Supporting information for

Vanadium-oxo immobilized onto Schiff base modified Graphene oxide for efficient catalytic oxidation of 5-hydroxymethyfurfural and furfural into maleic anhydride

Guangqiang Lv,[a,b] Chunyan Chen,[a,c] Boqiong Lu,[a,b] Jinlong Li,[a,b] Yongxing Yang,[a] Chengmeng, Chen,[d] Tiansheng Deng,[a] Yulei Zhu,[e] Xianglin Hou*[a]

[a] Shanxi Engineering Research Center of Biorefinery, Institute of Coal Chemistry, Chinese Academy of Sciences, 27 South Taoyuan Road, Taiyuan 030001, People's Republic of China. E-mail: houxianglin@sxicc.ac.cn

[b] University of Chinese Academy of Sciences, Beijing, 100039 People's Republic of China

[c] Shanghai University, Shanghai, 200444 People's Republic of China

[d] Key Laboratory of Carbon Materials, Institute of Coal Chemistry, Chinese Academy of Sciences, 27 South Taoyuan Road, Taiyuan 030001, People's Republic of China

[e] State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, 27 South Taoyuan Road, Taiyuan, 030001 People's Republic of China.

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1. Preparation of vanadium-oxo immobilization onto Schiff base modified graphene oxide catalyst (VO-NH$_2$-GO)

1.1 Materials.

Graphite powder, maleic acid (Aladdin Chemistry Co., Ltd. Shanghai, China), H_2SO_4 (98 wt%, Xilong Chem. Co., Ltd, China), maleic anhydride, EtOH, toluene, acetic acid, $NaNO_3$, $KMnO_4$ (Kermel Chem. Reagent Co., Ltd. China), H_2O_2 (30%, Dong Fang Chem. Co., Ltd. China), 5-hydroxymethylfrufural (98%, DEMO Medical Tech Co., Ltd. China), 2,5-diformylfuran (98%, TCI)

1.2 Methods.

1.2.1 Preparation of graphene oxide (GO)

GO was prepared by modified Hummers' method. Typically, graphite powder (8000 meshes, 5 g) and $NaNO_3$ (2.5 g) were mixed with sulfuric acid (115 mL, 98 wt. %) under magnetic stirring for 0.5 h, then the mixture was put into an ice bath before $KMnO_4$ (15 g) was slowly added, during which the temperature was kept below 20 °C. Subsequently, the reaction system was transferred to a water bath of 35 °C and maintained for 0.5 h. After that, 230 mL water was slowly added to the system. The diluted suspension was then stirred at 98 °C for 15 min, followed by another 700 mL of water was added. And the reaction was terminated by the addition of H_2O_2 (50 mL, 30 wt. %). The mixture was filtered and washed with HCl (1 L, 1 mol·L^{-1}) and a large amount of distilled water in sequence. The resulting graphite oxide was separated from the colloid by spray drying method.

The obtained grapheite oxide (0.5 g) was dispersed into 500 mL deionized water. The suspension was ultra-sonicated under 40K Hz for 180 min and dried in a freeze dryer (-70 ^{o}C, 10-20 Pa), obtaining the stable and exfoliated GO.

1.2.2 Synthesis of amino-functionalized graphene oxide (NH_2-GO)

The exfoliated graphene oxide by ultrasonic (1.0 g) was taken into anhydrous toluene (100 mL), and 3-aminopropyltrimethoxysilane (APTES, 5 mL) was added under N_2 atmosphere. The resultant suspension was refluxed at 115 ^{o}C under N_2 atmosphere for 24 h. The resultant solid material was filtered and washed with toluene (4 ×100 mL) and ethanol (4 ×100 mL) sequentially, and then the resultant amion-functionalized graphene oxide (NH_2-GO) was dried in oven at 80 ^{o}C.

