Supporting Information

Glucose oxidation to formic acid and methyl formate in perfect selectivity

Table S1. Results of screening tests with various solvents.

Entry	Solvent	Physical properties		NMR Analysis	
		solubility of HPA-5	Color of solution	^{31}P	^{51}V
1	Distilled Water	+	orange red	reference	
2	Methanol	+	orange red	+	+
3	Ethanol	+	orange yellow	+	+
4	*n*-Propanol	+	yellow	+	+
5	*n*-Butanol	+	orange yellow	+	+
6	*n*-Pentanol	+	orange yellow	+	+
7	*n*-Hexanol	+	orange red	+	+
8	Dimethylsulfoxide	+	red orange	+	+
9	Acetone	+	dark green	-	-
10	gamma-Valerolactone	+	dark green	-	-
11	Butyl acetate	+	dark green	-	-
12	Polyethylene carbonate	+	dark green	-	-
13	Trimethylphosphate	+	dark green	-	-
14	Tri-*n*-butylphosphat	+	green	-	-
15	Triethyleneglycol-monomethyl ether	+	dark green	-	-
16	*n*-Heptanol	-	orange	n/a	
17	Tetrahydrofuran	-	blue green		
18	Limonene	-	dark green		
19	Ethyl acetate	-	dark orange		
20	Ethyl lactate	-	dark green		
21	Polyethylene glycol 200	-	dark green		
22	Tris(2-butoxyethyl)phosphate	-	green		
23	Diethyleneglycol-monomethyl ether	-	dark blue		
24	Tetraethyleneglycol-dimethyl ether	-	dark blue		

Reaction conditions: *0.1 mmol HPA-5 catalyst dissolved in 10 mL different solvents, 20 bar initial O_2, 90 °C, 24 h, 1000 rpm.*
Note*: The representation of (+) to be good for using as oxidative solvent, (-) show bad effect*

Headspace GC-MS analysis of liquid products from ^{13}C-labelled oxidation in methanol

The measurements using headspace GC-MS analysis showed spectra of the experiments using different ^{13}C-labelling of the substrate or solvent using the HPA-5 catalyst. The liquid samples after oxidation were analysed by headspace GC-MS using a Shimadzu QC 2010/ QP2010 SE GCMS-system equipped with CTC combi PAL headspace and separated with CP-Sil PONA CB column (50 m x 210 µm x 0.5 µm) and with liquid injection method.

