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Supporting Information

Catalytic Conversion of Biomass-Derived Carbohydrates to Formic Acid Using Molecular Oxygen

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This Supporting Information file includes:

Materials & methods

Chemicals. Sodium metavanadate, sulfuric acid (98 %), barium chloride, glucose, fructose, xylose, sucrose, cellose, xylan, cellulose, formic acid, acetic acid, glycol, lactic acid, 1, 3-dioxyacetone dimmer, glycerol, methylglyoxal, oxalic acid, formaldehyde, 1,2-propylene glycol, glyceraldehyde, glycolaldehyde dimer, glycolic acid, glyoxylic acid, 1,3-propylene glycol, glyoxal, butyl ether, ethyl acetate and diethyl ether were analytical grade and purchased from Aladdin Chemical Co., Ltd., Shanghai, China. O_2 (99.99 %), CO_2 (99.99 %), He (99.99 %), and N_2 (99.99 %) were provided by Beijing Analytical Instrument Co., Ltd., Beijing, China.

^{51}V-NMR and XPS studies of the catalyst. The ^{51}V-NMR signals were obtained on a Bruker DRX-300 spectrometer operating at 78.9 MHz using a 10 mm broadband probe, at (295±0.5) K. Chemical shifts were externally referenced to $VOCl_3$ at 0 ppm. The ^{51}V-NMR studies of the mixture before and after a reaction were carried out directly without any dilution. The XPS signals were obtained on an ESCALAB-250 spectrometer equipped with a monochromated 450 W Al Kα source (ThermoFisher Scientific Co., Ltd. USA). The base pressure of the system was below 1×10^{-7} Pa. Experiments were recorded with 220 W source power and an angular acceptance of ±7^{o}. The V2p core levels were recorded with a step of 0.05 eV and a pass energy of 11.75 eV. The reactions were carried out with and without oxygen (replaced by nitrogen). The excess barium chloride was added into the solutions after the reaction to react with sulfuric acid, then the aqueous solutions were evaporated at 80 ^{o}C with nitrogen as the sweeping gas. The resulted solids were studied by XPS to investigate the valence transformation in the reaction.

Conversion of carbohydrates. The conversion of carbohydrates was carried out in a high-pressure batch reactor made from Hastelloy alloy (HC276), supplied by Haian Petroleum Scientific Research Co., Ltd., Jiangsu, China. The reactor had a volume of 25 cm^3, an inner

diameter of 20 mm and a magnetic stirrer. In a typical procedure, 100 mg of substrate, 22 mg $NaVO_3$, 42 mg H_2SO_4 and 6 g of H_2O were loaded in the reactor, air was purged by oxygen, and then oxygen was charged into the reactor to 3 MPa monitored by a pressure transducer (KLP-800KG) and an indicator (Beijing Tianchen Instrument Co., Ltd.) with an uncertainty of ± 0.025 MPa. The reactor was placed into the furnace, which was controlled by a temperature controller (XTD-7000) to ± 0.5 ^oC and then heated up by (8 to10) ^oC/min to a desired temperature. During the reaction, the mixture was stirred by the magnetic stirrer at a constant speed of 500 rpm. After the reaction, the reactor was placed in ice water and the gas was released and collected in a gas bag. The gaseous samples were analyzed using a GC (Agilent 7890A) using a TCD detector with a Poropak Q column, with helium as the carrier gas. An HPLC (Waters 2695, USA) with SHODEX SH 1011 column (Shodex, Tokyo) and a differential refractive index detector (Waters, USA) was employed for the analysis of the liquid samples with the column oven temperature at 55 ^oC and the mobile phase was 0.01 mol/dm^3 aqueous sulfuric acid solution at a flow rate of 0.5 cm^3/min. The products were identified by HPLC-MS (mirOTOF-QII, Bruker), and the retention times were compared with those of standard substances.

Separation of formic acid and recycling of the catalyst system. The separation of formic acid (FA) from the reaction system after reaction using solvent extraction was examined. The tested solvents were butyl ether, dichloromethane, diethyl ether, ethyl acetate and n-octanol. The extraction was operated with a volume ratio of 2/1 (volume of extractant/volume of aqueous solution) at room temperature and repeated four times. The extract and the raffinate obtained after every extraction were analyzed by HPLC to determine the extractability. The ultimate raffinate (including H_2O, $NaVO_3$, H_2SO_4 and small amount of extractant) was swept with N_2 at 30 ^oC to remove the extractant before reused in the next run. The amount of extractant in the water at sweep time was quantified by HPLC. The recovered catalyst system

had a lesser amount of water (ca. 5 g) than that added initially (6 g) because of the loss in the separation and recovery processes. Thus, in the next run, the water was supplemented to 6 g when investigating the reusability of the catalyst system.

Carbon balance of the reaction system. The carbon balance before and after the reaction was examined by analysis of HPLC and GC. The carbon-containing gaseous products were quantified by internal standard methods using N_2 as the internal substance in the GC. The products in the liquid were quantified by HPLC using an external standard method.

