Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information
Tuning Cellulose Pyrolysis Chemistry: Selective Decarbonylation via Catalyst-Impregnated Pyrolysis

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Summary

This supplementary material section supports the data and conclusions presented in the main body of the paper. It contains a detailed breakdown of all oxygenate products detected in our catalyst impregnated pyrolysis experiments; additional results from catalyst-support impregnated pyrolysis (i.e., no metals); and catalyst metal and support surface areas.

Additional Results

Detailed furan yields are reported in the paper. Other pyrolysis-oil components detected in our experiments include levoglucosan, anhydroglucofuranose, glyceraldehyde and formic acid (see Table 1 and 2 for a comprehensive list). In the case of the Pd/C and Pd/SiO_2 experiments, levoglucosan (the most abundant product of cellulose pyrolysis) yield parallels that of the total pyrolysis oil yield.

The effect of various supports on condensed-phase cellulose pyrolysis chemistry is also reported in the supplementary section. Our results show that SiO_2 and C are the most inert support materials with the least effect on the pyrolysis product distribution (Figures 1 and 2). We show that for SiO_2 there is little effect on pyrolysis product yields for several biomass starting materials (see Table 3 for a comprehensive list).

For the catalysts tested in this work, metal surface areas (Table 4) were measured using H_2 chemisorption (except for Pd, Ni, and Co catalysts, where CO chemisorption was used) and found to consistent with previous work with these materials (1.1 - 6.2 m^2/g). Additionally, N_2 physisorption (BET) measurements (Table 5) show that Al_2O_3 and SiO_2 have the higher support surface areas (220 and 89 m^2/g) compared to carbon (15 m^2/g). It is important to note that carbon catalysts have similar metal surface areas to SiO_2 catalysts, for the same metal weight loading which shows that carbon is better at dispersing the metals compared to SiO_2.

Additional Experimental Details

Catalyst impregnated pyrolysis experiments were conducted at 500 °C with millimeter-scale powder samples. Twenty Seven vapor products were detected in addition to char. CO and CO_2 were detected using a Thermal Conductivity Detector (TCD) while all other C1-C6 oxygenates were detected using both an FID and Mass Spectrometer. Oxygenate identities were based on FID retention times as well as mass spectra. Burn off was used to quantify char for all catalysts except those that were carbon-supported, since support oxidation would give artificially high char yields. Samples were pyrolyzed using a drop tube reactor (Frontier 2020 Pyrolyzer) with quartz wall and a furnace capable of reaching 800 °C. Previous work has shown that pyrolysis products such as levoglucosan do not breakdown in the quartz furnace despite the high temperature because of the ten millisecond residence time employed.

Carbon supported catalysts and Pd/Al_2O_3 were purchased from Sigma-Aldrich, Pt/SiO_2 was purchased from STREM Chemicals, and all other catalysts were prepared via incipient wetness impregnation. The weight loading for each of the catalysts is shown in the header of Tables 1 and 2. In general, metals were added at 1.7, 5 and 10 wt% to achieve the desired metal surface area (1.1 - 6.2 m^2/g).

Table 1. Twenty seven products were identified and quantified for cellulose co-pyrolysis with varying degrees of metal loading for 5Pt/Carbon and 10Pd/Carbon.

	5 Pt/Carbon (0.75 m^2/g-cel)	10Pd/Carbon (0.75 m^2/g-cel)	5 Pt/Carbon (1.5 m^2/g-cel)	10Pd/Carbon (1.5 m^2/g-cel)
Anhydrosugars				
Levoglucosan	27.86	48.85	16.01	43.7
1,6 Anhydroglucofuranose	1.90	4.31	1.05	5.0
DAGP	0.75	0.84	0.62	0.83
Levoglucosenone	0.52	0.60	0.56	1.2
Pyrans				
ADGH	0.33	2.44	0.37	1.8
Furans				
Hydroxymethylfurfural	0.77	0.82	0.62	0.4
Furfural	0.60	0.67	0.38	0.2
5-Methyl Furfural	0.32	0.23	0.15	0.2
2-Furanmethanol	0.44	0.53	0.38	0.5
2,5 Dimethyl Furan	0.36	0.52	0.27	0.7
2-Methyl Furan	0.85	1.11	1.08	2.5
Furan	1.57	2.06	1.82	3.3
2(5H) Furanone	0.17	0.19	0.22	0.1
Light Oxygenates				
Methyl Glyoxal	1.51	0.74	0.41	0.2
Glycolaldehyde	2.41	2.60	2.08	3.6
Formaldehyde	0.9	3.3	0.3	1.1
Hydroxyacetone	0.87	0.14	0.66	0.2
Acetic Acid	0.49	0.11	0.39	0.2
2,3 Butanedione	1.12	0.52	1.72	0.1
Formic Acid	2.56	1.77	2.53	1.4
Glyoxal	3.75	1.19	4.58	1.0
Permanent Gases				
Carbon Dioxide	3.71	1.69	4.56	1.9
Carbon Monoxide	29.15	9.02	41.83	17.9
Other				
CPHM	0.29	0.13	0.12	0.3
Catechol	0.45	0.16	0.42	0.0
1,2-Cyclopentanedione	0.43	0.24	0.17	0.5
Char	-	-	-	-
Total	84.4	85.1	83.4	89.1

