

Article

Phosphorus-Doped Carbon Supported Vanadium Phosphate Oxides for Catalytic Oxidation of 5-Hydroxymethylfurfural to 2,5-Diformylfuran

Sha Wen [†], Kai Liu [†], Yi Tian, Yanping Xiang, Xianxiang Liu ^{*} and Dulin Yin

National & Local Joint Engineering Laboratory for New Petro-chemical Materials and Fine Utilization of Resources, Key Laboratory of the Assembly and Application of Organic Functional Molecules of Hunan Province, College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, China; wensha@smail.hunnu.edu.cn (S.W.); nelab2012@126.com (K.L.); t15111298327@163.com (Y.T.); xiangyp@smail.hunnu.edu.cn (Y.X.); dulinyin@126.com (D.Y.)

^{*} Correspondence: lxx@hunnu.edu.cn

[†] Sha Wen and Kai Liu contributed equally to this work.

Received: 12 August 2020; Accepted: 7 October 2020; Published: 11 October 2020



Abstract: 2,5-diformylfuran (DFF) is an important downstream product obtained by selective oxidation of the biomass-based platform compound 5-hydroxymethylfurfural (HMF). In this study, a phosphorus-doped carbon (P-C) supported vanadium phosphate oxide (VPO) catalyst was successfully prepared and showed remarkably high catalytic activity in the selective oxidation of HMF to produce DFF with air as an oxidant. The effects of the reaction temperature, reaction time, solvent, catalyst amount, and VPO loading amount were investigated. The results showed that an HMF conversion rate of 100% and a DFF yield of 97.0% were obtained under suitable conditions, and DMSO was found to be the most suitable solvent under an air atmosphere.

Keywords: vanadium phosphate oxides; 5-hydroxymethylfurfural; catalysis; selective oxidation; 2,5-diformylfuran

1. Introduction

Nowadays, with the decrease in non-renewable fossil resources and the increase in environmental problems, the use of alternative green and renewable resources is needed. Hence, biomass, the only renewable source of energy, has received great attention [1]. Along this line, value-added chemicals processed by biomass have been researched widely [2]. 5-hydroxymethylfurfural (HMF), a biomass-derived chemical, which is classified by the US Department of Energy as one of the “Top 10 + 4” platform molecules, can be obtained by losing three molecules of water from hexose obtained from cellulose [3–6]. As a multifunctional intermediate connecting a biomass resource to the chemical industry, HMF can be used to synthesize various chemical products through hydrogenation, oxidation, polymerization, and ring-opening reactions [7–11].

2,5-diformylfuran (DFF), a versatile compound obtained by HMF oxidation, is applied in plenty of areas; for example, in pharmaceuticals, antifungal agents, and fluorescent materials [12,13]. Plenty of research on HMF oxidation to DFF has been done. Nocito et al. [14] conducted an oxidation process under pressure. Ning et al. [15] used tert-butyl hydroperoxide as an oxidant and demonstrated that it is environmentally unfriendly. Nie et al. [16] obtained an excellent DFF yield of 95.8% with a noble metal catalyst, but using a noble metal catalyst increased the cost of the reaction. However, the need for the preparation of high-performance catalysts, severe operating conditions, and its environmental unfriendly nature make the effective conversion of HMF to DFF difficult. Hence, finding an appropriate approach to this conversion is needed. According to research by Lai et al. [3], the catalyst vanadium

phosphate oxide (VPO) has a bright future in catalytic oxidation. As a transition metal with multiple valences of vanadium species, vanadium has been considered for use in HMF oxidation. Moreover, this carrier can enhance the performance of the active components of the catalyst, further improving its catalytic effect. Carbon materials, as carriers with a high specific surface area, can greatly increase the contact area between active components and reactants. This can improve the selectivity or conversion rate of the reaction [17–19]. Meanwhile, the introduction of heteroatoms can further improve catalytic performance through the adsorption of active components and reaction substrates by increasing the number of surface defects or the electron cloud density of carbon materials [20–22].

Spurred on by the above investigations, this work successfully prepared a phosphorus-doped carbon supported VPO catalyst, which was confirmed by various characterization methods. Due to its porous carbon material structure, the catalyst can efficiently adsorb reaction substrates and increase the concentration of HMF on the catalyst surface. By optimizing the reaction conditions, the catalyst achieves a perfect catalytic performance in atmospheric air. This work provides a method that not only overcomes the demand for precious metals but also reduces the equipment and technology requirements of the reaction, laying a foundation for the industrialization of DFF.