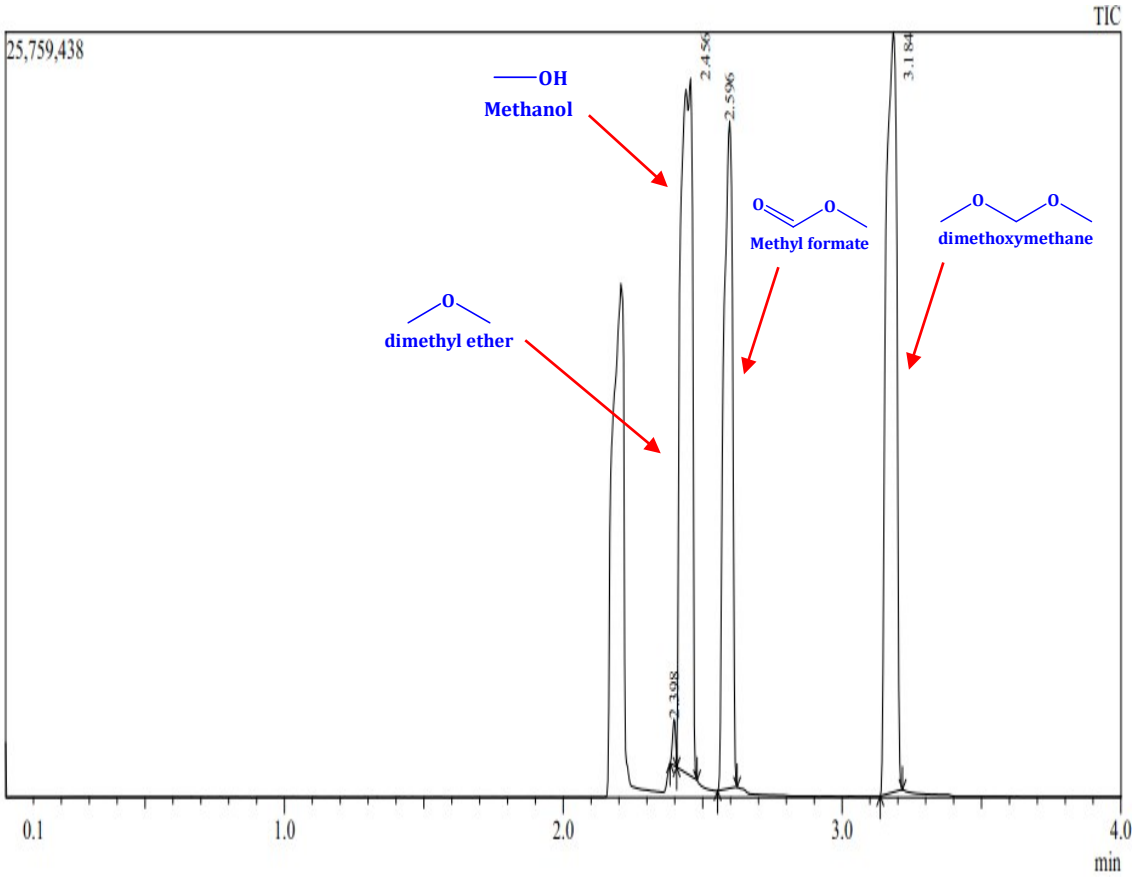

Figure S1. Chromatogram of ^{13}C-glucose:glucose (1:1) oxidative liquid products by headspace GC-MS analysis; reaction conditions: 0.5 mmol ^{13}C-glucose and 0.5 mmol glucose, 0.1 mmol HPA-5 catalyst dissolved in 10 mL MeOH, 20 bar initial O_2, 90 °C, 24 h, 1000 rpm.

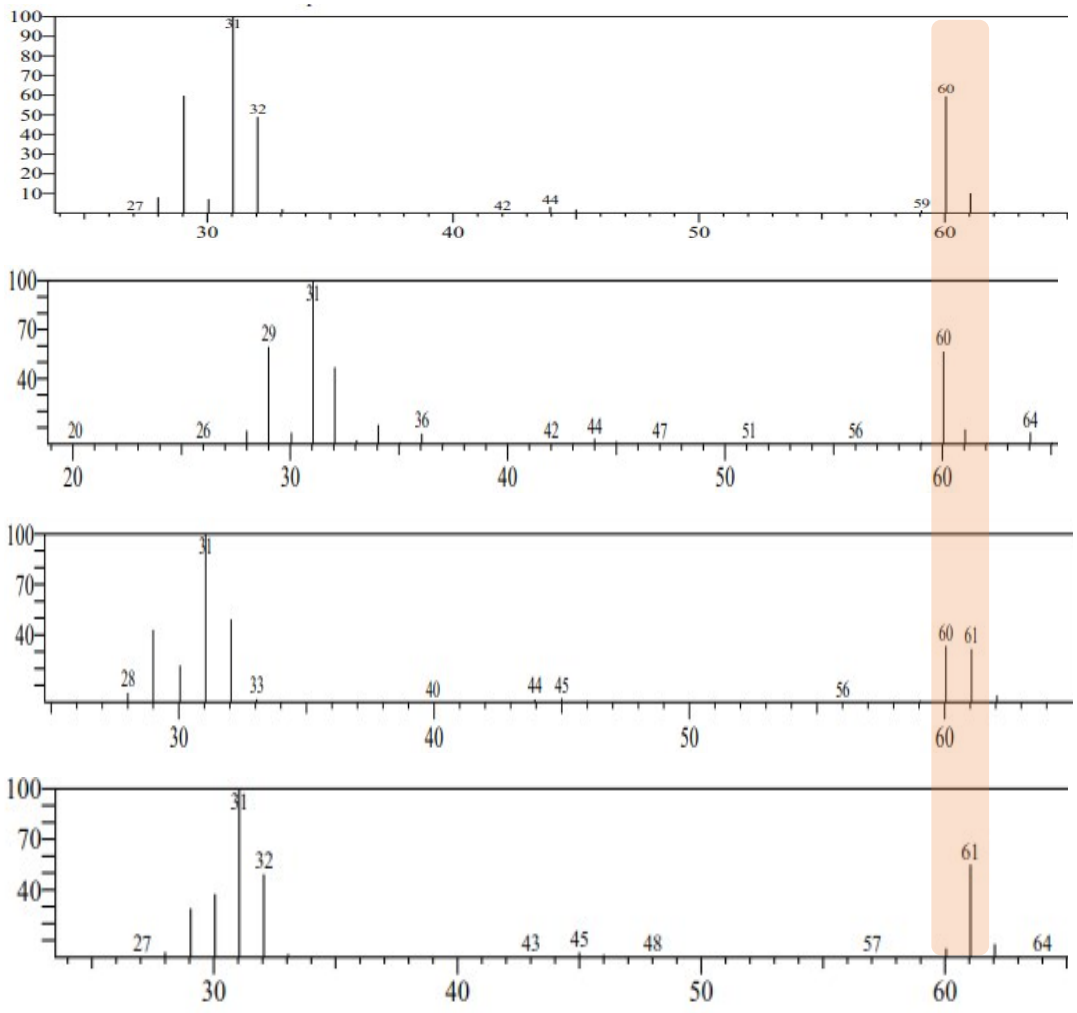

Figure S2. Mass spectrum of ^{13}C-labelled oxidative liquid products by GC-MS analysis; Mass spectrum of A. benchmark oxidative glucose in MeOH, B. oxidative glucose in ^{13}C-MeOH:MeOH (1:9), C. oxidative ^{13}C-glucose in MeOH, D. oxidative ^{13}C-glucose:glucose (1:1) in MeOH. Reaction conditions: 1 mmol glucose, 0.1 mmol HPA-5 catalyst dissolved in 10 mL MeOH, 20 bar initial O_2, 90 °C, 24 h, 1000 rpm.

