

Selective Oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran over Intercalated Vanadium Phosphate Oxides

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Supplementary information

Experimental section:

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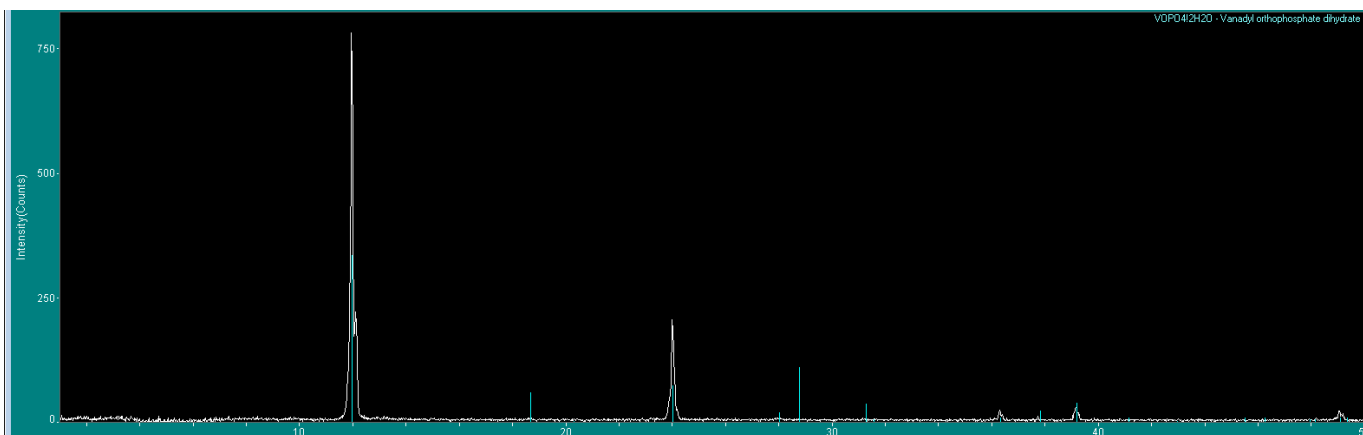
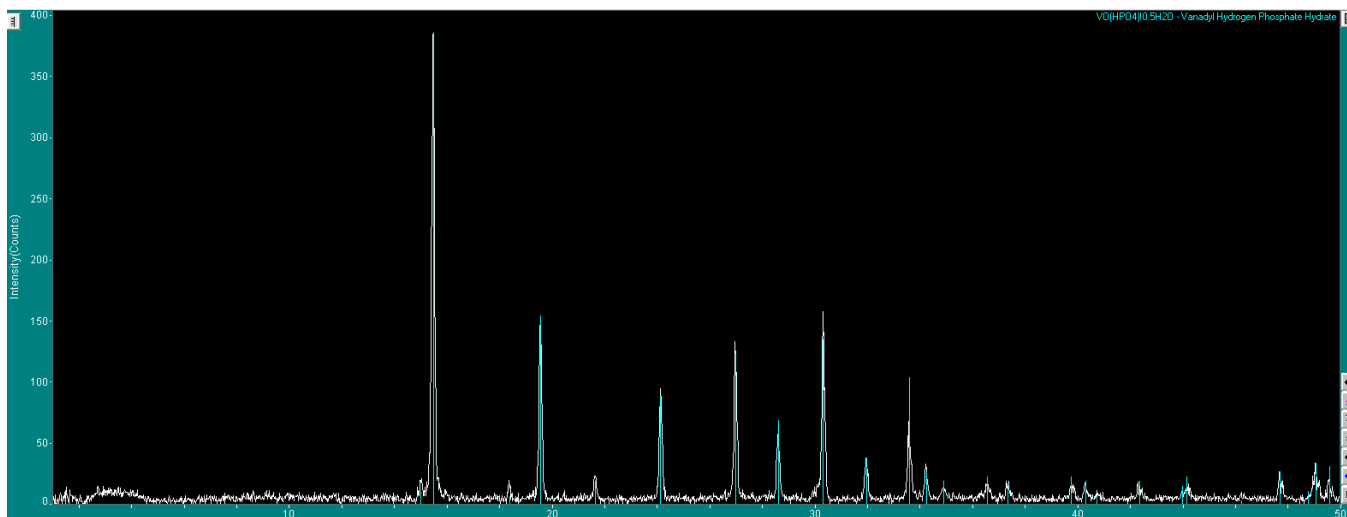