2. Experimental Methods

2.1. Materials

NH_4VO_3 was purchased from Tianjin Photovoltaic Technology Development Co. Ltd., Tianjin, China. Nano-silica, DMSO, acetonitrile, and acetic acid were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. HMF and DFF were purchased from Shanghai D&B Chemical Technology Co. Ltd., Shanghai, China. 5-Formyl-2-furancarboxylic acid (FFCA) was purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). The reagents were analytically pure. The experimental water was secondary distilled water.

2.2. Catalyst Preparation

2.2.1. Preparation of Phosphorus-Doped Carbon

Sucrose (3 g), H_3PO_4 (0.71 g), and nano-silica (1 g) were dissolved by ultrasound in deionized water and then, stirred at room temperature for 3 h. After that, they were dried in an oven at 100 °C for 12 h. They were calcined in a nitrogen atmosphere in a tubular furnace for 4 h at 700 °C at a rate of 10 °C/min. After soaking the ground product into HF, the powder was stirred at room temperature for 24 h and washed with deionized water and methanol ($3 \times 30\text{ mL}$). After drying at 100 °C, the product, labeled as P-C, was obtained.

2.2.2. Preparation of VPO/P-C Catalysts

The prepared P-C material was treated by ultrasound in water (10 mL). The mixtures with added NH_4VO_3 (0.0126 g) or $\text{VPO}_4 \cdot 2\text{H}_2\text{O}$ (0.14 g) were stirred for 2 h and dried in an oven at 100 °C for 12 h. They were calcined in a tubular furnace for 4 h at 500 °C at a rate of 10 °C/min under a nitrogen atmosphere. The catalyst was prepared after washing with deionized water and methanol ($3 \times 10\text{ mL}$) and drying at 100 °C. The obtained catalysts were marked as VPO/P-C and $\text{VPO}_4 \cdot 2\text{H}_2\text{O}/\text{P-C}$.

2.3. Catalyst Characterization

The FTIR spectrum was obtained with a Thermo Nicolet infrared spectrophotometer (Walsham, MA, USA) using the KBr pellet technique. Thermogravimetric and differential thermogravimetric (TG–DTG) curves were recorded on a TGA4000-FTIR Frontier Analyzer (Perkin Elmer, Walsham, MA, USA) with a heating rate of 10 °C/min under an N_2 atmosphere.

2.4. Synthesis of DFF from HMF

HMF (25.2 mg), a certain amount of catalyst, and DMSO (2 mL) were added to a round-bottomed flask equipped with a condenser and reacted in the oil bath pot. The cooled reaction liquid was diluted 20 times and filtered with an organic membrane before being analyzed by HPLC with an external standard method.

The product analysis was performed using the Agilent 1260 HPLC system equipped with a Venusil XBP C18 chromatographic column (4.6 × 250 mm, 5 μm, Phenomenex, Los Angeles, CA, USA) and a UV-Vis (280 nm) detector, Los Angeles, CA, USA. The mobile phase was composed of acetic acid solution (0.2%):acetonitrile (*v:v* = 95:5), and the samples were eluted at a rate of 0.5 mL/min at 30 °C. The amount of each compound was quantified by the external standard calibration curve method. According to the test results, the oxidation of HMF mainly leads to the production of DFF and FFCA. The peak locations and retention times of these products are shown in Figure S1 in Supplementary Materials. HMF conversion and product selectivity were calculated using the following equations:

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

$$\text{Product selectivity} = (\text{moles of product} / \text{moles of converted HMF}) \times 100\% \quad (2)$$

3. Results and Discussion

3.1. Catalyst Characterization

The catalyst was analyzed by FTIR and TG-DTG. The spectra of VPO/P-C and VPO₄·2H₂O/P-C presented in Figure 1 show a strong absorption band at 3371 cm⁻¹ associated with the hydroxyl group stretching vibration. The sharp absorption band at 1646 cm⁻¹ is assigned to the coordinated water molecule bending vibration. The characteristic peaks at 1199, 1105, and 1045 cm⁻¹ belong to the asymmetric stretching vibration of the phosphate radical. The peak at 977 cm⁻¹ is ascribed to the stretching vibration of the V=O bond. In addition, the 641 cm⁻¹ peak pertains to the P-OH bending vibration. The FTIR spectrum shows that the VPO/P-C catalyst was prepared successfully.