Catalyst characterisation

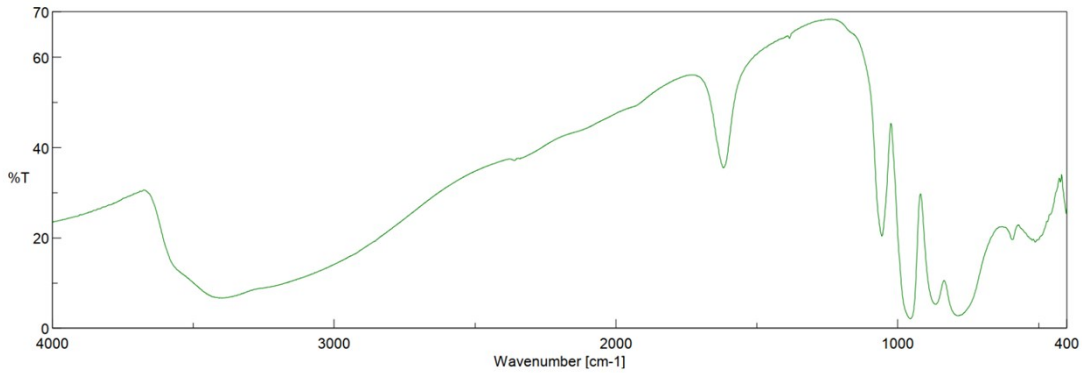

Figure S3. FT-IR spectrum of synthesized HPA-5 catalyst showing the respective stretching vibrations of the Keggin oxoanion including the stretching vibrations of the Keggin oxoanion at 1065 cm^{-1} (ν_{as} P-O_a), 959 cm^{-1} (ν_{as} Mo-O_d), 865 cm^{-1} (ν_{as} Mo O_b Mo) and 771 cm^{-1} (ν_{as} M-O_b-Mo).

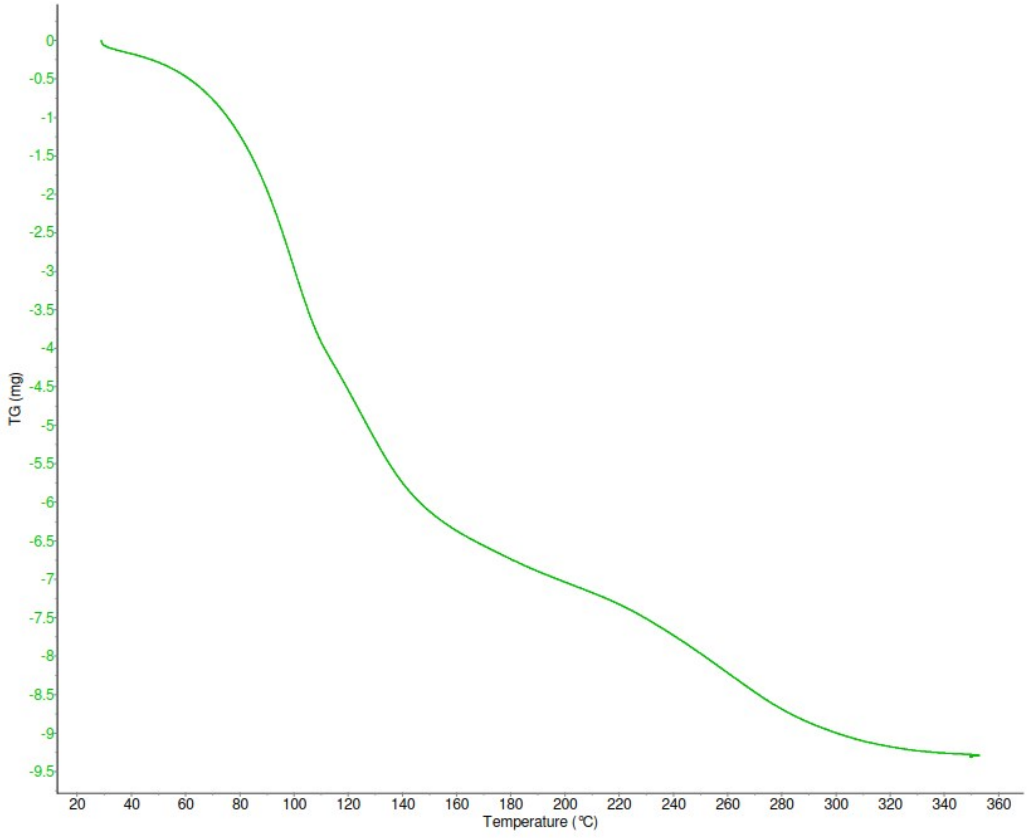

Figure S4. Thermogram of the solid HPA-5 catalyst. Conditions: 80 mg of the substance were weighed into a quartz crucible, heated at a constant rate of 10 °C min−1 up to 350 °C and kept there for 20 min. Helium was used as a carrier gas.

