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Ruthenium Complex Immobilized on Poly(4-vinylpyridine)-Functionalized Carbon-Nanotube for Selective Aerobic Oxidation of 5-Hydroxymethylfurfural to 2,5-Diformylfuran

Jinzhu Chen,*^a Jiawei Zhong,^{a,c} Yuanyuan Guo^a and Limin Chen^b

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Polymer-carbon composite material of poly(4-vinylpyridine)-functionalized carbon-nanotube (PVP/CNT) was prepared by *in situ* polymerization of 4-vinylpyridine monomer in the presence of CNT suspension. ¹⁰ Raman spectra analysis confirmed the almost unchanged graphitized surfaces of CNT moiety in the

PVP/CNT after the covalent functionalization of pristine CNT with PVP. Catalyst made of ruthenium complex immobilized on PVP/CNT (Ru-PVP/CNT) was fully characterized by ICP-OES, TG-DTA, FT-IR, Raman, XRD, UV-vis, BET, TEM, XPS and H₂-TPR. Moreover, Ru-PVP/CNT shows excellent catalytic performance towards the selective oxidation of biomass-based 5-hydroxymethylfurfural (HMF)

¹⁵ to 2,5-diformylfuran (DFF) with molecular oxygen as oxidant. The reaction parameters such as the reaction temperature, reaction time, solvent, catalyst amount, oxidant, and oxygen pressure were systematically investigated for this important biomass-related transformation. Under the optimal condition, a DFF yield of 94% with a full HMF conversion were obtained by using Ru-PVP/CNT in *N*,*N*-dimethylformamide (DMF) under 2.0 MPa O₂ at 120 °C.

1. Introduction

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With the rapid depletion of fossil fuel and the aggravation of global warming, much effort has been devoted to the production of fuels and chemicals from renewable resources. As the only carbon-containing renewable resource, biomass serves as an alternative feedstock to provide fuels and chemicals.^{1,2}

5-Hydroxymethylfurfural (HMF), obtained from acid-promoted dehydration of C6 based carbohydrate, has been identified as a key platform chemical compound which can be transformed to a variety of valuable chemicals and fuels.^{3, 4} In particular, the selective oxidation of HMF to 2,5-diformylfuran (DFF) has attracted considerable interests in recent decades, due to the applications of DFF in monomer, pharmaceuticals,⁵ fungicides,⁶ furan-urea resins⁷ as well as heterocyclic ligand.⁸ However, the selective oxidation of HMF is influenced by various parameters such as reaction temperature, reaction time, solvent, oxidants etc. In addition, some byproducts such as 5-hydroxymethyl-2-furancarboxylic acid (HMFCA), 5-formyl-2-furancarboxylic acid (FFCA), 2,5-furandicarboxylic acid (FDCA) can be produced during the process (Scheme 1). Therefore, it is still a challenging task for the selective oxidation of HMF to DFF.

The selective oxidation of HMF to DFF have been reported by using conventional oxidants such as NaOCl,⁹ BaMnO₄,¹⁰ Pb(OAc)₄-pyridine,¹¹ K₂Cr₂O₇-DMSO, trimethylammonium chlorochromate (TMACC),¹² oxalylchloride (OC), pyridinium chlorochromate (PCC) and 2,2,6,6-tetramethylpiperidine-1-oxide

(TEMPO).¹³⁻¹⁵ Nevertheless, the requirement of stoichiometric oxidants and the release of hazardous wastes are unavoidable for these methods. Therefore, selective oxidation of HMF to DFF with environment friendly molecular oxygen as oxidant satisfied the requirement of green chemistry.



Scheme 1. Pathway of oxidation of HMF.