Abbreviations: DAGP, dianhydroglucopyranose; ADGH, 1,5-anhydro-4-deoxy-D-glycero-hex-1-en-3-ulose; CPHM, 2-hydroxy-3-methyl-2-cyclopenten-1-one

Table 2. Twenty seven products were identified and quantified for cellulose co-pyrolysis Pt, Pd, Co, and Ni supported on silica and alumina.

	5 Pt/Silica [0.75 m²/g-cel]	**10 Pd/Silica [0.75 m²/g-cel]**	**1.7 Pt/Alumina [0.75 m²/g-cel]**	**10 Pd/Alumina [0.75 m²/g-cel]**	**10 Ni/Alumina [0.75 m²/g-cel]**	**10 Co/Alumina [0.75 m²/g-cel]**
Anhydrosugars						
Levoglucosan	32.95	52.80	39.26	34.77	40.71	33.98
1,6 Anhydroglucofuranose	1.94	4.31	2.48	2.14	2.84	2.12
DAGP	0.90	0.94	1.64	1.82	1.58	1.90
Levoglucosenone	0.17	0.23	0.69	0.27	0.58	1.55
Pyrans						
ADGH	0.57	3.16	3.08	2.82	2.52	2.32
Furans						
Hydroxymethylfurfural	0.81	0.81	4.77	4.47	4.88	6.30
Furfural	1.33	1.09	3.33	3.44	3.63	4.60
5-Methyl Furfural	0.51	0.35	0.59	0.60	0.68	1.00
2-Furanmethanol	0.51	0.62	0.43	0.46	0.42	0.43
2,5 Dimethyl Furan	0.52	0.25	0.13	0.29	0.18	0.35
2-Methyl Furan	0.34	0.60	0.56	0.77	0.49	0.55
Furan	0.79	1.50	1.28	2.13	1.04	1.01
2(5H) Furanone	0.51	0.12	0.11	0.14	0.13	0.13
Light Oxygenates						
Methyl Glyoxal	5.64	1.62	3.08	2.70	3.60	4.52
Glycolaldehyde	4.92	2.12	3.09	2.98	3.04	3.29
Formaldehyde	6.1	3.9	2.3	3.2	2.6	3.1
Hydroxyacetone	2.79	0.27	0.13	0.18	0.17	0.61
Acetic Acid	0.62	0.14	0.14	0.13	0.21	0.28
2,3 Butanedione	0.75	0.43	0.42	0.46	0.50	0.66
Formic Acid	1.92	2.21	3.60	2.58	2.50	2.51
Glyoxal	0.91	0.75	0.76	0.83	0.74	0.85
Permanent Gases						
Carbon Monoxide	4.46	1.69	1.77	1.87	2.39	2.92
Carbon Dioxide	6.28	6.69	4.90	6.01	3.73	3.20
Other						
CPHM	0.45	0.07	0.10	0.14	0.13	0.17
Catechol	0.62	0.14	0.21	0.27	0.21	0.23
1,2-Cyclopentanedione	0.81	0.15	0.24	0.33	0.25	0.32
Char	6.2	3.3	4.1	6.1	6.1	7.4
Total	84.9	90.4	83.5	82.3	86.2	83.1

Table 3. Twenty seven products were identified and quantified for cellulose co-pyrolysis with eight different support materials.