Determination of pH. The pH of the sodium metavanadate aqueous solution with different content of sulfuric acid (0 to 0.02 mass fraction) were determined by a pH meter (PHS-25, Shanghai Leici Instrument Co., Ltd., China) at 25 ^{o}C. The pH meter was calibrated by two standard buffer solution before the measurement.

Supporting Information Figures

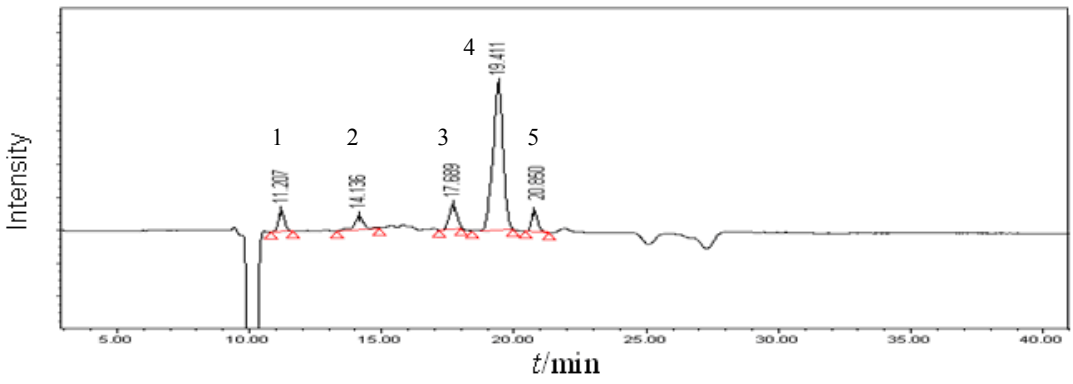


Fig. S1 A typical HPLC spectrum of glucose oxidation products in sodium metavanadate aqueous solution at 160^{o}C. (1) oxalic acid, (2) glucose, (3) glycolic acid, (4) formic acid, (5) acetic acid. The peak before the oxalic acid peak were caused by the mobile phase and was also observed in the standard sample. At times longer than the acetic acid peak, no additional peaks was observed.

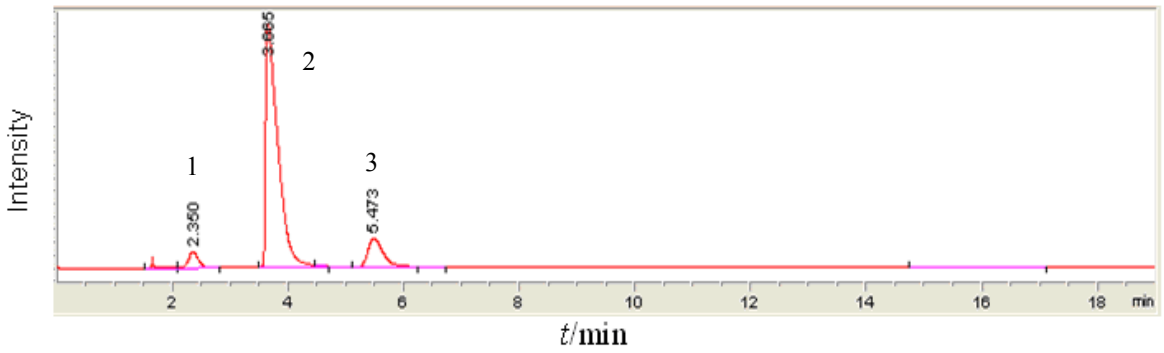


Fig. S2 A typical GC spectrum of gas-phase products from oxidation of glucose in sodium metavanadate aqueous solution at 160°C. (1) CO_2, (2) O_2, (3) N_2. N_2 was injected into the autoclave after reaction as the internal substance for quantification of CO_2. O_2 was the residual after consumption in the reaction and CO_2 was produced in the reaction.

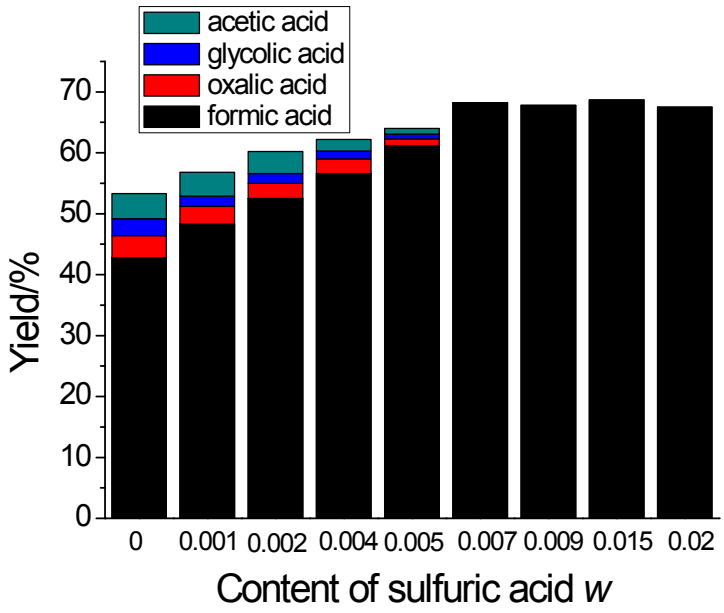


Fig. S3 The distribution of products in liquid with glucose as substrate as a function of mass faction of sulfuric acid *w*. Reaction conditions: glucose, 100 mg; sodium metavanadate, 22 mg; water, 6 g; temperature, 160 ^{o}C; reaction time, 1 min.

