Supporting Information

Amphiphilic dipyridinium-phosphotungstate as efficient and recyclable catalyst for triphasic fatty-ester epoxidation and oxidative cleavage with hydrogen peroxide

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Literature comparison

Table S1: Reported activities of selected, best performing tungstate catalysts for the epoxidation of methyl oleate or olefins

Catalyst	Substrate	Eq. H_2O_2	Solvent	Temp (°C)	Time (h)	Conv.[a]	Sel.	TON	TOF (h^{-1})	Acc. TON	REF
$[DP^{2+}]_3[PPW^{3-}]_2$	Methyl oleate	1.32	Neat	60	3	98%	96%	447	149	1868 (5 cycles)	This work
$[Me(n\text{-}C_8H_{17})_3N]_3[PO_4[WO(O_2)_2]_4]$	Methyl oleate	2	Neat	60	5	94%	95%	940	188	940 (not recyclable)	[1]
Fe@PILPW-AM	Methyl oleate	0.4	MeCN	70	6	37%	95%	124	21	375[b] (3 cycles)	[2]
DIM-CIM-PW	Cyclooctene	1.2	EtOAc	60	6	100%	100%	167	28	830 (5 cycles)	[3]
$(Bu_4N)_4(SiW_{10}O_{34}(H_2O)_2)$	Cyclooctene	0.2	MeCN	32	2	20%	99%	124	62	620 (5 cycles)	[4]
W-Zn/SnO_2	Cyclooctene	2[c]	DMC	60	4	99%	99%	30	8	149 (5 cycles)	[5]
Poly(dipyridinium) $PW_{12}O_{40}$	4-decen-1-ol	2.5	Neat	50	24	92%	100%	460	19	2885 (6 cycles)	[6]

[a] Conversions in this table are shown respective to the alkene. Entries with low conversions used H_2O_2 as limiting reagent.

[b] Recycling tests performed with DL-Limonene, not methyl oleate.

[c] H_2O_2 60% was used in this case, which increases the reaction rate. Most of the literature uses 30% or 35%.

Complimentary Experimental Section

Synthesis of $(C_{41}H_{72}N_2)(WO_6)$

$(C_{41}H_{72}N_2)(WO_6)$ was recognized as a possible side product during the synthesis of $(C_{41}H_{72}N_2)_3(PW_4O_{24})_2$. Therefore $(C_{41}H_{72}N_2)(WO_6)$ was purposely synthesized and tested for the epoxidation of methyl oleate as a control experiment to determine the detrimental effects of this side product.

Tungstic acid (100 mg, 0.4 mmol, 1 eq.) is suspended in 8 mL of H_2O_2 30% (79.7 mmol, 200 eq.). The suspension is heated to 60 °C for 10 minutes, until the solid has dissolved and the solution becomes transparent. The solution is then diluted with 10 mL of methanol. A solution of 4,4’-(trimethylene)bis(1-tetradecylpyridinium) dibromide (300 mg, 0.4 mmol, 1 eq.) in 10 mL of methanol is slowly added to the first solution over 10 minutes, during which the product precipitates in solution as a bright orange solid. The mixture is left to cool down to room temperature and stirred for 1 h. The solid is filtered and washed with water and acetonitrile. 288 mg recovered (83% yield).

Catalytic epoxidation of methyl oleate using $(C_{41}H_{72}N_2)(WO_6)$ as catalyst

Methyl oleate (500 mg, 1.69 mmol, 1 eq.), $(C_{41}H_{72}N_2)(WO_6)$ (16.2 mg, 0.02 mmol, 0.01 eq.) and H_2O_2 30% (222 µL, 2.23 mmol, 1.32 eq.) were added to a 20 mL flask and stirred at room temperature for 20 h. After the reaction, the mixture was diluted with 10 mL of ethyl acetate. A sample of the organic phase was removed, filtered and analysed by GC-MS.

Analysis showed 3% conversion with 94% selectivity for the epoxidation using $(C_{41}H_{72}N_2)(WO_6)$. In comparison, the active catalyst $(C_{41}H_{72}N_2)_3(PW_4O_{24})_2$ achieved 84% conversion and 100% selectivity in only 4 hours at room temperature, using the same catalyst loading (0.01 eq.). Therefore, the production of the side product $(C_{41}H_{72}N_2)(WO_6)$ is significantly detrimental to the activity of the catalyst and must be avoided.

