

Supporting Information

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Conversion of Fructose into 5-(Hydroxymethyl)furfural in Sulfolane

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Table S1. Effect of metal chlorides on the conversion of D-fructose to HMF

Catalyst, wt% ^[a]	LiCl Additive, wt% ^[a]	HMF Yield (%) ^[b]
LiCl, 100	0	67
CrCl ₂ , 5	100	52
CuCl, 5	100	59
CuCl ₂ , 5	100	56
AlCl ₃ , 5	100	49
KCl, 5	100	58
MgCl ₂ ·6H ₂ O, 5	100	59
MnCl ₂ ·4H ₂ O, 5	100	60
NaCl, 5	100	59
RbCl, 5	100	60
ZnCl ₂ , 5	100	60
BaCl ₂ ·2H ₂ O, 5	100	26
CdCl ₂ ·2.5H ₂ O, 5	100	51
CaCl ₂ ·2H ₂ O, 5	100	44
CsCl, 5	100	44
CoCl ₂ ·6H ₂ O, 5	100	46
PdCl ₂ , 5	100	62
NiCl ₂ ·6H ₂ O, 5	100	39
RuCl ₃ (H ₂ O) ₃ , 5	100	64
FeCl ₃ , 5	100	62
VaCl ₃ , 5	100	56
MoCl ₃ , 5	100	51
PtCl ₂ , 5	100	63
LaCl ₃ ·7H ₂ O, 5	100	50

^[a]Catalyst and additive wt% are relative to fructose (83 mg/g) in the reaction mixture. ^[b]Yields are based on HPLC analysis of reactions in sulfolane for 2 h at 90°C.

Table S2. Effect of LiCl:fructose on the conversion of D-fructose to HMF

LiCl:fructose, w/w ^[a]	HMF Yield (%) ^[b]
1.0:1.0	58
1.5:1.0	60
2.0:1.0	55
2.5:1.0	57

^[a]The concentration of fructose was 83 mg/g in the reaction mixture. ^[b]Yields are based on HPLC analysis of reactions in sulfolane for 2 h at 90°C.

Table S3. Effect of LiCl:fructose and sulfolane:fructose ratios on the conversion of D-fructose to HMF in sulfolane

LiCl:fructose, mol/mol	sulfolane:fructose, mol/mol	Time (h)	HMF Yield (%) ^[a]
4.25:1.00	16.5:1.0	2	65
4.25:1.00	16.5:1.0	3	65
4.25:1.00	16.5:1.0	4	58
3.25:1.00	16.5:1.0	2	62
3.25:1.00	16.5:1.0	3	62
3.25:1.00	16.5:1.0	4	60
2.25:1.00	16.5:1.0	2	62
2.25:1.00	16.5:1.0	3	62
2.25:1.00	16.5:1.0	4	60
1.25:1.00	16.5:1.0	2	56
1.25:1.00	16.5:1.0	3	59
1.25:1.00	16.5:1.0	4	60
4.25:1.00	13.5:1.0	2	63
4.25:1.00	13.5:1.0	3	62
4.25:1.00	13.5:1.0	4	58
3.25:1.00	13.5:1.0	2	60
3.25:1.00	13.5:1.0	3	60
3.25:1.00	13.5:1.0	4	59
2.25:1.00	13.5:1.0	2	60
2.25:1.00	13.5:1.0	3	60
2.25:1.00	13.5:1.0	4	59
1.25:1.00	13.5:1.0	2	58
1.25:1.00	13.5:1.0	3	59
1.25:1.00	13.5:1.0	4	59
4.25:1.00	10.5:1.0	2	60
4.25:1.00	10.5:1.0	3	60
4.25:1.00	10.5:1.0	4	58
3.25:1.00	10.5:1.0	2	60
3.25:1.00	10.5:1.0	3	60
3.25:1.00	10.5:1.0	4	59
2.25:1.00	10.5:1.0	2	59
2.25:1.00	10.5:1.0	3	59
2.25:1.00	10.5:1.0	4	58
1.25:1.00	10.5:1.0	2	54
1.25:1.00	10.5:1.0	3	58
1.25:1.00	10.5:1.0	4	59

^[a]Yields are based on HPLC analysis of reactions in sulfolane at 90°C.