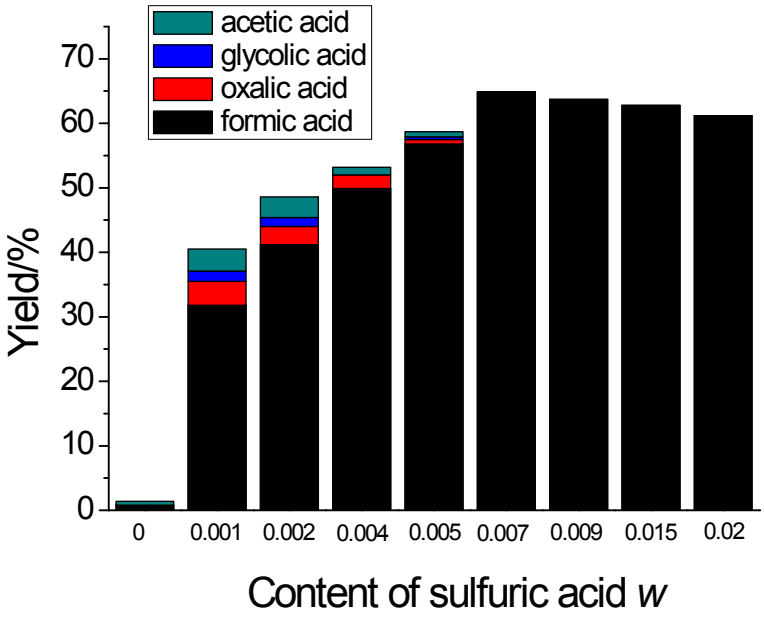


Fig. S4 The distribution of products in liquid with cellulose as substrate as a function of sulfuric acid mass fraction *w*. Reaction conditions: cellulose, 100 mg; sodium metavanadate, 22 mg; water, 6 g; temperature, 160 °C; reaction time, 2 h.

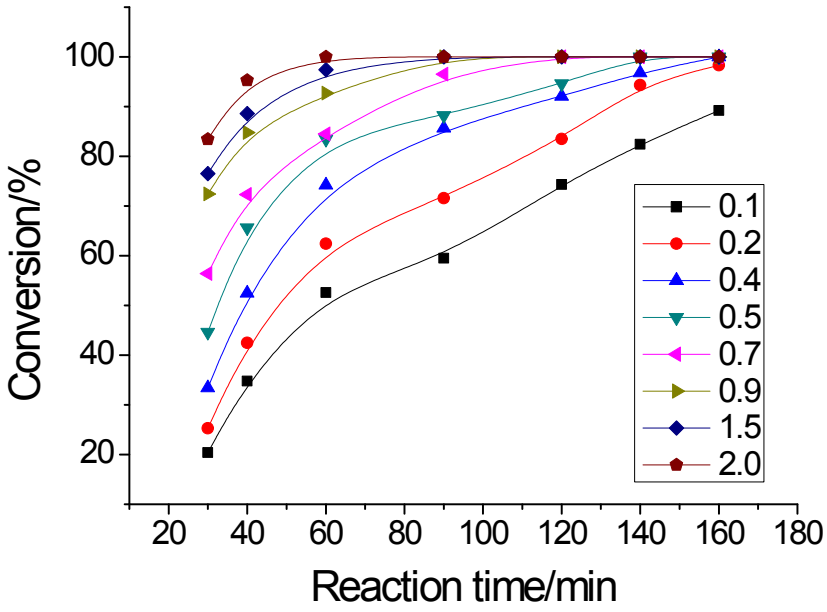


Fig. S5 The conversion of cellulose as a function of time under different mass fractions of sulfuric acid 100*w*. Reaction conditions: cellulose, 100 mg; sodium metavanadate, 22 mg; water, 6 g; temperature, 160 °C.

