## **Supporting Information for**

# Speciation and Kinetic Study of Iron Promoted Sugar Conversion to 5-Hydroxymethylfurfural (HMF) and Levulinic Acid (LA)

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## Characterization of Iron Species as Determined by MS, UV-Vis and

#### XANES



Mass Spectra of Iron and Fructose Reactions at Elevated Temperature

Figure S1. Mass spectra of (a) 0.25 M fructose and 0.10 M FeCl<sub>3</sub> in water, (b) after microwave heating at 140 °C for 1 s, and (c) 0.25 M glucose and 0.10 M FeCl<sub>2</sub> in water.

#### UV-Vis Spectra of Iron Fructose Solutions and Comparison of HMF Peak

As shown in the UV-Vis results, Fe<sup>III</sup> in fructose solution shows characteristic absorption band at 300 nm, while the UV-Vis spectrum of Fe<sup>II</sup> in fructose solution is featureless. The rising peak at 280 nm in the spectra for reaction mixtures at 1 s, 1 min, and 5 min reaction times indicated the formation of HMF at elevated temperature (Figure S2 a).<sup>1</sup> When mixed with HMF, the absorbance of Fe<sup>III</sup> overlaps with that of HMF at 280 nm. However, shoulder at about 300-360 nm is characteristic of Fe<sup>III</sup> in the mixture and can be utilized to confirm presence of Fe<sup>III</sup> (Figure S2 b).



Figure S2. (a) UV-Vis spectra of 0.25 M fructose and 0.10 M FeCl<sub>3</sub> in water (red), after 1 s at 140°C (blue), after 1 min at 140°C (green), and after 5 min at 140°C (black). Pink spectrum is a solution of 0.25 M fructose and 0.10 M FeCl<sub>2</sub> in water for comparison. (b) Comparison of spectra of FeCl<sub>3</sub> (red), HMF (blue), and the combination of FeCl<sub>3</sub> and HMF (green).



#### **Differentiate Glucose and Fructose by CAD Experiments**

Figure S3. CAD spectra of (a) m/z 414 for Fe<sup>III</sup>-glucose, (b) m/z 414 for Fe<sup>III</sup>-fructose, (c) m/z 451 for Fe<sup>II</sup>-glucose, and (d) m/z 451 for Fe<sup>II</sup>-fructose. Condition: 0.10 M iron salts (FeCl<sub>3</sub> or FeCl<sub>2</sub>) and 0.25 M sugar (glucose or fructose) in water.

## Quantification of Fe<sup>III</sup> Reduction by XANES



Figure S4. (a) Fe K-edge XANES from 7.09 to 7.16 keV for 0.10 M FeCl<sub>3</sub> and 0.25 M fructose (red), after thermal heating at 140 °C for 16 min (blue), and 0.10 M FeCl<sub>2</sub> and fructose (green) for comparison. (b) Fraction of Fe<sup>III</sup> and Fe<sup>II</sup> in the reaction samples at elevated temperature. Condition: 0.10 M FeCl<sub>3</sub> and 0.25 M fructose under microwave (M) or thermal (T) heating at 140 °C from 0 to 16 min.<sup>2</sup>



## Identification of Unknown Solids by XRD Experiments

Figure S5. XRD spectrum of the solids obtained from 0.25 M glucose and 0.10 M FeCl<sub>3</sub> after 1 s reaction at 140 °C (red), and Akaganéite spectrum from database (blue).

#### **Control Experiments for Speciation Study**

#### Water and Microwave Effect

In order to eliminate the possibility that water and microwave heating alone results in the reduction of Fe<sup>III</sup> to Fe<sup>II</sup>, reactions without sugars have been performed. The Mass spectra of iron salts alone in water show that there is no reduction of Fe<sup>III</sup> to Fe<sup>II</sup> after microwave heating (Figure S5 a, b, and c). Additionally, when adding glucose to the solution of FeCl<sub>3</sub> in water that has been heated for 1 min at 140 °C, only peak m/z 414 is shown in the MS and peak m/z 451 is not in the spectrum, which indicates that iron in the solution is still Fe<sup>III</sup> (Figure S5 d). Furthermore, after putting reaction samples of FeCl<sub>3</sub> and sugars (glucose or fructose) at room temperature without microwave heating for very long time (16 days), there is small amount of Fe<sup>III</sup> reduced to Fe<sup>II</sup> (Figure S5 e and f). These control experiments prove that water and microwave heating alone do not result in Fe<sup>III</sup> reduced to Fe<sup>II</sup>, but microwave heating facilitates the reduction of Fe<sup>III</sup>.





Figure S6. Mass spectra of (a)  $FeCl_3$  (0.10 M) in water, (b) after microwave heating at 140 °C for 1 min, (c)  $FeCl_2$  (0.10 M) in water, (d) the addition of glucose (0.25 M) to the solution of  $FeCl_3$  (0.10 M) in water heated for 1 min at 140 °C, (e) glucose (0.25 M) and  $FeCl_3$  (0.10 M) solution at RT for 16 days, and (f) fructose (0.25 M) and  $FeCl_3$  (0.10 M) solution at RT for 16 days.

#### **Change of Iron Salts**

Other than iron chloride, iron sulfate also shows similar reduction behavior. Mass spectrum of solution of  $Fe_2(SO_4)_3$  and glucose has a dominant  $Fe^{III}$  peak at m/z 414, which corresponds to  $[Fe^{3+} + 2glucose - 2H^+]^+$ , as discussed above. In comparison, mass spectrum of solutions of  $FeSO_4$  and glucose has a dominant ion of m/z 464, which corresponds to  $[Fe^{2+} + 2glucose + 2SO_4^{2-}]^+$ . Upon microwave heating of  $Fe^{III}$ -glucose solution for 2 min, mass spectrum shows that the abundance of ion of m/z 414 decreases and that m/z 464 (corresponding to  $Fe^{II}$ ) increases.