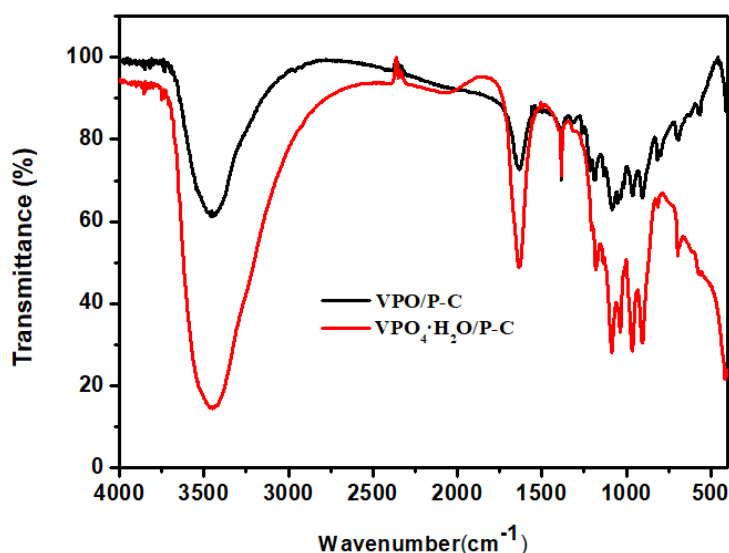


Figure 1. FTIR spectra of VPO₄·2H₂O/P-C and VPO/P-C.

The TG-DTG curves of the VPO/P-C catalyst are presented in Figure 2, showing three weight loss stages. The first stage appeared at 120 °C, owing to water absorption by porous carbon material. Then, the loss of crystal water led to mass loss at 150 °C. Finally, constant mass loss began at 250 °C with

the formation of $\text{VO}(\text{PO}_3)_2$ by VPO_4 pyrolysis. The structure of the catalyst above 400 °C began to stabilize without significant mass loss.

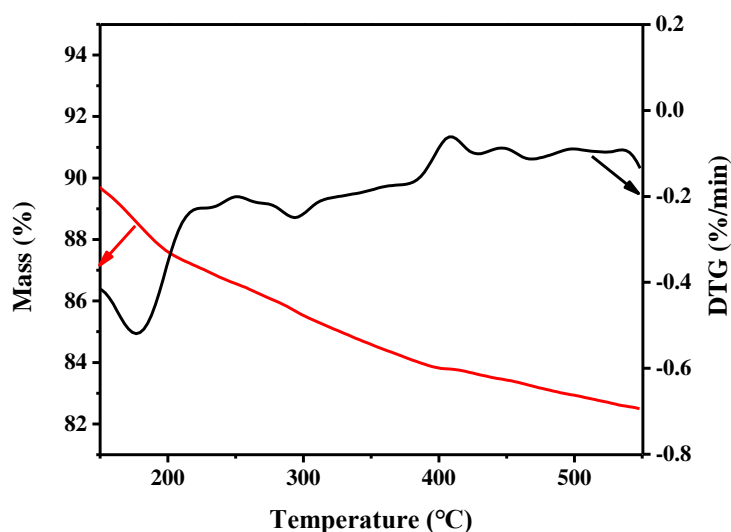


Figure 2. Thermogravimetric and differential thermogravimetric (TG-DTG) curves of the VPO/P-C catalyst.

3.2. Effects of VPO Loading Amount on the Selective Oxidation of HMF

As shown in Figure 3, the conversion of HMF rose with an increase in the VPO loading amount. At the VPO loading amount of 0.25 wt.%, the HMF converted completely. In terms of the selectivity of DFF, the VPO loading amount of 0.325 wt.% had the best effect, reaching a percentage of 98.0%. After that, a stabilization phase appeared in the conversion of HMF, and the selectivity of DFF remained almost unaltered.

