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One-Step Approach to 2,5-Diformylfuran from Fructose by Proton- and Vanadium-Containing Graphitic Carbon Nitride

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5-Hydroxymethylfurfural (HMF) was selectively synthesized from fructose by using protonated graphitic carbon nitride $[g-C_3N_4(H^+)]$ as a solid acid. With $g-C_3N_4$ as the same precursor material, 2,5-diformylfuran (DFF) was efficiently obtained from aerobic oxidation of HMF by using vanadium-doped $g-C_3N_4$ (V– $g-C_3N_4$) as an environmentally benign heterogeneous catalyst with atmospheric pressure of molecular oxygen as the oxidant. In addition, a combination of $g-C_3N_4(H^+)$ and V– $g-C_3N_4$ successfully afforded the direct synthesis of DFF from fructose through $g-C_3N_4(H^+)$ -promoted fructose dehydration and V– $g-C_3N_4$ -catalyzed successively aerobic oxidation of HMF to DFF in a one-pot and two-step process. Moreover, a bifunctional cata-

Introduction

In view of diminishing fossil reserves and degradation of the environment, a growing interest has recently been devoted to fuels and chemicals from the sustainable biomass resource.^[1-6] Carbohydrates, obtained from renewable biomass, are currently deemed as promising feedstocks for this purpose.^[7-9] Among the carbohydrate-derived platform chemical compounds, 5-hydroxymethylfurfural (HMF) was identified as a versatile molecule with particular interest.^[10,11] Moreover, selective oxidation of HMF to 2,5-diformylfuran (DFF) has received particular attention due to the various applications of DFF in fungicides,^[12,13] pharmaceuticals,^[14] heterocyclic ligands,^[15] and functional polymers.^[16,17]

In the literature for HMF-to-DFF transformation, a series of classical oxidants such as pyridinium chlorochromate (PCC), $BaMnO_4$, NaOCI, and 2,2,6,6-tetramethylpiperidine-1-oxide

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lyst made of protonated V–g-C₃N₄ [V–g-C₃N₄(H⁺)] allowed onepot as well as one-step direct transformation of fructose into DFF. Under optimized conditions, 80% yield of HMF and 82% yield of DFF were obtained from g-C₃N₄(H⁺)-promoted fructose dehydration and V–g-C₃N₄-catalyzed HMF oxidation, respectively. Stepwise addition of g-C₃N₄(H⁺) and V–g-C₃N₄ in the one-pot process improved the DFF yield up to 63% from fructose. In contrast, V–g-C₃N₄(H⁺)-catalyzed direct one-step transformation of fructose into DFF led to a DFF yield of 45%. The research highlights a one-step approach to DFF from fructose with functional g-C₃N₄ catalyst.

(TEMPO) show good performance for this aerobic oxidation process.^[18-20] Moreover, various catalyst systems, such as V₂O₅,^[21] VOPO₄·2H₂O,^[22]V-containing polymeric catalyst,^[23] Cu(NO₃)₂/VOSO₄,^[24] metal/bromide (Co/Mn/Br) catalyst,^[25] polymer-supported IBX amide,^[26] Ru/HT,^[27]K-OMS-2,^[28] Ru/C,^[29]Ag-OMS-2,^[30] TEMPO/Cu,^[31]PVP-Pd NP,^[32] and RuCo(OH)₂CeO₂^[33] were recently developed to achieve this important process under a more sustainable route with air or molecular O₂ as an oxidant. However, HMF, currently obtained from the acid-promoted dehydration of fructose, is of high cost as raw material for this purpose owing to its high energy cost for isolation and purification. The progress in green chemistry could realize an integrated chemical process in which multistep reactions are consolidated in one pot. Accordingly, the direct transformation of fructose to DFF in a one-pot process has recently attracted much attention and a series of combined catalytic system, including a H-form cation-exchange resin and VOHPO4,^[21] Amberlyst-15 and Ru/HT^[27], Fe₃O₄-SBA-SO₃H and K-OMS-2^[28], have been investigated as a potential route for DFF production from an economic and environmental point of view. In these combined catalytic systems, both acid catalyst and redox catalyst are essential for the one-pot but two-step approach to DFF from fructose. Under optimal conditions, the overall DFF yields from 45%^[21,27] to 80%^[28] calculated on fructose were obtained by stepwise addition of these dual catalysts. Notably, the coexistence of acid catalyst and redox catalyst in the initial stage of reaction generally resulted in significantly decreased DFF yields to 13%.^[27] The low yield of DFF from fructose in the one-step process was presumably related to the undesired decomposition of fructose by redox catalyst in the presence of molecular oxygen.^[27,28]In contrast to the one-pot but two-step process for DFF production by using the above combined catalytic system, a one-pot as well as one-step approach to DFF with the yield of 60%from fructose was recently achieved by us with Cs₃HPMo₁₁VO₄₀ as a bifunctional and recyclable catalyst and molecular oxygen as an oxidant under environmentally benign conditions. Cs₃HPMo₁₁VO₄₀ behaves as a heterogeneous catalyst and can be easily reused at least four times with only a slightly reduced DFF yield from 60 to 53%.^[34]

