

Selectivity enhancement in the aqueous acid-catalyzed conversion of glucose to 5-hydroxymethylfurfural induced by choline chloride

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Supporting information

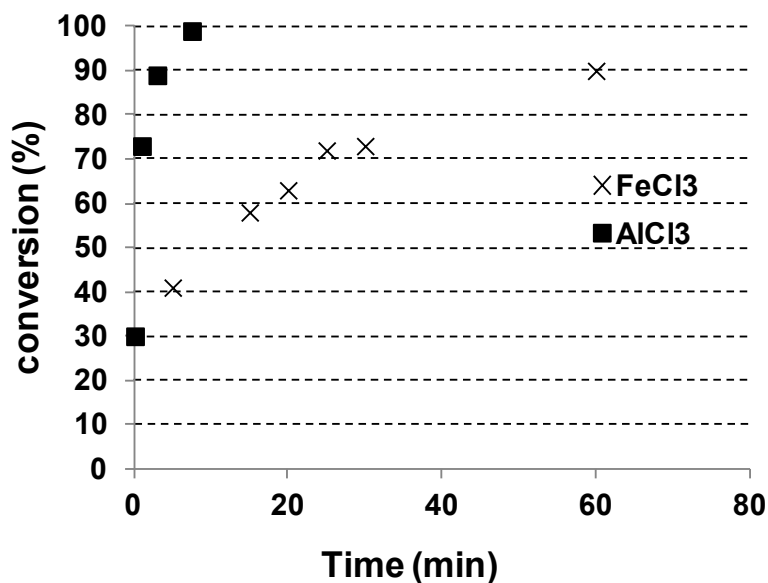


Fig. S1. Comparison between FeCl₃ and AlCl₃: Conversion of glucose vs Time (180°C, 3 mol% of MCl₃, 10 wt % of glucose, reaction media = ChCl-H₂O/MIBK)

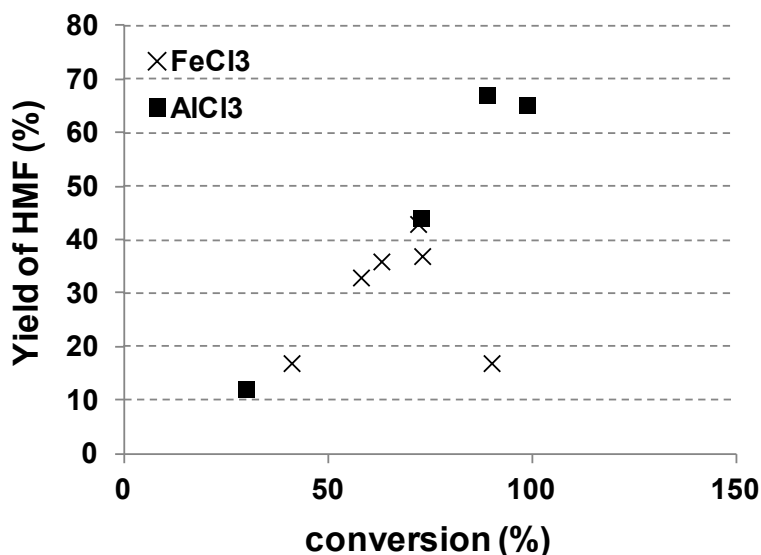


Fig. S2. Comparison between FeCl₃ and AlCl₃-Yield of HMF vs conversion of glucose (180°C, 3 mol% of MCl₃, 10 wt % of glucose, reaction media = ChCl-H₂O/MIBK)