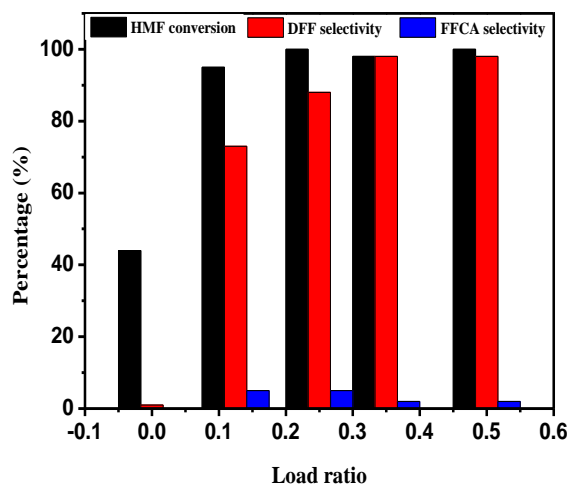


Figure 3. Effects of the VPO loading amount on the oxidation of HMF to DFF. HMF (25.2 mg, 0.2 mmol), VPO/P-C (10 mg), and DMSO (2 mL) for 10 h in air. HMF—5-hydroxymethylfurfural; DFF—2,5-diformylfuran.

3.3. Effects of the Reaction Time on the Selective Oxidation of HMF

The results of the reaction time effects are shown in Figure 4. The conversion rate of HMF increased quickly, within 0–3 h, and then, slowed down with time. This phenomenon shows that HMF was converted at high speed due to the rich concentration of HMF at the beginning of the reaction. After 6 h, HMF was fully converted, and the DFF yield was the highest—up to 83.2%. The selectivity of

DFF gradually stabilized after 10 h, while HMF conversion remained steady after 6 h, demonstrating a hysteresis effect. 5-hydroxymethyl-2-furancarboxylic acid (HFCA) and 2,5-furandicarboxylic acid (FDCA) were not detected during the reaction.

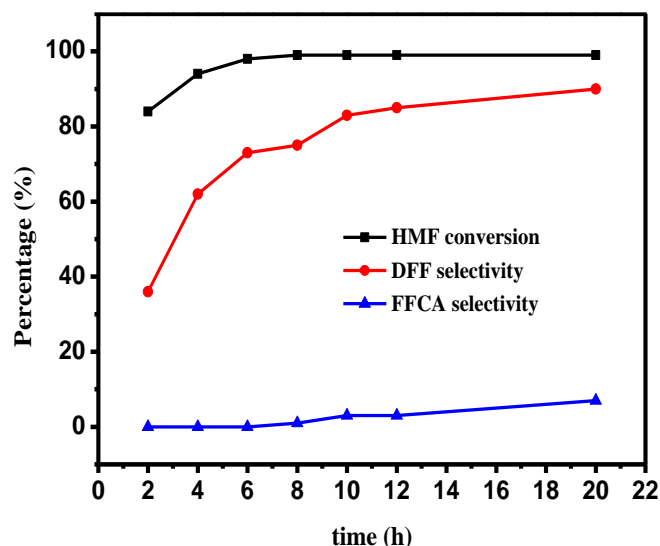


Figure 4. Effects of the reaction time on the oxidation of HMF to DFF. HMF (25.2 mg, 0.2 mmol), VPO/P-C (10 mg), and DMSO (2 mL) at 120 °C in air.

3.4. Effects of the Reaction Temperature on the Selective Oxidation of HMF

The effect of the reaction temperature on HMF oxidation was studied (Figure 5). When the reaction temperature was in the range of 80–120 °C, HMF conversion and the DFF yield increased. At 80 °C, the HMF conversion rate was 25.4%, and this further increased to 98.3% at 110 °C. When the reaction was performed at 120 or 140 °C, quantitative HMF conversion was reached. At 120 °C, the highest DFF yield was 83.6%. However, when the temperature increased by 10 °C, the yield was marginally lower than 71.7%. The above results indicate that a high reaction temperature promotes the selective oxidation of HMF to DFF. In terms of the DFF yield, it is greatly affected by the reaction temperature and increases gradually with an increase in the reaction temperature.