To date, homogeneous metal/bromide systems (Co/Mn/Br, Co/Mn/Zr/Br)¹⁶ and heterogeneous transition metal-based catalysts such as ruthenium,¹⁷⁻²¹ vanadium,²²⁻³¹ manganese,^{9, 32, 33} copper^{23, 26} and silver³⁴ have been developed for the production of DFF from HMF or directly from carbohydrate.³⁵⁻⁴⁰ Recently, our team achieved one-step approach to DFF directly from fructose by using acidic cesium salts of molybdovanadophosphoric heteropolyacids (CsMVP-HPAs)³⁹ as well as proton- and vanadium-containing graphitic carbon nitride [V-g-C₃N₄(H⁺)].⁴⁰

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Among the developed catalyst systems, ruthenium-based catalyst is proved to be more active and selective to this important biomass-related transformation of HMF to DFF. For example, Ebitani and coworkers obtained DFF from HMF with yield of 92% over hydrotalcite-supported ruthenium catalyst [Ru(OH)_x/HT] in N,N-dimethylformamide (DMF) using molecular oxygen as oxidant.³⁸ Antonyraj et al. achieved DFF from HMF with yield of 97% on RuCl₃/Al₂O₃ at 130 °C with molecular oxygen.¹⁹ Zhang and team members obtained DFF yield of 86.4% with Fe₃O₄@SiO₂-NH₂-Ru(III) at 120 °C. It was found that Ru³⁺ ions from RuCl₃ aqueous solution can be effectively immobilized by amino group of Fe₃O₄@SiO₂-NH₂.¹⁸ In addition, Corma et al. obtained a DFF yield of 82% on immobilized vanadyl pyridine complexes at 130 °C. It was observed that vanadyl groups can be fully coordinated with pyridine ligand.²⁹ Therefore, pyridine-Ru(III) complex was investigated as catalyst for selective aerobic oxidation of HMF to DFF in this research.

Currently, commercially available carbon materials such as carbon nanotubes (CNT) have attracted ever-increasing attention due to their high surface area, tunable surface properties, superior mechanical strength etc. However, the lack of solubility and the difficult manipulation of CNT in most solvents have limited their use. Therefore, CNT generally needs to undergo chemical functionalization to enhance solubility in various solvents and to produce novel hybrid materials for practical applications.⁴¹ By comparison, there is a large potential for the development and application of organic polymer with tailored physical and chemical properties in both selective catalysis and functional material science, owing to the possibility of employing the vast range of organic transformations developed by synthetic organic chemists.^{42, 43} Therefore, to combine the advantages of polymer and CNT, much effort has been put in polymer/CNT composite material. For instance, our group recently developed poly(pstyrenesulfonic acid)-functionalizd CNT (CNT-PSSA) as solid acid for effective conversion of biomass-based fructose to HMF and alkyl levulinate.44

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Fig. 1 Proposed structure of PVP/CNT and PVI/CNT. (x indicates the degree of polymerization).

In recent decades, transition metal complex with nitrogencontaining polymer as ligand or immobilizer has attracted great interests for catalysis purpose. Among the developed nitrogencontaining polymers, due to the strong affinity of the pyridyl group with transition metal ions, poly(4-vinylpyridine) (PVP)immobilized transition metal complexes⁴⁵⁻⁴⁷ have particularly been used in various applications such as chemoselective protection of aldehydes,⁴⁸ selective solid phase extraction,⁴⁹ hydrogenation and hydroformylation,⁵⁰ water gas shift reaction,⁵¹ reduction of nitrobenzene.⁵¹ Recently, our team investigated a series of nitrogen-containing polymer, including PVP- and poly(1-vinylimidazole) (PVI)-functionalized CNT (Figure 1). Moreover, the catalysts, made of palladium_supported_varticle_online polymer/CNT composite materials, showed excellent selectivity towards hydrogenation of phenol and derivatives. Our research results further indicate that the phenol conversion is related to the conductive property of polymer/CNT; whereas, the cyclohexanone selectivity is contributed to the nitrogencontaining nature of polymer/CNT.^{42, 43}

To explore the application of composite material PVP/CNT, ruthenium complex was immobilized on the PVP/CNT (Ru-PVP/CNT) through the formation of coordinative bond N: \rightarrow Ru³⁺ (Figure 2). Raman spectra analysis confirmed the almost unchanged graphitized surfaces of CNT moieties in both PVP/CNT and Ru-PVP/CNT after the functionalization of pristine CNT. Moreover, the coordinative bond of N: \rightarrow Ru³⁺ in Ru-PVP/CNT was confirmed by UV-vis and X-ray photoelectron spectroscopy (XPS) analysis. The synthesized catalyst Ru-PVP/CNT shows excellent catalytic performance towards the selective oxidation of HMF to DFF with molecular oxygen as oxidant (Scheme 1). Under the optimal condition, a DFF yield of 94% with full HMF conversion were obtained by using Ru-PVP/CNT in DMF under 2.0 MPa O₂ at 120 °C.