Support	No Support	Aluminum Oxide	Titanium Oxide	Magnesium Oxide	Zirconium Oxide	Tungsten Carbide	Calcium Oxide	Carbon	Silicon Dioxide
Anhydrosugars									
Levoglucosan	48	32	43	46	41	42	40	49	42
1,6 Anhydroglucofuranose	4.0	2.2	3.3	2.9	3.4	3.6	2.6	4.3	3.6
DAGP	0.1	2.1	1.1	0.9	1.1	1.8	0.7	1.3	1.2
Levoglucosenone	0.3	0.8	0.2	0.1	0.4	0.6	0.1	0.4	0.4
Pyrans									
ADGH	3.8	4.0	4.7	1.8	3.5	4.4	2.8	3.6	4.6
Furans									
Hydroxymethylfurfural	3.9	5.9	6.7	3.9	4.1	2.3	4.1	4.2	3.7
Furfural	1.6	4.5	2.6	2.0	2.5	2.1	1.5	2.6	1.9
5-Methyl Furfural	0.5	0.8	0.5	0.4	0.4	0.5	0.4	0.5	0.4
2-Furanmethanol	0.4	0.2	0.2	0.1	0.2	0.3	0.2	0.6	0.1
2,5 Dimethyl Furan	0.3	0.6	0.8	0.7	0.6	0.6	0.5	0.4	0.5
2-Methyl Furan	0.2	0.5	0.5	0.3	0.4	0.5	0.3	0.4	0.5
Furan	0.6	0.8	0.9	0.5	1.0	1.4	0.5	1.1	1.0
2(5H) Furanone	0.2	0.3	0.3	0.3	0.3	0.3	0.3	0.1	0.3
Light Oxygenates									
Methyl Glyoxal	2.0	3.0	4.4	7.1	2.5	3.2	4.1	2.3	2.4
Glycolaldehyde	1.9	3.5	3.0	2.8	1.9	3.0	2.2	2.6	2.2
Formic Acid	2	0.9	2.4	2.2	1.7	4.3	2.4	1.7	1.3
Formaldehyde	4.4	4.2	3.7	4.4	3.4	3.8	2.8	3.2	3.4
Hydroxyacetone	0.5	0.1	0.5	1.1	0.3	0.6	0.9	0.1	0.1
Acetic Acid	0.3	0.3	0.5	0.5	0.4	0.5	0.4	0.2	0.2
2,3 Butanedione	0.4	0.3	0.5	0.6	0.4	0.5	0.4	0.5	0.4
Glyoxal	0.3	0.6	0.7	0.9	0.4	0.6	0.5	0.3	0.8
Permanent Gases									
Carbon Monoxide	1.4	2.1	2.4	2.0	2.1	2.5	1.9	1.8	2.8
Carbon Dioxide	2	2.0	2.8	3.4	2.3	2.3	2.4	2.0	2.4
Other									
CPHM	0.2	0.1	0.2	0.2	0.1	0.1	0.2	0.1	0.1
1,2-Cyclopentanedione	0.2	0.3	0.4	0.3	0.2	0.2	0.3	0.2	0.3
Char	9	3.5	3.5	10.6	5.4	15.1	11.3	0.0	8.1
Catechol	0.2	0.2	0.3	0.3	0.1	0.3	0.2	0.0	0.1
Total	90	77	90	97	81	97	85	84	85

Abbreviations: DAGP, dianhydroglucopyranose; ADGH, 1,5-anhydro-4-deoxy-D-glycero-hex-1-en-3-ulose; CPHM, 2-hydroxy-3-methyl-2-cyclopenten-1-one

Table 4. Metal surface area for supported metal catalysts. Measurements were conducted using chemisoption with CO as the titration gas for Pd, Ni, and Co and H_2 for Pt.

Catalyst	Surface Area [m^2/g]	Dispersion [%]
1.7 Pt/Alumina	2.70	64
10Pd/Alumina	6.24	14
5Pt/Carbon	5.16	42
10Pd/Carbon	6.19	14
5Pt/Silica	1.27	10
10Ni/Alumina	2.51	3.8
10Co/Alumina	1.11	1.6
5Pd/Silica	1.95	4.4

Table 5. Eight support materials examined in impregnated pyrolysis of cellulose. BET surface area was measured using nitrogen adsorption. Particle size was measured using the Mastersizer 2000 and detailed plots of the particle size distribution for each support material are included in the supplementary section. R^2 values describe the variation between pyrolysis of cellulose with and without the support material and are also listed in Figure 1.