Fig. S1: Powder XRD pattern of VOPO₄·2 H₂O compared to the standard VOPO₄·2 H₂O (JCPDS 36-1472). The same reflexions were obtained by Kamiya *et al.*¹



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Fig. S2: Powder XRD pattern of VOHPO₄·0.5 H₂O compared to the standard VOHPO₄·0.5 H₂O (JCPDS 37-0269).

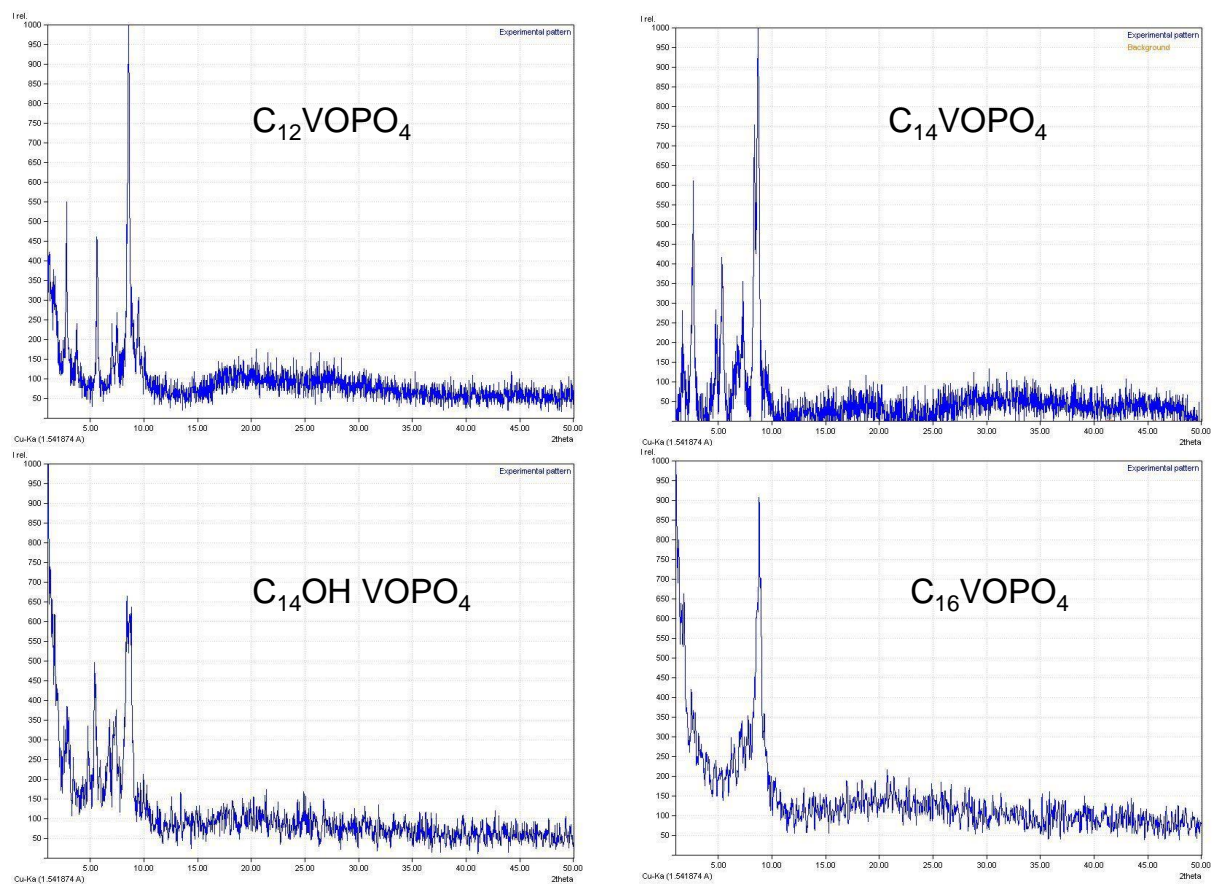


Fig. S3: Powder XRD patterns of the solids obtained by intercalation of C_n TAB in $VOPO_4 \cdot 2H_2O$ ($n = 10, 12, 14, 16$).