1.2.3 Immobilization of oxo-vanadium onto Schiff base modified graphene oxide (VO-NH_2-GO)

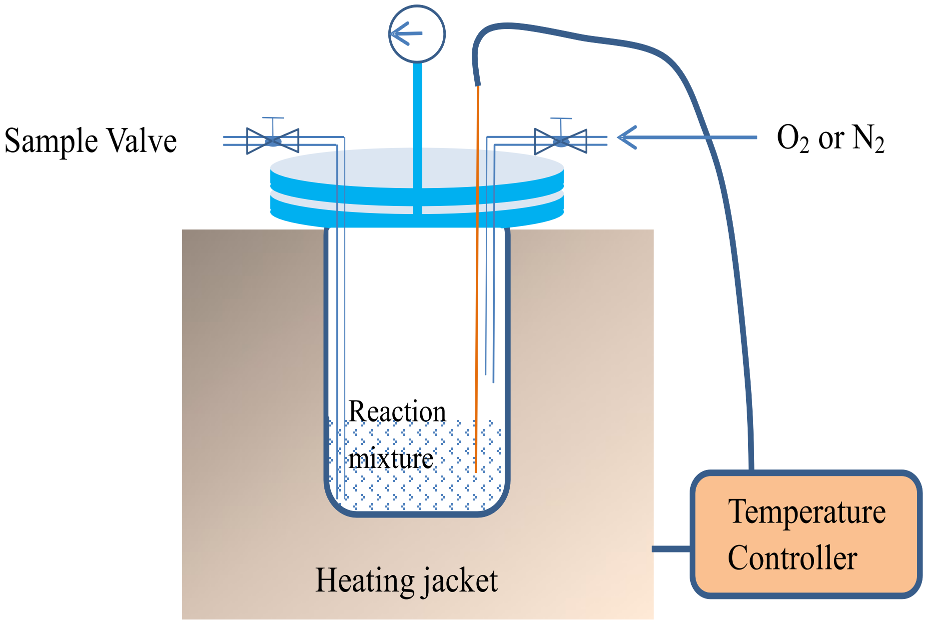
NH_2-GO (1.0 g) was dispersed in ethanol (60 mL), and then $VO(acac)_2$ (500 mg) was added. The mixture was heated at 75 ^{o}C for 6 h. After cooling the reaction mixture to room temperature, the heterogeneous vanadium-oxo immobilized and Schiff base modified graphene oxide was separated by filtration and washed with ethanol (4×100 mL), and then the obtained solid powder was dried at 80 ^{o}C in oven and labeled as VO-NH_2-GO.

1.3 Experimental procedure for reaction

In a typical experiment, a certain amount of investigated catalyst with HMF (252.2 mg, 2 mmol) and acetic acid (10 mL) were charged in a 100 mL

Teflon-lined stainless steel autoclave with vigorous stirring. The oxygen pressure in the autoclave was increased to 20 bar and the mixture was stirred and heated to 90 °C. After a fixed reaction time, the reactor system was quickly cooled to room temperature in an ice-water bath. For reusability tests, the spent VO-NH_2-GO was filtrated, washed in ethanol (4×50 mL) and dried at 80 °C in each cycle.

The schematic diagram of experimental set-up as following:

