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Supporting Information

One-pot synthesis of formic acid via hydrolysis-oxidation of potato starch in the presence of cesium salts of heteropoly acid catalysts

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Content

1. One-pot hydrolysis-oxidation of different types of plant materials to formic acid (Literature data)

Table S1. The main catalytic systems for one-pot hydrolysis-oxidation of monosaccharides into formic acid

Run	Catalyst		Experimental conditions		Results		Ref.
		Amount		Substrate	Conversion, (%)	Yield of FA (%)	
Substrate – Glucose							
1	$H_5PV_2Mo_{10}O_{40}$	0.735-38.8 mmol	333-363 K, 30 bar O_2, 3-22 h	16.7-50 mmol	98:	8-50	[1]
2	$H_8PV_5Mo_7O_{40}$	0.5 mmol	363 K, 20 bar O_2, 6-48 h, 1000 rpm V_{H2O} = 100 mL, $m_{alcohol}$ = 100 g. Alcohol: 1-Hexanol or 1-Heptanol	1.8 g	-	18-85	[2]
3	$H_5PV_2Mo_{10}O_{40}$	1 mmol	353 K, 60 bar O_2, 8 h, 1000 rpm, V_{H2O} = 200 mL	62.5-500 mmol L^{-1}	-	16-38	[3]
4	$H_8PV_5Mo_7O_{40}$	-	353 K, 60 bar O_2, 8 h, 1000 rpm	125 mmol L^{-1}	-	> 85	[3]
5	$H_5PV_2Mo_{10}O_{40}$,	10 mol %	373 K, 20 bar O_2, 2 h, 1000 rpm V_{H2O} = 50 mL	2.5 g	-	36	[4]
6	$NaVO_3$ - H_2SO_4	22 mg - 0.7 wt%	433 K, 30 bar O_2, 1 min V_{H2O} = 6 mL	100 mg	100	68	[5]
7	$H_4PVMo_{11}O_{40}$	0.1 mmol	453 K, 20 bar O_2, 3 h, 600 rpm V_{H2O} = 20 mL	0.2 g	100	55	[6]

Table S1. (Continue)

<table>
<tr><th rowspan="2">Run</th><th colspan="2">Catalyst</th><th colspan="2">Experimental conditions</th><th colspan="2">Results</th><th rowspan="2">Ref.</th></tr>
<tr><th></th><th>Amount</th><th></th><th>Substrate</th><th>Conversion, (%)</th><th>Yield of FA (%)</th></tr>
<tr><td colspan="8">Substrate – Xylose</td></tr>
<tr><td>8</td><td>$H_5PV_2Mo_{10}O_{40}$</td><td>0.03 mmol</td><td>353 K, 30 bar O_2, 26 h</td><td>120 mg</td><td>98</td><td>54</td><td>[1]</td></tr>
<tr><td>9</td><td>$NaVO_3 – H_2SO_4$</td><td>22 mg - 0.7 wt%</td><td>433 K, 30 bar O_2, 1 min
V_{H2O} = 6 mL</td><td>100 mg</td><td>100</td><td>66</td><td>[5]</td></tr>
<tr><td>10</td><td>$H_4PVMo_{11}O_{40}$</td><td>0.1 mmol</td><td>453 K, 20 bar O_2, 3 h, 600 rpm
V_{H2O} = 20 mL</td><td>0.2 g</td><td>100</td><td>33</td><td>[6]</td></tr>
<tr><td>11</td><td>$[MIMPS]_3HPMo_{11}VO_{40}$</td><td>0.05 mmol</td><td>453 K, 10 bar O_2, 1 h
V_{H2O} = 5 mL</td><td>2 mmol</td><td>100</td><td>55</td><td>[11]</td></tr>
<tr><td colspan="8">Substrate – Sorbitol</td></tr>
<tr><td>12</td><td>$H_5PV_2Mo_{10}O_{40}$</td><td>0.03 mmol</td><td>353 K, 30 bar O_2, 26 h</td><td>120 mg</td><td>98</td><td>56</td><td>[1]</td></tr>
<tr><td>13</td><td>$H_5PV_2Mo_{10}O_{40}$</td><td>1 mmol</td><td>353 K, 60 bar O_2, 8 h, 1000 rpm
V_{H2O} = 200 mL</td><td>125-500 mmol L^{-1}</td><td>-</td><td>15-31</td><td>[3]</td></tr>
<tr><td>14</td><td>$H_4PVMo_{11}O_{40}$</td><td>0.1 mmol</td><td>453 K, 20 bar O_2, 3 h, 600 rpm
V_{H2O} = 20 mL</td><td>0.2 g</td><td>100</td><td>44</td><td>[6]</td></tr>
</table>

Table S2. The main catalytic systems for one-pot hydrolysis-oxidation of disaccharides into formic acid