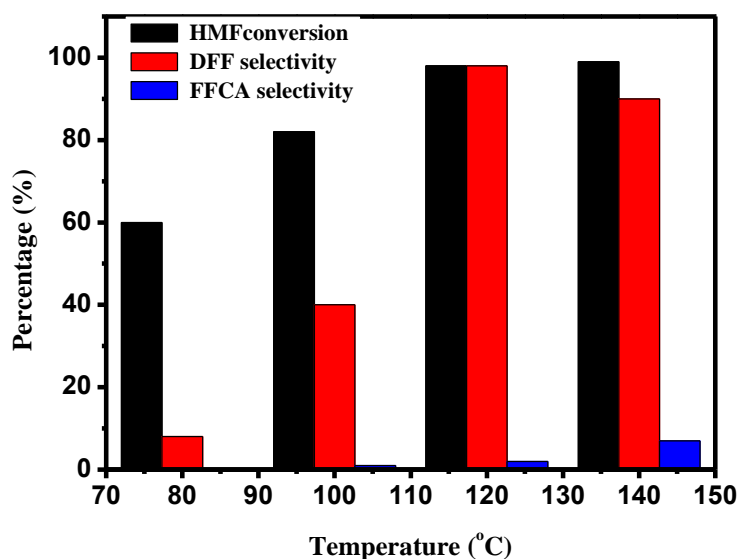


Figure 5. Effects of the temperature on the oxidation of HMF to DFF. HMF (25.2 mg, 0.2 mmol), VPO/P-C (10 mg), and DMSO (2 mL) for 10 h in air.

3.5. Effects of the Catalyst Amount on the Selective Oxidation of HMF

In general, the amount of catalyst will directly change the number of active sites on the catalyst, which will affect the conversion and selectivity of the reaction. Therefore, the effect of different catalyst amounts on HMF oxidation reaction was investigated, and the results are shown in Figure 6. As the amount of catalyst rose from 0 to 2.5 mg, the conversion rate of HMF changed from 48.0% to 91.0%, and the corresponding DFF selectivity also increased.

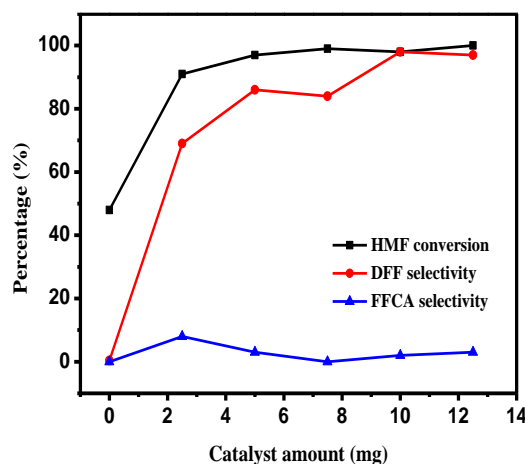


Figure 6. Effects of the catalyst amount on the oxidation of HMF to DFF. HMF (25.2 mg, 0.2 mmol), and DMSO (2 mL) for 10 h at 120 °C in air.

The above results indicate that increasing the amount of catalyst can promote the selective oxidation of HMF to DFF. When the amount of catalyst was further increased to 7.5 mg, the growth rate of HMF conversion decreased. In contrast, the selectivity of DFF rose from 69.0% to 86.0%, which may have been caused by the combination of intermediates and catalysts, causing a slow-release effect. As the amount of catalyst increased, there was no sign of a decline in DFF selectivity or an increase in by-products, probably due to the characteristic of porous carbon materials with a good adsorption effect on DFF.

3.6. Effects of Solvents on the Selective Oxidation of HMF

Solvents affect the oxidation of HMF. Among solvents, DMSO, which has strong polarity and a high boiling point, performed the best. HMF was completely converted and the DFF selectivity reached 97.0% with the DMSO solvent (Table 1, Entry 1). Compared with DMSO, there was moderate HMF conversion of 30.4% and 65.1%, respectively, in toluene and acetonitrile, and no further oxidation of DFF to FDCA was processed (Table 1, Entry 2 and Entry 3). In addition, HMF was slightly converted in water (Table 1, Entry 4). It is obvious that DMSO is a perfect solvent for the selective oxidation of HMF to DFF. Furthermore, the experiment was carried out in order to figure out the influences of VPO and P-C on the oxidation of HMF to DFF, as shown in Table S1 in Supplementary Materials.

Table 1. Effects of solvents on the oxidation of HMF to DFF.

Entry	Solvent ^a	HMF Conversion ^b (%)	Selectivity ^c (%)		
			FDCA	DFF	FFCA
1	DMSO	100	0	97.0	3.0
2	Toluene	30.4	2.2	30.4	3.2
3	Acetonitrile	65.1	0	65.1	2.2
4	H ₂ O	10.1	0	97.1	3.1

^a HMF (25.2 mg, 0.2 mmol), VPO/P-C (10 mg), solvent (2 mL) for 10 h at a reflux temperature in air ^b Conversion was determined by HPLC. ^c Selectivity was determined by HPLC.

