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Triazaheterocyclic compound as an efficient

catalyst for dehydration of fructose into

5-hydroxymethylfurfural*

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Hexachlorocyclotriphosphazene and cyanuric chloride are found to be high efficient homogeneous catalysts for dehydration of fructose into 5-hydroxymethylfurfural under mild conditions. The P–Cl or C–Cl bonds play important roles in the reaction, and the strong interaction between the fructose and the electron-withdrawing substituent will help to promote the dehydration.

To overcome the growing shortage of fossil resources, many strategies for efficient conversion of biomass into fuels and chemicals have been developed, in which the production of 5-hydroxymethylfurfural (HMF) has been considered as a promising intermediate in the bio-energy transformation in the past two decades.^{1,2} Furthermore, HMF as an important platform chemical derived from biomass can be an alternative compound to those from fossil resources. For example, it can be selectively oxidized into furan-2,5-dicarboxylic acid, which can serve as a substituent for terephthalic acid in the manufacturing of plastic, and converted into other valuable building blocks such as 2,5-di(hydroxymethyl)furan and levulinic acid.³ HMF can be derived from hexoses by losing three molecules of water in an acidic medium. Consequently, acids including mineral acids and organic acids (e.g., hydrochloric acid (HCl) and p-toluenesulfonic acid) were first to be used as catalysts in this process.³⁻⁵ However, the formation of soluble polymers and insoluble humins and the rehydration of HMF under acidic conditions have restricted the HMF production, especially in aqueous systems. Therefore much effort has been

expended in improving this situation. Kuster *et al.*⁶ introduced polyethylene glycol (PEG) as the solvent, and demonstrated that the improved HMF yield should be attributed to the formation of HMF–PEG esters, which exhibited better stability in the reaction system. Dumesic and co-workers⁷ described a method using phase modifier with various concentrations, and a high yield (approx. 76%) of HMF was obtained by using hydrochloric acid as catalyst in an aqueous solution containing dimethyl sulfoxide (DMSO) and poly(1-vinyl-2-pyrrolidone) with 2-meth-ylisobutylketone as the phase modifier. Nevertheless, the high energy consumption demanded by the required isolation procedures, becomes the disadvantage of these processes.

On the other hand, the industrial catalytic dehydration of saccharides has also been impeded due to the introduction of corrosive reaction medium. Therefore, the application of ionic liquids (ILs), which have greatly avoided the use of acids in the reaction systems, have improved the yield of HMF as well as the selectivity, and have drawn much attention in the biomass processing and production of HMF from sugars.8 For instance, Zhao et al. reported production of HMF from dehydration of glucose catalyzed by chromium(II) chloride in 1-alkyl-3-methylimidazolium chloride.9 Although it has been improved by many less or none toxic promoters such as SnCl₄,¹⁰ GeCl₄,¹¹ FeCl₂,¹² CoSO₄¹³ and B(OH)₃,¹⁴ it will significantly increase the cost of the process by employing ILs and the difficult separation and purification operations. The application of heterogeneous catalysts, as reported in the literature, still have been challenged by relatively low efficiency, high reaction temperature, and the product isolation process.15-19 From an eco-friendly and economic point of view, a noncorrosive, high efficiency and metal-free catalyst system is intensively needed for the HMF production from biomass in the future.

According to the references, triazaheterocyclic compounds, such as hexachlorocyclotriphosphazene (HCCP) and cyanuric chloride (CNC), have been reported as very effective catalysts instead of strong acids (*e.g.*, HCl) for the Beckmann rearrangement reactions.²⁰ Besides, these compounds, which possess variable and active substituents as well as stability, have

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been widely applied in organic synthesis and polymeric materials.²¹ Based on these and our previous works, we try to adopt HCCP and CNC as the catalysts for the dehydration of D-fructose into HMF by using these compounds in DMSO as a solvent under mild conditions.