Run	Catalyst		Experimental conditions		Results		Ref.
		Amount		Substrate	Conversion, (%)	Yield of FA (%)	
Substrate – Cellobiose							
1	$H_5PV_2Mo_{10}O_{40}$	0.03 mmol	353 K, 30 bar O_2, 26 h	120 mg	98	47	[1]
2	$H_5PV_2Mo_{10}O_{40}$	1 mmol	353 K, 60 bar O_2, 8 h, 1000 rpm V_{H2O} = 200 mL	125 mmol L^{-1}	-	($FA+CO_2$) = 10%	[3]
3	$H_8PV_5Mo_7O_{40}$	1 mmol	353 K, 30 bar O_2, 8 h, 1000 rpm V_{H2O} = 200 mL	125 mmol L^{-1}	-	($FA+CO_2$) = 19%	[3]
Substrate – Sucrose							
4	$H_5PV_2Mo_{10}O_{40}$	0.03 mmol	353 K, 30 bar O_2, 26 h	120 mg	98	48	[1]
5	$H_8PV_5Mo_7O_{40}$	0.5 mmol	363 K, 20 bar O_2, 6-48 h, 1000 rpm V_{H2O} = 100 mL, $m_{alcohol}$ = 100 g. Alcohol: 1-Hexanol, 1-Heptanol	3.44 g	-	45-76	[2]
6	$H_5PV_2Mo_{10}O_{40}$	1 mmol	353 K, 60 bar O_2, 8 h, 1000 rpm V_{H2O} = 200 mL	25 mmol L^{-1}	-	($FA+CO_2$) = 78%	[3]
7	$H_8PV_5Mo_7O_{40}$	1 mmol	353 K, 60 bar O_2, 8 h, 1000 rpm V_{H2O} = 200 mL	25 mmol L^{-1}	-	($FA+CO_2$) = 100 %	[3]
8	$NaVO_3 – H_2SO_4$	22 mg - 0.7 wt%	433 K, 30 bar O_2, 5 min V_{H2O} = 6 mL	100 mg	100	65	[5]

Table S3. The main catalytic systems for one-pot hydrolysis-oxidation of polysaccharides into formic acid

Run	Catalyst		Experimental conditions		Results		Ref.
		Amount		Substrate	Conversion, (%)	Yield of FA (%)	
Substrate – Starch							
1	$VOSO_4$	0.1 mmol	413 K, 20 bar O_2, 1.5 h V_{H2O} = 20 mL	1 mmol	-	46	[12]
Substrate – Cellulose							
2	$H_5PV_2Mo_{10}O_{40}$	0.03 mmol	353 K, 30 bar O_2, 26 h	120 mg	n.d	1	[1]
3	$H_8PV_5Mo_7O_{40}$ - p-toluenesulfonic acid	2 mmol 20 mmol	363 K, 50 bar O_2, 5-72 h, 1000 rpm V_{H2O} = 200 mL	100 mmol	-	3-31	[3]
4	$H_5PV_2Mo_{10}O_{40}$	5 mol %	443 K, 50 bar O_2, 9 h, 1000 rpm V_{H2O} = 50 mL	0.5 g	-	35	[4]
5	$NaVO_3$ – H_2SO_4	22 mg - 0.7 wt%	433 K, 30 bar O_2, 120 min V_{H2O} = 6 mL	100 mg	100	65	[5]
6	$Co_{0.6}H_{3.8}PMo_{10}V_2O_{40}$	0.01M	433 K, 20 bar O_2, 5 h, 1500 rpm V_{H2O} = 60 mL	0.6 g	-	66	[7]
7	$H_5PV_2Mo_{10}O_{40}$	0.75 mmol	363 K, 30 bar O_2, 24 h, 1000 rpm V_{H2O} = 100 mL	2.7 g	-	(FA + CO_2) – 15%	[8]
8	$H_5PV_2Mo_{10}O_{40}$ - p-toluenesulfonic acid	0.75 mmol 1.9 g	363 K, 30 bar O_2, 66 h, 1000 rpm V_{H2O} = 100 mL	2.7 g	-	(FA + CO_2) – 68%	[8]
9	$H_4PVMo_{11}O_{40}$	0.1 mmol	453 K, 20 bar O_2, 3 h, 600 rpm V_{H2O} = 20 mL	0.2 g	-	61	[6]
10	$H_4PVMo_{11}O_{40}$	0.1 mmol	453 K, 6 bar O_2, 3 h, 600 rpm V_{H2O} = 20 mL	0.2 g	100	68	[6]

Table S3. (Continue)

Run	Catalyst		Experimental conditions		Results		Ref.
		Amount		Substrate	Conversion, (%)	Yield of FA (%)	
Substrate – Cellulose							
11	$Co_{0.6}H_{3.8}PMo_{10}V_2O_{40}$	0.01M	423 K, 20 bar O_2, 7 h, 1500 rpm V_{H2O} = 60 mL	0.6 g	-	29	[9]
12	$NaVO_3$-H_2SO_4	2% - 0.35%	433 K, 30 bar O_2, 5 min V_{H2O} = 6 mL	0.05 g	98	95	[10]
13	$[MIMPS]_3HPMo_{11}VO_{40}$	0.05 mmol	453 K, 10 bar O_2, 1 h V_{H2O} = 5 mL	0.335 g	93	51	[11]
14	$VOSO_4$	0.2 mmol	453 K, 20 bar O_2, 2 h V_{H2O} = 20 mL	1 mmol	-	39	[12]
Substrate – Xylan (hemicellulose)							
15	$H_5PV_2Mo_{10}O_{40}$	0.03 mmol	353 K, 30 bar O_2, 26 h	120 mg	n.d.	33	[1]
16	$NaVO_3$ – H_2SO_4	22 mg - 0.7 wt%	433 K, 30 bar O_2, 30 min V_{H2O} = 6 mL	100 mg	100	64	[5]
17	$H_5PV_2Mo_{10}O_{40}$	0.75 mmol	363 K, 30 bar O_2, 24 h, 1000 rpm V_{H2O} = 100 mL	2.7 g	-	(FA + CO_2) – 88%	[8]
18	$H_5PV_2Mo_{10}O_{40}$ - p-toluenesulfonic acid	0.75 mmol 1.9 g	363 K, 30 bar O_2, 66 h, 1000 rpm V_{H2O} = 100 mL	2.7 g	-	(FA + CO_2) – 100%	[8]
19	$Co_{0.6}H_{3.8}PMo_{10}V_2O_{40}$	0.01M	393 K, 20 bar O_2, 2 h, 1500 rpm V_{H2O} = 60 mL	0.6 g	-	42	[9]