Fig. 2 Proposed structure of Ru-PVP/CNT.

2. Results and discussion

2.1 PVP/CNT and Ru-PVP/CNT

PVP/CNT composite material was prepared by polymerization of 4-vinylpyridine monomer with azobisisobutyronitrile (AIBN) as a radical initiator in the presence of CNT suspension. According to literature,^{41, 43, 52} the CNT is functionalized by poly(4vinylpyridine) through covalent chemical grafting in PVP/CNT. The catalyst of Ru-PVP/CNT was synthesized by treating PVP/CNT with aqueous solution of RuCl₃, followed with filtration and drying under vacuum. The inductively coupled plasma-optical emission spectroscopy (ICP-OES) analysis of the Ru-PVP/CNT showed that 2.2 wt% of Ru was immobilized on PVP/CNT.

The thermal stabilities of CNT, PVP and PVP/CNT were investigated by thermal gravimetric-differential thermal analysis (TG-DTA). As shown in Figure 3, CNT shows no significant weigh lose before 800 °C. By contrast, PVP shows the weight loss of 2.4% at 100 °C, which is attributed to the loss of residual moisture associated with PVP. In addition, PVP further shows weight loss of 97.6% at 418 °C as supported with a sharp DTA at

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405 °C. As for PVP/CNT, beside the weight loss of 2.5% at 100 °C attributed to the loss of residual moisture, the main decomposition started at 290 °C with the weight loss of 26.3% which was supported by DTA at 330 °C. The similar TG-DTA results were observed in Fullerene[60]-polyvinylpyridine composites.⁵³ TG-DTA of PVP/CNT thus confirmed that CNT was successfully functionalized by polymer PVP.



Fig. 3 (a) TG and (b) DTA analysis of CNT, PVP, and PVP/CNT.

The Fourier transform infrared (FT-IR) spectra of PVP and PVP/CNT are compared in Figure 4. As we have investigated previously, the FT-IR spectrum of pristine CNT is practically featureless with extremely low infrared absorption intensities.^{42,44} For PVP/CNT, the IR bands at 2919 and 2850 cm⁻¹ were assigned to asymmetric and symmetric vibration absorptions, respectively, for C–H band of the aliphatic CH₂ in vinyl chain. In the case of PVP, the corresponding bands are observed at 2926 and 2854 cm⁻¹, respectively. In addition, the absorption bands of PVP/CNT around 1580 cm⁻¹ are assigned to the C=C stretching vibration of pyridine ring. The absorption bands at 1462 and 1441 cm⁻¹ are attributed to C=N stretching vibration of pyridine ring in PVP/CNT, which are in accordance with the reported observance.⁵⁴ The spectrum shifts between PVP and PVP/CNT are attributed to the strong π - π interaction between PVP and CNT moiety in the PVP/CNT composite.^{42, 43} Therefore, FT-IR results further verify the existence of PVP chain segments in the asprepared PVP/CNT composite materials.

Raman spectroscopy is used to determine the changes of defect density in the CNT moiety of PVP/CNT and Ru-PVP/CNT after the polymerization and immobilization process (Figure 5). The peak near 1576 cm⁻¹ (G-band) corresponds to the E_{2g} mode of graphite. Whereas, the peak around 1342 cm^{-1} (D-band) is associated with the vibrations of carbon atoms in the disordered graphite structure, *i.e.*, the defect sites. Generally, the intensity ratio of the D-band to G-band (I_D/I_G) is used to determine the defect density of CNT. The I_D/I_G is 0.85 for the pristine CNT and then slightly increases to 0.88 for PVP/CNT and to 0.89 for Ru-PVP/CNT. Therefore, Raman spectra analysis indicates that graphitized surfaces of CNT moieties in both PVP/CNT and Ru-PVP/CNT were almost unchanged after the covalent functionalization of CNT with polymer PVP to give PVP/CNT and the immobilization of Ru complex on PVP/CNT to afford Ru-PVP/CNT, respectively.