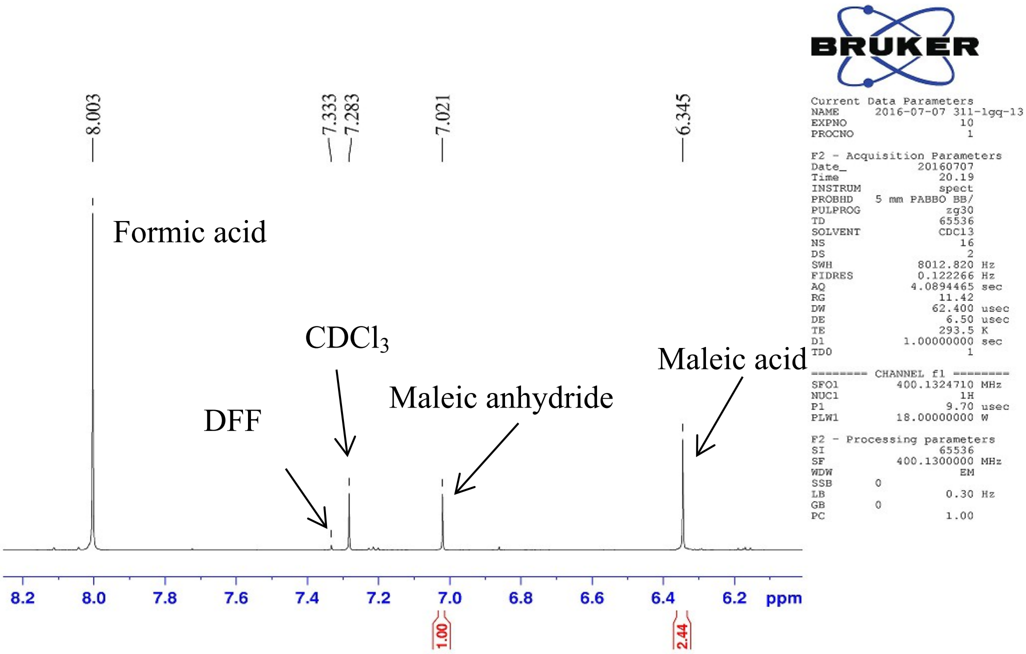


1.4 Analytical method

The reaction mixture was diluted with hot water (50 °C) and maintained in hot water for 2 h, after that, the mixture was filtered with 0.45 µm syringe filer prior to analysis. The HMF conversion and byproducts yield, such DFF, FFCA were separated by using a Shimadu high-pressure liquid chromatograph (LC-10AT) with a reversed-phased C18 column (200 × 4.6 mm) at 25 °C with a UV detector at wavelength of 280 nm. The mobile phase was acetonitrile and water with acetic acid (volume ratio 60:39:1 v/v) at 0.3 mL/min. The HMF conversion and DFF yield were expressed in mol%, based on the total HMF amount.

Maleic anhydride in reaction mixture can be converted into maleic acid totally after hot water treated, which is proved to be valid by early researchers.[1] For the analysis of maleic anhydride and maleic acid, a 4.6 mm ×250 mm Shodex sugar column (SC1011) was used, and distilled water was used as the mobile phase at a flow rate of 1.0 mL min^{-1}. The column temperature was maintained at 75 ^{o}C. The yield of maleic acid, DFF and conversion of HMF were calculated on the basis of external standard curves constructed with authentic standards.

The product distribution (without hot water treated) was identified by NMR. The maleic anhydride and maleic acid ratio after reaction was determined by NMR:



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PROCNO                     1

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LB                      0.30 Hz
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2. Figure S1. XRD pattern of graphite, GO, NH_2-GO, fresh VO-NH_2-GO and recycled VO-NH_2-GO for five times.

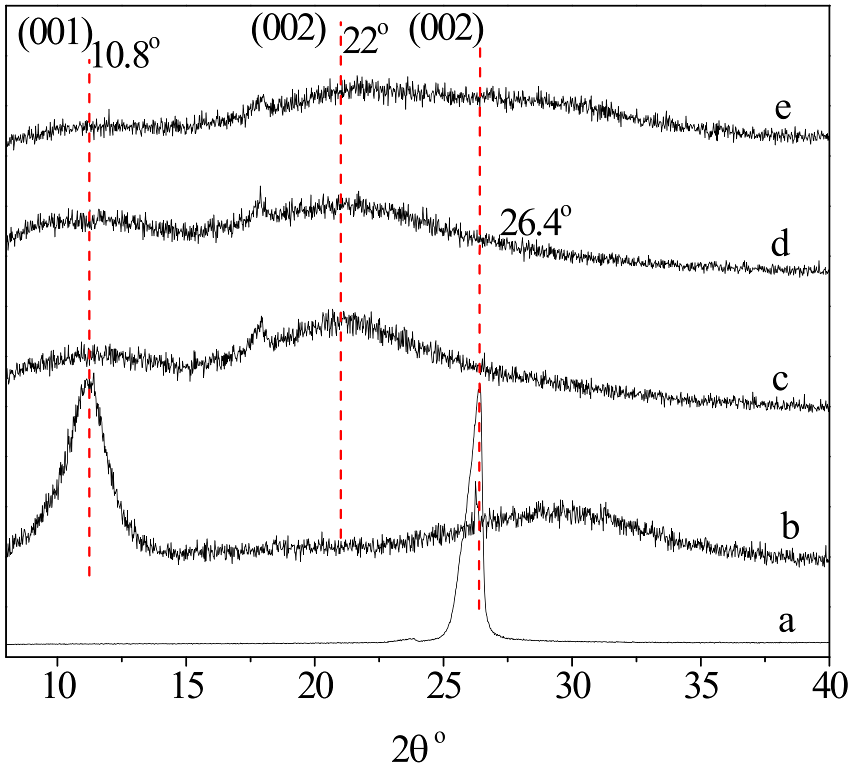

Figure S1. XRD pattern of (a) graphite, (b) GO, (c) NH_2-GO, (d) fresh VO-NH_2-GO, and (e) recycled V-NH_2-GO for five times