Table S3. (Continue)

Run	Catalyst		Experimental conditions		Results		Ref.
		Amount		Substrate	Conversion, (%)	Yield of FA (%)	
Substrate – Xylan (hemicellulose)							
20	$NaVO_3$-H_2SO_4	2% - 0.35%	433 K, 30 bar O_2, 5 min V_{H2O} = 6 mL	0.05 g	-	86	[10]
21	$K_5V_3W_3O_{19}$	1 mmol	363 K, 30 bar O_2, 24 h, 1000 rpm V_{H2O} = 100 mL	100 mmol	-	24	[13]
Substrate – Arabinogalactan (hemicellulose)							
22	$Co_{0.6}H_{3.8}PMo_{10}V_2O_{40}$	0.01 M	393 K, 20 bar O_2, 1 h, 1500 rpm V_{H2O} = 60 mL	0.6 g	-	40	[9]

Table S4. The main catalytic systems for one-pot hydrolysis-oxidation of lignin into formic acid

Run	Catalyst		Experimental conditions		Results		Ref.
		Amount		Lignin	Conversion, (%)	Yield of FA (%)	
1	$H_5PV_2Mo_{10}O_{40}$	0.03 mmol	353 K, 30 bar O_2, 26 h	120 mg	n.d.	14	[1]
2	$H_5PV_2Mo_{10}O_{40}$	0.75 mmol	363 K, 30 bar O_2, 66 h, 1000 rpm V_{H2O} = 100 mL	2.7 g	-	($FA + CO_2$) – 100%	[8]
3	$H_5PV_2Mo_{10}O_{40}$ - p-toluenesulfonic acid	0.75 mmol 1.9 g	363 K, 30 bar O_2, 66 h, 1000 rpm V_{H2O} = 100 mL	2.7 g	-	($FA + CO_2$) – 100%	[8]
4	$NaVO_3$-H_2SO_4	2% - 0.35%	433 K, 30 bar O_2, 5 min V_{H2O} = 6 mL	0.05 g	88	17	[10]
5	$K_5V_3W_3O_{19}$	1mmol	363 K, 30 bar O_2, 24 h, 1000 rpm V_{H2O} = 100 mL	100 mmol	-	7	[13]

Table S5. The main catalytic systems for one-pot hydrolysis-oxidation of biomass into formic acid

Run	Catalyst		Experimental conditions			Results		Ref.
		Amount		Biomass		Conversion, (%)	Yield of FA (%)	
					Amount			
1	$H_5PV_2Mo_{10}O_{40}$	0.03 mmol	353 K, 30 bar O_2, 26 h	poplar sawdust	120 mg	n.d.	1	[1]
2	$H_5PV_2Mo_{10}O_{40}$	0.75 mmol	363 K, 30 bar O_2, 24 h, 100 rpm V_{H2O} = 100 mL	poplar	2.7 g	-	(FA + CO_2) – 77%	[8]
3	$H_5PV_2Mo_{10}O_{40}$ - p-toluenesulfonic acid	0.75 mmol 1.9 g	363 K, 30 bar O_2, 66 h, 1000 rpm V_{H2O} = 100 mL	poplar	2.7 g	-	(FA + CO_2) – 80%	[8]
4	$H_4PVMo_{11}O_{40}$	0.1 mmol	453 K, 6 bar O_2, 3 h, 600 rpm V_{H2O} = 20 mL	bagasse	0.2 g	100	61 AA - 20%	[6]
5	$H_4PVMo_{11}O_{40}$	0.1 mmol	453 K, 20 bar O_2, 3 h, 600 rpm V_{H2O} = 20 mL	hay	0.2 g	100	55 AA – 14%	[6]
6	$H_8PV_5Mo_7O_{40}$	0.5 mmol	363 K, 20 bar O_2, 6-48 h, 1000 rpm V_{H2O} = 100 mL, $m_{alcohol}$ = 100 g. Alcohol: 1-Hexanol, 1-Heptanol	beech wood	1.63 g	-	10-61	[2]
7	$H_8PV_5Mo_7O_{40}$ - p-toluenesulfonic acid	2 mmol 20 mmol	363 K, 50 bar O_2, 1-24 h, 1000 rpm V_{H2O} = 200 mL	beech wood	100 mmol	-	2-29	[3]
8	$H_5PV_2Mo_{10}O_{40}$	0.75 mmol	363 K, 30 bar O_2, 24 h, 1000 rpm V_{H2O} = 100 mL	beech	2.7 g	-	(FA + CO_2) – 52%	[8]
9	$H_5PV_2Mo_{10}O_{40}$ - p-toluenesulfonic acid	0.75 mmol 1.9 g	363 K, 30 bar O_2, 66 h, 1000 rpm V_{H2O} = 100 mL	beech	2.7 g		(FA + CO_2) – 87%	[8]