Fig. 5 Raman spectra of CNT, PVP/CNT and Ru-PVP/CNT.

The Ultraviolet visible (UV-vis) spectra of PVP/CNT and Ru-

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PVP/CNT are compared in Figure S1 (ESI). For PVP/CNT, the bands at 207 and 255 nm are attributed to the absorptions of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ orbits of PVP, respectively. In the case of Ru-PVP/CNT, the corresponding absorption band shift to 210 and 258 nm, respectively. Therefore, the presence of Ru³⁺ ions in Ru-PVP/CNT lead to red shifts of PVP/CNT in both bands, which is attributed to the formation of coordination bonds between pyridyl ligand in PVP and Ru³⁺ ions in the Ru-PVP/CNT.

The Brunauer-Emmett-Teller (BET) surface areas and the pore sizes of PVP/CNT and Ru-PVP/CNT were calculated with BET and Barrett-Joyner-Halenda (BJH) methods. As determined from the nitrogen adsorption/desorption isotherm in Figure S2 (ESI), the average pore diameter and total pore volume for PVP/CNT are 16.5 nm and 0.35 cm³ g⁻¹, respectively. By comparison, the average pore diameter and total pore volume for Ru-PVP/CNT decrease to 14.6 nm and 0.33 cm³ g⁻¹, respectively. However, BET surface areas of PVP/CNT and Ru-PVP/CNT are 84.8 and 89.4 m² g⁻¹. The slightly increased surface area can be attributed to the formation of new pore in the matrix of PVP/CNT.⁴²

The Powder X-ray diffraction (XRD) patterns of PVP/CNT and Ru-PVP/CNT show no distinct difference (Figure 6), though a slight attenuation of the diffraction peaks at 26°, indicating that the immobilization process does not greatly damage the crystallinity structure of PVP/CNT. The diffraction peaks of both PVP/CNT and Ru-PVP/CNT located at a 20 value of about 26° and 43° were assigned to the characteristic peaks of the (002) and (100) packing of graphitic CNT, respectively.^{42, 43} Moreover, the distinct reflections for Ru(0) and RuO₂ were unobserved in XRD results,⁵⁵ which proves the unchanged valence state of Ru(III) during the catalyst preparation process.^{18, 55}



Fig. 6 XRD patterns of PVP/CNT and Ru-PVP/CNT.



Fig. 7 TEM images of PVP/CNT.

The surface morphologies of the CNT and PVP/CNT were further observed by transmission electron microscopy (TEM). The outside diameter of pristine CNT falls into the rate online 20 nm with the CNT length around 10~30 um (Figure S3, ESI). In contrast, PVP/CNT shows a thin polymer coating of 2-4 nm over CNT (Figure 7). Thus, TEM analysis of PVP/CNT effectively confirmed the functionalization of CNT with polymer PVP.

The surface composition of PVP/CNT and Ru-PVP/CNT were investigated with X-ray photoelectron spectroscopy (XPS). Peaks corresponding to carbon, oxygen, nitrogen, ruthenium and chlorine are presented in the survey scan (Figure 8a). Corresponding O1s signals were possibly arose from surface impurities.56 For Ru-PVP/CNT, there is an overlap between Ru 3d and C 1s peak at around 282.5 eV.18, 56 The presence of chlorine peak indicated that Cl⁻ ion acts as the counter ion of Ru³⁺ ion.⁴⁵ The binding energy at 461.8 and 484.2 eV are assigned to Ru 3p3/2 and Ru 3p1/2, respectively, which demonstrates that the oxidation state of the ruthenium species is Ru³⁺ (Figure 8b).^{18, 57} The N 1s binding energies are 397.0 and 397.4 eV for PVP/CNT and Ru-PVP/CNT, respectively (Figure 8c). The observed shift in N 1s binding energies indicates that coordination bonds are presumably formed between nitrogen atom of pyridyl ligand and Ru³⁺ ion in Ru-PVP/CNT.



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Fig. 8 (a) XPS scan survey for PVP/CNT and Ru-PVP/CNT, (b) Ru 3p XPS spectra of Ru-PVP/CNT, (c) N 1s XPS spectra of PVP/CNT and Ru-PVP/CNT.