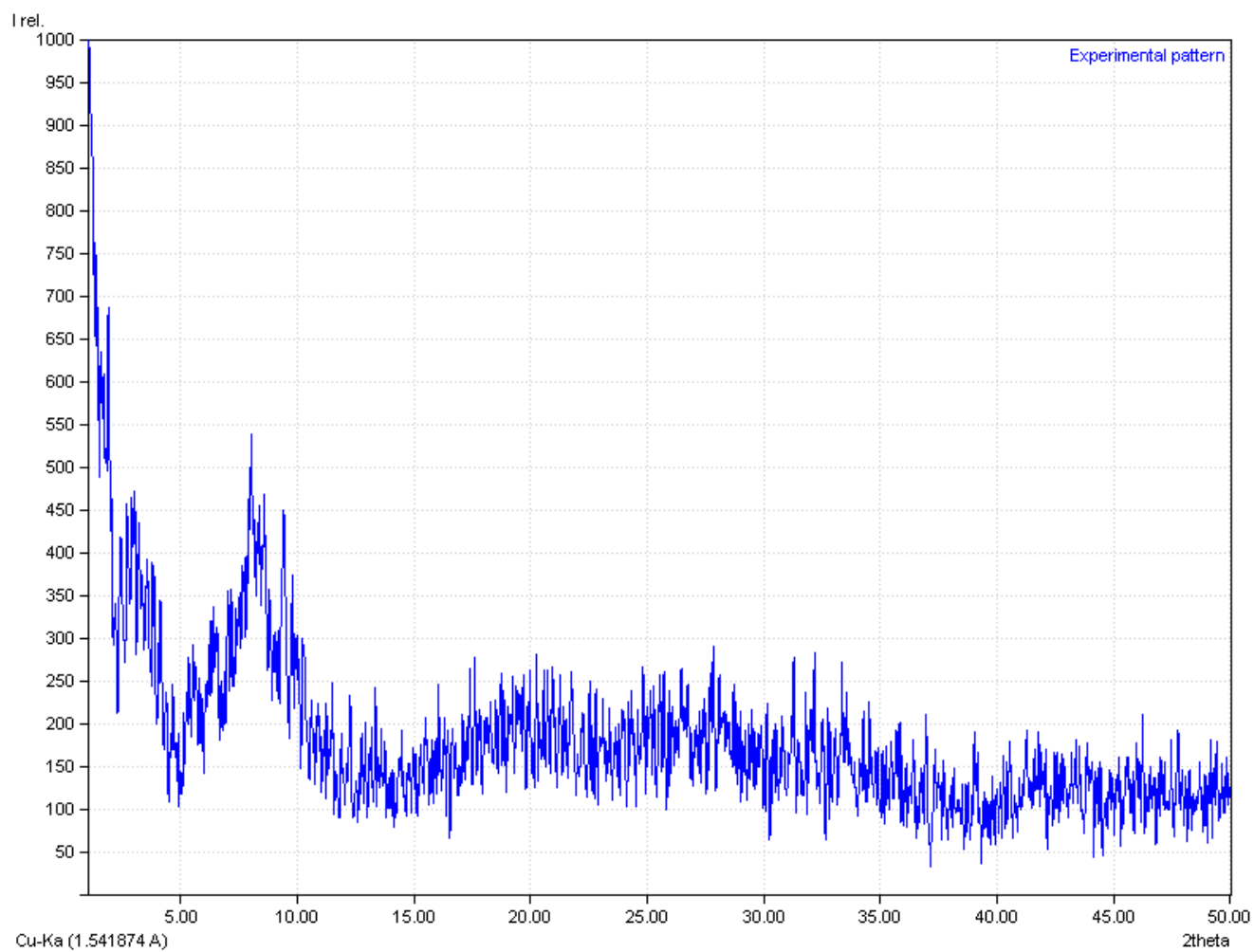


Fig. S4: Powder XRD pattern of $C_{14}VOHPO_4$.