Recently, Jiang and Han reported a selective synthesis of phenol from benzene using a vanadium-doped graphitic carbon nitride catalyst (V–g-C₃N₄) with hydrogen peroxide as the oxidant.^[35] Moreover, owning to the multifunctional catalytic nature, the g-C₃N₄, upon deprotonation with *t*BuOK, exhibits high efficiency for promoting Knoevenagel condensations and transesterification reactions as a heterogeneous solid base catalyst, on the one hand.^[36] On the other hand, g-C₃N₄ could be reversibly protonated by strong mineral acids, thus modifying acidity, solubility/dispersibility, and surface area.^[37] Inspired by these works, herein, we report that a combination of g-C₃N₄(H⁺) and V–g-C₃N₄ catalysts successfully catalyzed direct synthesis of DFF from fructose by acid-catalyzed dehydration and successive aerobic oxidation in a one-pot reaction (Scheme 1). Stepwise addition of g-C₃N₄-derived binary cata-



Scheme 1. Conversion of fructose into HMF and DFF catalyzed by functionalized g-C_3N_4.

lysts gave DFF in 63% yield. Moreover, a bifunctional catalyst made of protonated V–g-C₃N₄ [V–g-C₃N₄(H⁺)] allowed one-step direct transformation of fructose to DFF with a yield of 45% (Scheme 1).

Results and Discussion

Dehydration of fructose to HMF over g-C₃N₄(H⁺)

According to the literature, $g-C_3N_4(H^+)$ was obtained by stirring $g-C_3N_4$ with hydrochloric acid followed by centrifugal washing with water until neutral condition.^[37]In Figure 1 a, the influence of reaction temperature and time on the dehydration of fructose catalyzed by $g-C_3N_4(H^+)$ using DMSO as solvent is shown. Both the conversion of fructose and the yield of HMF increased with reaction time at all temperatures investigated. The yield of HMF increased slowly to 34% after 2 h at 100 °C, whereas it increased quickly to 80% after 0.5 h at 140 °C, confirming that increasing the reaction temperature promotes the conversion of fructose to HMF. The influences of acid density of $g-C_3N_4(H^+)$ on fructose-to-HMF transformation suggested that





Figure 1. a) Effect of reaction temperature and time on fructose dehydration to HMF using $g-C_3N_4(H^+)$ as a solid acid. Reaction conditions: fructose (200 mg), $g-C_3N_4(H^+)$ (100 mg, acid density 0.32 mmol g^{-1}), DMSO (2 mL).b) Effect of acid density of $g-C_3N_4(H^+)$ on fructose conversion and HMF yield. Reaction conditions: fructose (200 mg), $g-C_3N_4(H^+)$ (100 mg), DMSO (2 mL), 120 °C. The acid density of $g-C_3N_4(H^+)$ was determined by potentiometric acid–base titration.

both the conversion of fructose and the yield of HMF increased with proton loading level in $g-C_3N_4(H^+)$ (Figure 1 b).

The developed g-C₃N₄(H⁺) was further compared with commercial acid catalysts such as Amberlyst-15, H-ZSM-5 (Si/Al = 25), HY-zeolite (Si/Al \geq 5.2), and H-Beta (Si/Al = 12.5) for fructose-to-HMF transformation. In Table 1it is shown that the catalytic activity for fructose-to-HMF transformation at 130 °C decreases in the order of g-C₃N₄(H⁺) > HCl > Amberlyst-15 (run 3) > H-ZSM-5 (Si/Al = 25) > HY-zeolite (Si/Al \geq 5.2) > H-Beta (Si/Al = 12.5). The reusability of g-C₃N₄(H⁺) was performed and in Figure 2the activity of g-C₃N₄(H⁺) catalyst is shown during six consecutive uses. The recovered g-C₃N₄(H⁺) was separated and cleaned, and then applied in the next run under the same

