# Polyaniline-Grafted VO(acac)<sub>2</sub>: An Effective Catalyst for the Synthesis of 2,5-Diformylfuran from 5-Hydroxymethylfurfural and Fructose<sup>\*\*</sup>

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Herein, polyaniline-grafted vanadyl acetylacetonate  $[VO(acac)_2]$  was prepared and used as an effective catalyst for the oxidation of 5-hydroxymethylfurfural (HMF) under atmospheric oxygen pressure. A high HMF conversion of 99.2% was obtained after 12 h at 110 °C, and 2,5-diformylfuran (DFF) was obtained in 86.2% yield. More importantly, the one-pot conversion of fructose into DFF was also realized with two binary catalysts: Amberlyst-15 and polyaniline–VO(acac)<sub>2</sub>. Amberlyst-15

Introduction

Nowadays, much attention is paid to the search of renewable resources to supply chemicals and fuels owing to the decrease in fossil resources.<sup>[1]</sup> Biomass is a promising renewable feed-stock that can serve as a substitute of fossil resources because it is inexpensive and abundant in the earth.<sup>[2–5]</sup> In addition, biomass maintains the carbon balance in the earth, as biomass is synthesized with carbon dioxide and water using sunlight as the energy source. In this context, much effort has been devoted to the conversion of biomass into useful chemicals and valuable fuels.<sup>[6,7]</sup>

Among various biomass-based chemicals, 5-hydroxymethylfurfural (HMF) is one of the most promising platform chemicals in the biorefinery area. Therefore, the synthesis of HMF from various carbohydrates with various homogeneous and heterogeneous catalysts has been extensively studied.<sup>[8–10]</sup> Nowadays, there is a growing interest in the transformation of HMF into valuable chemicals and liquid fuels.<sup>[11–14]</sup> The catalytic oxidation of HMF can generate several important furan compounds, such as 2,5-diformylfuran (DFF), 5-hydroxymethyl-2-furancarboxylic acid, and 2,5-furandicarboxylic acid (FDCA).<sup>[15–17]</sup> FDCA has been identified as one of the top 12 valuable chemicals from biomass by the U.S. Department of Energy. It has a structure similar to that of petroleum-derived terephthalic acid; thus, it can serve as a substitute for terephthalic acid in manufacturing poly(ethylene terephthalate) plastics.<sup>[18]</sup> DFF, one of

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 [\*\*] acac = acetvlacetonate.

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was used for the acid-catalyzed dehydration of fructose into HMF, followed by the in situ oxidation of HMF catalyzed by polyaniline–VO(acac)<sub>2</sub>. DFF could be obtained in a yield of 42.1% from fructose by using the one-pot reaction, whereas two consecutive steps gave a higher DFF yield of 71.1%. Owing to the facile catalyst preparation and low cost, this method showed a promising potential for the synthesis of DFF from abundant carbohydrates.

the oxidation products of HMF, has also been found to be useful in many fields. It can be used as a versatile precursor for the synthesis of furanic polymers, pharmaceuticals, antifungal agents, nematocides, fluorescent materials, and porous organic frameworks.<sup>[19-23]</sup> DFF is generally obtained by the selective oxidation of the hydroxyl group in HMF. However, the existing furan and aldehyde functionalities in HMF make it susceptible to undergo many side reactions, such as overoxidation to FDCA and cross-polymerization to produce unwanted byproducts.

In early reports, the oxidation of HMF to DFF was performed with conventional oxidants such as NaOCI,<sup>[24]</sup> BaMnO<sub>4</sub>,<sup>[25]</sup> and C<sub>5</sub>H<sub>5</sub>NH[CrO<sub>3</sub>Cl].<sup>[26]</sup> These methods not only required stoichiometric oxidants but also released serious toxic wastes. Therefore, the use of molecular oxygen or air and heterogeneous catalysts is highly favored from both sustainable chemistry and economical point of views. To date, several metal-based catalytic systems such as Pt-Bi/C,[27] hydrotalcite supported Ru nanoparticles (Ru/HT),<sup>[28]</sup> and KMn<sub>8</sub>O<sub>16</sub>·nH<sub>2</sub>O<sup>[29]</sup> have been reported for the aerobic oxidation of HMF with varied catalytic performances. Among the heterogeneous catalysts, vanadiumbased catalysts have attracted much attention for the aerobic oxidation of HMF to DFF because the cost of vanadium-based catalysts is low as compared with other metal catalysts such as ruthenium and platinum. Carlini et al. reported that a high HMF conversion of 98% was obtained with the vanadyl phosphate catalyst in methyl isobutyl ketone (MIBK) under an oxygen pressure of 0.1 MPa, but the selectivity toward DFF was only 50%.[30] Later, Riisager et al. reported that the use of the zeolite-supported vanadia catalyst afforded 50% HMF conversion with approximately 45% DFF yield; however, the catalyst lost its catalytic activity significantly owing to leaching of active metal species.<sup>[31]</sup>