The Temperature-programmed reduction (H₂-TPR) profile for Ru-PVP/CNT is provided in Figure S4 (ESI). Two reduction peaks take place around 173 and 540 °C for Ru-PVP/CNT, the peak at 173 °C results from the reduction of Ru complex; whereas, hydrogen consumption observed at 540 °C is attributed to the methanation of PVP/CNT.⁵⁸ Therefore, the H₂-TPR profile effectively testifies that Ru species is in the form of Ru³⁺ rather than Ru⁰ in Ru-PVP/CNT.

2.2 Selective aerobic oxidation of HMF over Ru-PVP/CNT

The prepared Ru-PVP/CNT was investigated as potential catalyst for selective aerobic oxidation of HMF to DFF. The reaction is typically carried out in DMF under 2.0 MPa O₂. Figure 9 shows the effects of reaction temperature and time on the aerobic oxidation of HMF to DFF. Both the HMF conversion and DFF yield increased with reaction time at all temperatures investigated. The yield of DFF increased slowly to 67% after 12 h at 100 °C; whereas, it increased quickly to 94% after 12 h at 120 °C, confirming that increasing the reaction temperature promotes the aerobic oxidation of HMF to DFF. The result was consistent with the previous reports.^{17-19, 32, 34}



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Fig. 9 The influences of reaction temperature and time on the aerobic oxidation of HMF to DFF. Reaction conditions: HMF (63 mg, 0.5 mmol), Ru-PVP/CNT (60 mg, Ru 2.2 wt%), DMF (5 mL), O₂ (2.0 MPa).

It is widely accepted that the nature of solvent have great impacts on the conversion rate of HMF and selectivity to DFF. Therefore, various solvents such as high boiling and polar solvents [DMF and dimethylsulfoxide (DMSO)], low boiling and polar solvents [isopropyl alcohol (IPA), ethanol (EtOH), acetonitrile (MeCN), 1,4-dioxane and water] and non-polar solvent (toluene) are investigated so as to study the solvent effect on the aerobic oxidation of HMF. Among all the solvents tested, DMF showed HMF conversion of >99% with DFF selectivity of 95% (Table 1, Entry 1), which may be ascribed to the high solubility of oxygen in DMF.34 Satisfying result can also be achieved with the use of toluene (Table 1, Entry 2).^{19, 20} 1,4dioxane and water achieved high HMF conversion but low DFF selectivity (Table 1, Entries 4-5), which may be attributed to the decomposition of 1.4-dioxane molecule¹⁹ and the hydration of the aldehyde groups in HMF and DFF to germinal diols,^{21, 59} respectively. Alcohol-type solvents (IPA and EtOH) also achieved great HMF conversion and selectivity toward DFF (Table 1, Entries 3, 6).¹⁹ MeCN and DMSO attained modest level of HMF conversion (Table 1, Entries 7-8), the poor performance of DMSO may be ascribed to the strong coordination effect of DMSO molecule with Ru³⁺ center.^{20, 60} Besides, it has been reported that DMSO tend to undergo disproportionation to yield toxic Me₂SO₂ and Me₂S under oxidizing conditions.²¹

Table 1 Effect of solvents on the aerobic oxidation of HMF to DFF^a

Entry	Solvent	HMF conversion (%)	DFF yield (%)	DFF selectivity (%)
1	N,N-dimethylformamide	>99	94	95
2	Toluene	>99	87	88

3	Isopropyl alcohol	>99	77	78
4	1,4-Dioxane	>99	35	35
5	Water	>99	13	13
6	Ethanol	92	83	89
7	Acetonitrile	70	66	94
8	Dimethylsulfoxide	60	52	86

^aReaction conditions: HMF (63 mg, 0.5 mmol), Ru-PVP/CNT (60 mg, Ru 2.2 wt%), solvent (5 mL), O₂ (2.0 MPa), 120 °C, 12 h.



Fig. 10 Aerobic oxidation of HMF to DFF with various catalyst dosages. Reaction conditions: HMF (63 mg, 0.5 mmol), Ru-PVP/CNT (Ru 2.2 wt%), DMF (5 mL), O_2 (2.0 MPa), 120 °C, 12 h.