3. Figure S2. FT-IR analysis of GO, NH_2-GO, fresh VO-NH_2-GO and recycled VO-NH_2-GO for five times.

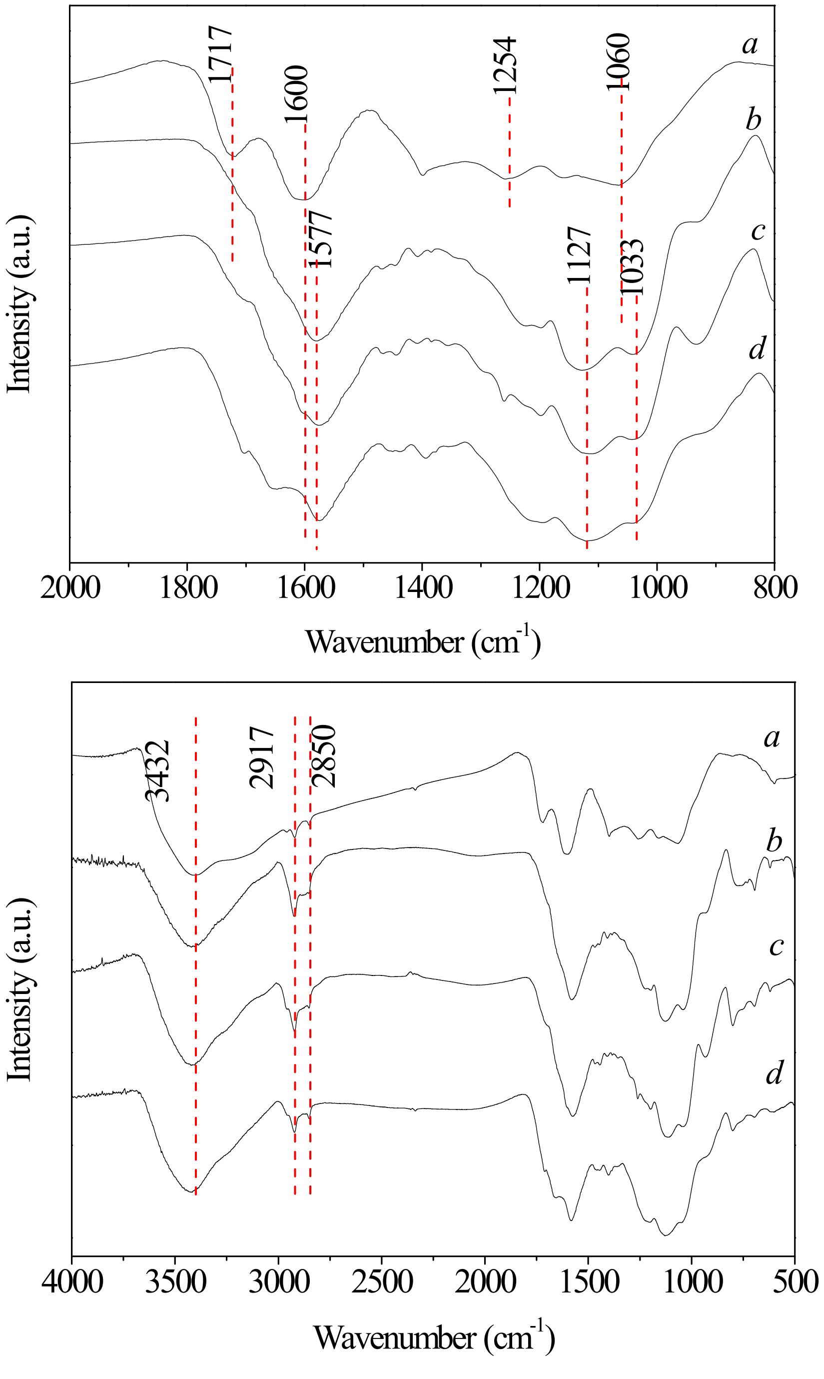

Figure S2. FT-IR analysis of (a) GO, (b) NH_2-GO, (c) fresh VO-NH_2-GO, and (d) recycled VO-NH_2-GO for five times.

