Supporting information

Contents

Kinetic study

To estimate the kinetic parameters, cellulose conversion experiments were carried out at different reaction temperatures (170, 180 and 190 ^{o}C) and water contents (0, 0.2 and 0.6 mL). The experimental rate date of cellulose conversion and yields of all intermediates and products in the reaction model were recorded and depicted in Figure S1. Based on the overall reaction model, the change of products concentrations as a function of time are presented by the following differential equations:

$$\frac{dC_{cellulose}}{dt} = -(k_1 + k_2 + k_3)C_{cellulose}$$

$$\frac{dC_{coke}}{dt} = k_1 C_{cellulose}$$

$$\frac{dC_{glucose}}{dt} = k_2 C_{cellulose} + k_{-5} C_{MG} - (k_4 + k_5 + k_6)C_{glulose}$$

$$\frac{dC_{MG}}{dt} = k_3 C_{cellulose} + k_5 C_{glucose} - (k_{-5} + k_7 + k_8)C_{MG}$$

$$\frac{dC_{HMF}}{dt} = k_4 C_{glucose} + k_{-9} C_{MMF} - (k_9 + k_{10} + k_{11})C_{HMF}$$

$$\frac{dC_{MMF}}{dt} = k_7 C_{MG} + k_9 C_{HMF} - (k_{-9} + k_{12} + k_{13})C_{MMF}$$

$$\frac{dC_{LA}}{dt} = k_{10} C_{HMF} + k_{-14} C_{ML} - (k_{14} + k_{15})C_{LA}$$

$$\frac{dC_{ML}}{dt} = k_{12} C_{MMF} + k_{14} C_{LA} - (k_{-14} + k_{16})C_{ML}$$

$$\frac{dC_{humin}}{dt} = k_6 C_{glucose} + k_8 C_{MG} + k_{11} C_{HMF} + k_{13} C_{MMF} + k_{15} C_{LA} + k_{16} C_{ML}$$

where $C_{cellulose}$, C_{coke}, $C_{glucose}$, C_{MG}, C_{HMF}, C_{MMF}, C_{LA}, C_{ML} and C_{humins} represent the concentration of cellulose, coke, glucose, methyl glucoside, 5-hydroxymethylfurfural, 5-methoxymethylfurfural, levulinic acid, methyl levulinate and humins at time t (min), in mg/mL. By solving these ordinary differential equations (ODEs) simultaneously using MATLAB program, the kinetic parameters k_1-k_{16} were determined. The function of lsqnonlin nonlinear fitting in MATLAB was also utilized to minimize the error between experimental and predicated data. The obtained reaction rate constants were then used to evaluate the apparent activation energy (Ea) by plotting -ln k versus 1000/RT through Arrhenius equation (Figure S2a)

Table S1 Conversion of cellulose in methanol at low temperatures.

Entry	Temperature (°C)	Time (min)	Conv. (%)	ML yield (%)
1	150	40	10.4	1.9
2		120	29.7	8.3
3	160	40	20.3	4.5
4		120	49.5	16.2

Reaction condition: cellulose 3 mmol, 0.6 mmol $Al_2(SO_4)_3$, 0.6 mL H_2O, 14 mL MeOH, 800 W.

Table S2 Effect of reaction temperature

Temp. (°C)	Time (min)	Conv. (%)	Products yields (%)						
			ML	MMF	Glucose	MG	Fructose	Humins	Coke
170	10	6.6	0.6	0.2	3.1	1.6	0.2	0.4	0.1
	20	14.3	2.6	0.7	5.6	2.8	0.2	1.3	0.3
	30	28.5	8.4	1.7	7.8	3.8	0.4	3.0	1.1
	40	46.7	17.8	2.4	11.1	5.2	0.7	4.5	2.1
	50	64.7	27.9	3.1	12.7	6.0	1.5	6.8	3.1
	60	88.7	44.1	3.9	12.3	7.9	0.9	10.7	4.6
	70	100	58.9	1.3	6.2	6.1	0.5	16.2	5.5
	80	100	68.4	0.2	0.2	0.6	0	19.6	6.1
	90	100	67.1	0	0	0	0	22.7	6.3
180	10	67.4	15.4	3.3	25.4	11.0	1.3	1.0	6.5
	20	99.4	47.3	4.1	17.2	10.3	1.5	3.1	9.1
	30	100	64.0	1.9	6.6	5.3	0.9	7.1	10.7
	40	100	70.6	0.1	0	0.5	0	14.5	11.1
	50	100	66.3	0	0	0	0	17.1	11.9
190	10	91.5	23.7	4.5	28.7	15.3	1.7	1.4	11.1
	20	100	53.2	2.5	12.9	8.1	0.3	5.9	13.3
	30	100	66.1	0	0	0.2	0	16.1	13.9
	40	100	59.6	0	0	0	0	21.3	15.0