4. Conclusions

A high-performance VPO/P-C catalyst was successfully prepared and characterized by TF-IR and TG-DTG. The effects of various single factors on the oxidation of HMF to DFF were investigated. The catalyst showed good performance as a catalyst during the oxidation of HMF to DFF with a yield of 97.0%. This work presents a viable method for producing the high value-added product DFF in air.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2227-9717/8/10/1273/s1>, Table S1. The results of HMF oxidation over the different catalysts, Figure S1. Liquid chromatography of HMF oxidation products.

Author Contributions: Conceptualization, X.L.; Data curation, K.L.; Investigation, S.W. and K.L.; Methodology, S.W. and Y.T.; Project administration, X.L.; Resources, X.L. and D.Y.; Software, Y.X.; Supervision, X.L. and D.Y.; Visualization, Y.X.; Writing—original draft, S.W.; Writing—review & editing, X.L. All authors have read and agreed to the published version of the manuscript.

Funding: The authors gratefully acknowledge the financial support of the National Natural Science Foundation of China (21606082), Hunan Provincial Natural Science Foundation of China (2018JJ3334), and China Postdoctoral Science Foundation (2019M662787).

Conflicts of Interest: The authors declare no conflict of interest.

References

- Hong, M.; Min, J.; Wu, S.; Cui, H.; Zhao, Y.; Li, J.; Wang, S. Metal nitrate catalysis for selective oxidation of 5-hydroxymethylfurfural into 2,5-diformylfuran under oxygen atmosphere. *ACS Omega* **2019**, *4*, 7054–7060. [CrossRef]
- Zhang, H.; Feng, Z.; Zhu, Y.; Wu, Y.; Wu, T. Photocatalytic selective oxidation of biomass-derived 5-hydroxymethylfurfural to 2,5-diformylfuran on WO₃/g-C₃N₄ composite under irradiation of visible light. *J. Photochem. Photobiol. A* **2019**, *371*, 1–9. [CrossRef]
- Lai, J.; Liu, K.; Zhou, S.; Zhang, D.; Liu, X.; Xu, Q.; Yin, D. Selective oxidation of 5-hydroxymethylfurfural into 2,5-diformylfuran over VPO catalysts under atmospheric pressure. *RSC Adv.* **2019**, *9*, 14242–14246. [CrossRef]
- Liu, L.-J.; Wang, Z.-M.; Lyu, Y.-J.; Zhang, J.-F.; Huang, Z.; Qi, T.; Si, Z.-B.; Yang, H.-Q.; Hu, C.-W. Catalytic mechanisms of oxygen-containing groups over vanadium active sites in an Al-MCM-41 framework for production of 2,5-diformylfuran from 5-hydroxymethylfurfural. *Catal. Sci. Technol.* **2020**, *10*, 278–290. [CrossRef]
- Qin, Y.-Z.; Li, Y.-M.; Zong, M.-H.; Wu, H.; Li, N. Enzyme-catalyzed selective oxidation of 5-hydroxymethylfurfural (HMF) and separation of HMF and 2,5-diformylfuran using deep eutectic solvents. *Green Chem.* **2015**, *17*, 3718–3722. [CrossRef]
- Sádaba, I.; Gorbanev, Y.Y.; Kegnaes, S.; Putluru, S.S.R.; Berg, R.W.; Riisager, A. Catalytic performance of zeolite-supported vanadia in the aerobic oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran. *ChemCatChem* **2013**, *5*, 284–293. [CrossRef]
- Zhang, H.; Wu, Q.; Guo, C.; Wu, Y.; Wu, T. Photocatalytic selective oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran over Nb₂O₅ under visible light. *ACS Sustain. Chem. Eng.* **2017**, *5*, 3517–3523. [CrossRef]
- Liu, X.; Ding, H.; Xu, Q.; Zhong, W.; Yin, D.; Su, S. Selective oxidation of biomass derived 5-hydroxymethylfurfural to 2, 5-diformylfuran using sodium nitrite. *J. Energ. Chem.* **2016**, *25*, 117–121. [CrossRef]
- Lv, G.; Wang, H.; Yang, Y.; Deng, T.; Chen, C.; Zhu, Y.; Hou, X. Graphene oxide: A convenient metal-free carbocatalyst for facilitating aerobic oxidation of 5-hydroxymethylfurfural into 2, 5-diformylfuran. *ACS Catal.* **2015**, *5*, 5636–5646. [CrossRef]
- Mittal, N.; Nisola, G.M.; Malihan, L.B.; Seo, J.G.; Lee, S.-P.; Chung, W.-J. Metal-free mild oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran. *Korean J. Chem. Eng.* **2014**, *31*, 1362–1367. [CrossRef]
- Mittal, N.; Nisola, G.M.; Seo, J.G.; Lee, S.-P.; Chung, W.-J. Organic radical functionalized SBA-15 as a heterogeneous catalyst for facile oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran. *J. Mol. Catal. A-Chem.* **2015**, *404–405*, 106–114. [CrossRef]