Firstly, we compared the catalytic performance of HCCP, CNC, HCl and some reference compounds in a 5 wt% fructose/ DMSO solution under 90 °C for 2 h. As listed in Table 1 (entry 1 and 2), HCCP showed the best activity which gave a HMF yield of 91.0%, and a good catalytic performance with an 86.9% yield of HMF was conducted by CNC. In contrast, a lower HMF yield of 76.4% (entry 3) was received when HCl was used as the catalyst under the same conditions. By considering the special structure of HCCP and CNC molecules, we supposed that the active substituent chloride atoms should be associated with the catalyst activity, which had been approved to have strong interaction with fructose.²² Thus we repeated the reactions with different dosages of HCl (3 mol% and 6 mol% to fructose). As a result (entry 4 and 5), HCCP still had a better performance in activity than HCl, while CNC was slightly inferior. Moreover, the catalytic performance tests of high concentrate of substrate (entry 11-14) also reveal the superiority of HCCP and CNC over HCl on the dehydration of fructose. In order to demonstrate the active site of the catalysts, we designed and carried out a series of experiments. Firstly, HCCP was capped with phenol by replacing the substituent chlorine atoms with phenoxy groups, which formed hexaphenoxycyclo-triphosphazene (PCP). However, PCP showed nearly no catalytic activity on the reaction (entry 6), which only gave a 2.1% of HMF yield in 2 h, by comparison with the control experiment which was carried out with no catalyst (entry 10) under the same conditions. Similarly, when cyanuric acid (CNA) was used instead of CNC, only 10.3% yield of HMF (entry 7) was received after the reaction. As referred above, the strong interaction between Cl⁻ anion and fructose through hydrogen bonds bridging structure OH····Cl···HO could help fructose to lose the

Table 1 Catalytic performance of HCCP, CNC and relative catalysts on dehydration of fructose into HMF^a

| Entry | Catalyst | Fructose content (wt%) | Catalyst dosage (mol%) | Fructose conversion (%) | HMF yield (%) |
|-------|----------|------------------------------|------------------------------|-------------------------------|------------------|
| 1 | HCCP | 5.0 | 1.0 | 98.9 | 91.0 |
| 2 | CNC | 5.0 | 1.0 | 96.3 | 86.9 |
| 3 | HCl | 5.0 | 1.0 | 90.0 | 76.4 |
| 4 | HCl | 5.0 | 3.0 | 96.7 | 87.8 |
| 5 | HCl | 5.0 | 6.0 | 98.2 | 88.5 |
| 6 | PCP | 5.0 | 1.0 | 12.2 | 2.1 |
| 7 | CNA | 5.0 | 1.0 | 28.5 | 10.3 |
| 8 | BTPPCl | 5.0 | 1.0 | 14.6 | 6.9 |
| 9 | MTPPBr | 5.0 | 1.0 | 34.6 | 12.3 |
| 10 | None | 5.0 | 1.0 | 9.8 | 1.9 |
| 11 | HCCP | 30.0 | 1.0 | 98.6 | 75.7 |
| 12 | CNC | 30.0 | 1.0 | 97.2 | 69.6 |
| 13 | HCl | 30.0 | 1.0 | 91.9 | 56.9 |
| 14 | HCl | 30.0 | 3.0 | 97.3 | 69.3 |
| | | | | | |

 a Reaction conditions: all reactions were performed with 12.5 g fructose/ DMSO solution and the catalyst (mol% to fructose) under 90 $^\circ C$ for 2 h.

water molecules.²¹ In view of this, some phosphonium salts such as benzyltriphenylphosphonium chloride (BTPPCl) and methyltriphenylphosphonium bromide (MTPPBr), in which a type of ionic bond exist between halogen atoms and phosphorus, had been employed as the catalyst. But the results showed (entry 8 and 9) poor activity of BTPPCl and MTPPBr, only giving a HMF yield of 6.9% and 12.3%, respectively. Thus, based on these results, it can be presumed that the bonded chlorine on the triazine derivatives (P–Cl or C–Cl) should play a key role in the catalytic activity.

In addition, the catalytic performance of a serials of s-triazine derivatives with different substituent groups including 2,4,6-tris-(trifluoromethyl)-1,3,5-triazine (TFTZ), trithiocyanuric acid (TCA), melamine and CNA had been compared, and the results are illustrated in Fig. 1. A moderate HMF yield of 28.7% with 51.5% fructose conversion was received under the given reaction conditions in the presence of TCA. But when the functional groups of triazine were replaced by amino groups (melamine), there was no conversion of fructose detected after the reaction. By comparing with that of HCCP and CNC, it was found that the different electro-withdrawing ability of the substituent on each triazine derivative should be responsible for the catalytic activity. Furthermore, a fluoride-rich analogue, TFTZ, which possessed a stable structure with carbon-carbon bonded trifluoromethyl groups was adopted to catalyse the dehydration of fructose, and a small amount of HMF with 10.3% in yield was obtained. However, when this compound was reperformed together with HCl (0.1 mol% to fructose), an obvious increase of fructose conversion and HMF yield was achieved after a reaction time of 0.5 h, which was 30.3% and 10.4% respectively, compared to the isolated performance of TFTZ (3.9% conversion, 1.1% yield) and HCl (12.0% conversion, 1.9% yield) (Table S1, ESI[†]). These results revealed that there might be a synergetic effect on the reaction due to the substituent groups with electron-withdrawing ability, which acted in the form of hydrogen bonds between the groups and the fructose. Moreover, further evidence from mass spectrometric analysis had proved that an