In addition to the solvent effect, the catalyst Ru-PVP/CNT loading level also exhibits a dramatic influence on the aerobic oxidation of HMF to DFF. As shown in Figure 10, HMF conversions of 82% and 95% were obtained after 12 h with 40 mg and 50 mg of Ru-PVP/CNT, respectively, the corresponding DFF yields were 77% and 88%. Notably, HMF conversion and DFF yield increased to >99% and 94%, respectively, after 12 h by the use of 60 mg of Ru-PVP/CNT. The higher the catalyst loading, the higher both HMF conversion and DFF yield. The results indicate that the increase of the catalyst amount leads to the increase of the aerobic oxidation rate of HMF to DFF, which should be ascribed to the increase in the number and availability of catalytically active sites.³⁴ Notably, the selectivity of DFF almost always maintained around 92-95% regardless of catalyst loading level (Figure 10). This result suggests that the use of Ru-PVP/CNT can effectively avoid further oxidation of DFF to FFCA under the investigated conditions, thus leading to a high selectivity to DFF. In fact, the DFF selectivity is mainly determined by the reaction temperature, the solvent as well as the oxidant in this research.^{17, 18, 32}

In general, oxidant plays a vital role on the conversion rate of HMF and selectivity to DFF. As shown in Table 2, molecular oxygen, the clean and easily available oxidant, was most effective for the oxidation of HMF to DFF. An increase of the oxygen pressure leads to an increase of both HMF conversion and DFF yield (Table 2, Entries 1-4), which is ascribed to an enhanced molecular oxygen concentration in the solvent with the increase of oxygen pressure.^{20, 34} In addition to O_2 , common oxidants such as *tert*-butyl hydroperoxide (*t*-BuOOH) and hydrogen peroxide (H₂O₂) were also explored for the oxidation of HMF to DFF. However, DFF yield was rather low with *t*-BuOOH as the oxidant though nearly quantitative HMF conversion was observed (Table

2, Entry 5), which can be attributed to the strong oxidative capability of *t*-BuOOH leading to the breakage of the furan ring.^{17, 18} By contrast, low HMF conversion of 47% and 2%% water obtained by using H₂O₂ (Table 2, Entry 6), which is presumably attributed to the quick decomposition of H₂O₂ catalyzed by ruthenium species.^{17, 61} Therefore, the mild oxidant H₂O₂ was not effective for the oxidation of HMF to DFF, which is consistent with the previous results.^{18, 32}

Table	2 Cataly	ic oxidation	of HMF	using	various	oxidants ^a
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Entry	Oxidant	HMF conversion (%)	DFF yield (%)	DFF selectivity (%)
1	O_2^{b}	>99	94	95
2	O_2^{c}	95	90	95
3	O_2^{d}	83	80	96
4	O_2^e	26	25	96
5	<i>t</i> -BuOOH ^f	98	13	13
6	H ₂ O ₂ ^g	47	32	68

^a Reaction conditions: HMF (63 mg, 0.5 mmol), Ru-PVP/CNT (60 mg, Ru 2.2 wt%), DMF (5 mL), 120 °C, 12 h. $^{b}O_{2}$ (2.0 MPa), $^{c}O_{2}$ (1.0 MPa), $^{d}O_{2}$ (0.5 MPa), $^{e}O_{2}$ (0.1 MPa), f *t*-BuOOH (3.5 mmol), $^{g}H_{2}O_{2}$ (3.5 mmol) were used, respectively.



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Fig. 11 Aerobic oxidation of HMF to DFF with various catalysts. Reaction conditions: HMF (63 mg, 0.5 mmol), catalyst (60 mg), DMF (5 mL), O_2 (2.0 MPa), 120 °C, 12 h.