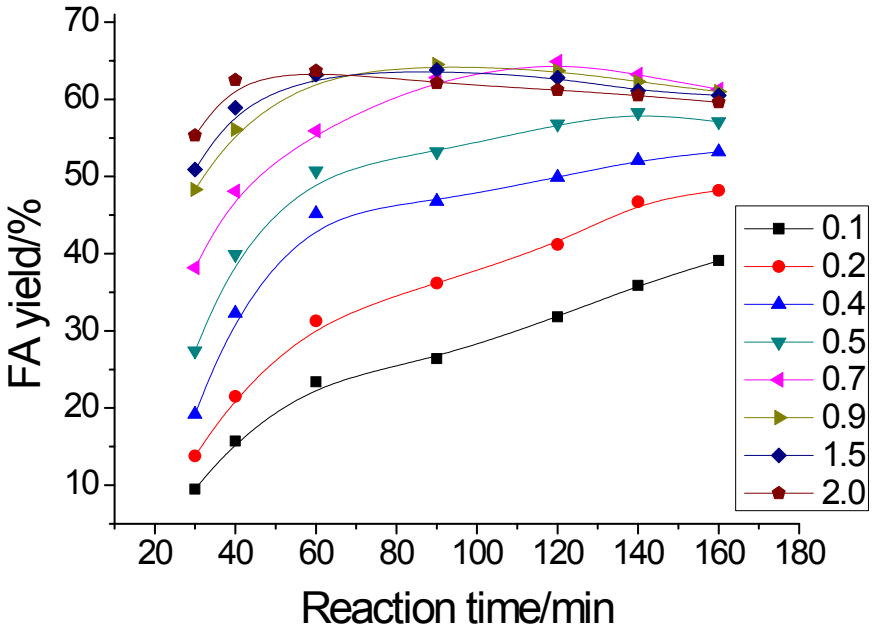


Fig. S6 The yield of FA from cellulose as a function of time under different mass fractions of sulfuric acid 100*w*. Reaction conditions: cellulose, 100 mg; sodium metavanadate, 22 mg; water, 6 g; temperature, 160 °C.

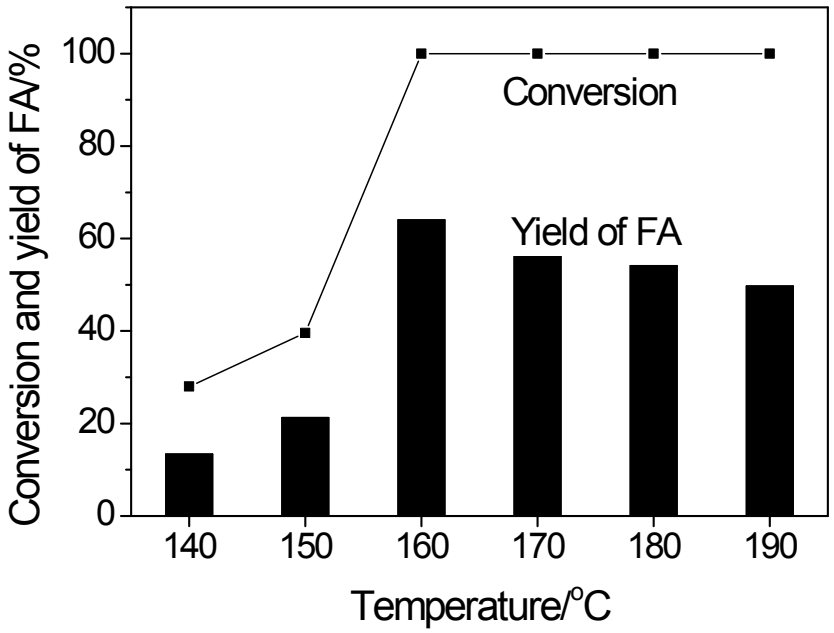


Fig. S7 The effect of temperature on the conversion of substrate and yield of FA. Reaction conditions: cellulose, 100 mg; sodium metavanadate, 22 mg; sulfuric acid, 42 mg; water, 6 g.

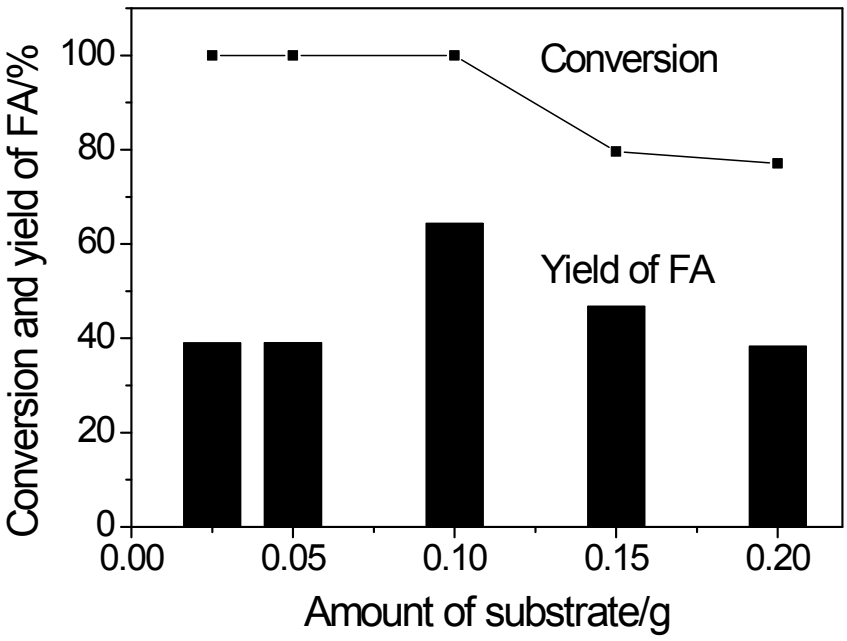
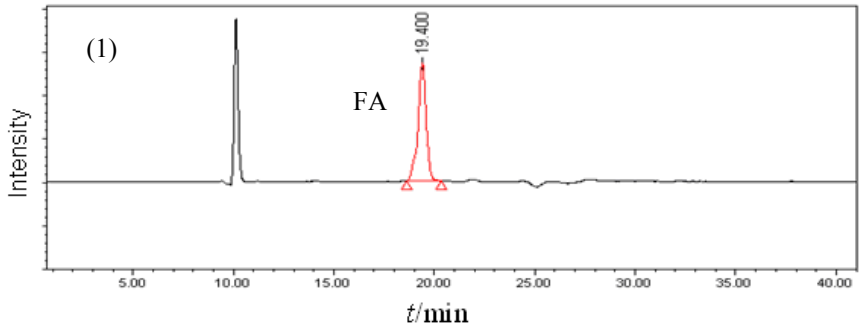
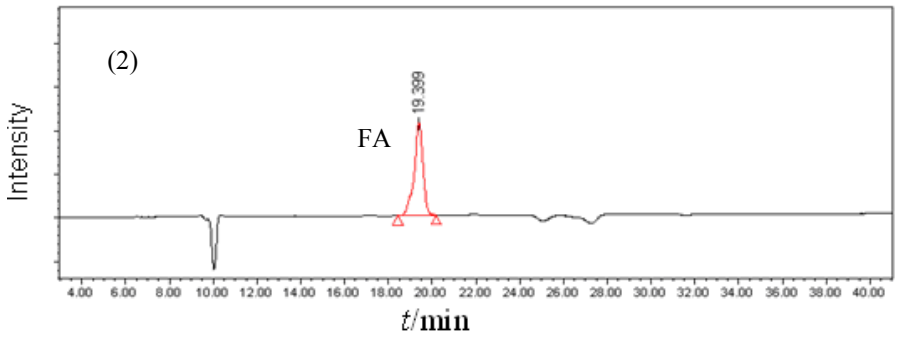