4. Table S1. BET analysis of GO and VO-NH_2-GO

Sample	S(m^2/g)[a]	V (cm^3/g)[b]	*D(nm)*[c]
GO	379.0	1.36	14.4
VO-NH_2-GO	148.8	1.13	14.6

[a] BET surface area

[b] Average pore volume

[c] Average pore diameter

5. **Table S2.** Elemental analysis of the prepared GO, fresh VO-NH_2-GO and recycled VO-NH_2-GO for five times[a]

Sample	C (wt%)	O (wt%)	H (wt%)	N (wt%)	V (mmol g^{-1})
GO	43.3	46.5	3.3	---	---
Fresh VO-NH_2-GO	46.7	24.9	3.6	3.4	0.32
[b]Recycled VO-NH_2-GO	46.8	25.2	3.5	3.3	0.30
[c]Recycled VO-NH_2-GO	47.1	25.5	3.7	3.2	0.27

[a] The content of C, O, N ,H was determined by elemental analysis method and the content of V was determined by ICP method.

[b] Recycled V-NH_2-GO in aerobic oxidation of HMF for 5 cycles.

[c] Recycled V-NH_2-GO in aerobic oxidation of furfural for 5 cycles.

6. Affinities of different materials to HMF.

The adsorption of HMF on different material such as GO, VO-NH_2-GO, Graphene (G), V_2O_5/SiO_2 and V_2O_5 was tested with method reported previously.[2] In these experiments, 1 mmol HMF dissolved in 10 mL acetic acid was mixed with 100 mg different materials. The mixtures were stirred at room temperature for 8 h. After that, the mixtures were centrifuged and the supernatant solution was analyzed by HPLC.

Table S3. The adsorption capacity of HMF by GO, VO-NH_2-GO, G, V_2O_5/SiO_2, V_2O_5[a]

Entry	Catalyst	C_1 (mol L^{-1})	C_2 (mol L^{-1})	R (%)
1	blank	0.1	0.099	---
2	GO	0.1	0.082	18.0
3	V-NH_2-GO	0.1	0.086	14.5
4	G[b]	0.1	0.094	6.2
4	V_2O_5/SiO_2	0.1	0.096	3.8
5	V_2O_5	0.1	0.091	7.5

[a] C_1 represents the initial concentration of HMF in acetic acid solvent. C_2 represents the final concentration of HMF in acetic acid solvent. R represents the concentration percentage decreased by solid material.

[b] The G material was made by thermal reduction of GO in helium at 800 °C for 10 h. The oxygen content in G was determined as ~2 wt%.

7. Effect of the reaction temperature on the HMF conversion and product yield.

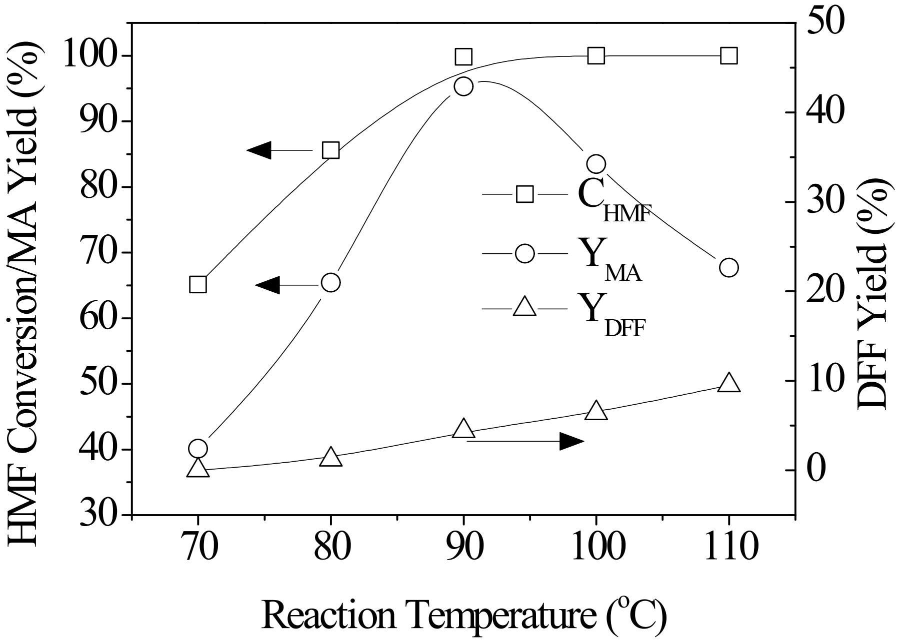

Figure S3. Effect of the reaction temperature on the HMF conversion and product yield

