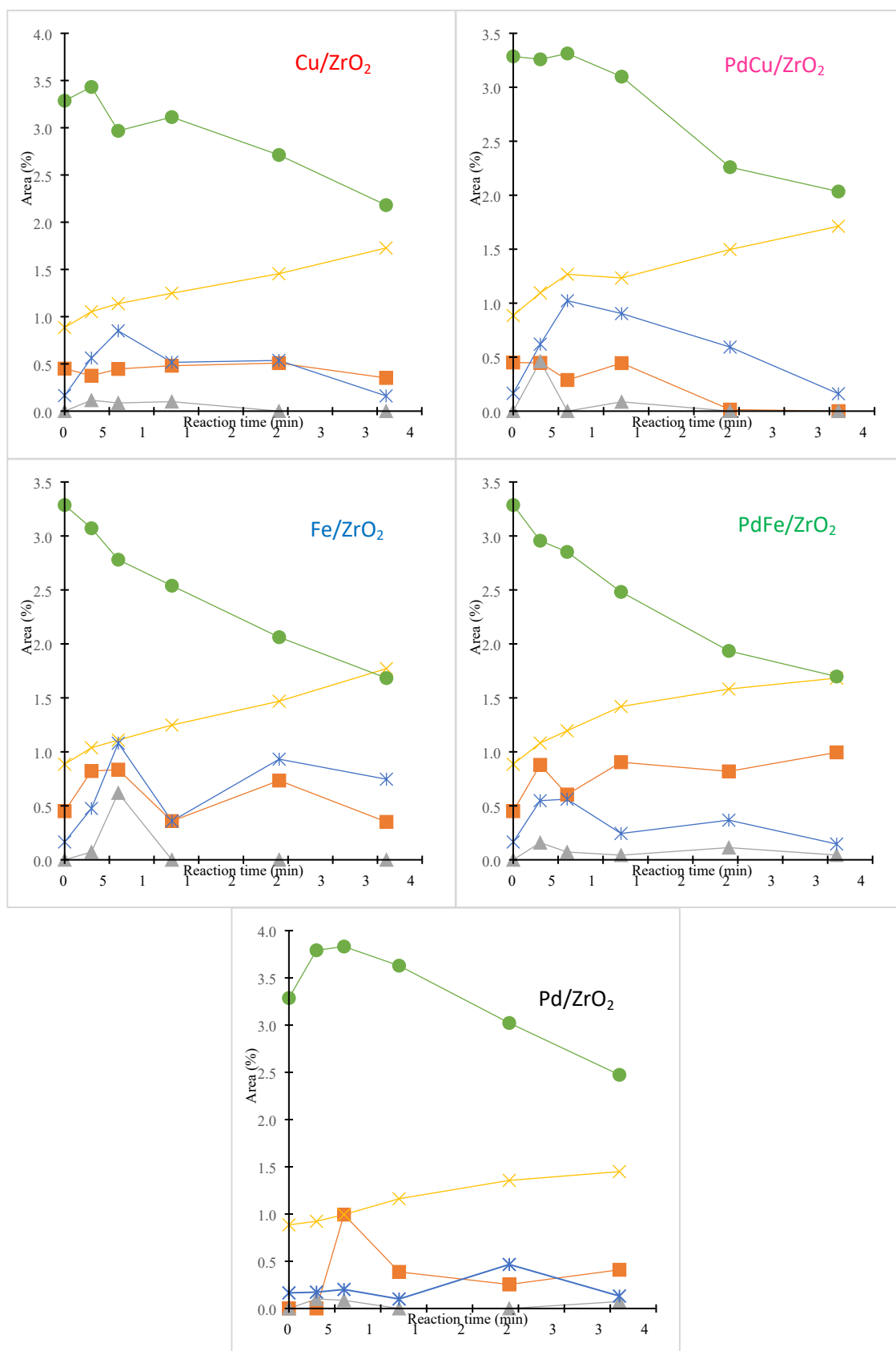


Figure S6. GC-MS qualitative analysis for cellulose fraction. — Glycero-d-galacto-heptose, — Butanediol, — Ethanediol, — Ethanol, — Acetaldehyde, hydroxy-.