Reaction condition: cellulose 3 mmol, 0.6 mmol $Al_2(SO_4)_3$, 0.6 mL H_2O, 14 mL MeOH, 800 W.

Table S3 Effect of catalyst loading

Catalyst loading (mol%)	Conv. (%)	Products yields (%)						
		ML	MMF	Glucose	MG	Fructose	Humins	Coke
6.7	57.3	19.1	0.3	10.1	4.9	0.2	4.1	15.3
13.3	98.4	55.1	2.5	7.4	5.8	0.7	9.8	12.8
20	100	70.6	0.1	0	0.5	0	14.5	11.1
26.7	100	67.3	0	0	0	0	18.9	10

Reaction conditions: 3 mmol cellulose, 14 mL MeOH, 0.6 mL H_2O, 800 W, 180 ^oC, 40 min.

Table S4 Effect of water content on the formation of coke, humins and DME.

Water content (mL)	Coke (%)	Humins (%)	DME (%)
0	35.9	17.8	21
0.2	24.4	16.5	13.2
0.4	15.3	14.1	7.5
0.6	11.1	14.5	4.1
0.8	10.1	16.8	3.3
1	9.9	21.9	3.1

Reaction conditions: cellulose 3 mmol, 0.6 mmol $Al_2(SO_4)_3$, 14 mL MeOH, 800 W, 40 min.

Table S5 Products distribution of cellulose methanolysis with different water content.

Water content (mL)	Time (min)	Conv. (%)	Glucose (%)	MG (%)	ML (%)
0	5	14.8	2.5	4.6	2.1
	10	43.1	6.9	13.1	7.3
	20	74.9	4.3	11.4	28.6
	40	100	0	0	45.1
0.2	5	20.8	5.3	5.9	3.4
	10	55.7	13.4	14.6	10.2
	20	87.3	10.8	11.7	34.4
	40	100	0	0.2	56.3
0.6	5	24.1	8.1	3.5	5.3
	10	67.4	25.4	11.0	14.9
	20	99.4	17.2	10.3	47.3
	40	100	0	0.5	70.6

Reaction condition: cellulose 3 mmol, 0.6 mmol $Al_2(SO_4)_3$, 14 mL MeOH, 800 W, 180 ^oC.

Table S6 Conversion of cellulose using conventional heating

Entry	Time (min)	Conv. (%)	ML (%)
1	40	7.4	1.3
2	120	22.1	4.3
3	240	62.2	11.2
4	360	87.1	21.9
5	480	100	36.8
6	600	100	54.1
7	720	100	64.2
8	840	100	58.1

Reaction condition: cellulose 3 mmol, 0.6 mmol $Al_2(SO_4)_3$, 0.6 mL H_2O, 14 mL MeOH, 180 ^oC.

Table S7 Measurement of the formation of dimethyl ether over different acidic catalysts [a]

Entry	Substrates	Catalyst	Cellulose conv. (%)	DME (g)	Solvent loss (%)
1	Cellulose+MeOH	$Al_2(SO_4)_3$	100	0.33	4.1
2	MeOH		-	0.31	3.8
3	Cellulose+MeOH	H_2SO_4	100	1.85	23.2
4	MeOH		-	1.79	22.5
5	Cellulose+MeOH	Amberlyst-15	100	0.45	5.6
6	MeOH		-	0.44	5.5
7	Cellulose+MeOH	$H_3O_{40}PW_{12} \cdot xH_2O$	100	1.56	19.5
8	MeOH		-	1.53	19.2
9	Cellulose+MeOH	$H_4[Si(W_3O_{10})_4] \cdot xH_2O$	100	1.41	17.7
10	MeOH		-	1.39	17.3

[a]Reaction Conditions: 3 mmol cellulose, 0.6 mmol $Al_2(SO_4)_3$/ 1.2 mmol H_2SO_4/ 500 mg Amberlyst-15(H^+, 4.8 mmol/g)/ 200 mg HPAs ,14 mL MeOH, 0.6 mL H_2O, 800 W, 180 ^oC, 40 min.