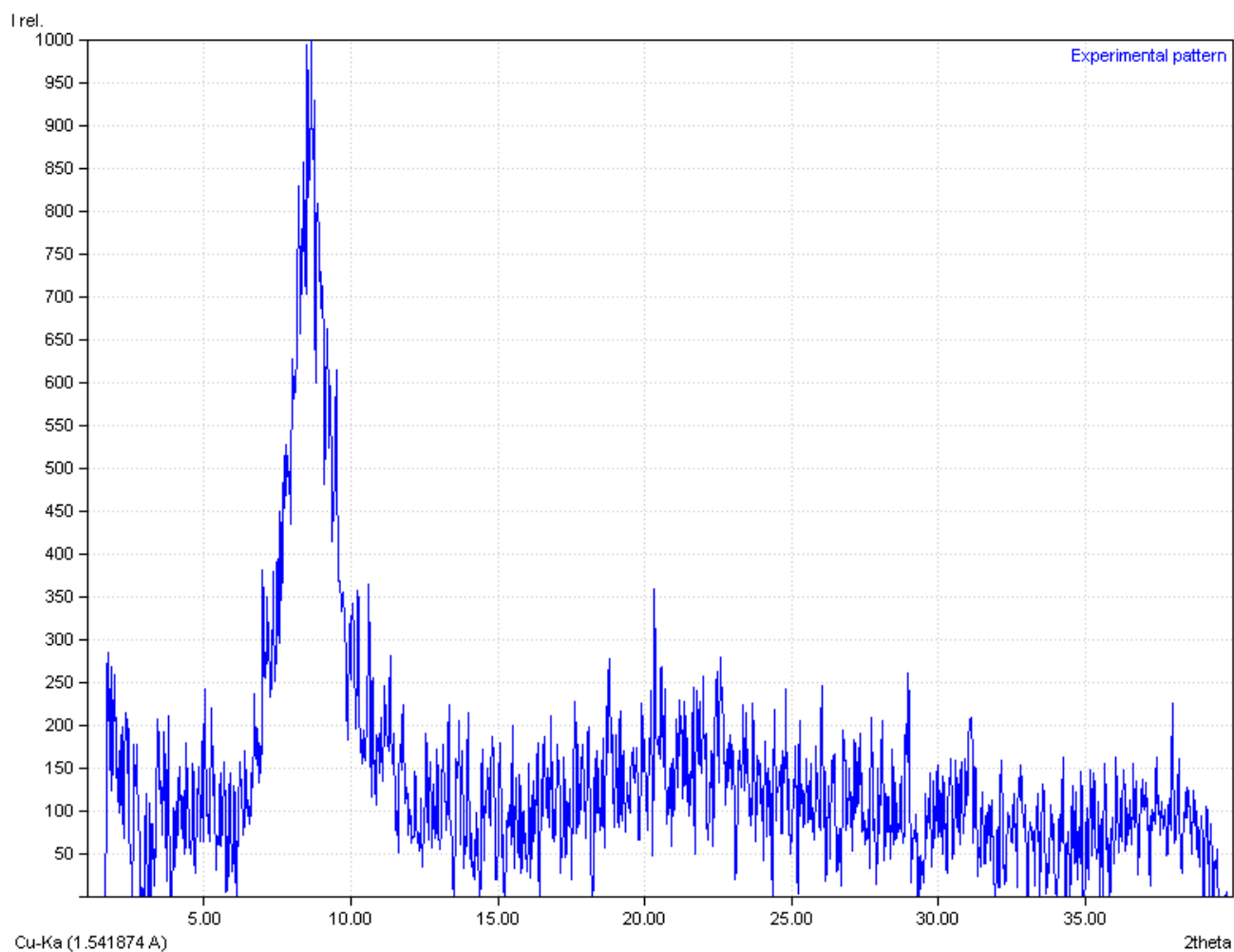


Fig. S5: Powder XRD pattern of spent $C_{14}VOPO_4$.

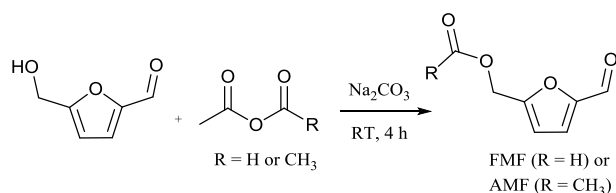
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Table S1: Elemental analysis of intercalated VPOs.

Catalyst	V (wt.%)	P (wt.%)	N (wt.%)	Br (wt.%)	V/P	N/P	Br/P
$C_{10}VOPO_4$	30.12	1.16	2.62	0.55	26.0	2.3	0.5
$C_{12}VOPO_4$	28.63	1.08	2.59	0.50	26.5	2.4	0.5
$C_{14}VOPO_4$	27.24	1.10	2.44	0.57	24.8	2.2	0.5
$C_{14}VOHPO_4$	26.60	1.61	2.44	0.68	16.5	1.5	0.4
$C_{14}OHVOPO_4$	26.68	1.05	2.65	-	25.4	2.5	-
$C_{16}VOPO_4$	25.81	0.97	2.34	0.34	26.6	2.4	0.4
Spent $C_{14}VOPO_4$	22.57	0.91	1.89	< 0.2	24.8	2.1	< 0.2

Synthesis of reference molecules:

The synthesis of AMF and FMF was performed by adapting a literature procedure.²



Scheme S1: Synthesis of AMF and FMF.

5 Synthesis of AMF:

5-HMF (0.13 g, 1.0 mmol, 1 eq.), acetic anhydride (1 mL) and Na₂CO₃ (0.21 g, 2.0 mmol, 2 eq.) were stirred at room temperature for 4 h. The mixture was extracted with diethylether (3 × 2 mL), and the organic layer was washed with water (3 × 5 mL) and brine (5 mL). Removal of the volatiles gave an orange oil, which was analysed without any further purification. ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 2.10 (s, 3H, CH₃), 5.11 (s, 2H, CH₂), 6.58 (d, *J* = 3 Hz, 1H, C-H), 7.20 (d, *J* = 3 Hz, 1H, C-H), 9.63 (s, 1H, COH). GC-MS: [M]⁺
10 (*m/z*) = 168.

Synthesis of FMF:

Acetic anhydride (0.75 mL) and formic acid (0.25 mL) were mixed at room temperature and then stirred at 60 °C for 1 h. After cooling the solution to room temperature, 5-HMF (0.13 g, 1.0 mmol, 1 eq.) and Na₂CO₃ (0.21 g, 2.0 mmol, 2 eq.) were added, and the mixture was stirred at room temperature for 4 h. The mixture was then extracted with diethylether (3 × 2 mL), and the organic layer was washed with
15 water (3 × 5 mL) and brine (5 mL). Removal of the volatiles gave an orange oil, which was analysed without any further purification. ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 5.20 (s, 2H, CH₂), 6.60 (d, *J* = 3 Hz, 1H, C-H), 7.21 (d, *J* = 3 Hz, 1H, C-H), 8.09 (s, 1H, OCOH), 9.60 (s, 1H, COH). The product was contaminated by a small amount of AMF (15 mol.% based on NMR). GC-MS: [M]⁺ (*m/z*) = 154.