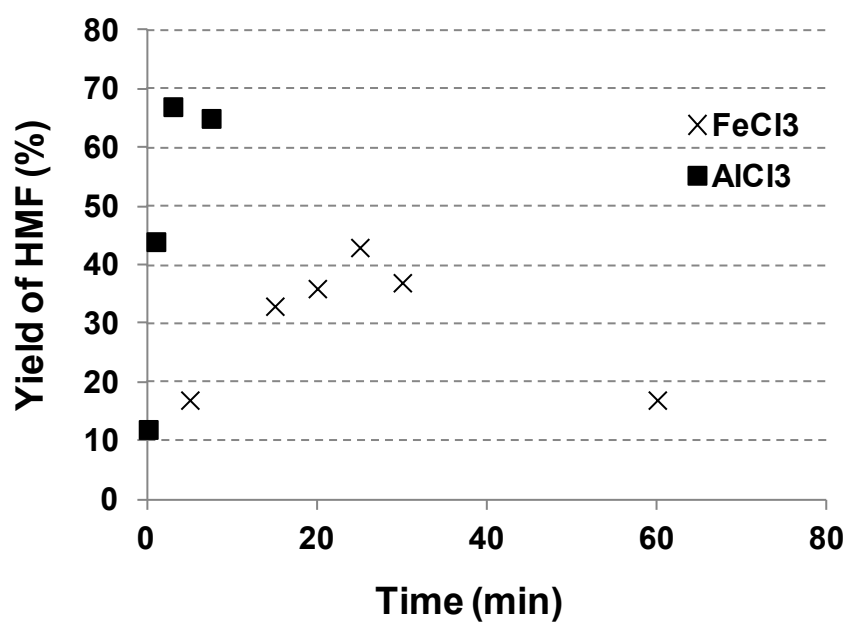


Fig. S3. Comparison between FeCl₃ and AlCl₃ in the conversion of glucose to HMF in a ChCl-H₂O/MIBK mixture-180°C, 3 mol% of MCl₃, 10 wt % of glucose

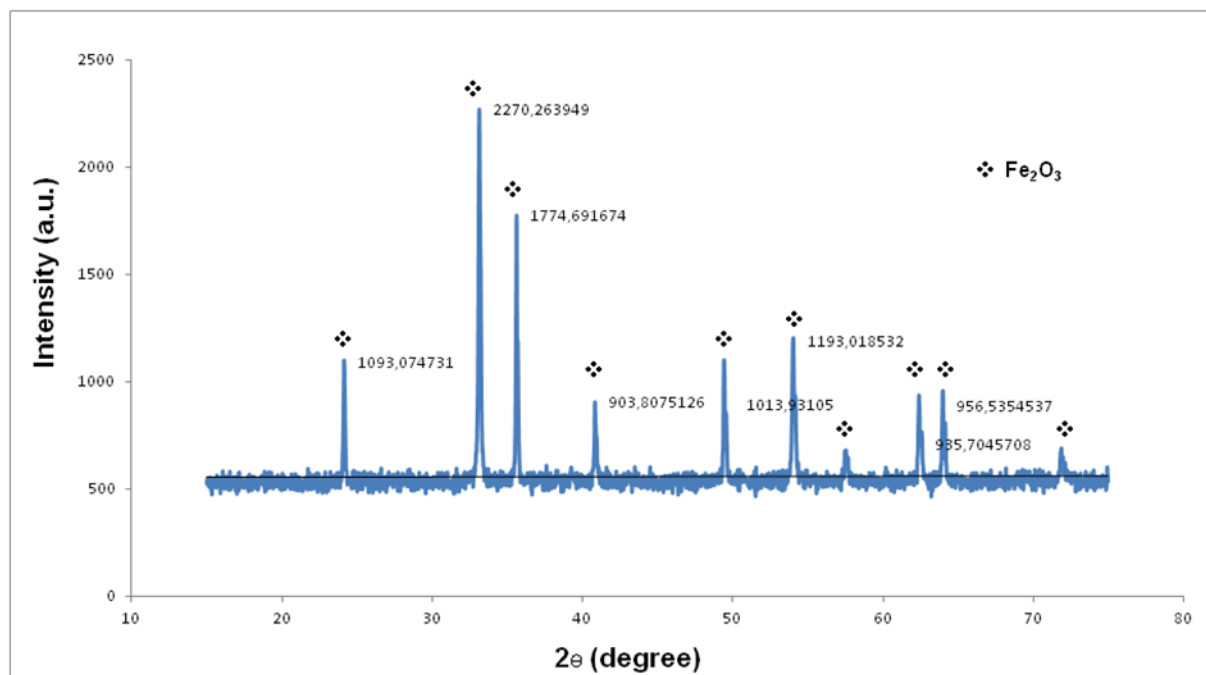


Fig.S4. XRD patterns of recovered hydrated iron oxide after heating FeCl₃ in water for 30 min at 165°C under microwaves (250W)

