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Mechanistic Understanding of Humins Formation in the Conversion of Glucose and Fructose to 5-Hydroxymethylfurfural in [BMIM]Cl Ionic Liquid

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1. Typical humins preparation procedure

In a three-necked round bottom (100 mL) with a stir bar, $CrCl_3$ (0.74 g) and [BMIM]Cl (10.0 g) were mixed and heated to 110 °C (a purple homogeneous solution formed). Glucose (5.0 g) was added in one portion to the homogeneous phase. The final mixture was heated at 110 °C for 4 h, resulting in forming a black phase. After cooling to room temperature by water bath, water (80 mL) was added and stirred at room temperature for 1 h. The water diluted mixture was filtrated to separate solid 1 and liquid. The solid 1 was washed with water (200 mL). The combined filtrate was analyzed by HPLC. The washed solid was air-dried for 1 day (solid 2), and extracted by water through Soxhlet extraction for 2 d (solid 3), followed by THF extraction for 2 d (solid 4). The solid 4 was vacuum dried at about 60 °C for 6 h to obtain the final humins (1.592 g). The filtrate and water phase were analyzed by HPLC using DMSO as an internal standard. Humins was analyzed by elemental analysis (Table 1), IR (Figure S1), microscope (Figure 1a), TEM (Figure 1b), XRD (Figure S2), TG/DTG (Figure S3), and XRF (Table S1). The others humins preparation also followed this procedure with relative modifications.

2. Preparation of model compounds

2.1 Synthesis of 2-(5-methylfuran-2-yl)-1,3-dioxane (M1)

A mixture of 5-methylfuran-2-carbaldehyde (2.2 g, 20 mmol), propane-1,3-diol (1.52 g, 20 mmol), and 4-methylbenzenesulfonic acid (172 mg) was stirred in dry toluene (50 mL) under N2 atmosphere at refluxing for 8 h. The in situ generated water was removed during the reaction. The final solution was purified through rotary evaporation to remove the toluene solvent, followed by vacuum distillation to give the product M1 as a colorless oil (2.08 g, yield 62%). GC-MS (EI): $[M]^+$ (*m/z* = 168.1).

2.2 Synthesis of (5-methylfuran-2-yl)methanol (M2)

In a three-necked round flask, 5-methylfuran-2-carbaldehyde (2.2 g, 20 mmol) was dissolved in methanol (50 mL). $NaBH_4$ (0.38 g) was carefully added into methanol. After 6 hours at room temperature, water (5 mL) was added into methanol. The solvent was then removed by rotary evaporation to give a viscous oil. The viscous oil was purified through a short silica gel column to give the product M2 as a colorless oil (2.15 g, yield 96%). GC-MS (EI): $[M]^+$ (*m/z* = 112.1).

2.3 Synthesis of 2-(methoxymethyl)-5-methylfuran (M3)

In a three-necked round flask, (5-methylfuran-2-yl)methanol (1.12 g, 10 mmol) was dissolved in dry THF (50 mL). NaH (0.5 g, 60% dispersion in mineral oil) was carefully added into THF. CH_3I (1.7 g) was then added to the THF. After 24 hours at room temperature, the reaction mixture was extracted by water (20 mL × 3) and THF (20 mL × 3). The combined organic phase was evaporated by rotary evaporation to give an oil. The oil was then purified through a short silica gel column to give the product M3 as a colorless oil (1.07 g, yield 85%). GC-MS (EI): $[M]^+$ ($m/z = 126.1$).