However, the large-scale synthesis of DFF from HMF is limited owing to the high cost of HMF. Because HMF can be readily generated from the dehydration of fructose in the presence of an acid catalyst, the synthesis of DFF from fructose is desirable through an integrated chemical process in which multistep reactions are consolidated into a one-pot reaction. Therefore, the one-pot conversion of fructose into DFF with a series of combined catalytic systems has received great attention.<sup>[28,29]</sup> For example, Takagaki et al.<sup>[28]</sup> demonstrated a one-pot conversion of fructose into DFF via two consecutive steps with use of Amberlyst-15 and Ru/HT catalysts in DMF. First, HMF was produced from the dehydration of fructose in the presence of Amberlyst-15, and then HMF was oxidized in situ to DFF over the Ru/HT catalyst. DFF was obtained from fructose in a yield of 49%. Chen et al. demonstrated the dehydration of fructose into HMF catalyzed by protonated graphitic carbon nitride  $[q-C_3N_4(H^+)]$ as a solid acid as well as the aerobic oxidation of HMF to DFF promoted by vanadium-doped g-C<sub>3</sub>N<sub>4</sub>, which gave DFF in approximately 63% yield.[32]

In recent years, polymer-supported metal complexes have gained much attention in organic synthesis because they offer high economic prospects in developing reusable catalysts.<sup>[33]</sup> In polymer-supported catalysts, the fixed position of the metal ion on the polymer matrix may contribute to greater isolation of catalytically active sites and can thus increase the catalytic activity. Polyaniline has recently received a great interest in catalytic applications owing to its ease of synthesis, performance stability, and low synthesis cost. It can be synthesized easily by the oxidation of the monomer in the liquid phase. Recently, polyaniline-supported metal catalysts have been used as heterogeneous catalysts for some chemical reactions.<sup>[34,35]</sup> Herein, these findings have motivated us to explore the use of polyaniline to immobilize vanadium complex and use it as a new heterogeneous catalyst for the oxidation of HMF with molecular oxygen. More importantly, much more attention has been devoted to the one-pot conversion of fructose into DFF in two wavs.

### **Results and Discussion**

#### Catalyst preparation and characterization

The synthesis of polyaniline–vanadyl acetylacetonate  $[VO(acac)_2]$  catalyst was performed in two steps (Scheme 1). First, the polymerization of aniline under acidic conditions in the presence of the oxidant reagent  $(NH_4)_2S_2O_8$  produced the polyaniline hydrochloride salt. The deprotonation of polyani-



**Scheme 1.** Synthesis of polyaniline–VO(acac)<sub>2</sub> catalyst.

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line hydrochloride was then achieved with aqueous ammonia (3 wt%). Polyaniline can be used as an effective support for the immobilization of a transition metal complex. On the one hand, it is insoluble in common organic solvents and water. On the other hand, there are many nitrogen atoms in polyaniline that have lone pair electrons to coordinate with the free orbit of the transition metal complex. Thus, the polyaniline-supported transition metal complex can be used as an effective and stable heterogeneous catalyst. The weight percentage of vanadium was determined to be 6.3% from inductively coupled plasma atomic emission spectroscopy analysis.

The nitrogen adsorption-desorption isotherms of the polyaniline-VO(acac)<sub>2</sub> catalyst are shown in Figure 1. The isotherm



Figure 1. Nitrogen adsorption-desorption isotherms of the catalyst.

is a typical type IV isotherm with H<sub>3</sub>-type hysteresis loop. The BET surface area of the catalyst was determined to be  $31.5 \text{ m}^2\text{g}^{-1}$ , and its pore volume was  $0.21 \text{ cm}^3\text{g}^{-1}$ . However, the BET surface area and pore volume of the parent polyaniline were calculated to be  $41.9 \text{ m}^2\text{g}^{-1}$  and  $0.36 \text{ cm}^3\text{g}^{-1}$ , respectively. This decrease in surface area and pore volume of the catalyst was due to VO(acac)<sub>2</sub> in the porous framework of the parent material. The BET results indicated that VO(acac)<sub>2</sub> was grafted onto the surface and pores of polyaniline.