Catalytic epoxidation of linoleic acid using $(C_{41}H_{72}N_2)_3(PW_4O_{24})_2$ as catalyst

Linoleic acid (500 mg, 1.78 mmol, 1 eq.), $(C_{41}H_{72}N_2)_3(PW_4O_{24})_2$ (8.00 mg, 0.0039 mmol, 0.0022 eq.) and H_2O_2 30% (427 µL, 4.28 mmol, 2.4 eq.) were added to a 20 mL flask and stirred at 60 °C for 2 h. After the reaction, a sample of the organic phase was diluted with $CDCl_3$ and analysed by ^1H NMR.

Catalytic epoxidation of ricinoleic acid using $(C_{41}H_{72}N_2)_3(PW_4O_{24})_2$ as catalyst

Ricinoleic acid (500 mg, 1.68 mmol, 1 eq.), $(C_{41}H_{72}N_2)_3(PW_4O_{24})_2$ (7.52 mg, 0.0036 mmol, 0.0022 eq.) and H_2O_2 30% (221 µL, 2.21 mmol, 1.32 eq.) were added to a 20 mL flask and stirred at 60 °C for 2 h. After the reaction, a sample of the organic phase was diluted with $CDCl_3$ and analysed by ^1H NMR.

Catalytic epoxidation of cyclooctene using $(C_{41}H_{72}N_2)_3(PW_4O_{24})_2$ as catalyst

Cyclooctene (591 µL, 4.54 mmol, 1 eq.), $(C_{41}H_{72}N_2)_3(PW_4O_{24})_2$ (18.5 mg, 0.009 mmol, 0.0022 eq.) and H_2O_2 30% (598 µL, 5.99 mmol, 1.32 eq.) were added to a 20 mL flask and stirred at 60 °C for 3 h. After the reaction, the mixture was diluted with 10 mL of ethyl acetate. A sample of the organic phase was removed, filtered and analysed by GC-MS.

Catalytic epoxidation of cyclohexene using $(C_{41}H_{72}N_2)_3(PW_4O_{24})_2$ as catalyst

Cyclohexene (247 µL, 2.43 mmol, 1 eq.), $(C_{41}H_{72}N_2)_3(PW_4O_{24})_2$ (10.93 mg, 0.005 mmol, 0.0022 eq.) and H_2O_2 30% (321 µL, 3.21 mmol, 1.32 eq.) were added to a 20 mL flask and stirred at 60 °C for 3 h. After the reaction, the mixture was diluted with 10 mL of ethyl acetate. A sample of the organic phase was removed, filtered and analysed by GC-MS.

Catalytic epoxidation of styrene using $(C_{41}H_{72}N_2)_3(PW_4O_{24})_2$ as catalyst

Styrene (275 µL, 2.40 mmol, 1 eq.), $(C_{41}H_{72}N_2)_3(PW_4O_{24})_2$ (10.77 mg, 0.005 mmol, 0.0022 eq.) and H_2O_2 30% (276 µL, 2.76 mmol, 1.32 eq.) were added to a 20 mL flask and stirred at 60 °C for 3 h. After the reaction, the mixture was diluted with 10 mL of ethyl acetate. A sample of the organic phase was removed, filtered and analysed by GC-MS.

Colorimetric analysis

The inactive species $(C_{41}H_{72}N_2)(WO_6)$ showed a bright orange color that could be used to determine its presence during the catalyst optimization experiments (Table 1), compared to the white color of $(C_{41}H_{72}N_2)_3(PW_{12}O_{40})_2$ and $(C_{41}H_{72}N_2)_3(PW_4O_{24})_2$. Although these samples could not be dissolved in any solvents for a proper UV-vis analysis, the activity of the catalyst could still be visually correlated with the color of the catalyst.