Fig. S8 The effect of amount of initial substrate on the conversion of substrate and yield of FA. Reaction conditions: substrate, cellulose; sodium metavanadate, 22 mg; sulfuric acid, 42 mg; water, 6 g; temperature, 160 ^{o}C.


(1)
19.400
FA
Intensity
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
t/min


(2)
19.399
FA
Intensity
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
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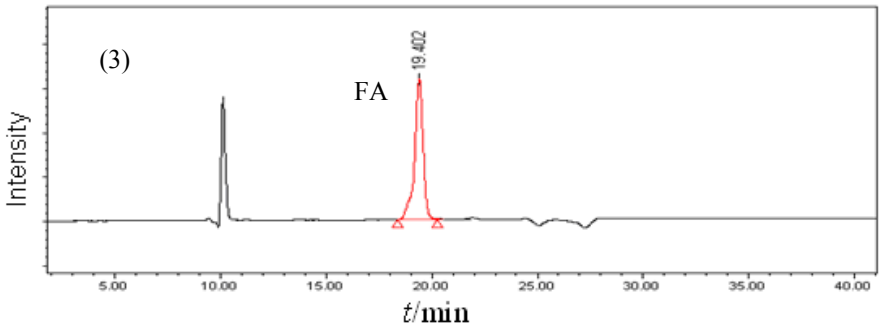
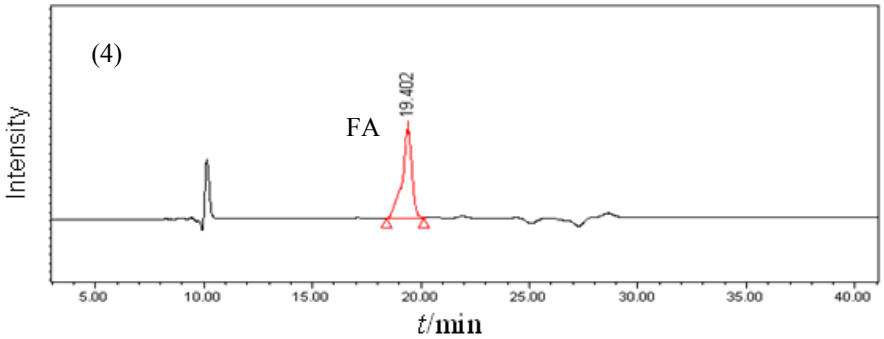
32.00
34.00
36.00
38.00
40.00
t/min


(3)
19.402
FA
Intensity
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
t/min


(4)
19.402
FA
Intensity
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t/min