Support	BET Surface Area [m^2/g]	Particle Size [μm]
Aluminum Oxide	89	2.8
Titanium Dioxide	3.6	3.9
Zirconium Oxide	21	7.1
Magnesium Oxide	120	41
Tungsten Carbide	1.3	3.6
Calcium Oxide	7.9	60
Carbon	15	5.9
Silicon Dioxide	220	130

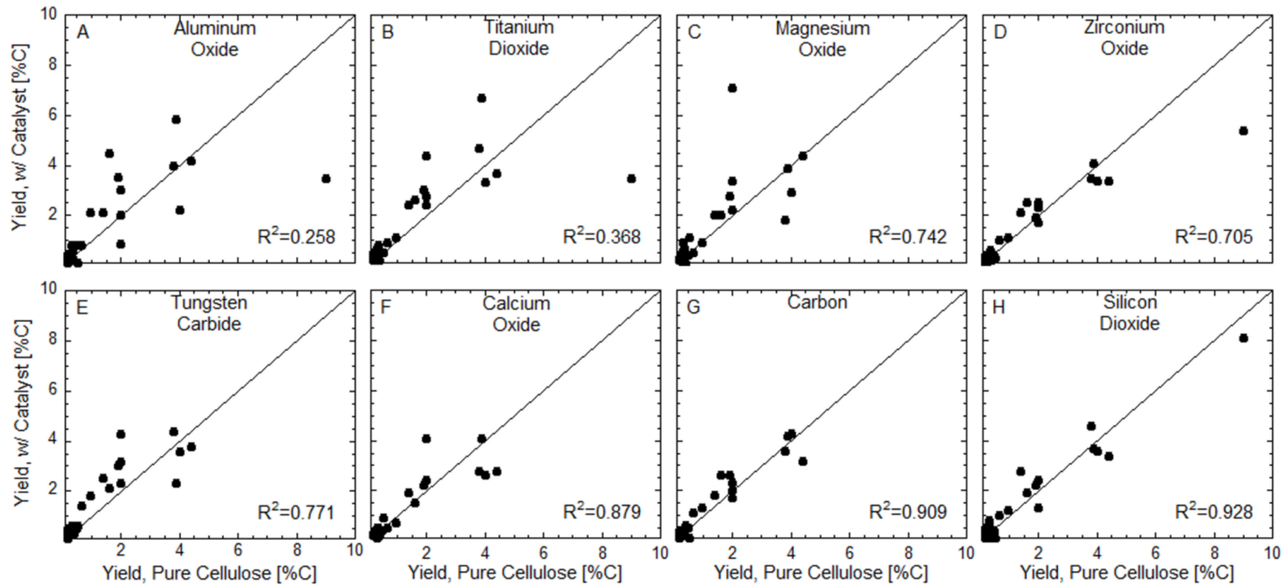

Figure 1. Parity plots comparing cellulose pyrolysis products with and without a catalyst support. All data points of an inert support fall on the parity line y = x. Included in each plot is the 'coefficient of determination' (R^2) value calculated using only yield values below 10%. A value of one represents a perfectly inert support.

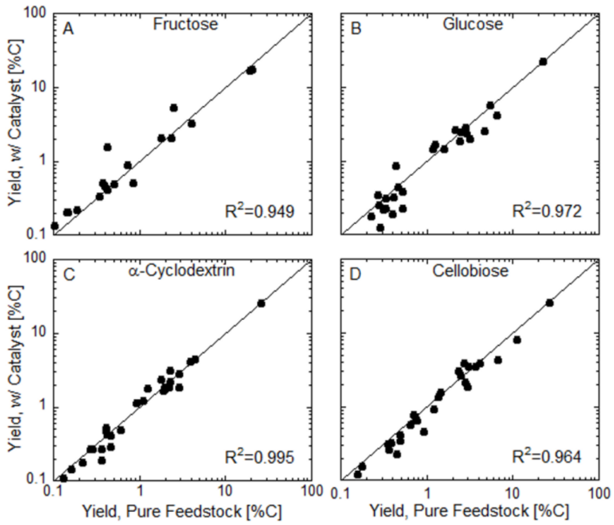

Figure 2 Parity plots comparing four different saccharides pyrolyzed with and without silicon dioxide. Included in each plot is the 'coefficient of determination' (R^2) value where a value of one represents a perfectly inert support.