Of particular interest was the optimization of the ratio between **DP**$^{2+}$ and $H_3PW_{12}O_{40}$ used (Table 1, entries 4, 6 and 7). When using a 3:2 ratio (Table 1, entry 4) to produce (**DP**$^{2+}$)$_3$(**PPW**$^{3-}$)$_2$, the solid obtained was a pale yellow, which we attributed to the contamination of (**DP**$^{2+}$)$_3$(**PPW**$^{3-}$)$_2$ with inactive (**DP**$^{2+}$)(WO_6^{2-}). When using an excess of **DP**$^{2+}$ in a 5:1 ratio (Table 1, entry 6), the solid obtained was orange. Under these conditions, there is enough excess of **DP**$^{2+}$ to precipitate all of the phosphptungstate species, leaving 2.5 equivalents of **DP**$^{2+}$, which is able to entrain a large amount of WO_6^{2-}. So now a large amount of (**DP**$^{2+}$)(WO_6^{2-}) is produced, consistent with the orange color observed. When using an excess of $H_3PW_{12}O_{40}$ in a 1:2 ratio (Table 1, entry 7), a white product was obtained, which was much more active than previous experiments. The white color is consistent with absence of (**DP**$^{2+}$)(WO_6^{2-}).

The speed of reagent addition was also a critical point in our experiment. The synthesis of (**DP**$^{2+}$)$_3$(**PPW**$^{3-}$)$_2$ was repeated by adding the solution of **DP**$^{2+}$ at different rates. It was found that a fast addition would always yield a yellow, less active catalyst, no matter how high the excess of $H_3PW_{12}O_{40}$ and H_2O_2 used. In order to obtain a white active catalyst, the solution of **DP**$^{2+}$ had to be added dropwise. The slow addition enhances the difference of reaction rates between $PW_4O_{24}^{3-}$ and WO_6^{2-}, in favour of the active product. Since the solvent used is polar (a mixture of acetonitrile, water and hydrogen peroxide), the higher charge trianion of $PW_4O_{24}^{3-}$ will bind to the cationic **DP**$^{2+}$ faster than the dianion WO_6^{2-}.

NMR study of solvent effects

In order to produce the catalyst, the phase transfer agent (**DP^{2+}**)(Br$^-$)$_2$ had to be dissolved and added to the solution of phosphotungstic acid in hydrogen peroxide. This requires an additional solvent to dissolve (**DP^{2+}**)(Br$^-$)$_2$. Since (**DP^{2+}**)(Br$^-$)$_2$ was purified by recrystallization in boiling water, this was the obvious solvent to use, as hydrogen peroxide is already diluted in water. However, water was found to be a poor solvent because the product would precipitate too quickly and it would always yield a yellow product, which shows the presence of the inactive (**DP^{2+}**)(WO_6^{2-}). (**DP^{2+}**)(Br$^-$)$_2$ could only be dissolved using small alcohols (methanol, ethanol), $CHCl_3$, DMF, DMSO and warm acetonitrile (above 50 °C). DMSO was immediately discarded as it reacts violently with the phosphotungstate in hydrogen peroxide. DMF gave similar results to methanol but was discarded for its toxicity and price.

The effect of solvents on the equilibrium of peroxidized phosphotungstate species was studied by ^{31}P NMR before the addition of (**DP^{2+}**)(Br$^-$)$_2$. The results are shown in fig. S1.