The FTIR spectra of polyaniline and polyaniline–VO(acac)<sub>2</sub> are shown in Figure 2. With regard to the structure of polyaniline, the characteristic peaks at 1583 and 1490 cm<sup>-1</sup> were assigned to the C=C stretching mode of quinoid and benzenoid rings.<sup>[36]</sup> Importantly, the band at 1301 cm<sup>-1</sup> was assigned to the C–N stretching vibration of secondary aromatic amine in the alternative unit of quinoid–benzenoid sequences of polyaniline. Another strong peak at 1149 cm<sup>-1</sup> was assigned to the in-plane bending vibration of the C–H bond, and the peak at 825 cm<sup>-1</sup> was attibuted to the out-plane bending of the C–H bond.<sup>[37]</sup>

With regard to the characteristic peaks of VO(acac)<sub>2</sub>, the peak at approximately 1575 cm<sup>-1</sup> was assigned to the streching vibration  $v_9$  of the C=O bond.<sup>[38]</sup> The peak at approximately 930 cm<sup>-1</sup> was assigned to the streching vibration  $v_3$  of the C=O bond,<sup>[38]</sup> and the peak at 640 cm<sup>-1</sup> was attibuted to the





Figure 2. FTIR spectra of a) polyaniline and b) the polyaniline–VO(acac)<sub>2</sub> catalyst.

stretching vibration of the V–O bond.<sup>[38,39]</sup> On comparing the FTIR spectra of the catalyst and the support, only two distinct peaks at approximately 930 and 640 cm<sup>-1</sup> were observed in the catalyst. These results indicated that VO(acac)<sub>2</sub> was immobilized on the polyaniline support. As shown in Figure 2b, the characteristic peaks of the catalyst in the region from 1100 to 1600 cm<sup>-1</sup> were similar to those of the parent polyaniline.

The results of X-ray photoelectron spectroscopy (XPS) of polyaniline–VO(acac)<sub>2</sub> are presented in Figure 3a. The strong signal of carbon with the C1s binding energy of approximately 285 eV was observed, and its atomic percentage was approximately 76.1%, which included adventitious carbon and the sample carbon. A peak at 399 eV was an evidence of the presence of nitrogen, which was assigned to the binding energy of N1s. Two peaks with the binding energy of approximately 531 and 516 eV were attributed to O1s and V2p, respectively, which confirmed the presence of oxygen and vanadium in the catalyst. The atomic percentage of vanadium and oxygen was determined to be 1.54 and 8.05%, respectively, from XPS analysis, which was close to the atomic molar ratio of vanadium and oxygen in VO(acac)<sub>2</sub>. These results suggested that VO(acac)<sub>2</sub> should be immobilized through the coordination of the nitrogen atom in polyaniline with vanadium in VO(acac)<sub>2</sub>. In addition, the atomic percentage of nitrogen was 8.81%, and it was much higher than that of vanadium, which indicated that only part of nitrogen in polyaniline was used to immobilize VO(acac)<sub>2</sub>. In addition, the survey spectrum showed the presence of a small emission peak at approximately 270 eV and it was assigned to the binding energy of Cl2s. This result indicated that chlorine ions still remained on the catalyst surface.

The high-resolution XPS spectra of O1s and V2p are shown in Figure 3c. The high-resolution XPS spectrum of O1s has been deconvoluted into three peaks. The binding energy of the three deconvoluted peaks was 530.2, 531.7, and 533.2 eV, and these peaks were assigned to C=O, V–O, and C–O bonds, respectively. The binding energy of vanadium(V) is usually larger than 518 eV. For example, Cornaglia et al.<sup>[40]</sup> treated  $(VO)_2P_2O_7$  in oxygen atmosphere at different temperatures and found that the binding energy of vanadium in all the samples



Figure 3. XPS spectra of a) the polyaniline–VO(acac)\_2 complex, b) O1s and V2p, and c) O1s.

was larger than 518 eV. However, the binding energy of vanadium was 517. 3 eV when  $(VO)_2P_2O_7$  was treated in nitrogen atmosphere. In the high-resolution XPS spectrum of vanadium, there was no peak for vanadium(V). Thus, we can conclude that  $VO(acac)_2$  in the catalyst was stable. The high-resolution XPS spectrum of vanadium should present only one peak for vanadium(IV) with the binding energy of 170.0 eV. Cornaglia et al. reported that the difference in the binding energy of O1s and  $V2p_{3/2}$  in VOHPO<sub>4</sub> [vanadium(IV)] was 14.7 eV, whereas it was 12.9 eV in  $V_2O_5$  [vanadium(V)]. As shown in Figure 3 b, the difference in the binding energy of V–O1s (531.7 eV) and  $V2p_{3/2}$  (517.0 eV) in our prepared catalyst was 14.7 eV. Thus, this result again confirmed that the oxidation state of vanadium in our prepared catalyst was +4, which was in accordance



with the results reported by Cornaglia et al. Our results were consistent with the previous results reported by Pereira et al.,<sup>[39]</sup> which indicated that the valence state of vanadium(IV) in VO(acac)<sub>2</sub> did not change after immobilization.