12. Wang, F.; Jiang, L.; Wang, J.; Zhang, Z. Catalytic conversion of fructose and 5-hydroxymethylfurfural into 2,5-diformylfuran over SBA-15 supported Ruthenium catalysts. *Energ. Fuels* **2016**, *30*, 5885–5892. [\[CrossRef\]](#)
13. Yan, Y.; Li, K.; Zhao, J.; Cai, W.; Yang, Y.; Lee, J.-M. Nanobelt-arrayed vanadium oxide hierarchical microspheres as catalysts for selective oxidation of 5-hydroxymethylfurfural toward 2,5-diformylfuran. *Appl. Catal. B-Environ.* **2017**, *207*, 358–365. [\[CrossRef\]](#)
14. Nocito, F.; Ventura, M.; Aresta, M.; Dibenedetto, A. Selective oxidation of 5-(hydroxymethyl)furfural to DFF using water as solvent and oxygen as oxidant with earth-crust-abundant mixed oxides. *ACS Omega* **2018**, *3*, 18724–18729. [\[CrossRef\]](#)
15. Ning, L.; Liao, S.; Sun, Y.; Yu, L.; Tong, X. The efficient oxidation of biomass-derived 5-hydroxymethylfurfural to produce 2,5-diformylfuran over supported Cobalt catalysts. *Waste Biomass Valori.* **2018**, *9*, 95–101. [\[CrossRef\]](#)
16. Nie, J.; Xie, J.; Liu, H. Activated carbon-supported ruthenium as an efficient catalyst for selective aerobic oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran. *Chin. J. Catal.* **2013**, *34*, 871–875. [\[CrossRef\]](#)
17. Lee, J.; Kim, J.; Hyeon, T. Recent progress in the synthesis of porous carbon materials. *Adv. Mater.* **2006**, *18*, 2073–2094. [\[CrossRef\]](#)
18. Zhai, Y.; Dou, Y.; Zhao, D.; Fulvio, P.F.; Mayes, R.T.; Dai, S. Carbon materials for chemical capacitive energy storage. *Adv. Mater.* **2011**, *23*, 4828–4850. [\[CrossRef\]](#)
19. Zhang, L.; Sadanandam, G.; Liu, X.; Scurrrell, M.S. Carbon surface modifications by plasma for catalyst support and electrode materials applications. *Topics in Catal.* **2017**, *60*, 823–830. [\[CrossRef\]](#)
20. Yang, D.-S.; Bhattacharjya, D.; Inamdar, S.; Park, J.; Yu, J.-S. Phosphorus-doped ordered mesoporous carbons with different lengths as efficient metal-free electrocatalysts for oxygen reduction reaction in alkaline media. *J. Am. Chem. Soc.* **2012**, *134*, 16127–16130. [\[CrossRef\]](#)
21. Yeh, M.-H.; Leu, Y.-A.; Chiang, W.-H.; Li, Y.-S.; Chen, G.-L.; Li, T.-J.; Chang, L.-Y.; Lin, L.-Y.; Lin, J.-J.; Ho, K.-C. Boron-doped carbon nanotubes as metal-free electrocatalyst for dye-sensitized solar cells: Heteroatom doping level effect on tri-iodide reduction reaction. *J. Power Sources* **2018**, *375*, 29–36. [\[CrossRef\]](#)
22. Yang, Z.; Wu, J.; Zheng, X.; Wang, Z.; Yang, R. Enhanced catalytic activity for the oxygen reduction reaction with co-doping of phosphorus and iron in carbon. *J. Power Sources* **2015**, *277*, 161–168. [\[CrossRef\]](#)



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).