Table S1. Comparison between RAMAN frequencies reported in the literature for α -Fe₂O₃ and those collected in this work

Vibration mode	RAMAN frequencies (cm ⁻¹) reported by Shim and Duffy for α -Fe ₂ O ₃ - see ref 1 and 2	RAMAN frequencies collected in this study (cm ⁻¹)
A _{1g}	224	226
E _g	243	246
E _g	290	293
E _g	297	298
E _g	408	411
A _{1g}	496	497
E _g	609	612
Eu	659	660
2Eu	1316	1320

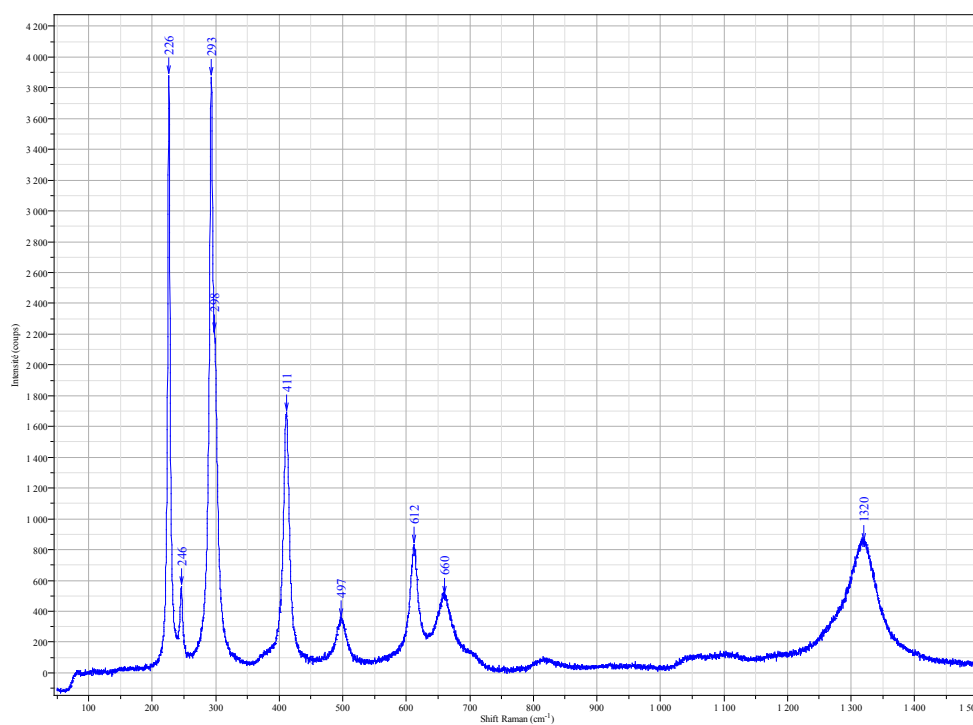


Fig.S5. RAMAN spectrum of precipitated iron oxide (from 50 to 1500 cm⁻¹)