In addition, the binding energy of V2p<sub>3/2</sub> was found to be 517.0 eV, though it was reported that the binding energy of the V2p<sub>3/2</sub> peak of free VO(acac)<sub>2</sub> was 516.8 eV.<sup>[41]</sup> These results suggested that VO(acac)<sub>2</sub> should be chemically bonded to the support through the coordination of lone pair electrons of nitrogen with the free orbit of vanadium, as shown in Scheme 1. Jarrais et al. also found that the binding energy of vanadium(V) in free VO(acac)<sub>2</sub> was 516.8 eV, which shifted to 517.0 eV after VO(acac)<sub>2</sub> was bonded to the surface of the amine-functionalized active carbon.<sup>[41]</sup>

Thermogravimetric analysis (TGA) was performed to detect the difference between polyaniline and the polyaniline–vanadium complex, and the results are presented in Figure 4. Ther-



Figure 4. TGA of a) polyaniline and b) the polyaniline–VO(acac)<sub>2</sub> complex.

mal analysis was performed in nitrogen atmosphere at a heating rate of 10°C min<sup>-1</sup> in the temperature range of 40–700°C. The small weight loss was almost the same between the support and the catalyst before 150°C in nitrogen atmosphere, which was due to the loss of physically absorbed water. In the temperature range of 150-450 °C, the weight loss of the catalyst was much higher than that of the support, which was due to the decomposition of the acetylacetonate complex in the catalyst. Baltes et al. reported that the thermal decomposition of alumina-VO(acac)<sub>2</sub> underwent three steps in the temperature range of 150–325 °C.<sup>[42]</sup> However, polyaniline started to decompose at 300 °C and decomposed quickly at approximately 600 °C. As shown in Figure 4, the weight loss of polyaniline was slightly greater than that of the polyaniline-vanadium complex, which was due to the decomposition products of vanadium species, mainly vanadium oxide, present in the sample.

#### Aerobic oxidation of HMF in various solvents

The catalytic activity of the as-prepared polyaniline–VO(acac)<sub>2</sub> catalyst was evaluated by the aerobic oxidation of HMF. Experi-

ments were initially performed in various solvents to study the effect of the reaction solvent on the oxidation of HMF, as different solvents show different properties such as polarity, dielectric constant, steric hindrance, and acid–base property, which would affect chemical reactions.<sup>[43]</sup> The aerobic oxidation of HMF was greatly affected by the reaction solvent (Table 1).

Table 1. Results of the oxidation of HMF in various solvents. <sup>[a]</sup>							
Entry	Solvent	HMF conversion [%]	DFF yield [%]	FDCA yield [%]			
1	ethanol	16.1	8.7	4.1			
2	acetonitrile	17.2	14.1	2.0			
3	DMSO	43.6	31.1	7.6			
4	MIBK	91.7	70.1	17.6			
5	toluene	94.1	62.1	29.6			
6	4-chlorotoluene	99.2	86.2	11.7			
[a] Read	ction conditions: pol	yaniline–VO(acac) <sub>2</sub> ( $t = 30 \text{ ml min}^{-1} T =$	80 mg), HMF	(100 mg), sol-			

Generally speaking, the strong polar solvents were not beneficial for the aerobic oxidation of HMF over the polyaniline-VO(acac)<sub>2</sub> catalyst (Table 1, entries 1-3 vs entries 4-6). Low HMF conversions were obtained in ethanol and acetonitrile with low boiling point and strong polarity (Table 1, entries 1 and 2). A moderate HMF conversion of 43.6% was obtained in DMSO with strong polarity (Table 1, entry 1). High HMF conversions were obtained in MIBK, toluene, and 4-chlorotoluene with relatively low polarity (Table 1, entries 4-6). However, the product distribution was quite different in each solvent. In all cases, DFF was determined to be the major oxidation product during the formation of FDCA. The ratio of DFF to FDCA strongly depended on the specific solvent. Although a high HMF conversion of approximately 90% was obtained in MIBK, toluene, and 4-chlorotoluene (Table 1, entries 4-6), the selectivity toward DFF in MIBK and toluene was much lower than that in 4-chlorotoluene (Table 1, entries 4 and 5 vs entry 6). With regard to both HMF conversion and DFF selectivity, 4-chlorotoluene was found to be the best solvent, which afforded a high HMF conversion of 99.2% and a DFF selectivity of 86.2%.