8. Reaction kinetics of HMF oxidation over V_2O_5 and $VO(acac)_2$

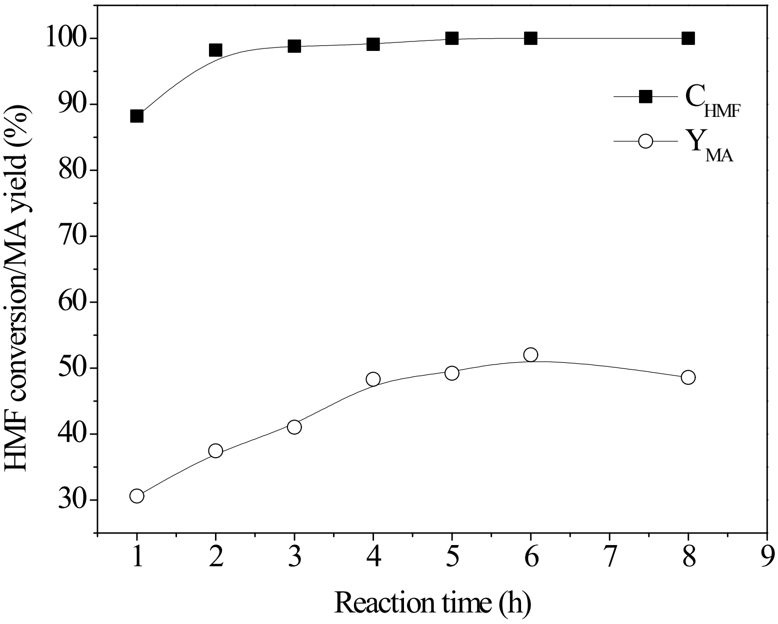

Figure S4. Reaction kinetics of HMF oxidation over V_2O_5. Reaction condition: HMF 252.2 mg (2.0 mmol); acetic acid 10.0 mL; V_2O_5, 10 mg; 90 °C; O_2 20 bar. The yield of MA in graph involves maleic anhydride and maleic acid.

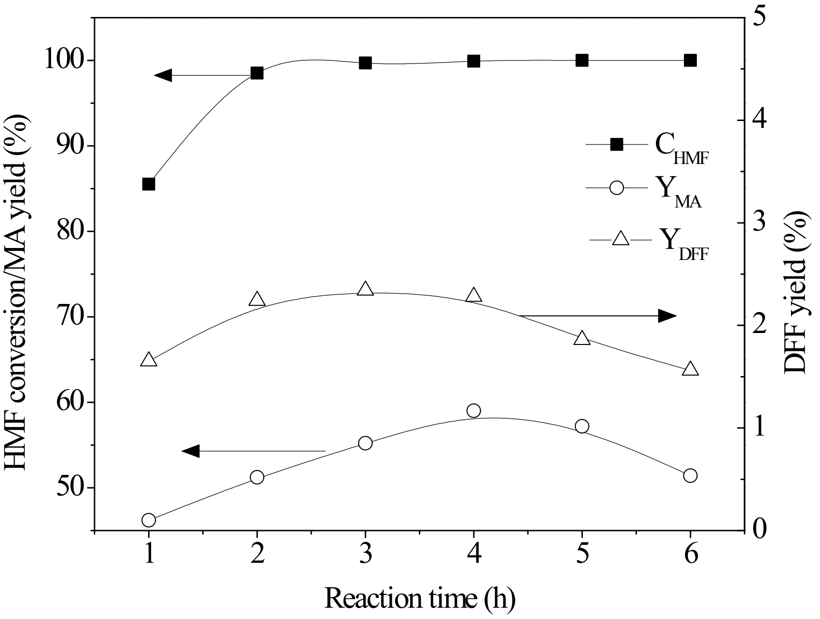

Figure S5. Reaction kinetics of HMF oxidation over $VO(acac)_2$. Reaction condition: HMF 252.2 mg (2.0 mmol); acetic acid 10.0 mL; $VO(acac)_2$, 10 mg; 90 °C; O_2 20 bar. The yield of MA in graph involves maleic anhydride and maleic acid.