Table S5. (Continue)

Run	Catalyst		Experimental conditions			Results		Ref.
		Amount		Biomass		Conversion, (%)	Yield of FA (%)	
					Amount			
10	$K_5V_3W_3O_{19}$	1mmol	388 K, 50 bar O_2, 72 h, 1100 rpm V_{H2O} = 10 mL	beech	4 mmol	-	13	[13]
11	$Co_{0.6}H_{3.8}PMo_{10}V_2O_{40}$	0.01M	423 K, 20 bar O_2, 7 h, 1500 rpm V_{H2O} = 60 mL	aspen wood	0.6 g	-	53	[9]
12	$H_8PV_5Mo_7O_{40}$ - p-toluenesulfonic acid	2 mmol 20 mmol	363 K, 50 bar O_2, 5-24 h, 1000 rpm V_{H2O} = 200 mL	spruce wood	100 mmol	-	17-35	[3]
13	$H_5PV_2Mo_{10}O_{40}$	0.75 mmol	363 K, 30 bar O_2, 24 h, 1000 rpm V_{H2O} = 100 mL	pine	2.7 g	-	(FA + CO_2) – 48%	[8]
14	$H_5PV_2Mo_{10}O_{40}$ - p-toluenesulfonic acid	0.75 mmol 1.9 g	363 K, 30 bar O_2, 24 h, 1000 rpm V_{H2O} = 100 mL	pine	2.7 g	-	(FA + CO_2) – 72%	[8]
15	$H_5PV_2Mo_{10}O_{40}$	0.75 mmol	363 K, 30 bar O_2, 24 h, 100 rpm V_{H2O} = 100 mL	waste paper	2.7 g	-	(FA + CO_2) – 26%	[8]
16	$H_5PV_2Mo_{10}O_{40}$ - p-toluenesulfonic acid	0.75 mmol 1.9 g	363 K, 30 bar O_2, 24 h, 1000 rpm V_{H2O} = 100 mL	waste paper	2.7 g	-	(FA + CO_2) – 68%	[8]
17	$H_5PV_2Mo_{10}O_{40}$	0.75 mmol	363 K, 30 bar O_2, 24 h, 1000 rpm V_{H2O} = 100 mL	cyanobacteria	2.7 g	-	(FA + CO_2) – 33%	[8]

Table S5. (Continue)

Run	Catalyst		Experimental conditions			Results		Ref.
		Amount		Biomass		Conversion, (%)	Yield of FA (%)	
					Amount			
18	$H_5PV_2Mo_{10}O_{40}$ - p-toluenesulfonic acid	0.75 mmol 1.9 g	363 K, 30 bar O_2, 24 h, 1000 rpm V_{H2O} = 100 mL	cyanobacteria	2.7 g	-	($FA + CO_2$) – 71%	[8]
19	$Co_{0.6}H_{3.8}PMo_{10}V_2O_{40}$	0.01M	423 K, 20 bar O_2, 7 h, 1500 rpm V_{H2O} = 60 mL	miscanthus	0.6 g	-	45	[9]
20	$Co_{0.6}H_{3.8}PMo_{10}V_2O_{40}$	0.01M	423 K, 20 bar O_2, 7 h, 1500 rpm V_{H2O} = 60 mL	waste paper	0.6 g	-	24	[9]
21	$NaVO_3$-H_2SO_4	2% - 0.35%	433 K, 30 bar O_2, 5 min V_{H2O} = 6 mL	wheat straw	0.05 g	100	75	[10]

2. Synthesis of heteropoly acids

2.1. Synthesis of $H_4PW_{11}VO_{40}$

Stage A: Commercially available $H_3PW_{12}O_{40}$ (15 g) were dissolved in 100 mL of H_2O at room temperature. When the acids were completely dissolved, pH of the solutions were adjusted to 4.8 for $[PW_{11}O_{39}]^{7-}$ by adding drop by drop concentrated NaOH solution.

Stage B: Synthesis of decavanadic acid $H_6V_{10}O_{28}$. Diluted aqueous solution of 0.0175 M $H_6V_{10}O_{28}$ was prepared from V_2O_5 by the "peroxide" method.

Stage C: The $H_6V_{10}O_{28}$ solution prepared at stage B was added to the solution of $[PW_{11}O_{39}]^{7-}$ prepared at Stage A. The solutions were mixed under stirring at room temperature.

2.1. Synthesis of $H_5SiW_{11}VO_{40}$

Stage A: synthesis of $[SiW_{11}O_{39}]^{8-}$ anions. Commercially available $H_4SiW_{12}O_{40}$ (15 g) were dissolved in 100 mL of H_2O at room temperature. When the acids were completely dissolved, pH of the solutions were adjusted to 5.5-6.0 for $[SiW_{11}O_{39}]^{8-}$ by adding drop by drop concentrated NaOH solution.