#### Effect of the reaction temperature on the oxidation of HMF

As discussed in the above section, the oxidation of HMF in 4chlorotoluene at the reaction temperature of  $110^{\circ}$ C gave a DFF yield of 86.2% and an FDCA yield of 11.7%. To increase the selectivity toward DFF and to inhibit the overoxidation of DFF to FDCA, oxidation reactions were performed at low reaction temperatures of 70 and 90°C, and the results are presented in Figure 5. It can be seen that the reaction temperature significantly affected HMF conversion and DFF selectivity. HMF conversion decreased gradually with the decrease in the reaction temperature from 110 to 70°C. Almost quantitative HMF conversion (99.2%) was observed at 110°C, whereas it sharply decreased to 55.2% at 90°C. With a decrease in the reaction temperature to 70°C, the oxidation of HMF proceeded slug-





**Figure 5.** Results of HMF oxidation at different reaction temperatures. Reaction conditions: polyaniline–VO(acac)<sub>2</sub> (80 mg), HMF (100 mg), 4-chlorotoluene (8 mL), oxygen flow rate = 30 mL min<sup>-1</sup>, t = 12 h.

gishly and afforded a low HMF conversion of only 25.7%. DFF and FDCA were also detected as the oxidation products at the three reaction temperatures. DFF selectivity (also the ratio of DFF to FDCA) increased with the decrease in reaction temperature. DFF selectivity was calculated to be 86.8% at 110°C, and it was 90.7 and 92.2% at 70 and 50°C, respectively.

### Synthesis of DFF and FDCA from fructose by using the onepot method

Although DFF could be produced from the oxidation of HMF with polyaniline–VO(acac)<sub>2</sub> as the catalyst, this method is limited to the large-scale synthesis of DFF owing to the high cost of HMF. Therefore, researchers tried to produce DFF directly from renewable carbohydrates such as fructose. To our knowledge, there are few examples of the one-pot conversion of fructose into DFF. To realize the one-pot conversion of fructose into DFF, we should solve the problem of solubility of fructose. DMSO was reported to have the strong ability to dissolve fructose and thus was the excellent reaction medium for the dehydration of fructose into HMF. As described above, the polyaniline-VO(acac)<sub>2</sub> catalyst showed high catalytic activity for the oxidation of HMF in 4-chlorotoluene and moderate activity in DMSO. Therefore, a mixed solvent of DMSO and 4-chlorotoluene with the volume ratio of 1:4 was used as the reaction solvent. The synthesis of DFF from fructose was performed by using the one-pot reaction catalyzed by two binary catalysts, Amberlyst-15 and polyaniline-VO(acac)<sub>2</sub>, simultaneously, in which Amberlyst-15 was used as the acid catalyst for the dehydration of fructose into HMF and polyaniline-VO(acac)<sub>2</sub> was used for the in situ oxidation of HMF to DFF. The results of the one-pot conversion of fructose into DFF are presented in Figure 6. It can be seen that HMF yield first increased and then decreased during the reaction. The initial increase in HMF yield was due to the high concentration of fructose in an early reaction stage, and the decrease in HMF yield was due to the flowing oxidation of HMF to DFF and FDCA. The highest HMF yield of 37.1% was obtained after 2 h. The DFF yield continuously increased during the reaction process. The highest DFF yield was observed to be 42.1% after 12 h in a one-pot reaction

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**Figure 6.** Results of the one-pot conversion of fructose catalyzed by two binary catalysts. Reaction conditions: fructose (145 mg) was first dissolved in a mixed solvent of DMSO and 4-chlorotoluene. Then, Amberlyst-15 (100 mg) and polyaniline–VO(acac)<sub>2</sub> (80 mg) were added to the fructose solution. The reaction was performed at 110 °C with an oxygen flow rate of 30 mL min<sup>-1</sup>.

starting from fructose. In addition, a low FDCA yield of 6.1% was observed.

#### Synthesis of DFF from fructose by two consecutive steps

To further increase DFF yield from fructose, two consecutive steps were applied for the synthesis of DFF from fructose to reduce side reactions (Scheme 2). First, HMF was produced by



Scheme 2. Synthesis of DFF from fructose by two consecutive steps.