Table 1. Fructose dehydration to HMF over various acid catalysts. ^[a]				
Run	Catalyst	Fructose conv. [%]	HMF yield [%]	
1	$g-C_{3}N_{4}(H^{+})^{[a,b]}$	> 99	80	
2	Amberlyst-15 ^[a]	>99	89	
3	Amberlyst-15 ^[a,c]	> 99	78	
4	HCI ^[a,d]	>99	76	
5	H-ZSM-5(Si/Al=25) ^[a]	>99	74	
6	HY-zeolite $(Si/Al \ge 5.2)^{[a]}$	> 99	71	
7	H-Beta(Si/Al=12.5) ^[a]	94	63	
[a] Reaction conditions: fructose (200 mg, 1.11 mmol), solid acid catalyst (100 mg), DMSQ (2 ml), 130 °C, 1.5 h, [b] $\sigma_{\rm c}$ C,N(H ⁺) (acid density				

(100 mg), DMSO (2 mL), 130 °C, 1.5 h. [b] g-C₃N₄(H⁺) (acid density 0.32 mmol g⁻¹). The acid density of g-C₃N₄(H⁺) was determined by potentiometric acid–base titration. [c] An amount of 14 mg Amberlyst-15 (acid density 2.25 mmol g⁻¹) was used instead of 100 mg as an equimolar amount of protons with g-C₃N₄(H⁺) (100 mg, acid density 0.32 mmol g⁻¹). [d] HCI (0.032 mmol) was used as the acid catalyst.



Figure 2. Fructose dehydration to HMF during six consecutive catalytic uses with $g-C_3N_4(H^+)$. Reaction conditions: fructose (200 mg), $g-C_3N_4(H^+)$ (100 mg, acid density 0.32 mmol g^{-1}), DMSO (2 mL), 120 °C, 1.0 h. C_{Fru} = conversion of fructose, Y_{HMF} = yield of HMF.

conditions. However, there was a dramatic decrease of conversion in the second run. The ion chromatography analysis of the reaction solution after the first run indicated that the content of chlorine in the solution was approximately 19% of the chlorine in the catalyst.Notably, a subsequent treatment of the catalyst with a 0.1 m aqueous solution of HCl allowed recovery of the catalytic activity of $g-C_3N_4(H^+)$. Apparently, the reduced activity of $g-C_3N_4(H^+)$ can presumably be related to the acidic proton lost from $g-C_3N_4(H^+)$ during its recovery.

Aerobic oxidation of HMF to DFF over V-g-C $_3N_4$

In addition to fructose dehydration to HMF catalyzed by solidacid g-C₃N₄(H⁺), we further explored aerobic oxidation of HMF to DFF promoted by V–g-C₃N₄. An initial experiment was performed to investigate the effect of the metallic sites on the aerobic oxidation of HMF to DFF using g-C₃N₄ doped with dif-

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Table 2. Catalytic activity of various metal-doped g-C_3N_4 for aerobic oxidation of HMF to DFF. $^{\rm (a)}$				
Run	Catalyst M–g-C ₃ N ₄ ^[b] (M [mmol g ⁻¹])	HMF conv. [%]	DFF yield [%]	
1	g-C₃N₄	33	7	
2	Cu–g-C ₃ N ₄ (1.53)	20	3	
3	Mn–g-C₃N₄ (1.25)	24	4	
4	$Co-g-C_3N_4$ (1.13)	24	3	
5	Ni–g-C ₃ N ₄ (1.27)	23	6	
6	$Ru-g-C_3N_4$ (1.66)	20	8	
7	Fe-g-C ₃ N ₄ (1.34)	35	16	
8	Mo-g-C ₃ N ₄ (1.44)	45	23	
9	$V-g-C_3N_4$ (0.66)	76	68	
10	$V-q-C_3N_4$ (1.01)	83	69	
11	$V-g-C_3N_4$ (1.09)	92	75	
12	$V-q-C_3N_4$ (1.39)	> 99	82	
13	V-g-C ₃ N ₄ (1.70)	>99	54	
[a] Reaction conditions: HMF (126 mg, 1 mmol), catalyst (100 mg), DMSO (2 mL), O_{2} (0.1 MPa), 130 °C, 6 h. [b] Metal content in the catalyst was de-				

termined by ICP-AES.