Stage B: Synthesis of decavanadic acid $H_6V_{10}O_{28}$. Diluted aqueous solution of 0.0175 M $H_6V_{10}O_{28}$ was prepared from V_2O_5 by the "peroxide" method (see our previous paper [14].

Stage C: The $H_6V_{10}O_{28}$ solution prepared at stage B was added to the solution of $[SiW_{11}O_{39}]^{8-}$ prepared at Stage A. The solutions were mixed under stirring at room temperature.

3. Characterization of Cs-salts of heteropoly acids

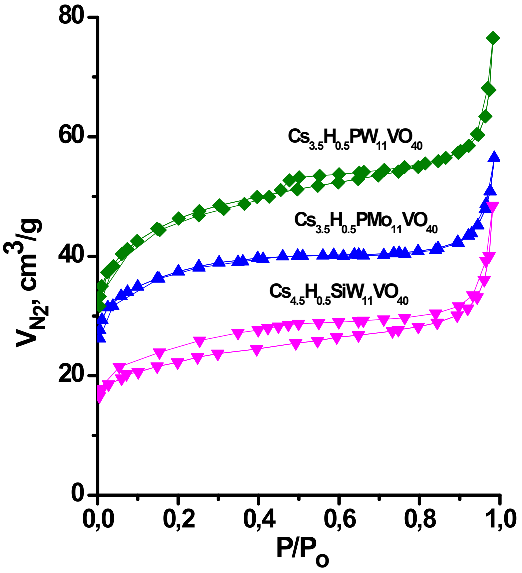


Figure S1. Adsorption-desorption isotherms of N_2 onto cesium salts of heteropoly acids

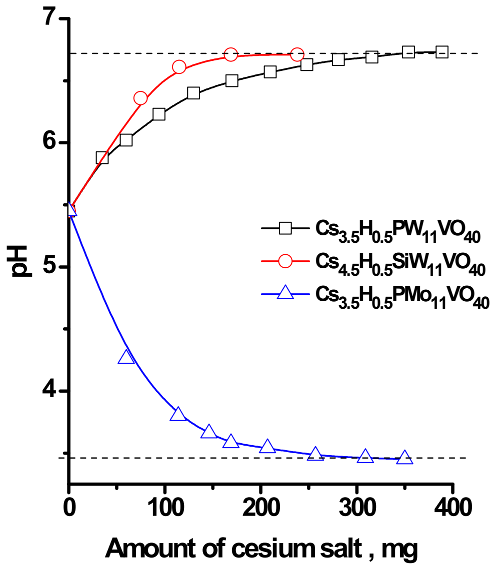


Figure S2. Correlation between pH and amount of cesium salts of heteropoly acids in water

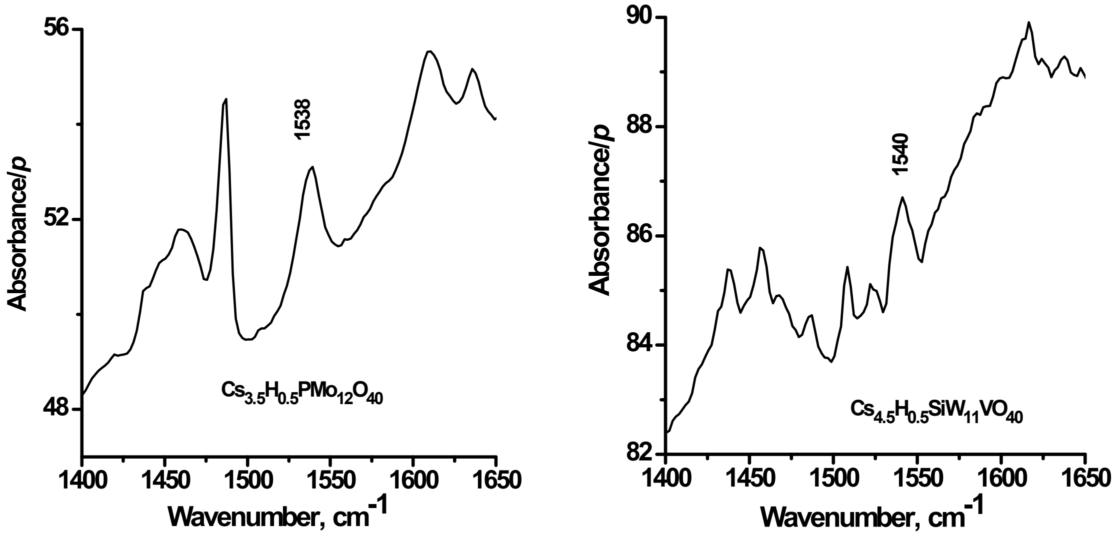


Figure S3. IR spectrum of adsorbed pyridine onto $Cs_{3.5}H_{0.5}PMo_{11}VO_{40}$ and $Cs_{4.5}H_{0.5}SiW_{11}VO_{40}$