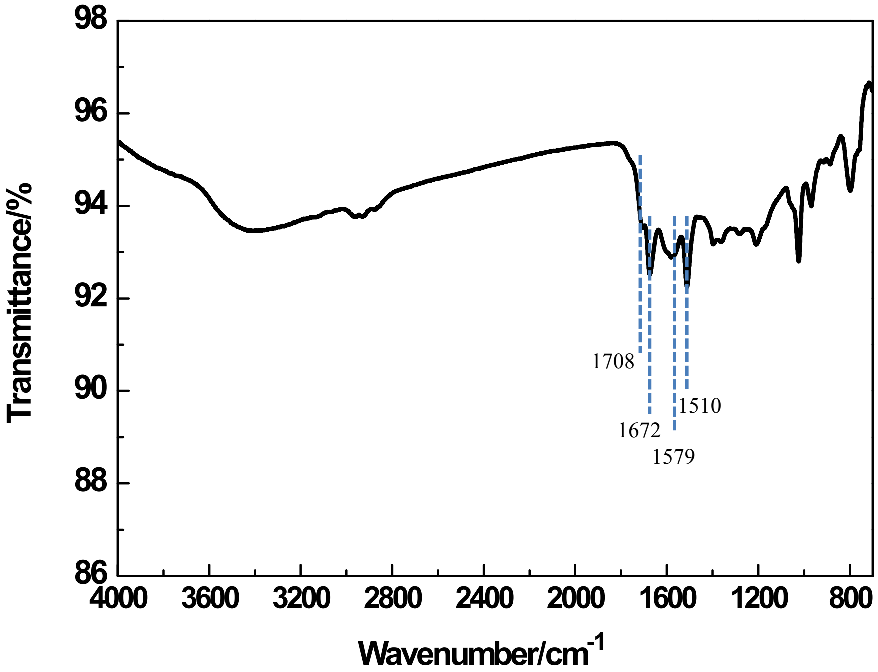


Figure S1. The IR spectrum of humins

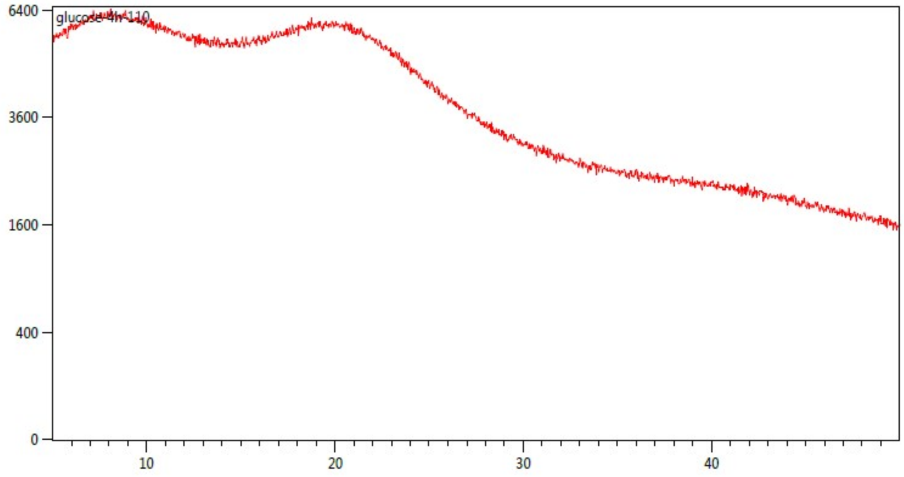


Figure S2. XRD spectrum of a typical solid humins.

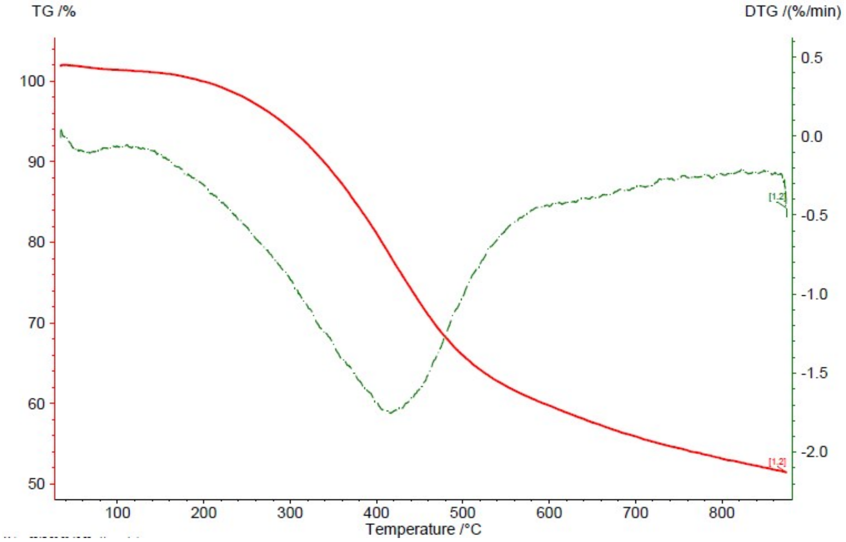
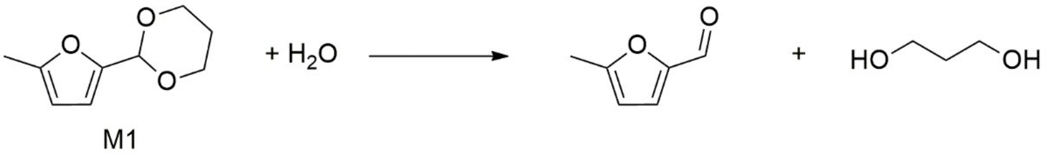


Figure S3. TG/DTG spectrum of humins.

Table S1. Reaction of M1 with water.[a]



Entry	Water (mg)	Temperature (°C)	Time (min)	Conversion (%)[b]
1	20	90	30	85
2	50	90	30	85
3	100	90	30	86
4	20	90	2	70
5	20	90	5	82
6	20	90	20	84

[a] Reaction conditions: [BMIM]Cl (0.5 g), $CrCl_3$ (6.6 mg), substrate (0.5 mmol), water (20 mg), 90 °C, 600 rpm, under air. [b] GC yield, 1,4-dioxane as an internal standard.

Table S2. Extraction of 5-HMF/protected 5-HMF (M4) from [BMIM]Cl by extraction.[a]

Entry	Compound	Organic in extractant (%)
1	5-HMF	12
2	M4	82

[a] Conditions: BMIMCl (1.0 g), $CrCl_3$ (13.3 mg), substrate (2 mmol), water (120 mg), GDE extractant (2 g), rt, 0.5 h, 600 rpm, under air.