ferent metals (M–g-C₃N₄) under atmospheric pressure of molecular oxygen. Without doping, pristine g-C₃N₄ exhibited extremely inferior activity towards the aerobic oxidation of HMF (Table 2, run 1). Moreover, the activity of Cu-, Mn-, Co-, and Nidoped g-C₃N₄ was negligible under the investigated conditions (runs 2–5). Ru was doped into g-C₃N₄ as a catalyst for comparison purpose. However, as shown in Table 2 (run 6), Ru–g-C₃N₄ was not efficient for aerobic oxidation of HMF to DFF in this reaction system. Fe- and Mo-doped g-C₃N₄ catalysts were found to be moderate active in the synthesis of DFF from HMF (runs 7–8). Notably, V–g-C₃N₄ was proved to be considerably more active and selective to afford DFF than other metals (runs 9– 13).

In addition to metallic sites, the influences of V contents on the catalytic performances of V-g-C₃N₄ catalysts were further explored for the HMF oxidation. The conversion of HMF increased with the V content in V-g-C₃N₄, whereas DFF yields smoothly increased with the V contents to a maximum DFF yield of 82% at the vanadium content of 1.39 mmol g^{-1} in V-g-C₃N₄. Further increased V content, however, led to a sharply reduced DFF yield (Table 2, runs 9-13). Such behavior may be explained as a result of the increase in the availability and number of catalytically active V sites in V-g-C₃N₄, which promotes the oxidation of HMF to DFF, on the one hand; however, it simultaneously promotes the subsequent oxidation of DFF to 5-formyl-2-furancarboxylic acid (FFCA) on the other hand as the V-loading increases. Notably, the desired DFF was always the predominantproduct under the investigated conditions.

In Figure 3, the influence of reaction temperature and time on the HMF-to-DFF transformation is shown with V-g-C₃N₄ as the catalyst. Generally, both the HMF conversion and DFF yield increased with reaction time at the temperatures investigated. In the case of the reaction temperature at 130 °C, the DFF yields increased with the reaction time with a maximum of 82% at 6 h. A further increased reaction time to 8 h, however,



Figure 3. Effect of reaction temperature and time on the aerobic oxidation of HMF to DFF over V–g-C₃N₄. Reaction condition: HMF (126 mg, 1 mmol), V–g-C₃N₄ (100 mg, V 1.39 mmol g⁻¹), DMSO (2 mL), O₂ (0.1 MPa).

led to a steeply reduced DFF yield to 65%, owing to subsequent oxidation of DFF to FFCA. The effect of reaction temperature demonstrated that increasing the reaction temperature promotes the aerobic oxidation of HMF to DFF.

To probe the reusability of V–g-C₃N₄, a five-cycle experiment was performed. The V–g-C₃N₄ catalyst was recovered by filtration, washed with DMSO, and then recycled for further reaction. Notably, the measured yields of the DFF reduced from 82 to 70% (Figure 4). Inductively coupled plasma atomic emission spectroscopy (ICP–AES) analysis of the reaction solution after the first run indicated that the content of V in the solution was approximately 2.7% of the V in the catalyst. Therefore, the de-



Figure 4. Catalyst V–g-C₃N₄ recycling. Reaction condition: HMF (126 mg, 1 mmol), V–g-C₃N₄ (100 mg, V 1.39 mmol g⁻¹), DMSO (2 mL), O₂ (0.1 MPa), 6 h, 130 °C.

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crease in catalytic activity could be presumably attributed to minor leaching of V from V–g-C_3N_4.

Recently, Fu and co-workers proposed a redox mechanism of K–OMS-2-promoted transformation of HMF into DFF using molecular oxygen under base-free conditions.^[28] The proposed mechanism involves the oxidation of HMF by $Mn^{4+}O_2^{-}$ through two-electron transfer, and a simultaneous reduction of $Mn^{4+}O_2^{-}$ to Mn^{3+} ion, which is reoxidized by O_2 . Moreover, Han and co-workers suggested a mechanism of hydroxylation of benzene to phenol using V–g– G_3N_4 as the catalyst with hydrogen peroxide as the oxidant.^[35] In principle, our reported results seemed to agree with the above mechanisms. HMF is oxidized by V^V species, simultaneously the V^V species is reduced to V^{IV} species (see the following X-ray photoelectron spectroscopy analysis for details). Furthermore, V^{IV} species could be converted to V^V species by O₂ (Scheme S1 in the Supporting Information).