the dehydration of fructose catalyzed by Amberlyst-15. Second, the Amberlyst-15 catalyst was removed from the reaction solution, and then the polyaniline-VO(acac)<sub>2</sub> catalyst was added to the resultant reaction solution to perform the following oxidation of HMF to DFF. In the first step, HMF was produced by the dehydration of fructose in the presence of Amberlyst-15 (Figure 7). This process was fast and effective, which gave a high HMF yield of 91.8% after 1.5 h at 110°C. Then, Amberlyst-15 was removed from the reaction mixture and polyaniline-VO(acac)<sub>2</sub> was added to the resultant reaction solution to promote the oxidation of HMF. In the second step, the HMF content decreased and DFF yield increased gradually. After the reaction time of 12 h in the second step, DFF was obtained from fructose in a yield of 71.1%. In addition, FDCA was produced in a small amount of 9.3%. DFF yield obtained by using the two consecutive method was much higher than that obtained by using the one-pot reaction. One of the main reasons for the lower DFF yield from fructose via a one-pot reaction was the possible oxidation of fructose, which resulted in other undesired byproducts.[44] For example, the oxidation of fructose over the Pt/C catalyst generated two oxidation prod-

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**Figure 7.** Results of the synthesis of DFF from fructose via two consecutive steps. Reaction conditions: fructose (145 mg) was first dissolved in a mixed solvent of DMSO and 4-chlorotoluene. Then, the dehydration of fructose was performed at 110 °C for 2 h. Finally, HMF oxidation in the reaction solution was performed with polyaniline–VO(acac)<sub>2</sub> (80 mg) at 110 °C with an oxygen flow rate of 30 mL min<sup>-1</sup>.

ucts 2-keto-D-gluconic acid and D-threo-hexo-2,5-diulose (5-ke-tofructose).<sup>[44]</sup>

#### **Catalyst recycling experiments**

The recycling experiment of the polyaniline–VO(acac)<sub>2</sub> catalyst was studied. The aerobic oxidation of HMF in 4-chlorotoluene at 110 °C was used as the model reaction. Polyaniline-VO(acac)<sub>2</sub> was insoluble in the reaction solvent and hence can be easily separated by centrifugation to avoid the weight loss of the catalyst. Then, the spent catalyst was washed several times with water and ethanol to remove any residue that remained in the catalyst. Finally, the spent catalyst was dried in a vacuum oven at 60°C. The spent catalyst was used in the next run under the same reaction conditions used for the first run. The results of recycling experiments of polyaniline-VO(acac)<sub>2</sub> are presented in Figure 8. Notably, HMF conversion and DFF yield showed a small decrease from the first run to the sixth run. HMF conversion decreased from 99.2% in the first run to 85.3% in the sixth run, and DFF yield decreased from 86.2% in the first run to 77.2% in the sixth run. The weight percentage of vanadium in the spent catalyst after the sixth run was determined to be 5.6% from inductively coupled plasma atomic emission spectroscopy analysis, and it was

6.3% in the fresh catalyst. Therefore, the small decrease in the catalytic activity was due to minor leaching of vanadium in the catalyst.

### Comparison of our method for the synthesis of DFF from HMF with other reported methods

To evaluate the advantages of our catalytic system for the synthesis of DFF from the oxidation CHEMCATCHEM Full Papers



Figure 8. Results of recycling experiments of the polyaniline–VO(acac) $_2$  catalyst.

of HMF, the method developed in our study was compared with other methods for the oxidation of HMF to DFF over vanadium-based catalysts, and the results are summarized in Table 2. To our knowledge, the use of homogeneous VOSO4 with Cu(NO<sub>3</sub>)<sub>2</sub> showed the best results for the oxidation of HMF to DFF, but the catalyst was difficult to recycle (Table 2, entry 1). Active carbon-supported V2O5 (AC/V2O5) and H-betasupported V<sub>2</sub>O<sub>5</sub> (H-beta/V<sub>2</sub>O<sub>5</sub>) could catalyze the oxidation of HMF to DFF with a relative selectivity; however, these catalytic systems were used under atmospheric oxygen pressure (Table 2, entries 2 and 3).  $g-C_3N_4-V_2O_5\cdot VO_2$  showed much higher catalytic activity than AC/V<sub>2</sub>O<sub>5</sub> and H-beta/V<sub>2</sub>O<sub>5</sub>, as it could catalyze the oxidation of HMF under atmospheric oxygen pressure. The reason was that VO<sub>2</sub> in the catalyst accelerated electron transfer between vanadium(V) and vanadium(IV), which was generally believed to be the redox cycle during the oxidation of HMF to DFF (Table 2, entry 4). Vanadium phosphate oxide-based heterogeneous catalysts also showed the catalytic activity for the oxidation of HMF to DFF (Table 2, entry 1). Although a high HMF conversion of 98% could be obtained in the presence of VOPO<sub>4</sub>·2H<sub>2</sub>O, the selectivity toward DFF was only 50% (Table 2, entry 5). The introduction of alkyl chain C14 into vanadium phosphate oxide (C14VOPO4) increased the DFF selectivity. However, the activity of the catalyst decreased significantly and HMF conversion decreased from 91% in the first run to 62% in the third run