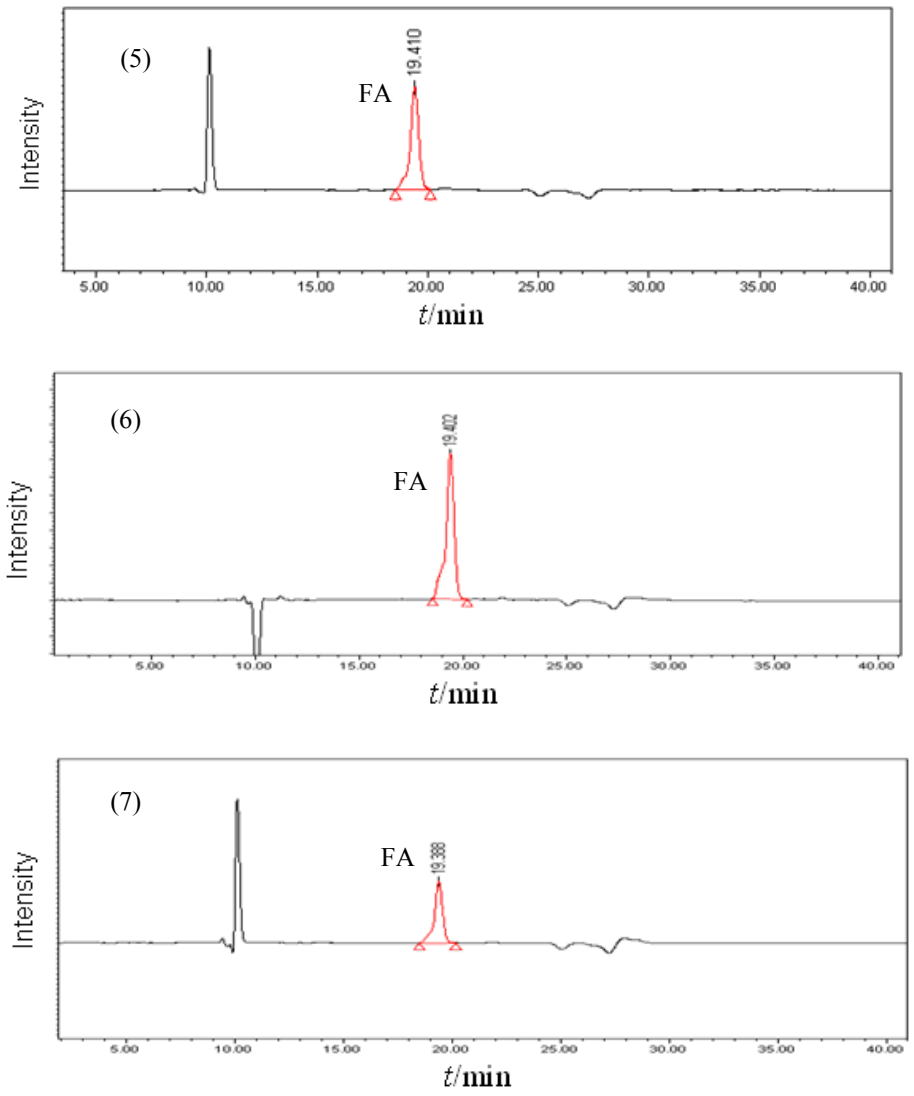

Fig. S9 The HPLC spectrum of oxidation products from carbohydrates in sodium metavanadate aqueous solution. Reaction conditions: substrate, 100 mg; sodium metavanadate, 22 mg; water, 6 g; sulfuric acid, 42 mg (w =0.007); temperature, 160 °C. (1) glucose; reaction time, 1 min. (2) cellulose; reaction time, 2 h. (3) fructose; reaction time, 1 min. (4) cellose; reaction time, 10 min. (5) sucrose; reaction time, 5 min. (6) xylose; reaction time, 1 min (7) xylan; reaction time, 30 min. The positive/negative peak before the FA peak was caused by the mobile phase or sulfuric acid; this peak was also observed in the standard sample.