One-pot conversion of fructose to DFF

We have examined the dehydration of fructose to HMF catalyzed by $g-C_3N_4(H^+)$ and aerobic oxidation of HMF to DFF promoted by V–g-C₃N₄. We thus further investigated the one-pot synthesis of DFF from fructose by using a combination of $g-C_3N_4(H^+)$ and V–g-C₃N₄ (Table 3). Addition of V–g-C₃N₄ as an ox-

Table 3. One-pot synthesis of DFF from fructose using $g-C_3N_4(H^+)$ and $V-g-C_3N_4$ under atmospheric pressure of molecular oxygen. ^[a]					
Run	$V-g-C_3N_4^{[c]}$ (V [mmol g ⁻¹])	Fructose conv. [%]	HMF yield [%]	DFF yield [%]	
1 ^[a]	V-g-C ₃ N ₄ (0.66)	>99	14	39	
2 ^[a]	V-g-C ₃ N ₄ (1.01)	>99	3	47	
3 ^[a]	V-g-C ₃ N ₄ (1.09)	>99	8	52	
4 ^[a]	V-g-C ₃ N ₄ (1.39)	>99	1	63	
5 ^[a]	V-g-C ₃ N ₄ (1.70)	>99	trace	25	
6 ^[a,b]	V-g-C ₃ N ₄ (1.39)	>99	18	26	
[a] Reacti	on conditions:	fructose (200 mg	. 1.11 mmol).	$a-C_2N_4(H^+)$	

(100 mg, acid density 0.32 mmolg⁻¹), DMSO (2 mL). After 2 h reaction under N₂ (0.1 MPa) at 120 °C, V-g-C₃N₄ (100 mg) was added under O₂ (0.1 MPa) at 130 °C for 6 h. [b] HCl (0.032 mmol) was used as the acid instead of g-C₃N₄(H⁺) (100 mg, acid density 0.32 mmolg⁻¹). [c] The vanadium content of catalyst was determined by ICP-AES.

idation catalyst afforded DFF directly from fructose in the presence of solid acid g-C₃N₄(H⁺). However, the existence of molecular oxygen from the initial stage of the fructose dehydration gave a trace amount (2% yield) of DFF, presumably owning to the undesired oxidation of fructose by V–g-C₃N₄ in the presence of molecular oxygen.^[27,28] Notably, the two-step synthesis in the one-pot reaction without catalyst separation improved the DFF yield of up to 63% (Table 3, run 4). In addition, with g-C₃N₄(H⁺) as a solid acid for the first step, DFF yields, again, increased with the vanadium contents in V–g-C₃N₄ to a maximum of 63% at the vanadium content of 1.39 mmol g⁻¹. Further increased vanadium content to 1.70 mmol g⁻¹, however, led to a sharply reduced DFF yield to 25% (run 5). Notably, a combination of HCl and V–g-C₃N₄ resulted in a decreased DFF yield to 26% (run 6), further indicating the high efficiency of g-C₃N₄(H⁺) and V–g-C₃N₄ system (run 4).

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In Figure 5, the reaction profile of these two-step sequential reactions in a one-pot process is shown, the addition of $g-C_3N_4(H^+)$ under atmospheric pressure of N_2 resulted in the dis-



Figure 5. Fructose conversion into HMF and DFF as a function of reaction time. Reaction condition: fructose (200 mg), g-C₃N₄(H⁺) (100 mg, acid density 0.32 mmol g⁻¹), DMSO (2 mL), 130 °C. After 2 h reaction under N₂ (0.1 MPa), V–g-C₃N₄ (100 mg, V 1.39 mmol g⁻¹) was added under O₂ (0.1 MPa).

appearance of fructose and simultaneous formation of HMF with a maximum yield of 80% at 2 h. Further addition of V–g- C_3N_4 without catalyst separation under atmospheric pressure of molecular oxygen afforded DFF from aerobic oxidation of HMF. The overall yield of DFF is up to 63% at 6 h based on fructose used under the investigated condition.