Table S4. Effect of sulfolane:fructose ratio on the conversion of D-fructose to HMF in sulfolane

sulfolane:fructose, mol/mol	Time (h)	HMF Yield (%) ^[a]
13.5:1.0	2	63
13.5:1.0	3	62
15.0:1.0	2	63
15.0:1.0	3	62
16.5:1.0	2	65
16.5:1.0	3	65
21.0:1.0	2	67
21.0:1.0	3	66
22.5:1.0	2	67
22.5:1.0	3	66
24.0:1.0	2	67
24.0:1.0	3	65
25.5:1.0	2	65
25.5:1.0	3	66
27.0:1.0	2	65
27.0:1.0	3	63

^[a]Yields are based on HPLC analysis of reactions containing LiCl:fructose 1/1 at 90°C.

Table S5. Effect of acid on the conversion of D-fructose to HMF in sulfolane

acid, mol% ^[a]	Time (min)	LiCl, mol% ^[b]	HMF Yield (%) ^[c]
HCl, 3	120	250	60
HCl, 6	60	250	61
H ₂ SO ₄ , 3	120	250	46
H ₂ SO ₄ , 6	120	250	48
HNO ₃ , 3	120	250	24
HNO ₃ , 6	120	250	23
HOAc, 3	60	250	66
HOAc, 6	60	250	56
HCl, 9	15	0	68
HCl, 9	30	250	60
HCl, 12	15	0	65
HCl, 12	15	250	63
HCl, 15	15	0	62
HCl, 15	15	250	63
HOAc, 9	45	0	0
HOAc, 9	60	250	21
HOAc, 12	45	0	2
HOAc, 12	60	250	61
HOAc, 15	45	0	3
HOAc, 15	15	250	32

^[a]Mol% relative to solvent.

^[b]Mol% is relative to fructose.

^[c]Yields are based on HPLC analysis of reactions at 90°C.

Table S6. Conversion of sugars to a furanic in sulfolane

Substrate	Time (h)	HMF Yield (%) ^[a]	Furfural Yield (%) ^[a]
Cellulose	1.5	4	—
Lactose	1.5	3	—
Glucose	1	6	—
Galactose	2	0	—
Mannose	0.5	2	—
Sorbose	0.5	41	—
Tagatose	0.5	43	—
Arabinose	0.5	—	2
Xylose	0.5	—	30

^[a]Reaction mixtures contained 5 wt% HBr relative to sugar (100 mg/g) at 100°C. Yields are based on HPLC analysis of reactions.

Table S7. Conversion of D-fructose to HMF in DMSO

HBr (wt%) ^[a]	Time (h)	HMF Yield (%) ^[b]
2	0.5	66
5	2	71
7	2	64
9	1.5	52

^[a]HBr wt% is relative to fructose (100 mg/g) in the reaction mixture.

^[b]Yields are based on HPLC analysis of reactions at 100°C.

Table S8. Extraction of HMF from sulfolane^[a]

Aqueous Phase Composition	Organic Phase Composition	R_{HMF} ^[b]	$R_{\text{sulfolane}}$ ^[c]
H ₂ O:sulfolane 9/1	MIBK	1.01	0.60
H ₂ O:sulfolane 9/1	MIBK:2-butanol 9/1	1.32	0.67
H ₂ O:sulfolane 9/1	MIBK:2-butanol 8/2	1.50	0.73
H ₂ O:sulfolane 8/2	MIBK	0.95	0.61
H ₂ O:sulfolane 8/2	MIBK:2-butanol 9/1	1.24	0.69
H ₂ O:sulfolane 8/2	MIBK:2-butanol 8/2	1.40	0.76
H ₂ O:sulfolane 7/3	MIBK	0.91	0.66
H ₂ O:sulfolane 7/3	MIBK:2-butanol 9/1	1.14	0.74
H ₂ O:sulfolane 7/3	MIBK:2-butanol 8/2	1.28	0.81
H ₂ O:sulfolane 6/4	MIBK	0.85	0.70
H ₂ O:sulfolane 6/4	MIBK:2-butanol 9/1	1.06	0.78
H ₂ O:sulfolane 6/4	MIBK:2-butanol 8/2	1.26	0.83

^[a]Water was added to sulfolane containing HMF, followed by MIBK and 2-butanol.

^[b] $R_{\text{HMF}} = [\text{HMF}]_{\text{org}}/[\text{HMF}]_{\text{aq}}$.

^[c] $R_{\text{sulfolane}} = [\text{sulfolane}]_{\text{org}}/[\text{sulfolane}]_{\text{aq}}$.