5-(2-furaldehyde)methyl formate (FMF) identification:

GC-MS analysis of the reaction media

$C_{14}VOPO_4$ (15 mg) was introduced to a reaction tube, and 3 vacuum/oxygen cycles were performed. A solution of 5-HMF (0.1 M, 3 mL) was added, and the mixture was heated to 110 °C under oxygen atmosphere while stirring (800 rpm). After 6 h, the tube was cooled down to room temperature and a clear solution was recovered by syringe filtration. The recovered solution was analyzed by GC-MS (Fig. S6).

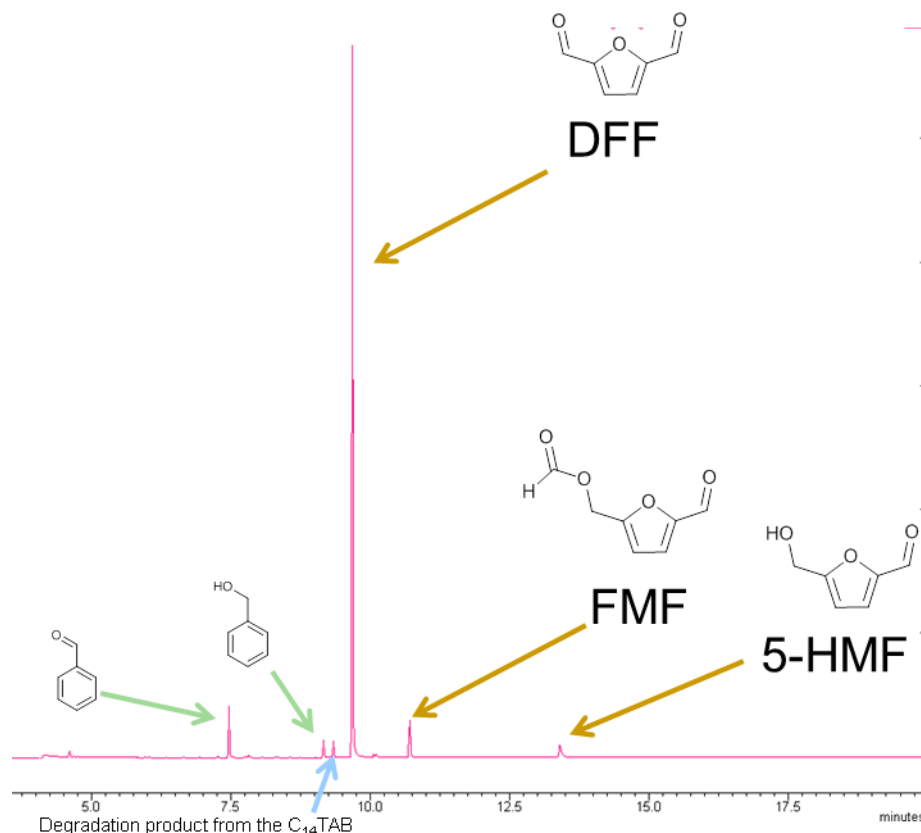


Fig. S6: GC-MS chromatogram of the 5-HMF oxidation reaction medium after reaction under O_2 (1 atm.) at 110 °C in toluene with $C_{14}VOPO_4$.