In addition to a dual catalyst system of g-C₃N₄(H⁺) and V-g-C₃N₄, a bifunctional catalyst made of protonated V-q-C₃N₄ $[V-g-C_3N_4(H^+)]$ was further investigated for one-step approach for fructose-to-DFF transformation. In Table 4, the results of DFF formation from fructose by successive dehydration and oxidation are listed using $V-g-C_3N_4(H^+)$ with variable acid density and V content. Under the investigated reaction conditions, optimal results of 36% yield in DFF were obtained by using the V–q-C₃N₄(H⁺) with acid density of 1.58 mmol q^{-1} and V content of 0.78 mmol g⁻¹ under atmospheric pressure of molecular oxygen (Table 4, run 2). In addition, the DFF yield, obtained from the direct fructose transformation, increased with the O₂ pressure to a maximum of 45% at 1.0 MPa (run 7). A further increased O₂ pressure to 2.0 MPa, however, led to a slightly reduced DFF yield to 39% (run 8). Moreover, the direct fructoseto-HMF transformation was further performed under scale-up conditions. A DFF yield of 19% was obtained with two grams of fructose and one gram of $V-g-C_3N_4(H^+)$ in the presence of molecular oxygen (Table S1 in the Supporting Information). The reusability of V-q-C₃N₄(H⁺) was investigated, the catalyst was regenerated by treatment with a 0.1 M aqueous solution

Table 4. One-step synthesis of DFF from fructose using bifunctional V–g-C $_3N_4(H^+)$ under atmospheric pressure of molecular oxygen.					
Run	Cata V [mmol g^{-1}]	$H^+ \ [mmol g^{-1}]$	Fructose conv. [%]	HMF yield [%]	DFF yield [%]
1 ^[a]	0.64	1.53	>99	37	21
2 ^[a]	0.78	1.58	>99	8	36
3 ^[a]	0.82	1.83	>99	18	34
4 ^[a]	0.94	0.68	>99	42	9
5 ^[a]	1.02	0.60	>99	39	11
6 ^[a]	1.11	0.59	>99	38	12
7 ^[b]	0.78	1.58	>99	2	45
8 ^[c]	0.78	1.58	>99	trace	39

[a] Reaction conditions: fructose (200 mg, 1.11 mmol), V–g-C₃N₄ (H⁺) (100 mg), DMSO (2 mL), 130 °C. After 2 h reaction under N₂ (0.1 MPa), the reaction was performed under O₂ (0.1 MPa) for 6 h. [b] Reaction condition as in [a], but O₂ pressure was 1.0 MPa. [c] Reaction condition as in [a], but O₂ pressure was 2.0 MPa. [d] The vanadium content and acid density of catalyst were determined by ICP–AES and potentiometric acid–base titration, respectively.

of HCl after each reuse. However, the DFF yield dramatically decreased from 45 % to 20 % in the third run (Table S2).

Recently, Riisager and co-workers reported the aerobic oxidation of HMF to DFF with zeolite-supported vanadia catalysts.^[38] Satsuma et al.,^[39] Nijhuis et al.,^[40] and our group^[41] obtained HMF by fructose dehydration using zeolite as solid acid. Therefore, for comparison purpose, zeolite-supported vanadia catalysts (V₂O₅/zeolite) were further investigated for one-pot approach to fructose-to-DFF transformation. Zeolites such as H-Beta (Si/AI = 12.5), HY-zeolite (Si/AI \geq 5.2), and H-ZSM-5 (Si/AI = 25, 50 and 150) were chosen as supports owing to their acidity, high thermal stability, and high surface areas. However, in sharp contrast to V–g-C₃N₄(H⁺), the V₂O₅/zeolite exhibited extremely inferior activity towards the direct synthesis of DFF from fructose under the investigated conditions (Table 5). According to the literature, the Lewis acidity of the zeolite de-

Table 5. Catalytic activity of V_2O_5 /zeolite for direct transformation of fructose to DFF.					
Run	Catalyst(V ₂ O ₅ /zeolite)	Fructose conv. [%]	HMF yield [%]	DFF yield [%]	
1 2 3 4 5	V_2O_5/H -Beta (Si/Al = 12.5) V_2O_5/HY -zeolite (Si/Al \ge 5.2) V_2O_5/H -ZSM-5 (Si/Al = 25) V_2O_5/H -ZSM-5 (Si/Al = 50) V_2O_5/H -ZSM-5 (Si/Al = 150)	> 99 > 99 > 99 > 99 > 99 > 99	12 24 9 7 6	5 7 8 5 4	
Reaction conditions: fructose (200 mg, 1.11 mmol), V_2O_5 /zeolite (100 mg, V_2O_5 3 wt%), DMSO (2 mL), 130 °C. After 2 h reaction under N_2 (0.1 MPa), the reaction was performed under O_2 (0.1 MPa) for 6 h.					

creases the selectivity of HMF formation by a fast initial condensation of fructose over the Lewis acid sites of the zeolite.^[40] The polymeric humins were thus presumably the major products.