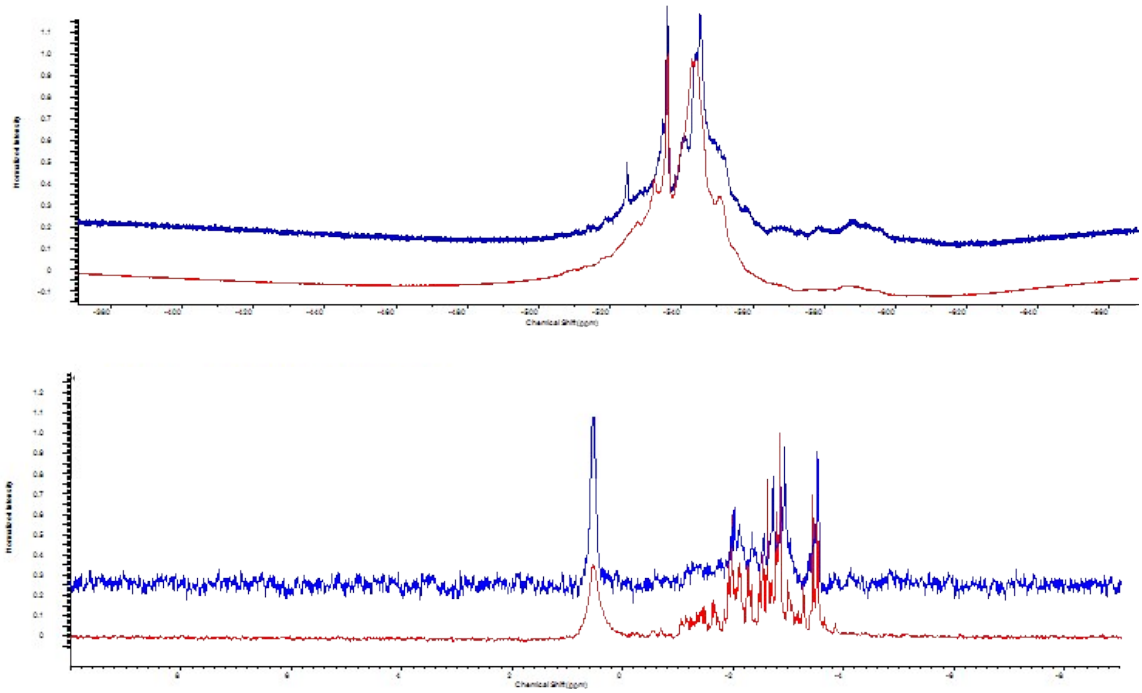

Figure S5. ^{51}V-NMR (above) and ^{31}P-NMR- (below) spectra of the synthesized HPA-5 catalyst (blue) in D_2O compared with a literature-known reference [27] (red) showing all expected isomers of the corresponding HPA-1, HPA-2, HPA-3/VO_2^+, HPA-4 and HPA-5 species.

Calculations of conversion, product selectivity and carbon mass balance:

$$\text{Gucose conversion (\%)} = \frac{\text{moles (of consumed C in glucose)}}{\text{moles (of initial C in glucose)}} \times 100 \quad (1)$$

Equation S1: Calculation of glucose conversion

$$Product\ selectivity\ (\%) = \frac{moles\ (C\ in\ product)}{moles\ (of\ \ initial\ \ C\ in\ glucose)} \times 100 \quad (2)$$

Equation S2: Calculation of product selectivity

The total carbon yield (TOC) was calculated by equation 3 and served as a representative for the carbon mass balance.

$$TOC = \frac{\sum_i n_{product,i}}{n_{C-atoms,glucose}} \quad (3)$$

^{13}C-NMR spectra of methanol oxidation products

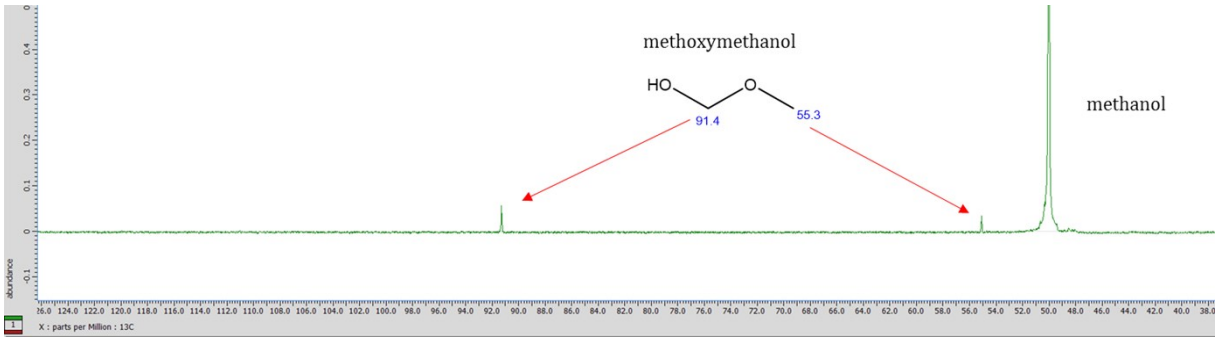

Figure S6. Substrate variation without catalyst; Reaction conditions: 1 mmol formaldehyde dissolved in 10 mL methanol, 20 bar O2 pressure, 90 °C, 24 h, 1000 rpm.