9. Recyclability of VO-NH_2-GO in catalytic oxidation of HMF and furfural

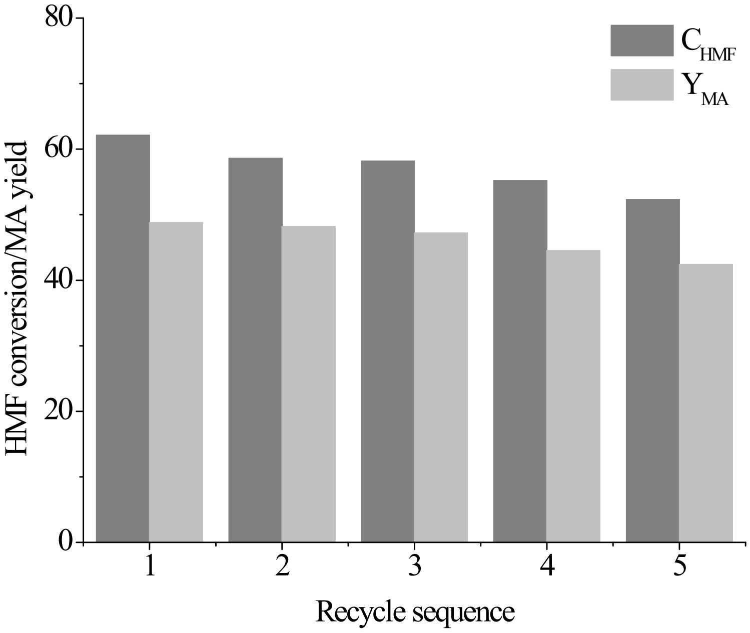

Figure S6. Recyclability of VO-NH_2-GO in HMF oxidation to MA. Reaction conditions: HMF 252.2 mg (2 mmol); acetic acid 10.0 mL; VO-NH_2-GO, 5 mg; 90 °C; O_2 20 bar; the reaction time was fixed at 2 h in each cycle.

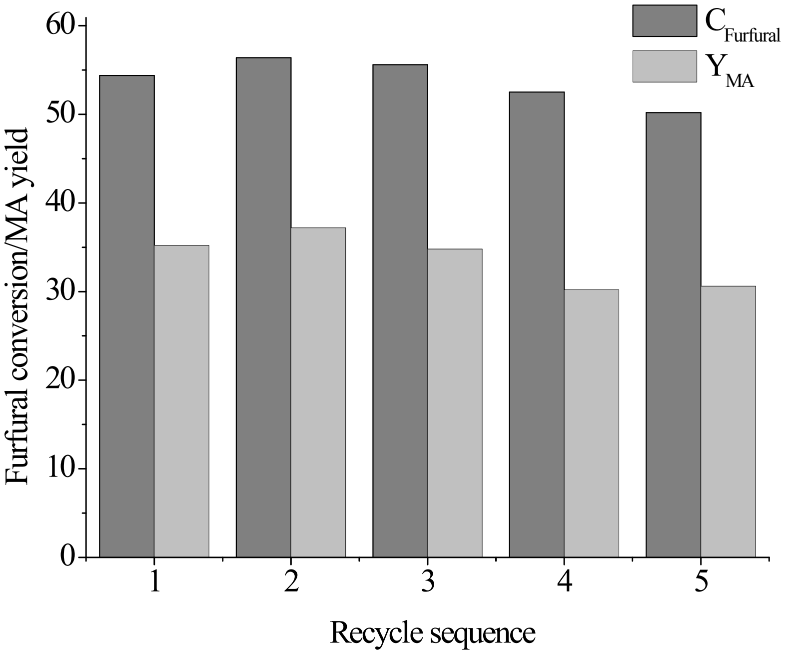

Figure S7. Recyclability of VO-NH_2-GO in furfural oxidation to MA. Reaction conditions: furfural, 252.2 mg (2 mmol); acetic acid 10.0 mL; VO-NH_2-GO, 10 mg; 90 °C; O_2 20 bar; the reaction time was fixed at 2 h in each cycle.

1. Li, X.; Ho, B.; Zhang, Y. *Green Chem.* **2016**, *18,* 2976-2980.
2. Wang, H.; Kong, Q.; Wang, Y.; Deng, T.; Chen, C.; Hou, X.; Zhu, Y. *ChemCatChem* **2014**, *6,* 728-732.