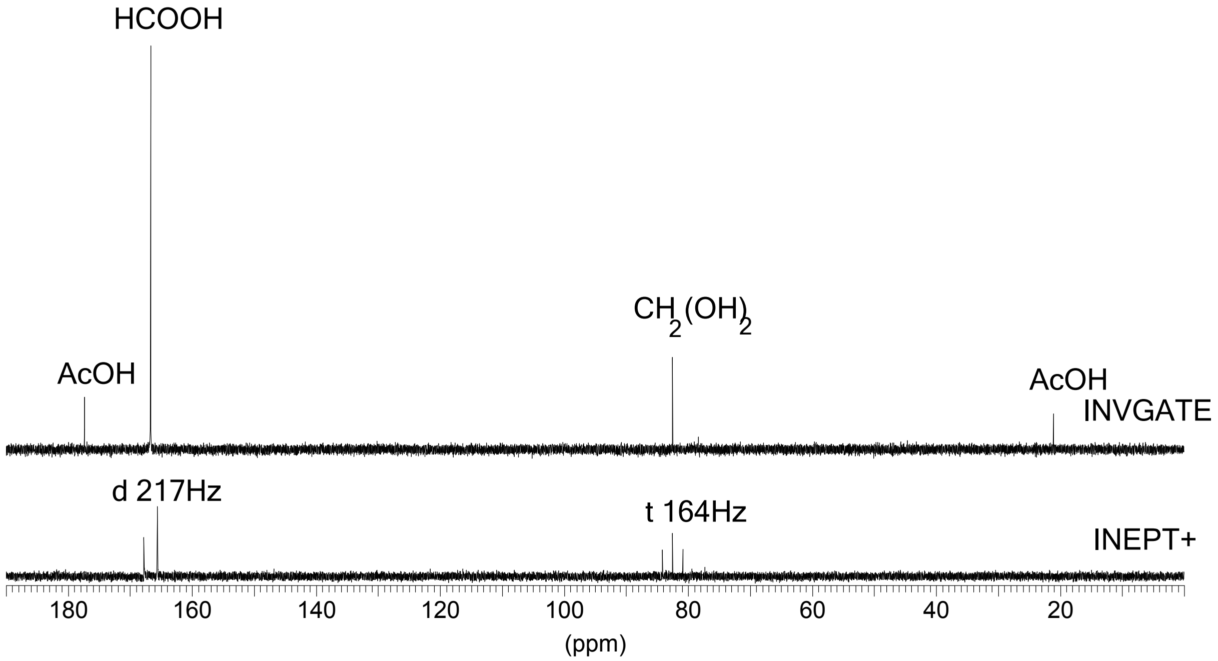


Figure S4 ^{13}C NMR spectra of the sample Cs-PMoV: inverse gated (top) and INEPT+ (no decoupling, bottom).

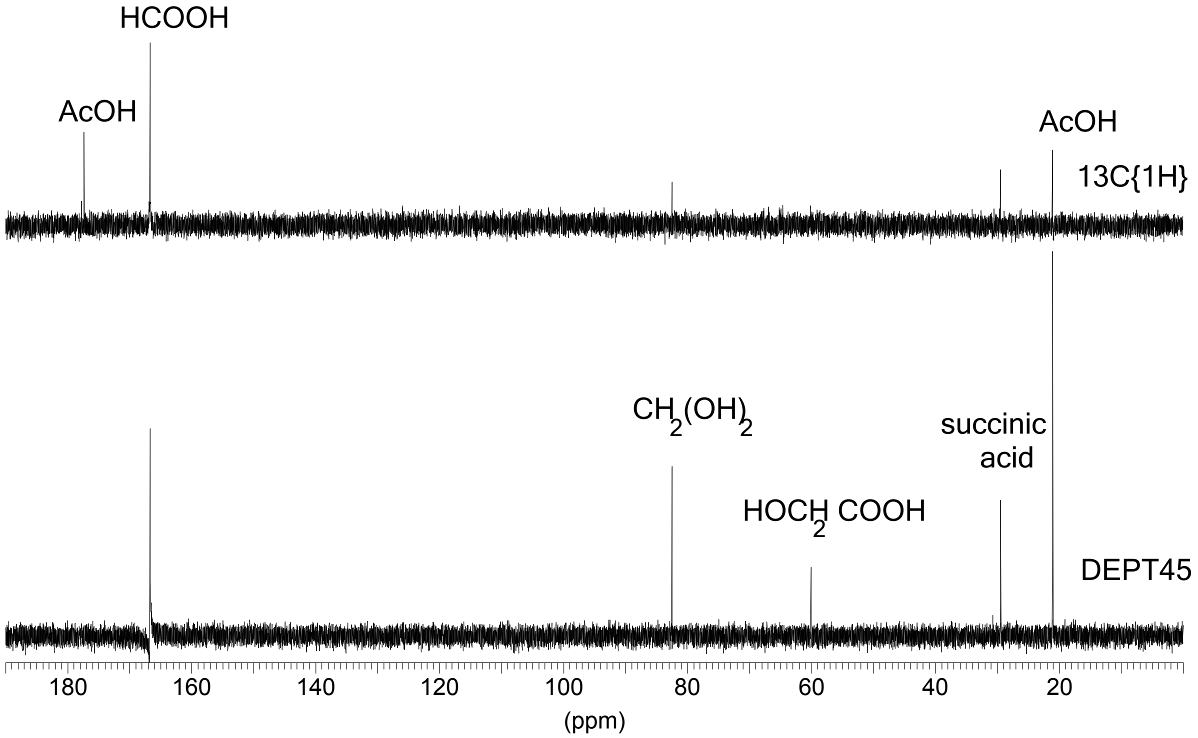


Figure S5 ^{13}C NMR spectra of the sample Cs-PWV: $^{13}C\{^1H\}$ (top) and DEPT45 (bottom).