Table S8 Conversion of glucose and MG with H_2SO_4.[a]

Entry	Substrates	Catalyst	Conv. (%)	ML (%)	Humins (%)
1	Glucose	H_2SO_4	100	39.0	56.3
2		H_2SO_4+Sn-beta[b]	100	77.9	17.8
3	MG	H_2SO_4	100	38.1	57.1
4		H_2SO_4+Sn-beta[b]	100	65.9	29.2

[a] Reaction conditions: 3 mmol Glucose or MG, 1.2 mmol H_2SO_4 ,14 mL MeOH, 0.6 mL H_2O, 800 W, 180 °C, 40 min. b: 100 mg Sn-beta.

Table S9. Conventional oil heating for cellulose conversion.

Entry	Heating method	Time (min)	ML (%)	MMF (%)	Glucose (%)_	Glucoside (%)	Fructose (%)
1	conventional	40	2	1.7	8.4	5.9	0.5
2	conventional	360	38.1	14.0	11.2	13.8	2.0
3	conventional	720	68.8	0.3	-	-	-
4	conventional	840	64.7	-	-	-	-

Reaction condition: cellulose 500 mg, metal salt (M^{n+} 1.2 mmol), 0.6 mL H_2O, 14 mL MeOH, 180 °C.

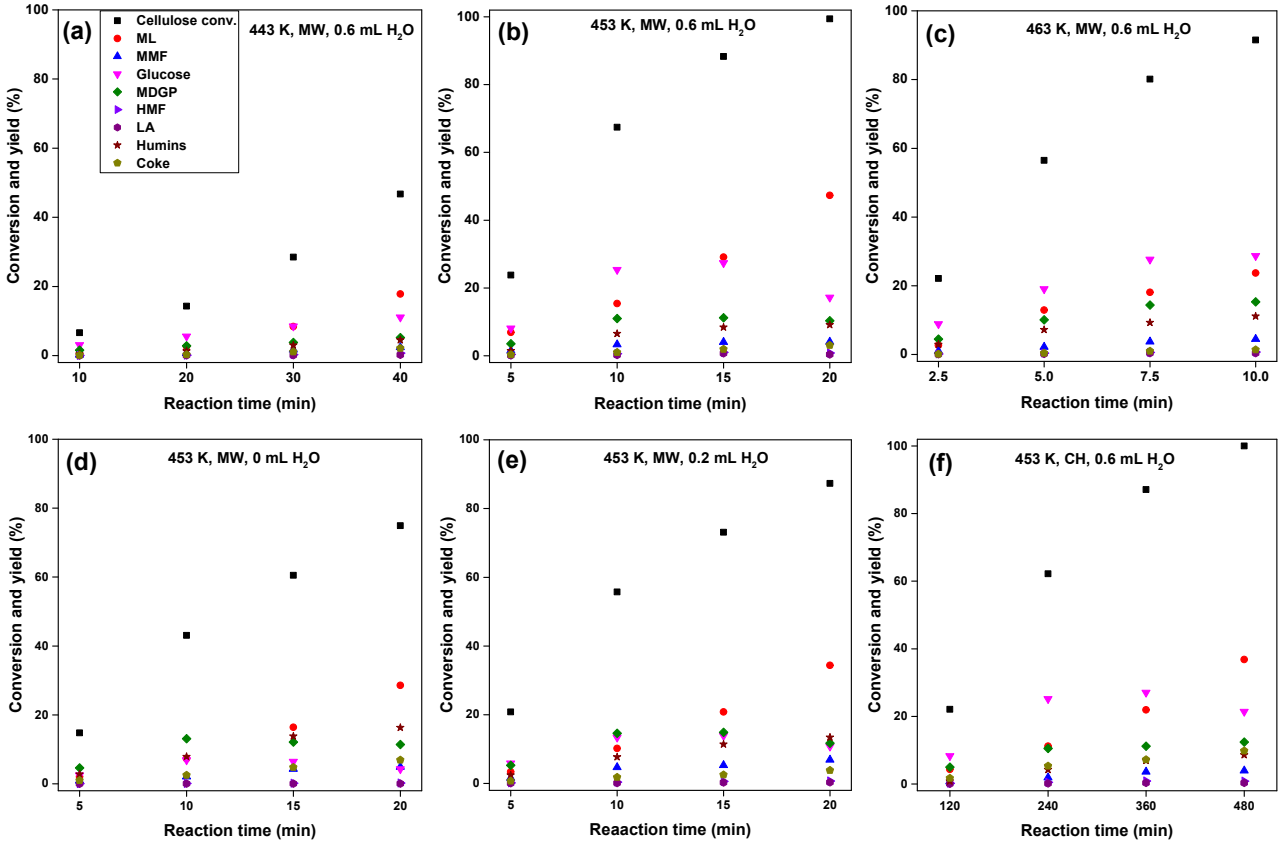

Figure S1. Experimental rate data as a function of reaction temperature and reaction time. Reaction conditions: cellulose 3 mmol, 0.6 mmol $Al_2(SO_4)_3$, 14 mL MeOH, (a): 800 W, 170 °C, 0.6 mL H_2O; (b): 800 W, 180 °C, 0.6 mL H_2O; (c): 800 W, 190 °C, 0.6 mL H_2O; (d): 800 W, 170 °C; (e): 800 W, 170 °C, 0.2 mL H_2O. (f): conventional heating, 180 °C, 0.6 mL H_2O; MW: microwave heating; CH: conventional heating.

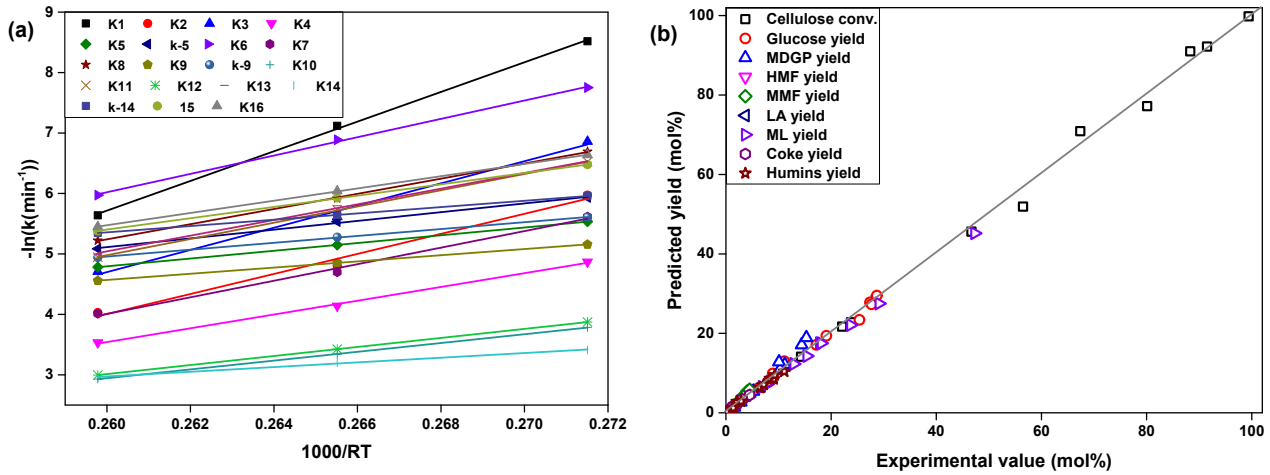

Figure S2. (a) Plots of -lnk ~ 1000/RT. (b) Parity plot of experimental data and model prediction. Reaction conditions: cellulose 3 mmol, 0.6 mmol $Al_2(SO_4)_3$, 14 mL MeOH, 800W, 170-190 °C.