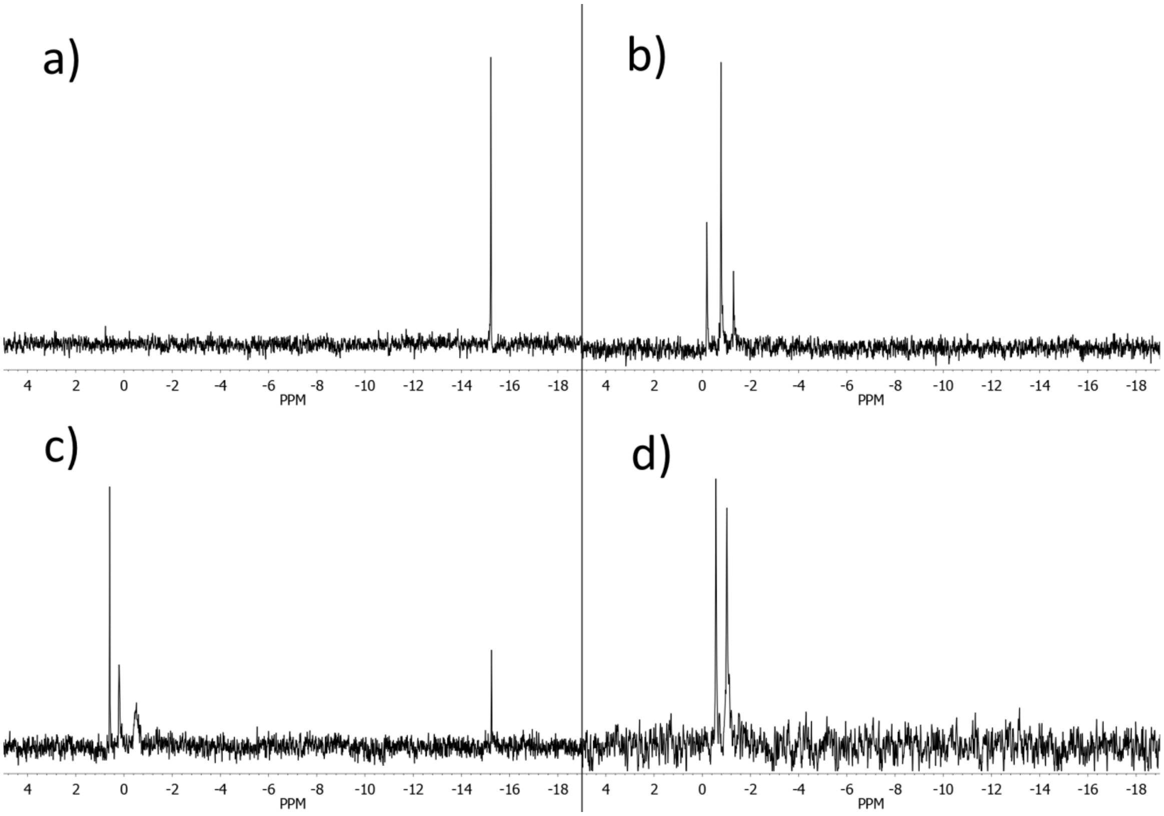

Fig. S1: ^{31}P NMR spectra. a) $H_3PW_{12}O_{40}$ in D_2O, b) $H_3PW_{12}O_{40}$ with 200 eq. of H_2O_2 in D_2O, c) $H_3PW_{12}O_{40}$ with 200 eq. of H_2O_2 in CD_3OD, d) $H_3PW_{12}O_{40}$ with 200 eq. of H_2O_2 in D_2O/MeCN.

The first notable result was that when phosphotungstic acid is oxidized with hydrogen peroxide, the ^{31}P NMR spectrum shows three peaks at -0.3 ppm, -0.9 ppm and -1.4 ppm. This result shows that the formation of the Venturello anion PW_4O_{24} does not occur exclusively in absence of a stabilizing counter cation. When methanol was used as co-solvent, the peaks shifted to 0.3 ppm, -0.2 ppm and a broadened peak at -0.8 pm, but more importantly, a peak at -15.3 ppm appeared, which belongs to the precursor, $H_3PW_{12}O_{40}$. This is possibly due to methanol being oxidized to formaldehyde as a side reaction, which depletes the active peroxophosphotungstate and allows the precursor to regenerate. Acetonitrile gave rise to two clean peaks at -0.6 ppm and -1.0 ppm with no precursor, which explains why the catalyst synthesized in acetonitrile gives better results.

A similar solvent effect can also be observed via solid state MAS ^{31}P NMR (Fig. S2).