Characterization of the catalyst

The catalysts $g-C_3N_4$, $V-g-C_3N_4$, and $g-C_3N_4(H^+)$ were compared by XRD and X-ray photoelectron spectroscopy (XPS) analyses.^[42-44] XRD patterns of $g-C_3N_4$ and $V-g-C_3N_4$ with different vanadium contents are shown in Figure S1 (Supporting Information). In the case of $g-C_3N_4$, the peaks at $2\theta = 27.5$ and 13.0° correspond to the stacking of the conjugated interlayers and in-plane ordering of tri-s-triazine units, respectively.^[45,46] V-g- C_3N_4 and $g\text{-}C_3N_4$ samples displayed similar diffraction peaks; however, the diffraction peaks of vanadium species were unobserved (Figure S1). Notably, the intensity of characteristic diffraction peaks observed in pristine g-C₃N₄ significantly decreased with increasing V contents if compared with V-g-C₃N₄ samples, which is in good agreement with the reported literature.^[35] For q-C₃N₄(H⁺), XRD patterns of q-C₃N₄(H⁺) exhibited a significant decrease of peak intensity at $2\theta = 13.0^{\circ}$, suggesting a slightly distorted structure of nitride pores after the protonation of g-C₃N₄ (Figure S2).^[37]

The XPS spectra of $g-C_3N_4$, $V-g-C_3N_4$, and $g-C_3N_4(H^+)$ are shown in Figure S3. In the case of $V-g-C_3N_4$, the photoelectron peaks of main elements on the surface appear at binding energies of 288.2 eV (C1s), 399.2 eV (N1s), 530.8 eV (O1s), and 517.1 eV (V2p), respectively. For the high-resolution V2p XPS spectra of V-g- C_3N_4 , two main peaks appeared at 523.5 and 517.3 eV corresponding to V2p1/2 and V2p3/2, respectively,^[47] which suggests that the V species is V₂O₅ (Figure 6a). In contrast, the other two peaks located at 522.1 and 515.2 eV correspond to V2p1/2 and V 2p3/2, respectively, confirming VO₂ species is formed.^[35] In Figure 6b–d, the N1s XPS spectra of g- C_3N_4 , V-g- C_3N_4 , and g- $C_3N_4(H^+)$ are shown, respectively. The two peaks at 401.2 and 399.8 eV can be assigned to tertiary nitrogen and amino functional groups, respectively. The peak at 398.6 eV corresponds to the nitrogen bonded to two carbon atoms. In the case of $q-C_3N_4(H^+)$, the additional signal at 402.3 eV can be attributed to the protonation of the nitrogen (C=NH⁺), indicating the formation of protonated $g-C_3N_4$.^[48]

Conclusions

We demonstrated the dehydration of fructose to HMF catalyzed by protonated graphitic carbon nitride $(g-C_3N_4(H^+))$ as a solid acid and aerobic oxidation of HMF to DFF promoted by vanadium-doped $g-C_3N_4(V-g-C_3N_4)$. In addition, a combination of $g-C_3N_4(H^+)$ and $V-g-C_3N_4$ successfully afforded direct synthesis of DFF from fructose in a one-pot reaction. Moreover, a bifunctional catalyst of $V-g-C_3N_4(H^+)$ achieved a one-step approach to fructose-to-DFF transformation by acid-catalyzed dehydration and successive aerobic oxidation. The research highlights a good prospect for catalytic application of $g-C_3N_4$ -derived catalysts for biomass carbohydrate conversion.

Figure 6. a) V2p XPS spectra of V–g-C₃N₄ (V 1.39 mmol g⁻¹); N1s XPS spectra of b) g-C₃N₄, c) V–g-C₃N₄ (V 1.39 mmol g⁻¹), and d) g-C₃N₄(H⁺) (acid density 0.32 mmol g⁻¹).



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Experimental Section

Materials and Characterization

Materials and their characterization are provided in the Supporting Information.

Synthesis of g-C₃N₄, M-g-C₃N₄, g-C₃N₄(H⁺), and V-g-C₃N₄(H⁺)

g-C₃N₄^[36] and metal-doped g-C₃N₄ (M–g-C₃N₄; M=V, Ni, Cu, Mo, Mn, Fe, and Co)^[49,50] were prepared according to the literature methods (see the Supporting Information for details). The V–g-C₃N₄ with different vanadium contents were labeled as V–g-C₃N₄ (*x*), in which *x* represents the molar concentration (mmolg⁻¹) of V in V–g-C₃N₄ determined by ICP–AES. g-C₃N₄(H⁺) and V–g-C₃N₄(H⁺) were prepared by protonation of g-C₃N₄ and V–g-C₃N₄, respectively, according to the literature methods (see the Supporting Information for details). The acid density of g-C₃N₄(H⁺) and V–g-C₃N₄(H⁺) was determined by potentiometric acid–base titration.