Figure S7. Mass spectra of (a) glucose (0.25 M) and  $\text{Fe}_2(\text{SO}_4)_3$  (0.05 M) in water, (b) after microwave heating at 140 °C for 2 min, and (c) glucose (0.25 M) and  $\text{FeSO}_4$  (0.10 M) in water for comparison.



**Iron and HMF Reactions at Elevated Temperature** 

Figure S8. Mass spectra of (a) HMF (0.25 M) and FeCl<sub>3</sub> (0.05 M) in water, (b) after microwave heating at 140 °C for 1 s, and (c) HMF (0.25 M) and FeCl<sub>2</sub> (0.10 M) in water for comparison.

#### **Testing of Mixture Solutions**

In the solution of fructose (0.25 M),  $FeCl_3$  (0.05 M) and  $FeCl_2$  (0.05 M), the dominant ion is m/z 451 ( $Fe^{II}$ -fructose), while ion abundance for m/z 414 ( $Fe^{III}$ -fructose) is very low (less than 5% relative abundance), suggesting that fructose favor coordination with Fe<sup>II</sup> over Fe<sup>III</sup> in MS (Figure S9 a). In the solution of glucose (0.25 M), FeCl<sub>3</sub> (0.05 M) and FeCl<sub>2</sub> (0.05 M), the dominant ion is m/z 451 (Fe<sup>II</sup>-glucose), while ion abundance for m/z 414 (Fe<sup>III</sup>-glucose) is low (about 35% relative abundance), suggesting that glucose also favor coordination with Fe<sup>II</sup> over Fe<sup>III</sup> in MS, but to a less extend than fructose (Figure S9 b). Not like MS, in the solution of glucose (0.25 M), FeCl<sub>3</sub> (0.05 M) and FeCl<sub>2</sub> (0.05 M), UV-Vis shows the absorption of Fe<sup>III</sup> at about half of that of solution of glucose (0.25 M) and FeCl<sub>3</sub> (0.10 M), indicating that the amount of Fe<sup>III</sup> in the solution detected by UV-Vis is not influenced by sugars or the instrument. In summary, MS favors Fe<sup>II</sup>-sugar (glucose or fructose) complexes to some extent in a mixture solution containing both Fe<sup>III</sup> to Fe<sup>II</sup> qualitatively. In addition, UV-Vis absorption which reflects the amount of Fe<sup>III</sup> present in the mixture solution confirms the reduction of Fe<sup>III</sup> to Fe<sup>II</sup> upon microwave heating in the catalytic reaction solutions.



Figure S9. Mass spectra of (a) fructose (0.25 M), FeCl<sub>3</sub> (0.05 M), and FeCl<sub>2</sub> (0.05 M) mixture in water, (b) glucose (0.25 M), FeCl<sub>3</sub> (0.05 M), and FeCl<sub>2</sub> (0.05 M) mixture in water.



Figure S10. Overlay of UV-Vis Spectrum of 0.25 M glucose, 0.05 M FeCl<sub>3</sub> and 0.05 M FeCl<sub>2</sub> in water (red), 0.25 M glucose and 0.1 M FeCl<sub>2</sub> in water (blue), and 0.25 M glucose and 0.1 M FeCl<sub>3</sub> in water (green).

## **Sugar Conversion Comparison**

Table 1. Comparison of 0.25 M sugar (glucose or fructose) conversion catalyzed by  $0.10 \text{ M FeCl}_3$ , versus  $0.10 \text{ M FeCl}_2$  and HCl, and versus HCl at the same pH (pH = 1), same temperature (140 °C), and same reaction time (60 min for glucose and 15 min for fructose).

Catalyst	Glucose Conversion	Fructose Conversion
FeCl <sub>3</sub>	22 %	94 %
FeCl <sub>2</sub> , HCl	21 %	94 %
HCl	13 %	89 %

## **Kinetic Profiles**



#### **Kinetic Modelling Using Different Iron Concentrations**

Figure S11. (a) Kinetic profiles for HMF conversion to LA and FA. (b) Kinetic profiles for reaction of fructose. (c) Kinetics profiles for reaction of glucose. Conditions: The reaction of 0.25 M substance and 0.025 M FeCl<sub>3</sub> at 140 °C. Points are data and solid lines represent kinetic modeling fits. Simulation starts from the point that after temperature reaches 140 °C. <sup>3,4</sup>

Kinetic Modeling in a Biphasic System



Figure S12. (a) Kinetic profiles for HMF conversion to LA and FA. (b) Kinetic profiles for reaction of fructose. Conditions: The reaction of 0.25 M substance and 0.025 M FeCl<sub>3</sub> at 140 °C in a water:MeTHF (1:3) biphasic system. Points are data and solid lines represent kinetic modeling fits. Simulation starts from the point that after temperature reaches 140 °C.



## **Characterization of Solvent Decomposition by GC-MS**

Figure S13. (a) GC-MS spectrum of the first unknown peak. (b) GC-MS spectrum of (Z)-3penten-1-ol from GC-MS library database. (c) GC-MS spectrum of the second unknown peak. (d) GC-MS spectrum of 1,4-Pentanediol from GC-MS library database. Reaction condition: 0.10 M FeCl<sub>3</sub> in 1 ml H<sub>2</sub>O and 3 ml MeTHF at 200 °C microwave heating for 5 min.

## References

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