TANDEM LEWIS/BRONSTED HOMOGENEOUS ACID CATALYSIS: CONVERSION OF GLUCOSE TO HMF IN AN AQUEOUS CrCl₃-HCl SOLUTION

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SUPPORTING INFORMATION

Supporting information

1.1 Excess of formic acid obtained from HMF

If all formic and levulinic acids are formed from Brønsted acid catalyzed HMF rehydration, the molar ratio should be one (line shown in Figure S1). The observed excess of FA indicates it must also form from a different pathway that does not produce LA as a co-product.



Figure S1. Molar ratio of formic to levulinic acids from HMF catalyzed by CrCl₃ as a function of time at two different temperatures. Experiments 5 and 6 in Table 1 used for these data.

1.2 Change in apparent rate constant with Lewis activity descriptor

The apparent rate constant was determined by linearizing the concentration of glucose at times < 40 minutes, where conversion remained low. The linear relationship between the activity descriptor (a_L) and the apparent rate constant suggest that the descriptor accurately captures the change in CrCl₃ reactivity at different HCl concentrations.



Figure S2. Apparent rate constant of glucose consumption as a function of Lewis activity descriptor evaluated at different HCl concentrations. Apparent rate determined using the slope of the log(1-X) vs t for short times. Experiments 9, 19-22 from Table 1 used for these data.



Figure S3. Parity plot based on Experiments 1-6, 9, and 11-16.

1.3 Model predictions for sensitivity of fructose and HMF yield from glucose

In agreement with experimental trends, the model predicts that fructose yield as a function of glucose conversion does not change with CrCl₃ concentration (Figure S4a) or temperature (Figure S5a). Again in agreement with experiment, HMF yield does not change with catalyst concentration (Figure S4b). The model predicts that HMF yields diverge (Figure S5b),

particularly at glucose concentrations > 80%. Experimentally, little difference is observed with temperature, though experimental glucose conversion is lower.



Figure S4. Predicted (a) fructose yield and (b) HMF yield as a function of glucose conversion for different $CrCl_3$ concentrations. Simulation at 10 wt% glucose and 130 °C.



Figure S5. Predicted (a) fructose yield and (b) HMF yield as a function of glucose conversion for different temperatures. Simulation at 10 wt% glucose and 5 mM CrCl₃.

1.4 HMF yield in combined Lewis and Brønsted acid systems

Unlike CrCl₃ concentration and temperature, adding HCl to a reactor changes the observed

HMF yield formed from glucose. Figure S6 shows that the addition of 0.1 M HCl to 17 mM

CrCl₃ increases HMF yield up to ~65% conversion but reduces the maximum HMF yield

achieved from glucose. Figure S7 shows glucose conversion, fructose yield, and HMF yield for

select concentrations of HCl added to CrCl₃.



Figure S6. Measured HMF yields as a function of glucose conversion in aqueous $CrCl_3$ and $CrCl_3 + HCl$ for experiments 13 and 15 from Table 1.



Figure S7. Effect of HCl concentration on (a) glucose conversion, (b) fructose yield, and (c) HMF yield in 5 mM CrCl₃ at 130 °C.

1.5 HMF yield in a biphasic reactor

The HMF yield in a biphasic reactor is shown in Figure S8 and includes both aqueous and organic fractions of HMF.



Figure S8. Predicted HMF yield as a function of time in a biphasic reactor at different HCl concentrations with (a) 5 mM CrCl₃ and (b) 17 mM CrCl₃. 10 wt% glucose, 140 °C, $V_{org}/V_{aq} = 5$ and a partition coefficient of 2.