Thermodynamical calculations

To obtain thermodynamic and structural information at a microscopic level, molecular simulations of the systems ChCl/H₂O/glucose and ChCl/H₂O/fructose were carried out. We chose to represent explicitly all atoms of the aqueous-DES phase containing the dissolved saccharides in order to compare energetic quantities and also the nature of the solvation environment. To respect the initial composition of the solution, the ChCl/H₂O/glucose phase was represented by 286 cholinium ions, 286 chloride ions, 2200 water molecules and 44 glucose molecules (of which 18 α -D-glucopyranose and 26 β -D-glucopyranose). The fructose systems contained the same number of ChCl, H₂O and sugar molecules as the glucose systems, but now with fructose represented by 6 β -D-fructopyranose, 23 β -D-fructofuranose and 15 α -D-fructofuranose molecules. The tautomer compositions were deduced from the literature.³ The force fields used to represent the molecular structures and interactions were OPLS-AA 2005 for the sugars,⁴ TIP4P for water,⁵ and specific parameters for cholinium ions.⁶ The systems were equilibrated and then simulated for 0.5 ns using molecular dynamics at 150°C and 5 bar, in periodic cubic boxes with Nosé-Hoover thermostat and barostat. Electrostatic interactions were calculated using the Ewald summation method. Please note that MIBK was not considered in our calculation since hexoses are not soluble in MIBK and isomerization of glucose to fructose only occurs in the aqueous phase.

Table S2 Energetic quantities obtained from molecular dynamics simulation

kJ/mol	E_{total}	E_{solute}	E_{solvent}	$E_{\text{solute-solvent}}$
ChCl/H ₂ O/glucose	-42.44±0.21	+4.40±0.07	-41.86±0.22	-4.98±0.23
ChCl/H ₂ O/fructose	-42.07±0.22	+4.34±0.07	-41.95±0.22	-4.46±0.23

As can be seen in Table S2, the total energy of the Glucose/ChCl and Fructose/ChCl systems are similar. The equilibrium constant of glucose-fructose isomerization also depends on entropic terms, which are unfortunately difficult to determine with accuracy using simulation. Differences in the microscopic structure of the solutions may give certain clues regarding differences of entropic nature. Analysis of site-site radial distribution function (RDF) shows similar positional correlations of atoms of the sugar molecules with the cholinium cation and with water, whether in terms of H-bond donor or H-bond acceptor sites. Important differences observed only concerning the correlations with Cl⁻. As shown in figure S1, the first peak of the RDF between the HO1 atom of glucose is much more intense than the corresponding one for fructose. The peak in the RDF of HO6, on the other hand, is slightly smaller for glucose, without compensating the large difference in HO1. (As an example of a H-bond donor site for which no significant differences are observed, we include in figure S1 the RDF between HO3

and Cl-) In other words, it suggests that fructose has a less organised solvation shell of chlorine anions around HO1 when compared to glucose.

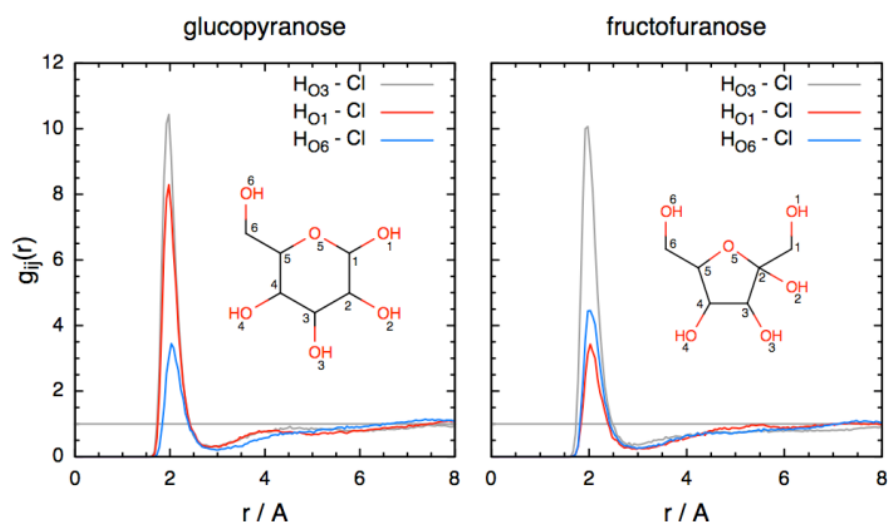


Fig. S5 – Radial distribution functions obtained from molecular dynamics simulations between H atoms of hydroxyl groups of the sugars and the chloride anion