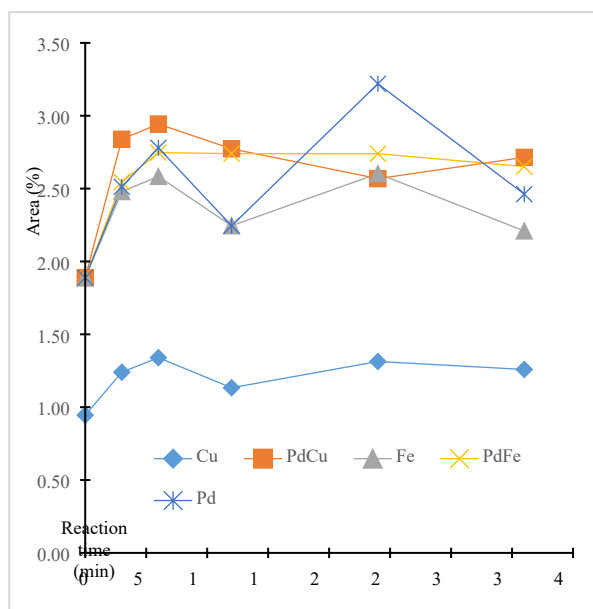


Figure S7. GC-MS qualitative analysis for Vanillin

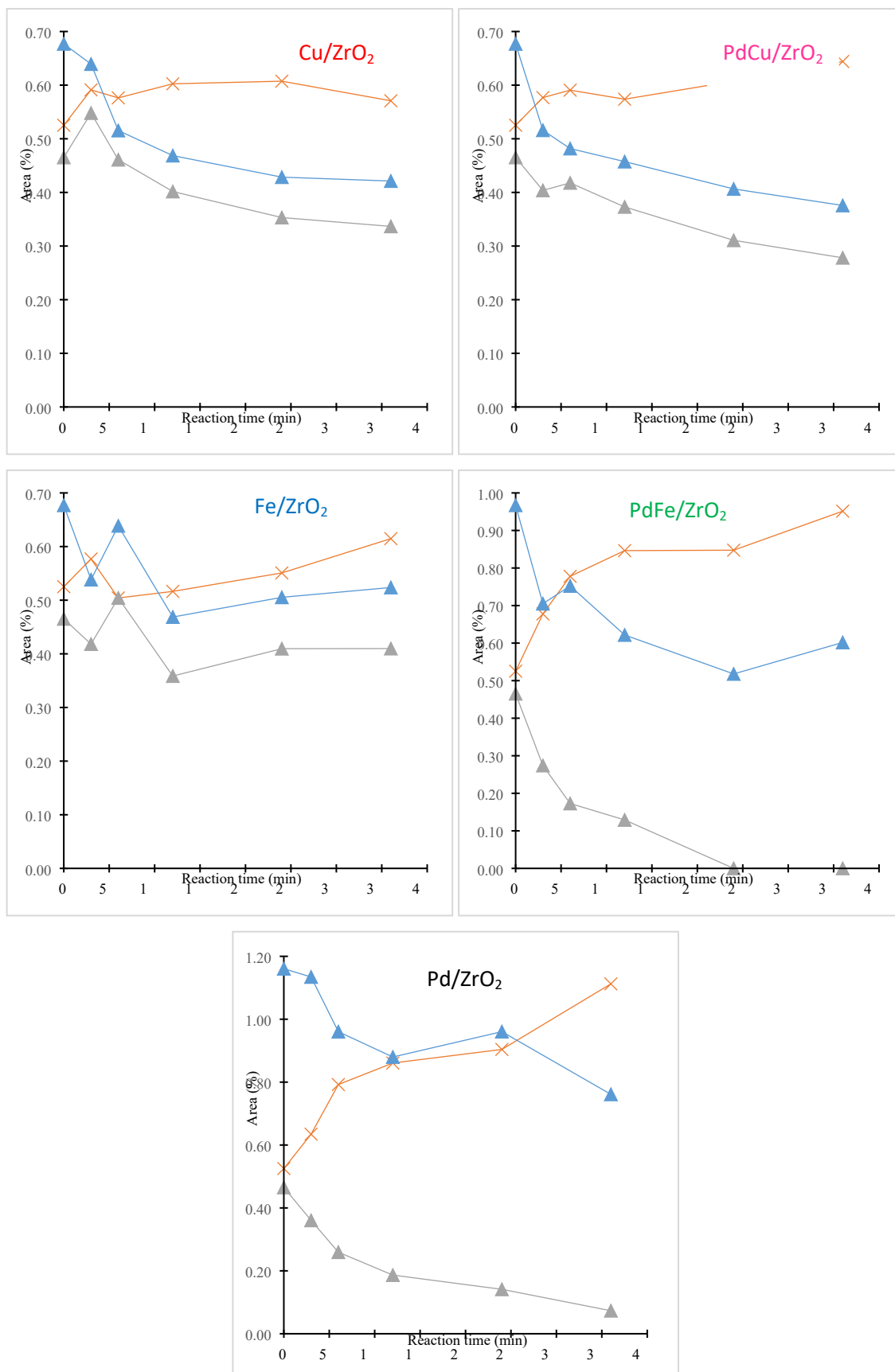


Figure S8. GC-MS qualitative analysis for hemicellulose fraction. —x— γ Butyrolactone, —▲— 2-Cyclopenten-1-one, —▲— Furfural.