The mass spectrum recorded for the peak of FMF is reported below in red (Fig. S7), while the proposed spectrum for AMF is represented in blue. Indeed, the software automatically interpreted the compound under the peak at 10.7 min as AMF with 80% of probability. However, the experimental spectrum displayed a peak at $m/z = 154$, which cannot be explained by the fragmentation of AMF, but can be attributed to the molecular ion of FMF ($M = 154$ g/mol). In addition, no peak at $m/z = 168$ corresponding to the molecular ion of AMF was observed in the experimental spectrum. In order to confirm this finding, AMF and FMF were synthesised using the aforementioned procedures, and the mass fragmentation obtained by GC-MS are reported below (Figs. S18 and S9). The ion $[M+H]^+$ ($m/z = 169$) is detected, and no ion at ($m/z = 154$) is present in the fragmentation of the AMF. In contrast, upon analysis of FMF, the molecular ion $[M]^+$ ($m/z = 154$) is detected while no ion at ($m/z = 168$) or 169 were collected. This study confirmed that the main by-product formed during the oxidation of 5-HMF by VPO compound is FMF.

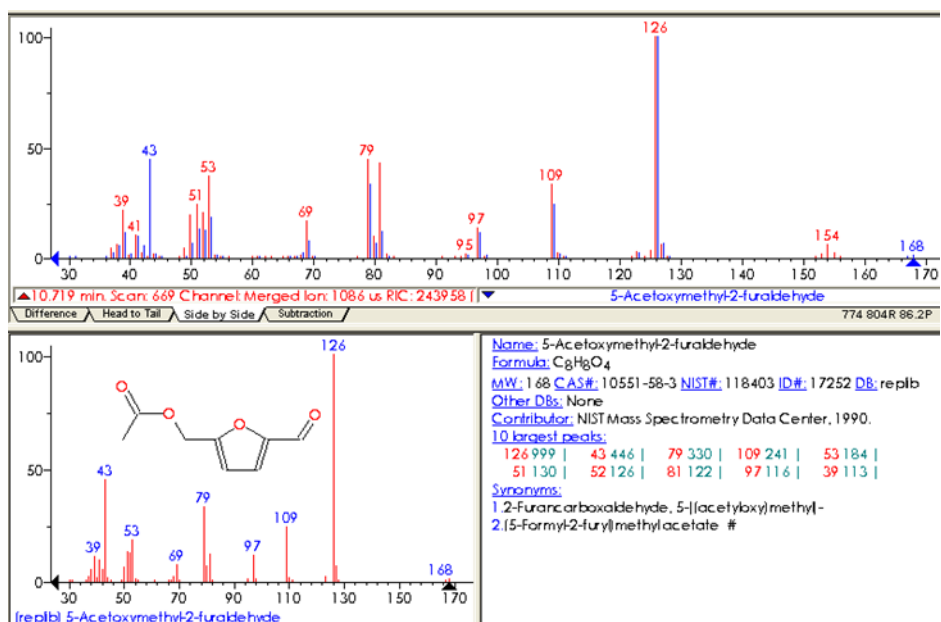


Fig. S7: MS spectrum of the by-product of the 5-HMF oxidation observed on GC-MS.

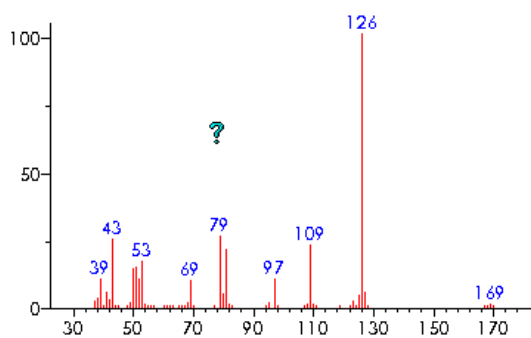


Fig. S8: MS spectrum of the synthesized AMF.

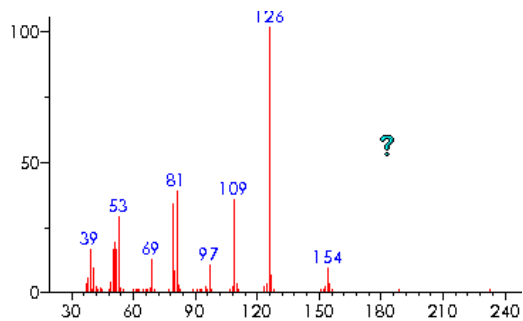


Fig. S9: MS spectrum of the synthesized FMF.