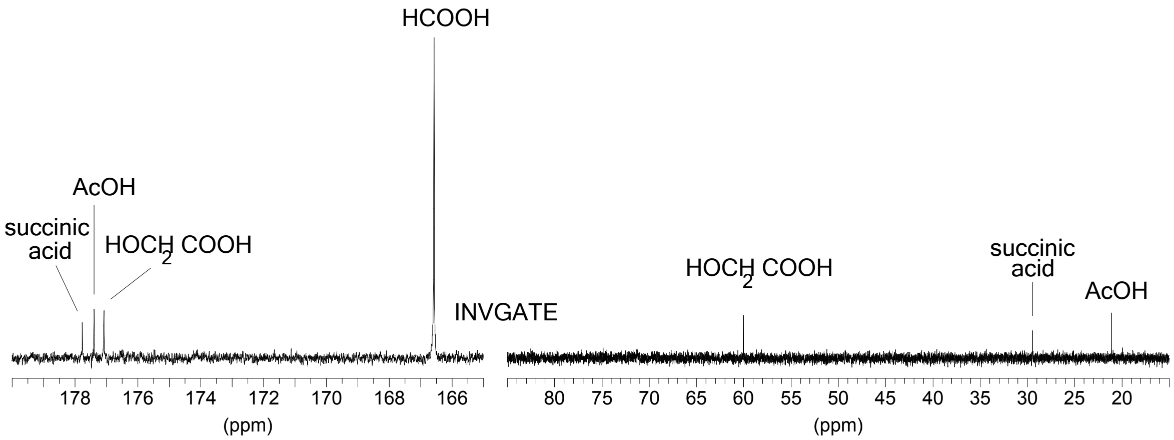
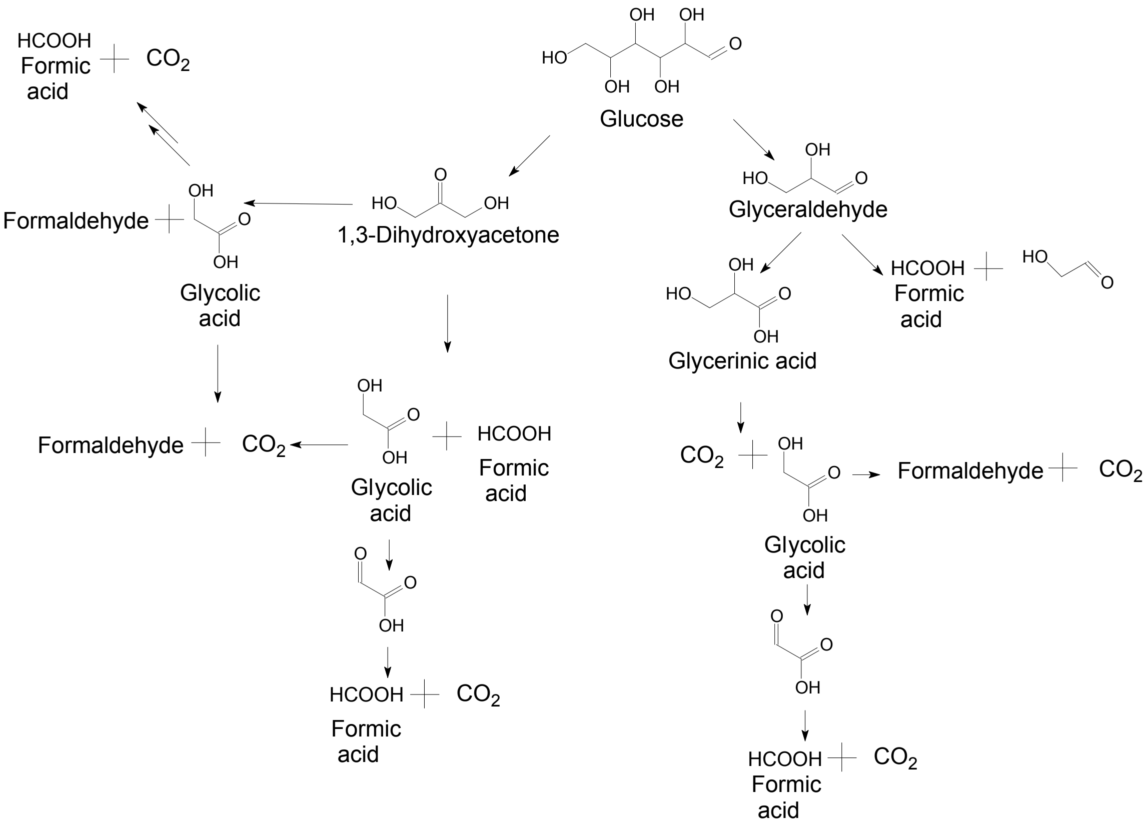


Figure S6 ^{13}C NMR spectrum of the sample Cs-SiWV (inverse gated).