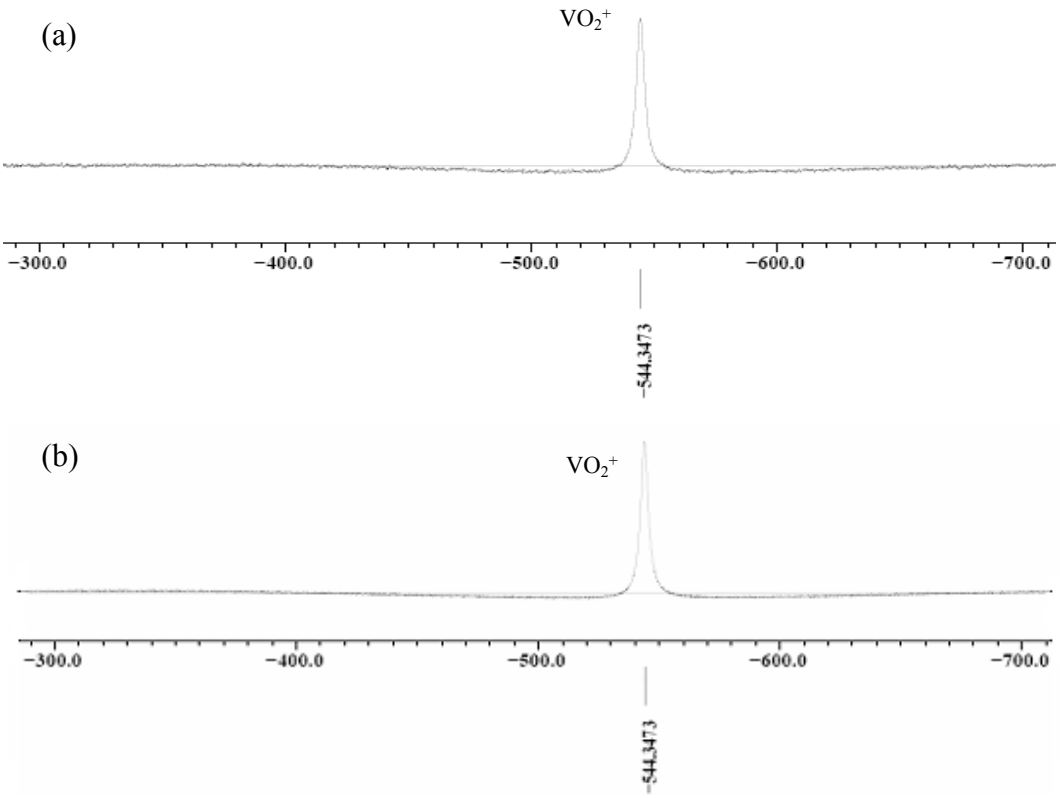

Fig. S10 ^{51}V-NMR spectras of the catalyst system before and after reaction (S1). (a), the catalyst system before reaction; (b), the catalyst system after reaction. Cellulose, 100 mg; sodium metavanadate, 22 mg; H_2O, 6 g; H_2SO_4, 42 mg (w =0.007); temperature, 160 ^oC; reaction time, 2 h.

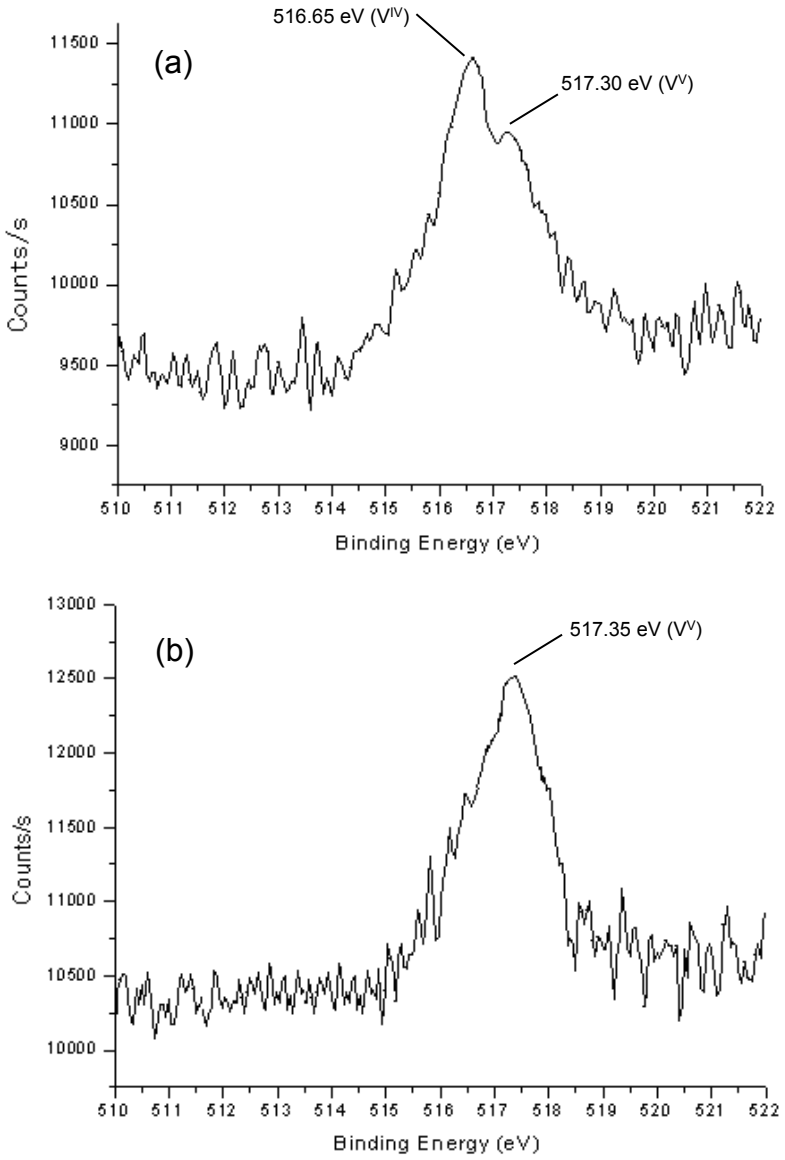

Fig. S11 XPS spectras of the catalyst system after reaction without and with oxygen (S2, S3). (a), the oxygen was substituted by nitrogen (initial pressure was 3 MPa) in the reaction; (b), the initial oxygen pressure was 3 MPa. Cellulose, 100 mg; sodium metavanadate, 22 mg; H_2O, 6 g; H_2SO_4, 42 mg (w =0.007); temperature, 160 ^oC; reaction time, 2 h.