Fig. 1 Catalytic activities of different triazine derivatives with varied substituent. (Reaction conditions: 12.5 g of 5 wt% fructose/DMSO solution, 1 mol% catalyst, 90 $^{\circ}$ C, 2 h).

intermediate consisting of a TFTZ molecule and a fructose molecule existed during the reaction (Fig. S2, ESI[†]). Another aspect should be mentioned that the unique triazine ring structure (-C=N-) could be another important factor to the catalytic activity. Herein, the catalytic dehydration of fructose using a phenyl containing analogue, 1,3,5-trichlorobenzene (TCB), had also been conducted, and only a 12.3% yield of HMF with a 38.1% conversion of fructose was received. By comparing the difference of CNC and TCB, the introduction of nitrogen to the body ring might result in the highly active structure, where the substituent groups were highly active and the carbon atoms could be easily attacked through the nucleophilic interaction. As for HCCP, the higher levels of activity observed when compared against CNC could be contributed to the greater number of chlorine atoms, which could lead to a stronger interaction with fructose and a more electropositive phosphorus atom as well, and to the easier accessible active sites due to the bigger sized phosphorus atoms.

As it was revealed, HCCP and CNC, as two chlorinesubstituted *s*-triazine derivatives, were both efficient homogeneous catalysts for dehydration of fructose into HMF under mild conditions. In Scheme 1, a possible mechanism for the reaction catalysed by HCCP had been presented. The high resolution mass spectrometric analysis of a reaction mixture, which was heated under 90 °C for only 5 min, had showed a very important intermediate (A, Scheme 1) (both mono- and dual-fructosesubstituent intermediates were discovered, see Fig. S3, ESI†) formed during the reaction. And the formation of the *O*-triazine compound should initialize the dehydration process, which was followed by the protonation step to form intermediate B. After the loss of the hydroxyl group (red in color) from fructose (in the form of fructofuranose), the intermediate product 2-hydroxymethyl-5-hydroxylmethylene-tetrahydrofuran-3,4-diol was formed by



Scheme 1 The possible mechanism of dehydration of fructose into HMF by HCCP.

deprotonation of intermediate C, and it would finally convert into the product HMF by loss of another two water molecules through a similar pathway. Then, reformation of HCCP by losing the water molecule would end the catalytic step of this process. Although there was HCl coming out in this mechanism, we believed that it should be involved as an instantaneous state during the reaction. Thus, we used triethylamine (TEA) as an additive to the reaction, which could capture the proton so as to inhibit the reaction. As a result (Table S2 \dagger), the addition of TEA had barely effect on the activity of HCCP (90.1%, 2 h) and CNC (81.1%, 2 h), while a clear decrease of HMF yield (76.1%, 2 h) was observed for HCl as the catalyst.

In summary, the triazaheterocyclic compounds with covalent bonded chlorine, HCCP and CNC, are proved as efficient catalysts for the dehydration on fructose into HMF, and a series of triazine analogues have also shown their catalytic activities in this reaction. The reason should be attributed to the active substituents with electron-withdrawing ability, which could have strong interactions with fructose through hydrogen bonds, and to the electropositive center (phosphorus or carbon atom) on the body ring structure. Moreover, O-triphosphazene compounds were considered as the important intermediates in this reaction system, based on which a possible mechanism of dehydration of fructose into HMF was proposed. And these triazine compounds provide a new pathway for synthesis of HMF from biomass with high efficiency and without pollutions. Finally, it is worthwhile to note that HCCP can be reused once it is immobilized (for example, poly-nanoparticles made by HCCP and 4,4'-sulfonyldiphenol have shown excellent catalytic activity on this reaction), and the relative work on this aspect is underway.

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