Fructose conversion into HMF

In a typical run, the procedure for fructose dehydration into HMF was as follows: fructose (200 mg), g-C₃N₄(H⁺) (100 mg), and DMSO (2 mL) were added into a 25 mL Schlenk tube. The tube was heated at 100–140 °C for 2 h under N₂. The concentrations of fructose and HMF were determined by HPLC (Shimadu LC-20AT) equipped with UV and refractive-index detectors. The analysis conditions were conducted with a Shodex Sugar SH-1011 column (300×8 mm) by using HPLC-grade 0.005 M H₂SO₄ water solution as the eluent at a column temperature of 50 °C and a flow rate of 0.5 mLmin⁻¹. Fructose and HMF were detected with a refractive-index detector, respectively. HMF: ¹H NMR (400 MHz, D₂O) δ = 9.33 (s, 1H), 7.40 (d, *J* = 3.6 Hz, 1H), 6.55 (d, *J* = 3.1 Hz, 1H), 4.57 ppm (s, 2H). ¹³C {¹H} NMR (101 MHz, D₂O) δ = 180.5, 161.3, 151.8, 126.8, 110.9, 56.0 ppm. IR (KBr): \hat{v} = 3377 (O–H), 1670 cm⁻¹ (C=O). Mass spectrum (EI) *m/z* = 126 (M⁺).

HMF conversion into DFF

In a typical run, the procedure for the HMF oxidation was as follows: HMF (126 mg, 1 mmol), V–g-C₃N₄ (100 mg, V 1.39 mmol g⁻¹) and DMSO (2 mL) were added into a 25 mL Schlenk tube. The tube was heated at 130 $^\circ\text{C}$ for 6 h under oxygen atmosphere (0.1 MPa). After the reaction mixture was cooled, distilled water (8 mL) was added and the mixture was filtrated; then the products were extracted by dichloromethane for qualitative analysis by GC-MS (Aglient, 5973 Network 6890N). Byproducts of dehydration such as levulinic acid and formic acid or further oxidation byproducts such as 2-carboxy-5-(formyl)furan and furan-2,5-dicarboxylic acid were undetected in the dichloromethane-extracted samples. The quantitative analysis of DFF was performed by GC (FILI, GC-9790II) with a KB-5 capillary column (30.0 m \times 0.32 µm \times 0.25 µm) and hydrogen flame-ionization detector (FID). The products were detected by using the following conditions: injector temperature 260 °C, detector temperature 280°C, oven temperature 100°C was held for 1 min, 25°C min⁻¹ to 200°C, and held at 200°C for 1.5 min. o-Cresol was used as an internal standard according to the literature. $^{\rm [51]}$ DFF: $^1{\rm H}$ NMR (400 MHz, CDCl_3) $\delta\!=\!9.86$ (s, 1 H), 7.33 ppm (s, 1 H).¹³C NMR (101 MHz, CDCl₃) δ = 179.3, 154.4, 119.3 ppm.

Fructose conversion into DFF

One-pot two-step: In a typical run, the procedure for one-pot twostep synthesis of DFF was as follows: the reaction was divided into two steps: firstly, fructose (200 mg), g-C₃N₄(H⁺) (100 mg), and DMSO (2 mL) were added into a 25 mL Schlenk tube, the dehydration reaction was performed at 130 °C for 2 h under nitrogen atmosphere (0.1 MPa). Then V–g-C₃N₄ (100 mg, V 1.39 mmol g⁻¹) was added into the Schlenk tube, the oxidation reaction was performed at 130 °C for 6 h under oxygen atmosphere (0.1 MPa).

One-pot one-step: In a typical run, the procedure for one-pot one-step synthesis of DFF was as follows: fructose (200 mg), V-g-C₃N₄(H⁺) (100 mg) and DMSO (2 mL) were added into a 25 mL Schlenk tube. The dehydration reaction was performed at 130 °C for 2 h under nitrogen atmosphere (0.1 MPa). Then, the oxidation reaction was performed at 130 °C for another 6 h under oxygen atmosphere (0.1 MPa).

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