CH_3COOH: ^{1}H (δ, ppm): 2.08; ^{13}C (δ, ppm): 21.03, 177.38
HCOOH: ^{1}H (δ, ppm): 8.23; ^{13}C (δ, ppm): 166.6
$HOCH_2COOH$: ^{1}H (δ, ppm): 4.20; ^{13}C (δ, ppm): 60.02, 177.06
$(CH_2COOH)_2$: ^{1}H (δ, ppm): 2.66; ^{13}C (δ, ppm): 29.39, 177.76
$CH_2(OH)_2$: ^{1}H (δ, ppm): 4.84; ^{13}C (δ, ppm): 82.47



Scheme S1. Mechanism of formic acid formation from glucose [15]

3. References

1 Wolfel R., Taccardi N., Bosmann A., Wasserscheid P. Selective catalytic conversion of biobased carbohydrates to formic acid using molecular oxygen // Green Chemistry. – 2011. – V.13. – P. 2759-2763. DOI:10.1039/C1GC15434F

2 Reichert J., Brunner B., Jess A., Wasserscheid P., Albert J. Biomass oxidation to formic acid in

aqueous media using polyoxometalate catalysts – boosting FA selectivity by in-situ extraction // Energy & Environmental Science. – 2015. – V.8. – P. 2985-2990. DOI: 10.1039/c5ee01706h

3 Reichert J., Albert J. Detailed Kinetic Investigations on the Selective Oxidation of Biomass to Formic Acid (OxFA Process) Using Model Substrates and Real Biomass // ACS Sustainable Chemistry & Engineering. – 2017. – V.5. – P. 7383-7392. https://doi.org/10.1021/acssuschemeng.7b01723

4 Li J., Ding D.-J., Deng L., Guo Q.-X., Fu Y. Catalytic air oxidation of biomass-derived carbohydrates to formic acid // ChemSusChem. – 2012. – V.5. – P. 1313-1318. DOI: 10.1002/cssc.201100466.

5 Wang W., Niu M., Hou Y., Wu W., Liu Z., Liu Q., Ren S., Marsh K.N. Catalytic conversion of biomass-derived carbohydrates to formic acid using molecular oxygen // Green Chemistry. – 2014. – V.16. – P. 2614–2618. https://doi.org/10.1039/C4GC00145A

6 Zhang J., Sun M., Liu X., Han Y. Catalytic oxidative conversion of cellulosic biomass to formic acid and acetic acid with exceptionally high yields // Catalysis Today. – 2014. – V. 233. – P. 77-82. http://dx.doi.org/10.1016/j.cattod.2013.12.010

7 Gromov N. V., Taran O. P., Delidovich I. V., Pestunov A.V., Rodikova Yu.A., Yatsenko D.A., Zhizhina E.G., Parmon V.N. Hydrolytic Oxidation of Cellulose to Formic Acid in the Presence of Heteropoly Acid Catalysts for Efficient Processing of Lignocellulosic Biomass // Catalysis Today. – 2016. –V. 278. – P. 74-81. http://dx.doi.org/10.1016/j.cattod.2016.03.030

8 Albert J., Wolfel R., Bosmann A., Wasserscheid P. Selective oxidation of complex, water-insoluble biomass to formic acid using additives as reaction accelerators // Energy & Environmental Science. – 2012. – V. 5. – P. 7956-7962. https://doi.org/10.1039/C2EE21428H

9 Gromov N.V., Medvedeva T.B., Rodikova Y.A., Pestunov A.V., Zhizhina E.G., Taran O.P. The Production of Formic Acid from Polysaccharides and Biomass via One-pot Hydrolysis-Oxidation in the Presence of Mo-V-P Heteropoly Acid Catalyst // Journal of Siberian Federal University. Chemistry 1. – 2018. – V.11. – P. 56-71. DOI: 10.17516/1998-2836-0058

10 Niu M., Hou Y., Ren S., Wu W., Marsh K.N. Conversion of wheat straw into formic acid in $NaVO_3$–H_2SO_4 aqueous solution with molecular oxygen // Green Chemistry. – 2015. – V.17. – P. 453-459. DOI: 10.1039/c4gc01440e

11 Xu J., Zhang H., Zhao Y., Yang Z., Yu B., Xu H., Liu Z. Heteropolyanion-based ionic liquids catalysed conversion of cellulose into formic acid without any additives //Green Chemistry. – 2014. – V.16. – P. 4931–4935. https://doi.org/10.1039/C4GC01252F

12 Tang Z., Deng W., Wang Y., Zhu E., Wan X., Zhang Q., Wang Y. Transformation of cellulose and its derived carbohydrates into formic and lactic acids catalyzed by vanadyl cations // ChemSusChem. – 2014. – V.7. – P. 1557–1567. DOI: 10.1002/cssc.201400150

13 Voß D., Pickel H., Albert J. Improving the fractionated catalytic oxidation of lignocellulosic biomass to formic acid and cellulose by using design of experiments // ACS ACS Sustainable Chemistry & Engineering. – 2019. – V.7. – P. 9754–9762. https://doi.org/10.1021/acssuschemeng.8b05095

14 V.F.Odyakov, E.G. Zhizhina, Russ. J. Inorg. Chem. 54 (2009) 361. https://doi.org/10.1134/S003602360903005X

15 Tang Z., Deng W., Wang Y., et al. Transformation of Cellulose and its Derived Carbohydrates into Formic and Lactic Acids Catalyzed by Vanadyl Cations // ChemSusChem. - 2014. - V. 7. - N. 6. - P. 1557-1567.