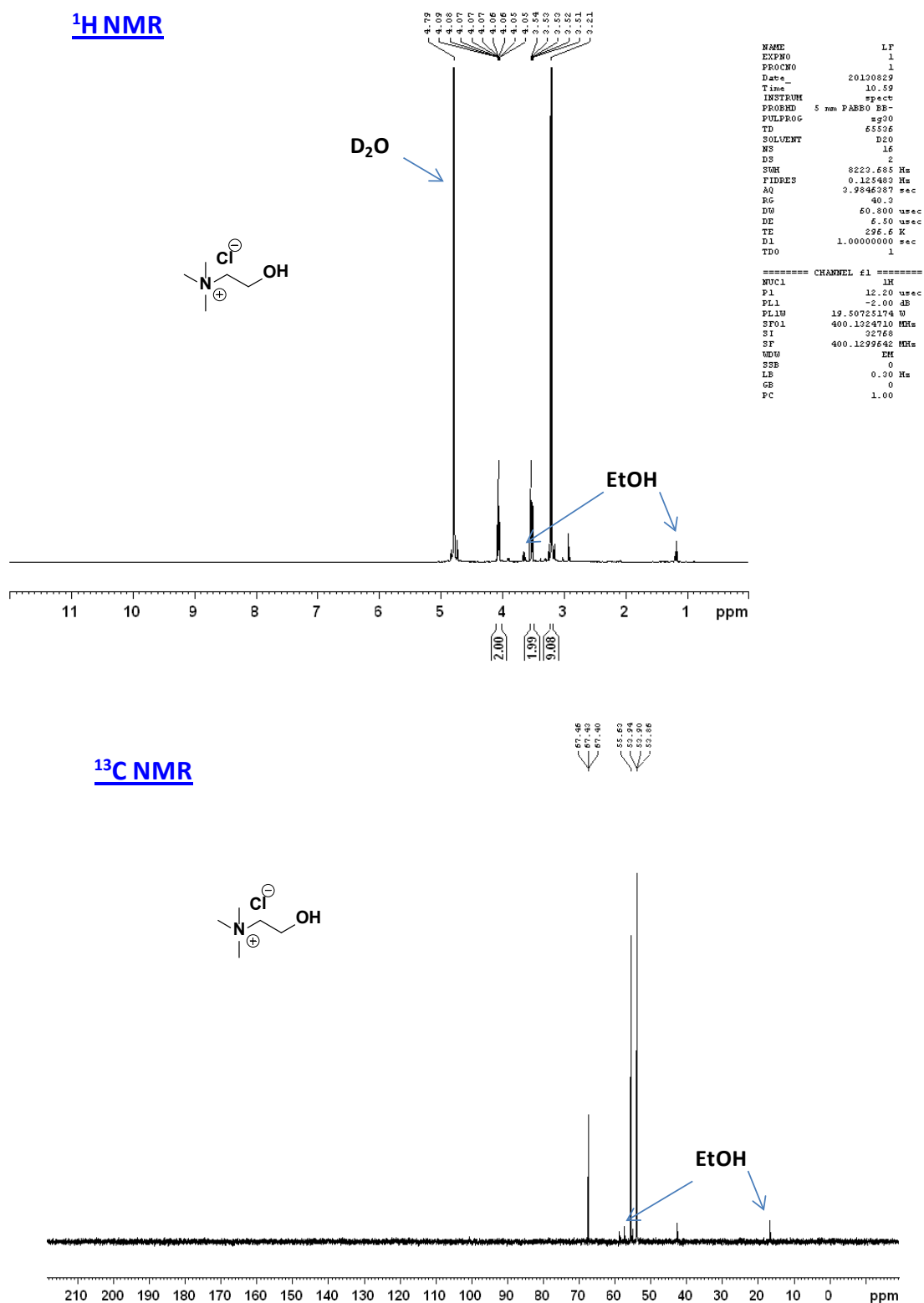


Fig. S6. ¹H and ¹³C NMR spectra of crude ChCl recovered after extraction

References

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