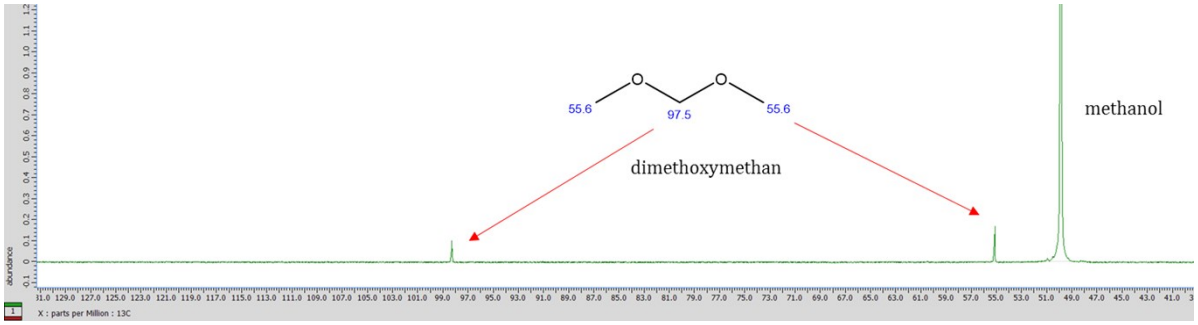

Figure S7. Substrate variation; Reaction conditions: 0.1 mmol HPA-5 catalyst 1 mmol dimethoxymethane dissolved in 10 mL methanol, 20 bar O2 pressure, 90 °C, 24 h, 1000 rpm.

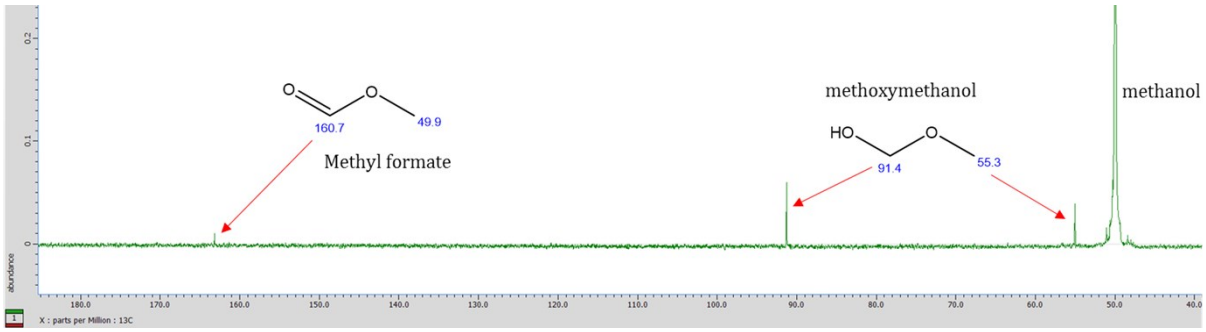

Figure S8. Substrate variation without catalyst; Reaction conditions: 1 mmol methyl formate dissolved in 10 mL methanol, 20 bar O2 pressure, 90 °C, 24 h, 1000 rpm.

Water content variation

Table S2. Detailed product composition depending on water content (Figures 6A and 6B). Reaction conditions: 1 mmol glucose, 0.1 mmol HPA-5 catalyst dissolved in 10 mL solvent, 20 bar initial O2, 90 °C, 24 h, 1000 rpm.

$w_{H2O,before}$ / wt%	$w_{H2O,after}$ / wt%	X_{Glu} / % (HPLC)	Y (FA) (NMR)	Y (MF) (NMR)	Y (CO_2) (GC)	Y (CO) (GC)	TOC /%
0	4.4	100	0	100	0	0	100
10	14.0	100	19.9	79.6	0.5	0	100
20	n.d.	99	24.6	73.8	0.6	0	99
30	n.d.	99	34.2	63.6	1.0	0.2	99
40	n.d.	98	40.6	56.0	1.2	0.2	98
48	n.d.	98	42.2	53.7	1.8	0.3	98
49	n.d.	98	44.3	51.9	1.6	0.2	98
70	n.d.	97	59.2	37.8	2.3	0.2	99
90	n.d.	93	72.4	16.9	3.3	0.3	93
100	n.d.	100	56	0	43	1	100

Kinetic experiments

Table S3. Kinetics of glucose oxidation in water. Reaction conditions: 20 mmol glucose, 2 mmol HPA-5 catalyst dissolved in 200 ml water, 90°C, 5 bar synthetic air (21 vol% oxygen), 1000 rpm, 22h.