Entry	Catalyst	Oxygen pressure [bar] <sup>[a]</sup>	HMF conversion [%]	DFF yield [%]	Reference
1	Cu(NO <sub>3</sub> ) <sub>2</sub> /VOSO <sub>4</sub>	1	99	99	[45]
2	AC/V <sub>2</sub> O <sub>5</sub>	2.8 (O <sub>2</sub> )	95.2	91.8	[46]
3	H-beta/V₂O₅	10 (O <sub>2</sub> )	84	82	[31]
4	$g-C_3N_4-V_2O_5\cdot VO_2$	1	99	82	[32]
5	VOPO <sub>4</sub> •2 H <sub>2</sub> O	1	98	49	[30]
6	C <sub>14</sub> VOPO <sub>4</sub>	1	99	83	[46]
7	polyaniline-VO(acac) <sub>2</sub>	1	99.2	86.2	this work

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(Table 2, entry 6). Compared with the above-mentioned method using the vanadium catalyst, our method did not require to perform the reaction under high atmospheric oxygen pressure and could gave high HMF conversion and DFF selectivity (Table 2, entry 7).

### Conclusions

Herein, the immobilization of vanadyl acetylacetonate [VO(acac)<sub>2</sub>] on polyaniline was performed and well characterized by using several technologies. The polyaniline-VO(acac)<sub>2</sub> catalyst showed high activity for the aerobic oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-diformylfuran (DFF). The oxidation of HMF proceeded smoothly under atmospheric oxygen pressure. A high HMF conversion of 99.2% was obtained after 12 h at 110 °C, and DFF and 2,5-furandicarboxylic acid were obtained in a yield of 86.2 and 11.7%, respectively. More importantly, the synthesis of DFF directly from fructose was also studied by using two methods using the two binary catalysts: Amberlyst-15 and polyaniline-VO(acac)<sub>2</sub>. Amberlyst-15 was used for the acid-catalyzed dehydration of fructose into HMF, and polyaniline-VO(acac)<sub>2</sub> was used for the oxidation of HMF. The one-pot method produced DFF in a yield of 42.1 %, whereas the two consecutive method gave a higher DFF yield of 71.1%. In addition, the polyaniline–VO(acac)<sub>2</sub> catalyst could be reused despite the slight loss of its catalytic activity. Owing to the low cost of the catalyst, this method showed a promising potential for the conversion of abundant carbohydrates into valuable bulk chemicals.

### **Experimental Section**

### Materials

Aniline and ammonium persulfate were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). VO(acac)<sub>2</sub> and Amberlyst-15 were purchased from Aladdin Chemicals Co. Ltd. (Beijing, China). HMF (98%) was purchased from Beijing Chemicals Co. Ltd. (Beijing, China). DFF and FDCA were purchased from the J&K Chemical Co. Ltd. (Beijing, China). All solvents were purchased from Sinopharm Chemical Reagent Co., Ltd.. Aniline was purified by distillation before use, and all other chemicals were of analytical grade and used without further purification. Acetonitrile (HPLC grade) was purchased from Tedia Co. (Fairfield, USA).

### Synthesis of polyaniline

Polyaniline was synthesized as described in a previous report.<sup>[36]</sup> In a typical synthesis, freshly distilled aniline (5 mL, 55 mmol) was first dissolved in HCl (63 mL, 1.5 M) in a 250 mL round flask. The flask was placed in an ice-salt bath, and the temperature was maintained at 0°C. Then, a solution of ammonium persulfate (55 mmol) in HCl (63 mL, 1.5 M) was added slowly for 1 h to the above solution at 0°C to keep the reaction temperature not higher than 5°C, as aniline polymerization is strongly exothermic. After the complete addition, the mixture was stirred for an additional 4 h. The resultant precipitate was separated by filtration and washed consecutively with water (3×30 mL), methanol (2×25 mL), and diethyl ether (2×15 mL) to remove the oligomers and any possible byproducts. The polymer was then dried in a vacuum oven for 24 h. The deprotonation of polyaniline hydrochloride was achieved with aqueous ammonia (3 wt%). The deprotonated polymer was washed with water, methanol, and diethyl ether and dried in a vacuum oven for 24 h.

### Synthesis of polyaniline-supported vanadium(VI) complex

First, VO(acac)<sub>2</sub> (0.5 g) was dissolved in dichloromethane (50 mL) and stirred with a magnetic stirrer. Then, polyaniline (1.0 g) was added and continuously stirred at RT for 48 h. After the completion of the reaction, the resultant precipitate was obtained by filtration and washed several times with hot ethanol to remove any unreacted metal complex. Finally, the catalyst was dried under vacuum at 60 °C for 12 h, which was labeled as polyaniline-VO(acac)<sub>2</sub>.