Catalytic oxidation of 5-HMF in CDCl_3

The oxidation of 5-HMF was performed using the general procedure described in the Experimental section of the manuscript, but with $\text{C}_{14}\text{VOPO}_4$ (15 mg) and CDCl_3 (3 mL) placed under reflux. The reaction mixture was analysed by $^1\text{H-NMR}$, which, in addition to the peaks of DFF and 5-HMF, confirmed the presence of small amounts of FMF (Fig. S10), this observation being definitely consistent with the GC-MS analysis.

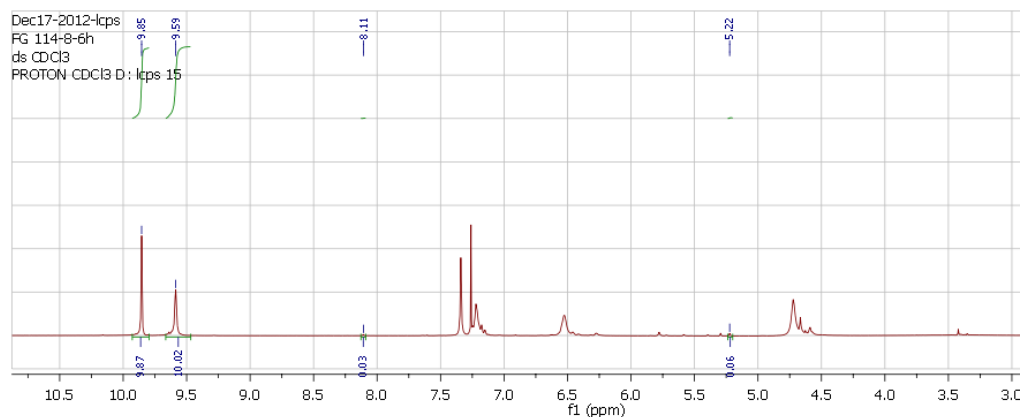
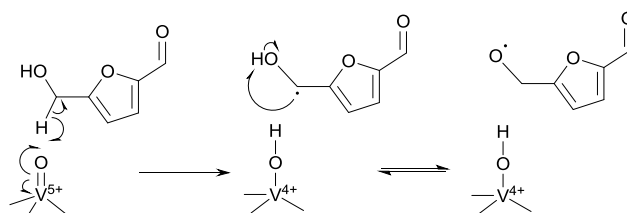


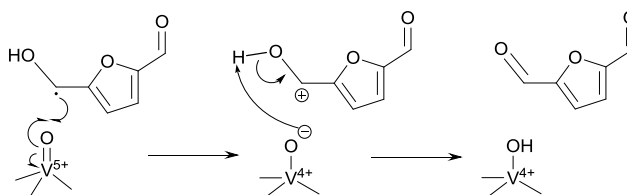
Fig. S10: $^1\text{H NMR}$ spectrum of the oxidation reaction medium in CDCl_3 .

All this body of experiments support that the by-product obtained in our work is actually FMF instead of AMF, as claimed by Carlini *et al.*³

Potential intermediate species:



Scheme S2 Possible interaction between $\text{C}_{14}\text{VOPO}_4$ and 5-HMF.



Scheme S3 Possible mechanism for the formation of DFF on $\text{C}_{14}\text{VOPO}_4$.

Notes and references

- 1 Y. Kamiya, N. Yamamoto, H. Imai, S. i. Komai, and T. Okuhara, *Micropor. Mesopor. Mat.*, 2005, **81**, 49.
- 2 Y. Katafuchi, T. Fujihara, T. Iwai, J. Terao, and Y. Tsuji, *Adv. Synth. Catal.*, 2011, **353**, 475.
- 5 3 C. Carlini, P. Patrono, A. M. R. Galletti, G. Sbrana, and V. Zima, *Appl. Catal. A: Gen.*, 2005, **289**, 197.