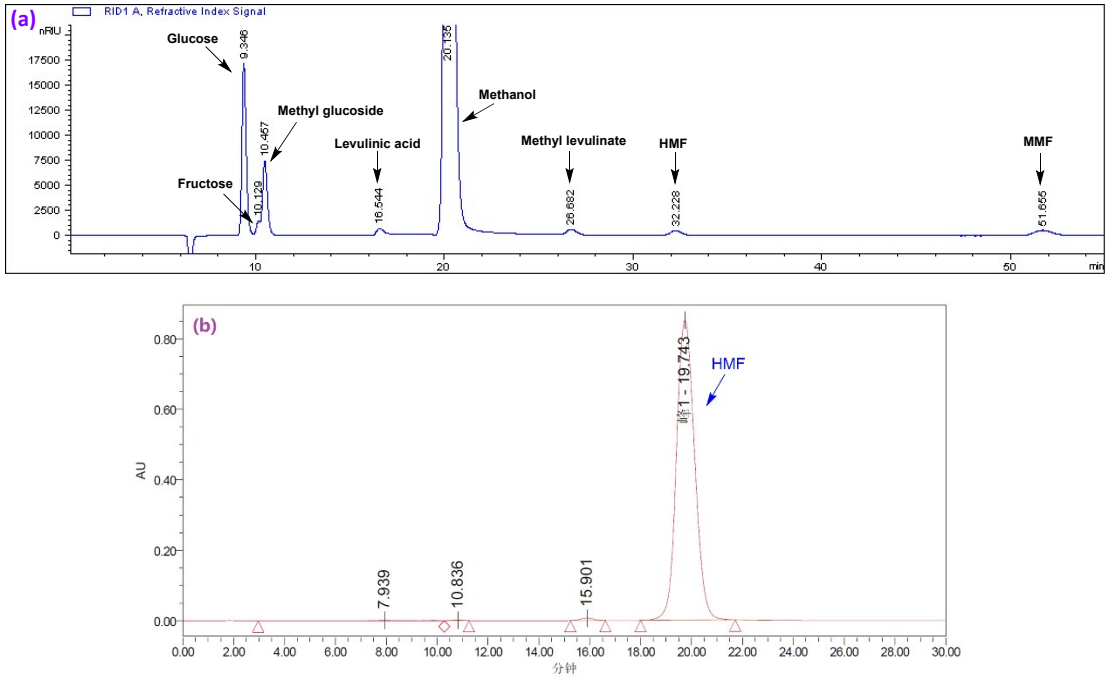

Figure S3 Typical HPLC chromatogram of the reaction mixture obtained from $Al_2(SO_4)_3$ catalyzed cellulose conversion; Reaction conditions: 3 mmol cellulose, 0.6 mmol $Al_2(SO_4)_3$, 0.6 mL H_2O, 14 mL MeOH, 800 W, 180 °C, 20 min; a: RI detector with a HPX-87H column; b: UV detector with a C18 column.

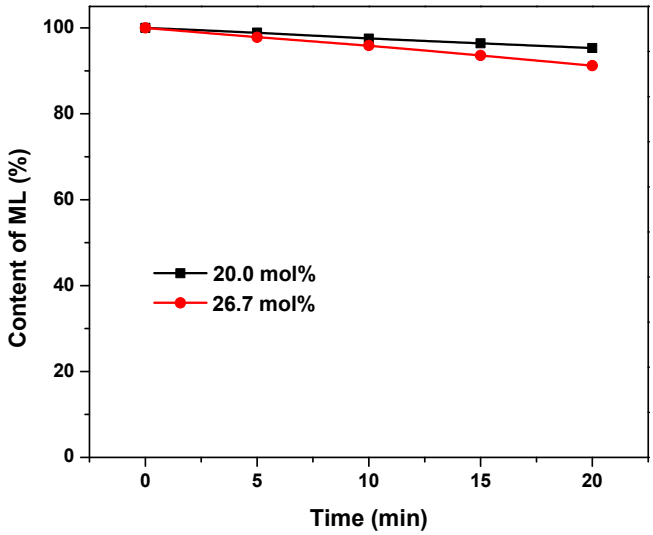

Figure S4. The degradation property of ML with different catalyst loading amount. Reaction conditions: ML 3 mmol, 0.6 mmol (20 mol%) or 0.8 mmol (26.7 mol%) $Al_2(SO_4)_3$, 14 mL MeOH, 0.6 mL H_2O, 800 W, 180 °C.