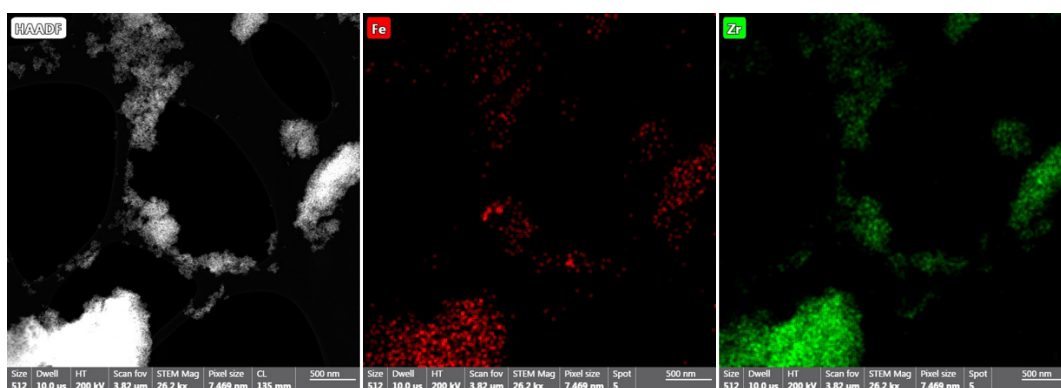


Figure S9. TEM-EDS of FeZrO₂

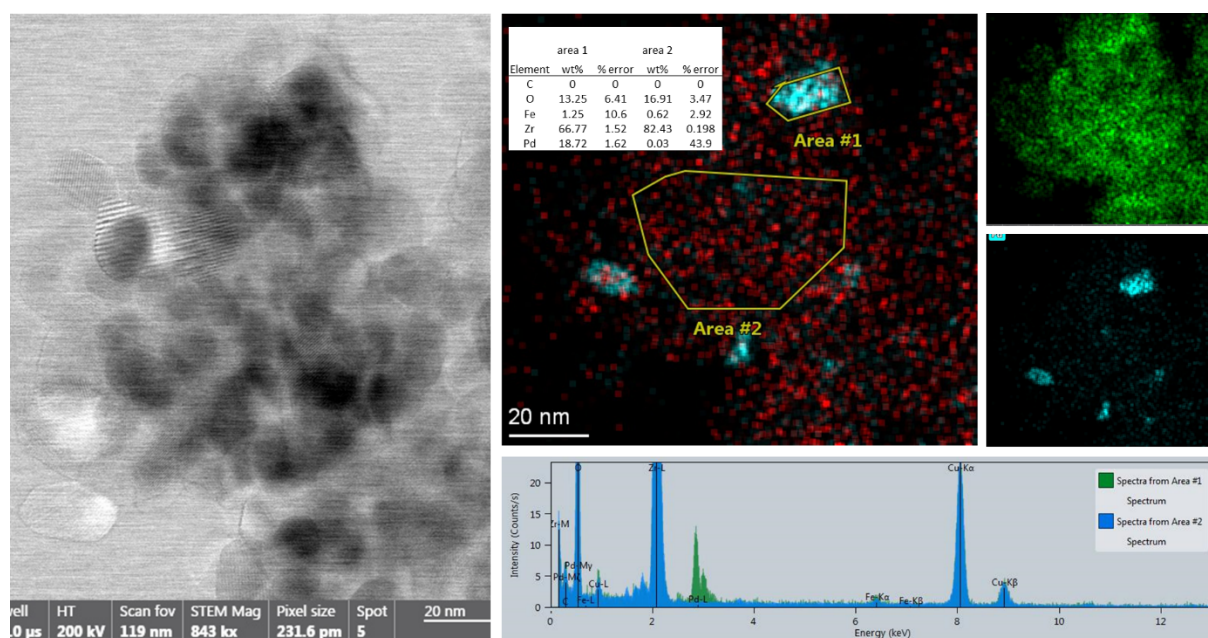


Figure S10. STEM-EDS of FePdZrO₂

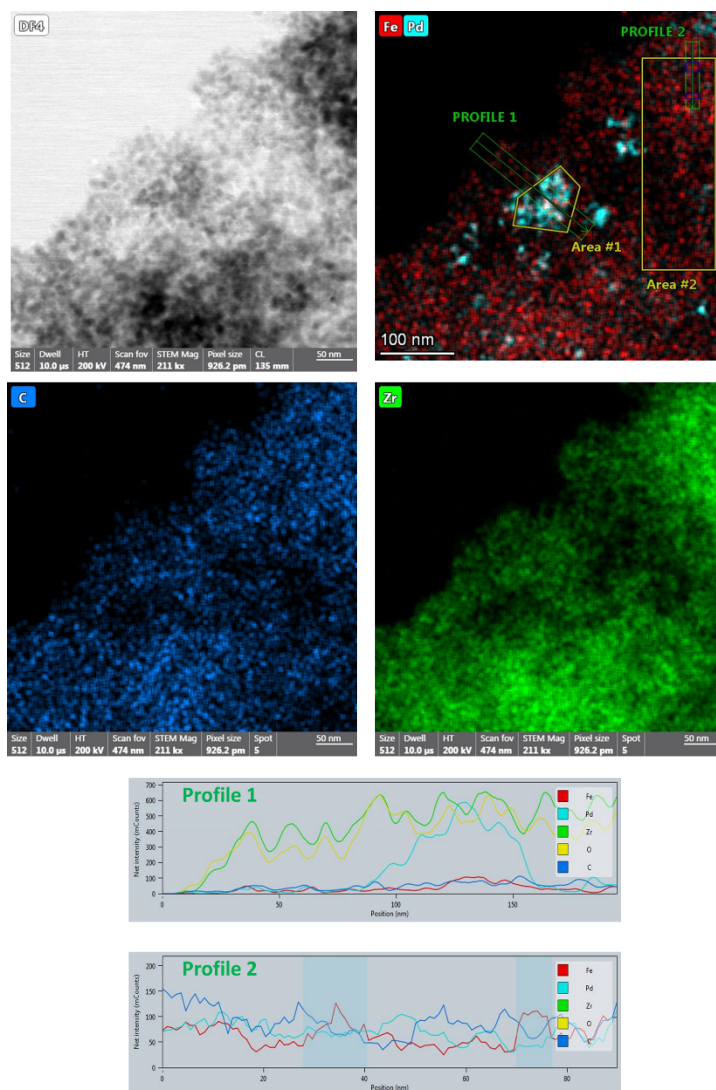


Figure S11. STEM-EDS of profiles for FePdZrO₂.

Table S2. Elemental analysis of areas 1 and 2 for FePdZrO₂ from Figure S8.

Element	area 1		area 2	
	wt%	% error	wt%	% error
O	11.21	1.90	11.92	2.55
Fe	1.04	2.75	0.54	2.79
Zr	77.43	0.35	87.33	0.07
Pd	10.31	0.63	0.21	3.32