In addition to Ru-PVP/CNT, various other ruthenium catalysts, made of Ru³⁺ immobilized on PVP and PVI/CNT (Figure 1), were further investigated to probe the influence of support on the selective aerobic oxidation of HMF to DFF (Figure 11). Without immobilization of Ru³⁺, no oxidation products were detected with the use of pristine PVP/CNT in the blank experiment (Figure 11), which indicated that the Ru rather than the support PVP/CNT showed catalytic activity in the aerobic oxidation of HMF.¹⁹ In the case of Ru-PVP and Ru-PVI/CNT, moderate HMF conversions and DFF yields were observed. Obviously, among all the catalysts explored, Ru-PVP/CNT is considerably more active and selective to afford DFF from HMF under the investigated conditions, presumably owing to the strong coordination ability of the pyridyl ligand to the ruthenium ion in the Ru-PVP/CNT. The decrease in HMF conversion with recycled Ru-PVP/CNT may be attributed to the leaching of active metal (ICP-OES

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analysis of the recycled Ru-PVP/CNT showed that 1.9 wt% of Ru was immobilized on PVP/CNT), the inevitable losses of catalyst during filtration¹⁸ and the insoluble polymeric furanic compounds adsorbed on the catalyst¹⁹.

3. Conclusions

In conclusion, the composite material of poly(4-vinylpyridine)functionalized carbon-nanotube (PVP/CNT) was prepared by in situ polymerization of 4-vinylpyridine monomer in the presence of CNT suspension. Raman spectra analysis confirmed the almost unchanged graphitized surfaces of CNT moiety in the PVP/CNT after the covalent functionalization of pristine CNT with PVP. The catalyst of ruthenium complex immobilized on PVP/CNT (Ru-PVP/CNT) shows excellent catalytic performance towards oxidation of biomass-based 5selective aerobic hydroxymethylfurfural (HMF) to 2,5-diformylfuran (DFF). Under the optimal condition, a DFF yield of 94% with a full HMF conversion were obtained by using Ru-PVP/CNT in N,Ndimethylformamide (DMF) under 2.0 MPa O2 after 12 h at 120 °C. The research highlights a good prospect for catalytic application of polymer-CNT composite material for biomassrelated transformations.

4. Experiment

Materials and Characterization

Materials and catalyst characterizations are provided in the Supporting Information.

Catalyst Preparation

Preparation of polymer/CNT and polymer: The polymer/CNT was prepared by the polymerization of the corresponding polymer monomer in the presence of CNT. The PVP/CNT,^{43, 52} PVI/CNT^{42, 62} and PVP^{43, 52} were prepared according to the published literature and the corresponding synthetic procedures were provided in the supporting Information.

Preparation of Ru-PVP/CNT: PVP/CNT (60 mg) was added to an aqueous ruthenium chloride solution (20 mL, 5×10^{-3} mol L⁻¹). The mixture was stirred for 12 h at room temperature. The resulting precipitates were filtrated and washed with de-ionized water twice to remove adsorbed and uncomplexed metal salt. Then the solid powder was dried in a vacuum oven at 60 °C until it attained constant weigh. Ru-PVI/CNT and Ru-PVP were prepared following the same procedures.

Typical Procedures for the Aerobic Oxidation of HMF to DFF.

Aerobic oxidation of HMF was carried out in Teflon-lined stainless steel autoclave (50 mL). Typically, HMF (63 mg, 0.5 mmol) and Ru-PVP/CNT (60 mg, Ru 2.2 wt%) was added into DMF (5 mL), and the mixtures were stirred at ca. 700 rpm during the reactions. The reaction was carried out at a given reaction

time at 120 °C under 2.0 MPa O_2 . After the reaction, the mixture was cooled to ambient temperature. The quantitative analysis methods of substrate and product are provided in the Supporting Information.

Reusability of the catalyst

The resulting precipitates were filtrated from the reaction mixture by nylon membrane and washed with de-ionized water. The solid powder was then dried in a vacuum oven at 60 °C until it attained constant weight. The recovered catalyst was used for the next circle, and other steps were the same as those described above.

5. Acknowledgements

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 ^a CAS Key Laboratory of Renewable Energy, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences. Guangzhou 510640 (PR China). E-mail: chenjz@ms.giec.ac.cn. Tel./Fax: +86-20-3722-3380.
 ^b College of Environment and Energy, South China University of Technology, Guangzhou 510006 (PR China)

^c University of Chinese Academy of Sciences. Beijing 100049 (PR China). † Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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Ruthenium complex, immobilized on poly(4-vinylpyridine)-functionalized carbon-nanotube, shows excellent catalytic performance towards selective aerobic oxidation of biomass-based 5-hydroxymethylfurfural to 2,5-diformylfuran.