### **Catalyst characterization**

The TEM images were obtained with an FEI Tecnai G<sup>2</sup> F20 instrument. The sample powder was dispersed in ethanol and dropped onto copper grids for observation. The XRD patterns of the samples were collected with a Bruker D8 ADVANCE X-ray diffractometer using CuK<sub>a</sub> radiation. All XRD patterns were collected in the  $2\theta$ range of  $10-80^{\circ}$  (scanning rate:  $0.016^{\circ} s^{-1}$ ). The XPS spectra were recorded on a Thermo VG Scientific ESCA MultiLab 2000 spectrometer with a monochromatized AlK<sub>a</sub> X-ray source (1486.6 eV) at a constant analyzer pass energy of 25 eV. The binding energy was estimated to be accurate within 0.2 eV. All binding energies were corrected referencing to the C1s (284.6 eV) peak of the contaminated carbon used as an internal standard. The FTIR spectra were recorded on a Nicolet Nexus 6700 FTIR spectrometer with a spectral resolution of  $4 \text{ cm}^{-1}$  in the wavenumber range of 500–4000 cm<sup>-1</sup>. TGA was performed with a Netzsch TG209 instrument at a heating rate of 10 Kmin<sup>-1</sup> and a nitrogen flow of 20 mLmin<sup>-1</sup>. Nitrogen adsorption-desorption isotherms were measured with an Autosorb-1 (Quantachrome, USA) at 77 K. Before the measurement, all the samples were degassed in a vacuum line at 200 °C for 6 h. The BET surface area was determined by a multipoint BET method using the adsorption data in the  $P/P_0$  range of 0.05–0.3. The mesoporous pore size distributions were derived from desorption branches of isotherms by using the BJH model.

### General procedure for the aerobic oxidation of HMF

In a typical run, HMF (0.8 mmol, 100 mg) was first dissolved in 4chlorotoluene (8 mL) and stirred with a magnetic stirrer. Then, polyaniline-VO(acac)<sub>2</sub> (80 mg) was added to the reaction mixture and oxygen was flushed (flow rate: 20 mLmin<sup>-1</sup>) from the bottom of the reactor under atmospheric pressure, and the reaction was performed at 110 °C at a constant stirring rate of 600 rpm. Time zero was recorded when oxygen was flushed into the reaction mixture. After the completion of the reaction, the catalyst was removed from the reaction mixture and the reaction mixture was analyzed by using HPLC.

### Quantification of the products

The amounts of furan compounds in the reaction solution were analyzed with a ProStar 210 HPLC system using the external standard calibration curve method. Furan compounds could be separated with a reversed-phase C18 column (200×4.6 mm) at a wavelength of 280 nm. Acetonitrile and acetic acid aqueous solution (0.1 wt%; 30:70 v/v) were used as a mobile phase, and the flow rate was



 $1.0 \text{ mLmin}^{-1}$ . The column temperature was maintained at  $30 \,^{\circ}$ C. The amounts of furan compounds in the samples were obtained directly by interpolation from calibration curves. The retention times of HMF, DFF, and FDCA were 3.0, 3.5, and 2.8 min, respective-ly.

The conversion of HMF was calculated by using Equation (1).

$$HMF \text{ conversion } (\%) = (\frac{\text{moles of converted HMF}}{\text{moles of starting HMF}}) \times 100$$
(1)

One molecule of HMF produced one molecule of DFF or FDCA; thus, DFF or FDCA yield was calculated by using Equation (2) or Equation (3), respectively.

DFF yield (%) = 
$$\left(\frac{\text{moles of DFF}}{\text{moles of starting HMF}}\right) \times 100$$
 (2)

$$FDCA \text{ yield } (\%) = \left(\frac{\text{moles of FDCA}}{\text{moles of starting HMF}}\right) \times 100 \tag{3}$$

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Take baby steps: Polyaniline-grafted vanadyl acetylacetonate shows high catalytic activity for the oxidation of 5-hydroxymethylfurfural (HMF) under atmospheric oxygen pressure. A high HMF conversion of 99% and a 2,5-diformyl-

furan (DFF) yield of 86% are obtained after 12 h. More importantly, the synthesis of DFF directly from fructose is also realized with two binary catalysts: Amberlyst-15 and polyaniline-vanadyl acetylacetonate.

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Polyaniline-Grafted VO(acac)<sub>2</sub>: An **Effective Catalyst** for the Synthesis of 2,5-Diformylfuran 5-Hydroxymethylfurfural and Fructose