time / h	$c_{Glucose}$ / mol L^{-1}	X_{Glu} / % (HPLC)	$Y_{FA/MF}$ / % (HPLC)	$Y_{CO2/CO}$ / % (GC)	Catalyst (Colour)
0	0.10	0	0.6		orange
0,25	0.094	8	1.3		dark brown
0,5	0.089	13	2.6		dark brown
0,75	0.084	17	4.5		dark brown
1,0	0.077	24	6.4		dark green
1,5	0.066	35	11.6		dark green
2	0.062	39	13.5		dark green
3	0.060	40	14.8		dark blue
4	0.060	41	15.4		dark blue
5	0.060	41	15.4		dark blue
6	0.058	43	15.4		dark blue
22	0.056	45	16.7	3.7 / -	dark blue

Table S4. Kinetics of glucose oxidation in methanol. Reaction conditions: 20 mmol glucose, 2 mmol HPA-5 catalyst dissolved in 200 ml methanol, 90°C, 5 bar synthetic air (21 vol% oxygen), 1000 rpm, 22h.

time / h	$c_{Glucose}$ / mol L^{-1}	X_{Glu} / % (HPLC)	w_{H_2O} / wt.-% (KFT)	$Y_{CO2/CO}$ / % (GC)	Catalyst (Colour)
0	0.018	82	0.84		orange
0.25	0.010	90	0.94		orange
0.5	0.007	93	0.94		orange
0.75	0.007	93	0.94		orange
1.0	0.005	95	0.99		orange
1.5	0.005	95	0.97		orange
2	0.004	96	0.94		orange
3	0.004	96			orange
4	0.004	97			orange
5	0.003	97	1.1		orange
24	0.000	100	1.6	0.04 / -	orange

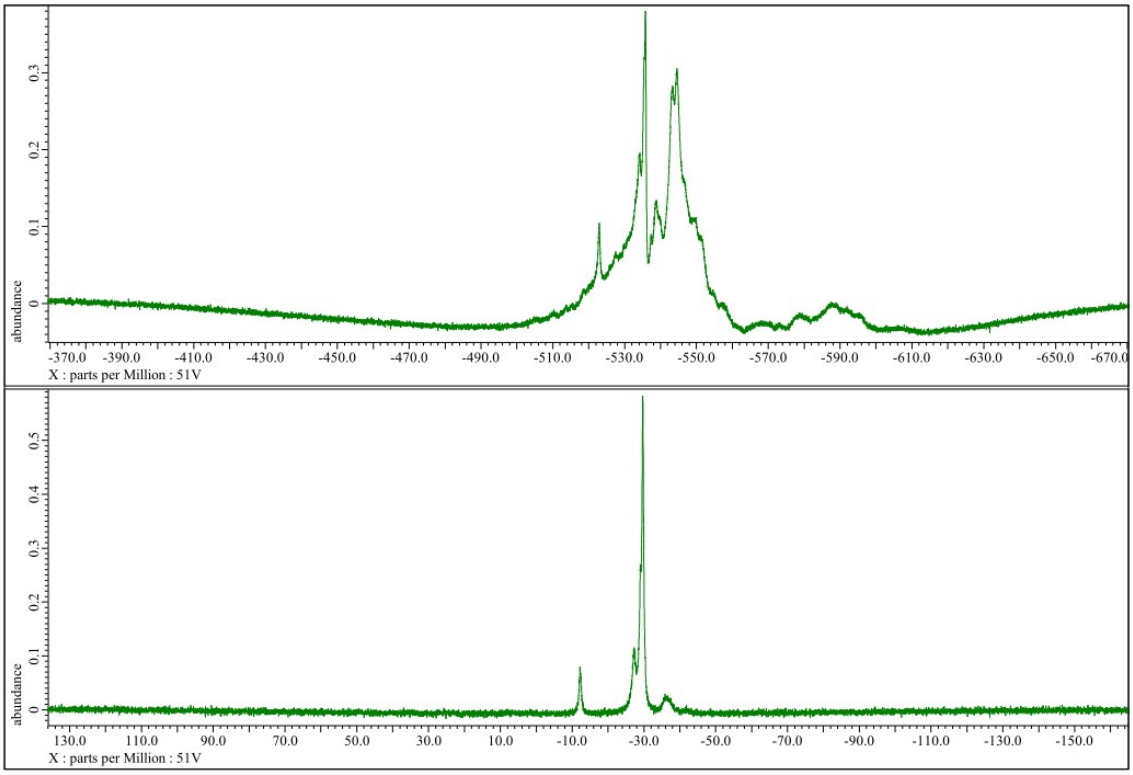

Figure S9. ^{51}V-NMR spectrum of aqueous HPA-5 solution before 0h (top) and after 24 h (bottom) catalytic oxidation of glucose.