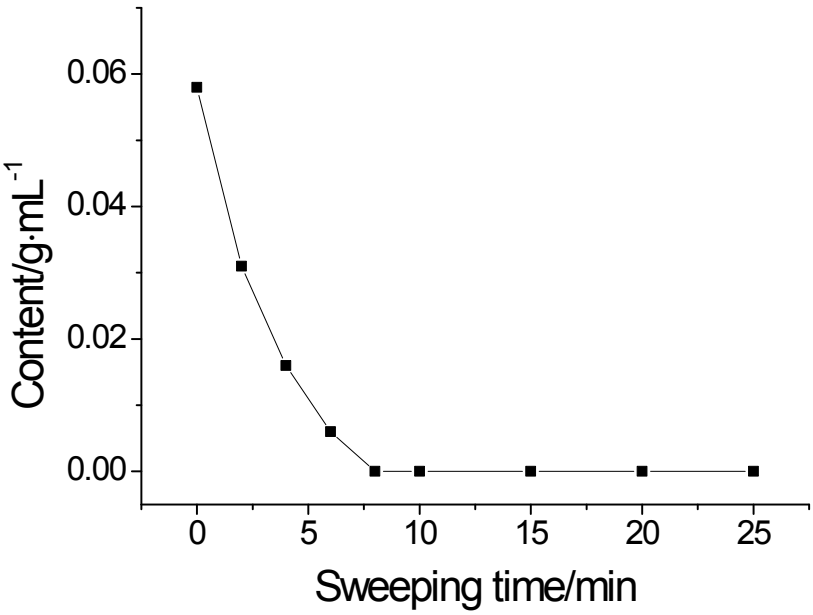

Fig. S12 The content of diethyl ether in water after exhaustive extraction as a function of sweeping time. Sweeping gas, nitrogen; flowrate of nitrogen, 20 cm^3/min; sweeping temperature, 30 ^oC.

Supporting Information Tables

Table S1 The corresponding pH of the sodium metavanadate aqueous solution as a function of the content of sulfuric acid at room temperature. Conditions: sodium metavanadate, 22 mg; H_2O, 6 g.

Amount of sulfuric acid/mg	0	6	12	24	31	42	54	91	120
Mass fraction of sulfuric acid 100*w*	0.0	0.1	0.2	0.4	0.5	0.7	0.9	1.5	2.0
pH	8.21	2.16	1.84	1.32	1.10	0.87	0.76	0.54	0.42

Table S2 Results of carbon balance before and after reaction. Reaction conditions: substrates, 100 mg; sodium metavanadate, 22 mg; H_2O, 6 g; H_2SO_4, 42 mg (w = 0.007); temperature, 160 ^oC.

Entry	Substrate	Reaction time/min	In*/mmol	Out*/ mmol		Total out/ mmol	Carbon balance/ %
				FA	CO_2		
1	glucose	--	3.33	0	0	3.33	100
2	glucose	1	3.33	2.26	1.13	3.39	101.8
3	cellulose	120	3.7	2.4	1.38	3.78	102.2
4	fructose	1	3.33	2.05	1.27	3.32	99.7
5	cellose	10	3.5	2.45	1.16	3.61	103.1
6	xylose	1	3.33	2.21	1.09	3.30	99.1
7	sucrose	5	3.33	2.15	1.25	3.40	102.1
8	xylan	30	3.79	2.41	1.43	3.84	101.3

*The “in” and “out” represent the carbon mole input and output, respectively.

Table S3 Calculations of the mean value and standard deviation for key experiments of carbohydrates investigated.

Substrate	Yield of FA/%					Mean value/%	Standard deviation/%
	1	2	3	4	5		
Glucose	67.4	65.4	69.8	68.1	70.3	68.2	2.0
Cellulose	66.3	61.1	67.5	63.1	66.5	64.9	2.7
Fructose	62.7	63.1	58.6	60.8	62.3	61.5	1.8
Cellose	63.2	67.8	63.0	66.5	66.0	65.3	2.1
Xylose	65.1	68.2	66.3	63.5	67.9	66.2	2.0
Sucrose	61.2	63.1	67.2	65.3	66.2	64.6	2.4
Xylan	66.2	61.3	64.5	60.2	65.3	63.5	2.6

Table S4 The extraction ratio of extractants including butyl ether, dichloromethan, diethyl ether, ethyl acetate and n-octanol at room temperature after reaction.

Extractant	Times	Extraction ratio/%	Total extraction ratio/%
Butyl ether	1	12.2	30.4
	2	8.3	
	3	5.6	
	4	3.2	
	5	1.1	
Dichloromethane	1	4.3	14.0
	2	3.2	
	3	2.8	
	4	2.1	
	5	1.6	
Diethyl ether	1	55.1	99.9
	2	26.4	
	3	12.3	
	4	5.8	
	5	0.3	
Ethyl acetate	1	23.4	56.7
	2	15.2	
	3	9.6	
	4	6.1	
	5	2.4	
n-Octanol	1	46.3	89.1
	2	25.6	
	3	10.3	
	4	4.5	
	5	2.4	

References in Supporting information

[S1] J. Min, L. F. Zhu, J. Y. Wang, J. Zhang, G. Y. Li, C. W. Hu, *J. Mol. Catal. A* **2006**, *253*, 1−7.

[S2] B. M. Weckhuysen, D. E. Keller, *Catal. Today* **2003**, *78*, 25−46.

[S3] G. Silversmit, D. Depla, H. Poelman, G. B. Marin, R. D. Gryse, *J. Electron. Spectrosc. Relat. Phenom.* **2004**, *135*, 167−175.