Supporting Information

Triazaheterocyclic compound as Efficient Catalyst for Dehydration

of Fructose into 5-Hydroxymethylfurfural

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Materials:

D-Fructose, hexachlorocyclotriphosphazene (HCCP), 2,4,6-tris-(trifluoromethyl)-1,3,5-triazine (TFTZ), benzyltriphenylphosphonium chloride (BTPPCl), methyltri-phenylphosphonium bromide (MTPPBr) and hydroxymethylfurfural (standard sample for HPLC analysis) were purchased from Sigma-Aldrich. Hexaphenoxycyclotriphosphazene (PCP) was purchased from J&K Scientific Ltd. Cyanuric chloride, dimethyl sulfoxide, hydrochloric acid and trithiocyanuric acid were purchased from Aladdin Chemistry Co., Ltd (China). Triethylamine and melamine were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were analytical reagent or higher grade, and used without further purification. Pure water was obtained through an ultra-pure water system (Millipore, 18.2 M Ω cm at 25 °C).

Experimental details:

Catalytic performance: In a typical reaction protocol for the dehydration of D-fructose, 12.5 g fructose/DMSO solution (5 wt%) was charged into a 50 mL flask, followed by the addition of the catalyst (1 mol% to fructose). The reaction was performed at 90 °C for 2 h with magnetic stirring. The point of zero time was taken to be when the reaction temperature reached the set point. After the reaction, the mixture was filtered with a PTFE syringe filter (40 μ m) and diluted 20 times with water before HPLC analysis. Before each reaction, a control sample for HPLC analysis was taken from the 5 wt% fructose/DMSO solution and diluted 20 times with water.

Product analysis: The composition analysis of the reaction mixture was conducted on a Shimadzu HPLC system equipped with refractive index detector. The saccharide and HMF were quantified by using HPLC with a Shodex SH1011 sugar column (300 mm \times 8.0 mm, 6 µm), sulfuric acid (0.0005M in water) as the mobile phase at a flow rate of 0.8 mLmin⁻¹, and a column temperature of 50 °C. The high resolution MASS analysis was conducted on a Bruker ApeXIII 7.0 TESLA FTMS using ESI mode.

Supplementary results:



Fig. S1 The effect of reaction time on the catalytic performances of HCCP, CNC and HCl on dehydration of fructose to HMF. (Reaction conditions: 12.5 g D-fructose/DMSO solution (5 wt%), catalyst (HCCP and CNC:1 mol% to fructose; HCl: 3 mol% to fructose), 90 °C, 2 h.)

| Catalyst | Time = 0.5 h | | Time = 2 h | | |
|------------|------------------------|-----------|----------------|-----------|--|
| | Conversion / % | Yield / % | Conversion / % | Yield / % | |
| HCl | 12.0 | 1.9 | 47.0 | 22.0 | |
| TFPZ | 3.9 | 1.1 | 20.5 | 10.3 | |
| TFPZ + HCl | 30.3 | 10.4 | 60.3 | 37.4 | |

Table S1 The catalytic performance of TFPZ with HCl on dehydration of fructose to HMF.^a

^{*a*} Reaction conditions: 12.5 g D-fructose/DMSO solution (5 wt%), catalyst (HCl: 0.1 mol% to fructose; TFPZ:1 mol% to fructose), 90 °C, 2 h.

The samples for HRMS analysis were prepared as described below. 12.5 g D-fructose/DMSO solution (5 wt%) was adding to a 50 ml flask, followed by adding the catalyst (1 mol% to fructose). The mixture was put into an oil bath of 90 °C and heated for only 10 min. The sample was directly used for mass analysis after being filtered with a PTFE syringe filter (40 μ m).



Fig. S2 The HRMS spectrum of the intermediate composed of TFPZ and fructose with the supposed molecular structure.



Fig. S3 The HRMS spectrum of the intermediate composed of HCCP and fructose with the supposed molecular structures.



Fig. S4 The HRMS spectrum of the furfural intermediate products and the final product HMF.

Table S2 The effect of TEA as an additive on the performance of dehydration of D-fructose to HMF.^a

| Entry | Catalyst | TEA - dosage ^b | Time = 0.5 h | | Time = 2 h | |
|-------|----------|------------------------------|--------------|-----------|------------|-----------|
| | | | Fruc. | HMF | Fruc. | HMF |
| | | | conv. (%) | Yield (%) | conv. (%) | Yield (%) |
| 1 | НССР | 3 | 81.2 | 74.7 | 96.2 | 90.1 |
| 2 | CNC | 3 | 56.7 | 45.3 | 92.4 | 81.1 |
| 3 | HC1 | 1 | 54.8 | 41.3 | 89.3 | 76.1 |

^{*a*} Reaction conditions: 12.5 g D-fructose/DMSO solution (5 wt%), catalyst (HCCP and CNC: 1 mol% to fructose; HCl: 3 mol% to fructose), 90 °C, 2 h. ^{*b*} mole ratio to catalyst.