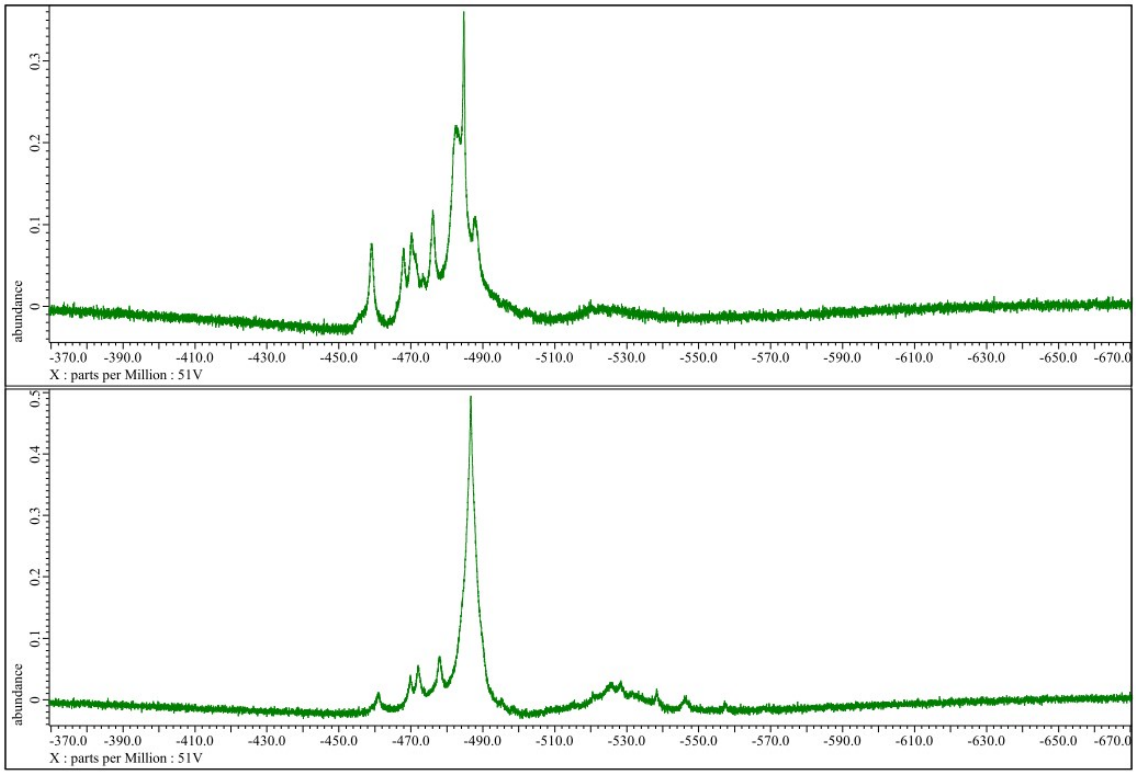

Figure S10. ^{51}V-NMR spectrum of methanolic HPA-5 solution before 0h (top) and after 24 h (bottom) catalytic oxidation of glucose.

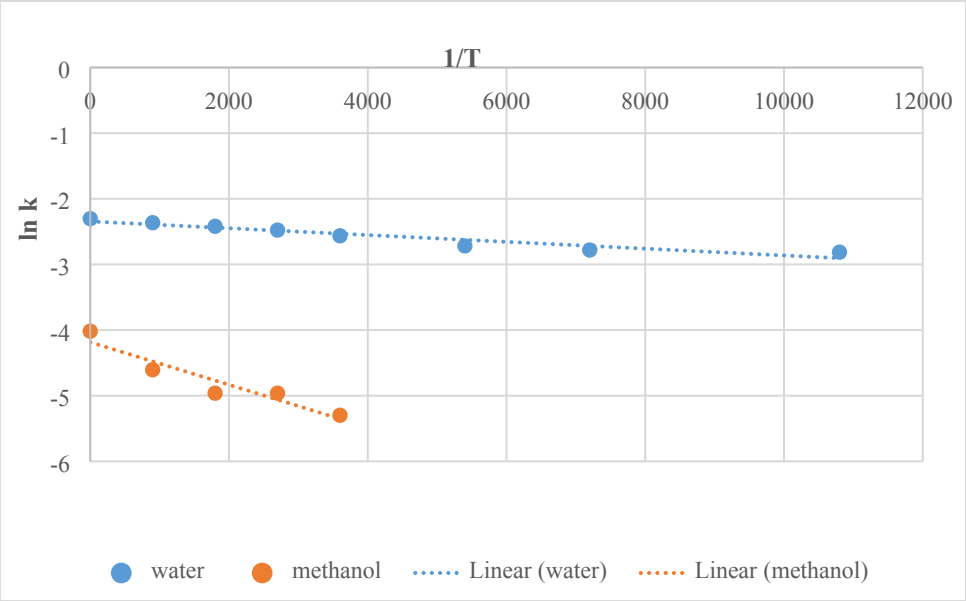

Figure S11. Determination of kinetic rate constants using Arrhenius' law.

