

# Supplementary Materials: Metal-Catalyzed Degradation of Cellulose in Ionic Liquid Media

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**Table S1.** Glucose, mannose and HMF contents in cellulose samples degraded in [BMIM]Cl using ZnCl<sub>2</sub>, MgCl<sub>2</sub>, CrCl<sub>3</sub>, tungsten (W-POM) and molybdenum (Mo-POM) oxide-based POMs as catalysts. Catalyst loading was 10 wt % from cellulose and cellulose loading was 10 wt %.

Catalyst	Glucose, %	Mannose, %	HMF, %	Total products yield, %
No catalyst	>0.04	>0.04	>0.04	>0.04
ZnCl <sub>2</sub>	>0.04	>0.04	4.64 ± 0.3	4.64
MgCl <sub>2</sub>	>0.04	>0.04	3.78 ± 0.3	3.78
CrCl <sub>3</sub>	>0.04	>0.04	55.3 ± 0.6	55.3
W-POM	33.7 ± 0.1	>0.04	5.82 ± 0.2	39.5
Mo-POM	4.96 ± 0.3	2.26 ± 0.1	2.95 ± 0.1	10.2

**Table S2.** Conversion of cellulose to glucose, mannose and HMF in [BMIM]Cl at 100 and 120 °C by using POMs based on molybdenum oxide. Catalyst loading was 10 wt % from cellulose and cellulose loading was 10 wt % from solvent.

Time, h	Glucose at 100°C	HMF at 100°C	Mannose at 100°C	HMF at 120°C
0	>0.04	>0.04	>0.04	>0.04
8	0.75 ± 0.2	1.21 ± 0.3	0.31 ± 0.1	1.39 ± 0.3
24	4.96 ± 0.3	2.95 ± 0.1	2.26 ± 0.3	3.43 ± 0.4
48	9.18 ± 0.3	5.11 ± 0.3	3.78 ± 0.2	0.97 ± 0.2
72	13.9 ± 0.1	7.15 ± 0.2	5.47 ± 0.3	0.46 ± 0.1

**Table S3.** Conversion of cellulose to glucose, mannose and HMF in [BMIM]Cl at 100 and 120 °C by using POMs based on tungsten oxide. Catalyst loading was 10 wt % from cellulose and cellulose loading was 10 wt % from solvent.

Time, h	Glucose at 100°C	HMF at 100°C	HMF at 120°C
0	>0.04	>0.04	>0.04
8	12.8 ± 0.7	1.50 ± 0.3	2.16 ± 0.2
24	33.7 ± 0.9	5.81 ± 0.4	1.36 ± 0.2
48	36.0 ± 0.5	9.54 ± 0.4	0.07 ± 0.0
72	36.7 ± 0.3	11.6 ± 0.7	0.01 ± 0.0

**Table S4.** Efficiency of cellulose degradation in [BMIM]Cl at 100°C by using phosphotungstic acid hydrate added 20 min before the substrate. Catalyst loading was 10 wt % from cellulose and cellulose loading was 10 wt % from solvent.

Time, h	Glucose, %	HMF, %
0	>0.04	>0.04
3	2.53 ± 0.3	0.30 ± 0.1
8	12.8 ± 0.4	1.50 ± 0.2
24	33.7 ± 0.7	5.81 ± 0.3
48	36.0 ± 0.5	9.54 ± 0.3
72	36.7 ± 0.4	11.6 ± 0.5

**Table S5.** Conversion of cellulose to HMF in [BMIM]Cl at 120°C by using tungsten and molybdenum oxides-based POMs at 5 and 10% substrate loading. Catalyst loading was 10 wt % from cellulose and cellulose loading was 5 or 10 wt % from solvent.

Time, h	W-pom*, %	W-POM**, %	Mo-pom*, %	Mo-pom**, %
0	>0.04	>0.04	>0.04	>0.04
8	4.33	4.65	2.79	2.93
24	2.72	3.07	6.86	6.59
48	0.20	0.43	1.93	3.25
72	0.01	0.16	0.92	1.12

\* substrate loading 5 wt %; \*\* substrate loading 10 wt %.

**Table S6.** Efficiency of cellulose degradation in [BMIM]Cl at 100°C by using phosphotungstic acid hydrate added 3 h after the substrate. Catalyst loading was 10 wt % from cellulose and cellulose loading was 10 wt % from solvent.

Time, h	Glucose, %	HMF, %	Cellobiose, %
1	>0.04	>0.04	>0.04
19	3.51 ± 0.2	0.44 ± 0.1	1.33 ± 0.1
24	6.87 ± 0.1	0.95 ± 0.2	2.10 ± 0.2
48	9.65 ± 0.5	3.20 ± 0.2	>0.04
72	>0.04	3.67 ± 0.3	>0.04

**Table S7.** Conversion of cellulose to glucose, mannose and HMF in [BMIM]Cl at 100 °C in the presence of water (10 wt % of solvent) by using POMs based on tungsten oxide. Catalyst loading was 10 wt % from cellulose and cellulose loading was 10 wt % from solvent.

Time, h	Glucose*, %	HMF*, %	Glucose, %	HMF, %
0	>0.04	>0.04	>0.04	>0.04
9	>0.04	0.15 ± 0.1	12.8 ± 0.4	1.50 ± 0.1
24	8.68 ± 0.4	1.36 ± 0.2	33.7 ± 0.6	5.81 ± 0.2
48	1.28 ± 0.2	3.23 ± 0.4	36.0 ± 0.5	9.54 ± 0.5
72	0.93 ± 0.1	3.78 ± 0.2	36.7 ± 0.4	11.6 ± 0.3

\* Reaction mixture contained 10 wt % water.

**Table S8.** Conversion of cellulose to glucose, mannose and HMF in [BMIM]Cl at 100 °C in the presence of water (10 wt % of solvent) by using POMs based on (a) tungsten oxide, (b) molybdenum oxide. Catalyst loading was 10 wt % from cellulose and cellulose loading was 10 wt % from solvent.

Time, h	Glucose*, %	Mannose*, %	HMF*, %	Glucose, %	HMF, %	Mannose, %
0	>0.04	>0.04	>0.04	>0.04	>0.04	>0.04
8	>0.04	>0.04	3.41 ± 0.1	0.75 ± 0.1	1.21 ± 0.1	0.30 ± 0.0
24	>0.04	>0.04	8.46 ± 0.3	4.96 ± 0.2	2.95 ± 0.3	2.26 ± 0.1
48	22.8 ± 0.2	7.91 ± 0.2	15.5 ± 0.2	9.18 ± 0.2	5.11 ± 0.2	3.78 ± 0.2
72	3.77 ± 0.1	14.8 ± 0.3	22.4 ± 0.2	13.9 ± 0.4	7.15 ± 0.2	5.47 ± 0.3

\* Reaction mixture contained 10 wt % water.