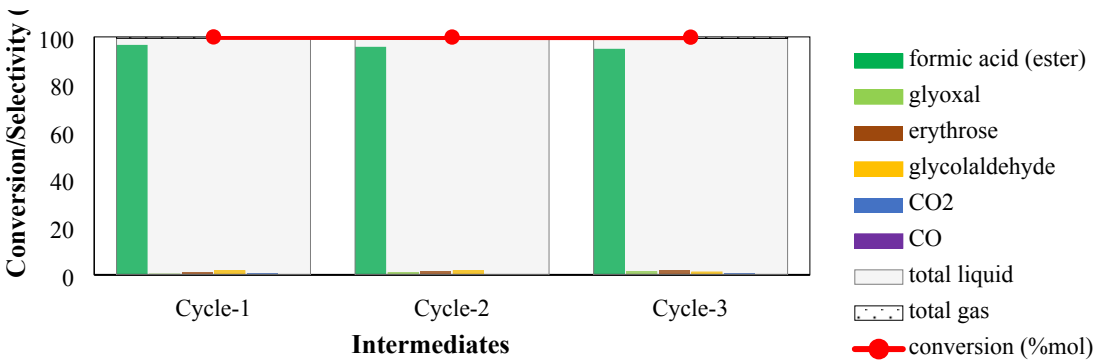

Figure S12. Catalyst recycling over three consecutive runs; Reaction conditions: 0.1 mmol HPA-5 catalyst 1 mmol glucose (added after each run) dissolved in 10 mL methanol, 20 bar O2 pressure, 90 °C, 24 h, 1000 rpm.

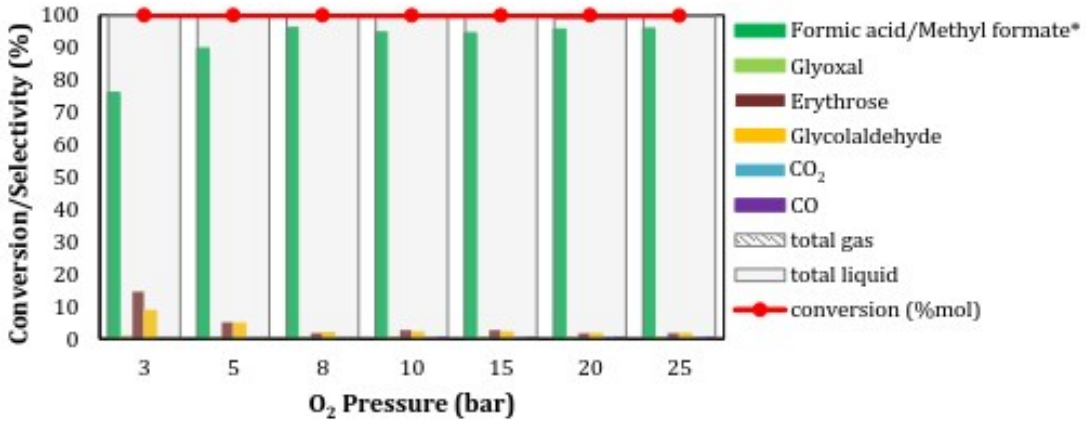

Figure S13. Variation of oxygen partial pressure; Reaction conditions: 0.1 mmol HPA-5 catalyst 1 mmol glucose dissolved in 10 mL methanol, 3-25 bar O2 pressure, 90 °C, 24 h, 1000 rpm.

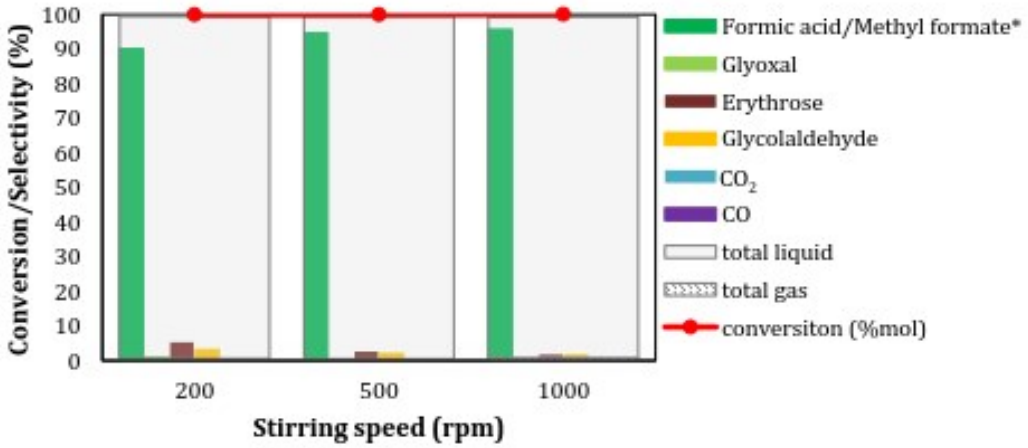

Figure S14. Variation of oxygen partial pressure; Reaction conditions: 0.1 mmol HPA-5 catalyst 1 mmol glucose dissolved in 10 mL methanol, 20 bar O2 pressure, 90 °C, 24 h, 200-1000 rpm.