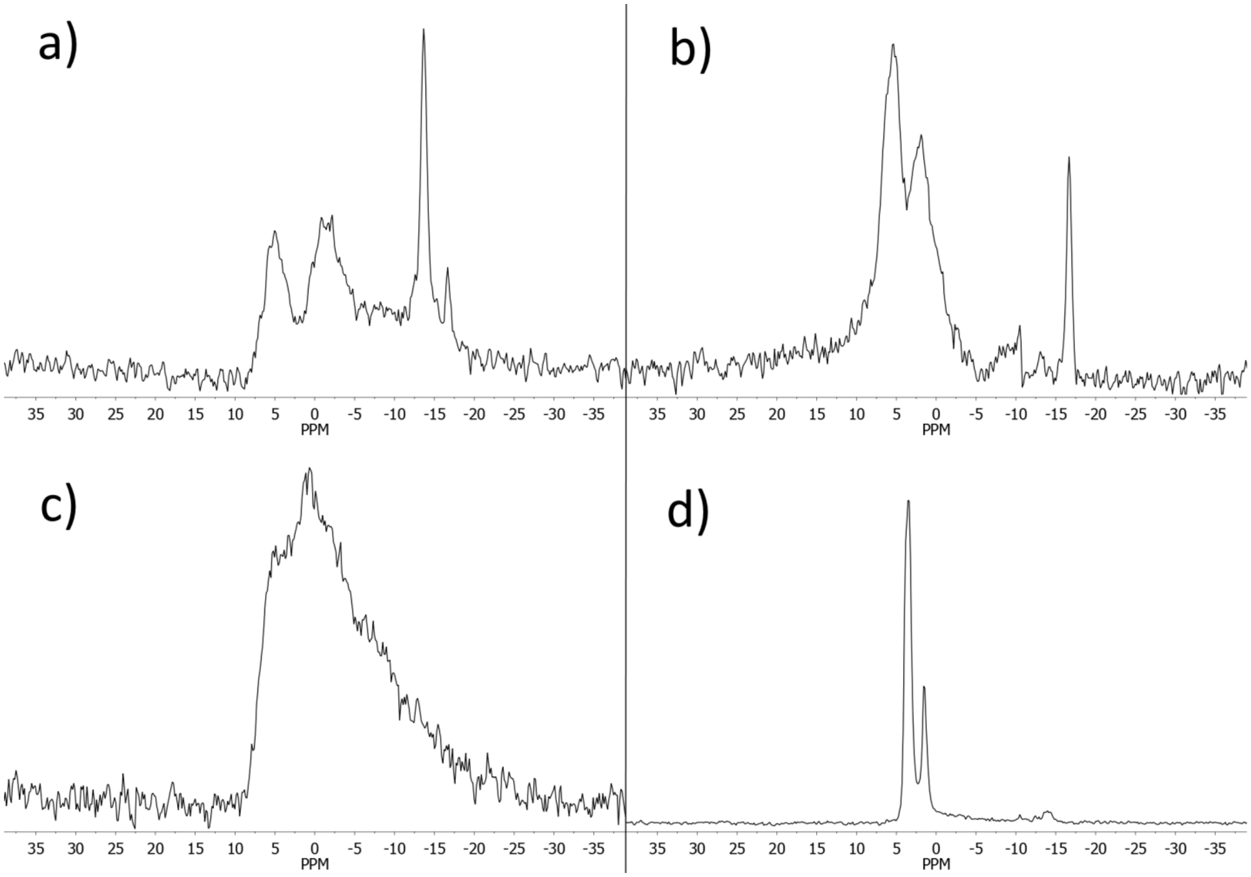

Fig. S2: MAS ^{31}P NMR spectra of catalyst $(C_{41}H_{72}N_2)_3(PW_4O_{24})_2$ synthesized with a) H_2O b) MeOH c) $CHCl_3$ d) MeCN.

When the catalyst was synthesized using water, multiple peaks were observed between 8 and 16 ppm, with the largest signal at -13.7 ppm, which belongs to an intermediate with a low degree of peroxidation. When using methanol, two broad signals were observed between 10 ppm and -5 ppm, which should be highly peroxidized species, as well as a peak at -16.5 which shows that some of the inactive non-oxidized phosphotungstate co-precipitated. When using chloroform, a very broad peak was observed between 8 and -20 ppm, which is likely a complex mixture of partially peroxidized phosphotungstates. The catalyst synthesized with acetonitrile shows the peaks of highly peroxidized species at 3.5 ppm, and 1.5 ppm, both peaks being much better resolved than with the other solvents. There is also a very small peak at -13.9 ppm, which should be an intermediate with a low degree of peroxidation. It is important to notice that the catalysts produced in water and chloroform were visibly yellow which demonstrates the presence of the inactive (**DP**$^{2+}$)(WO_6^{2-})$_2$, which does not contain phosphorus and is therefore not visible by ^{31}P NMR.

SEM characterization

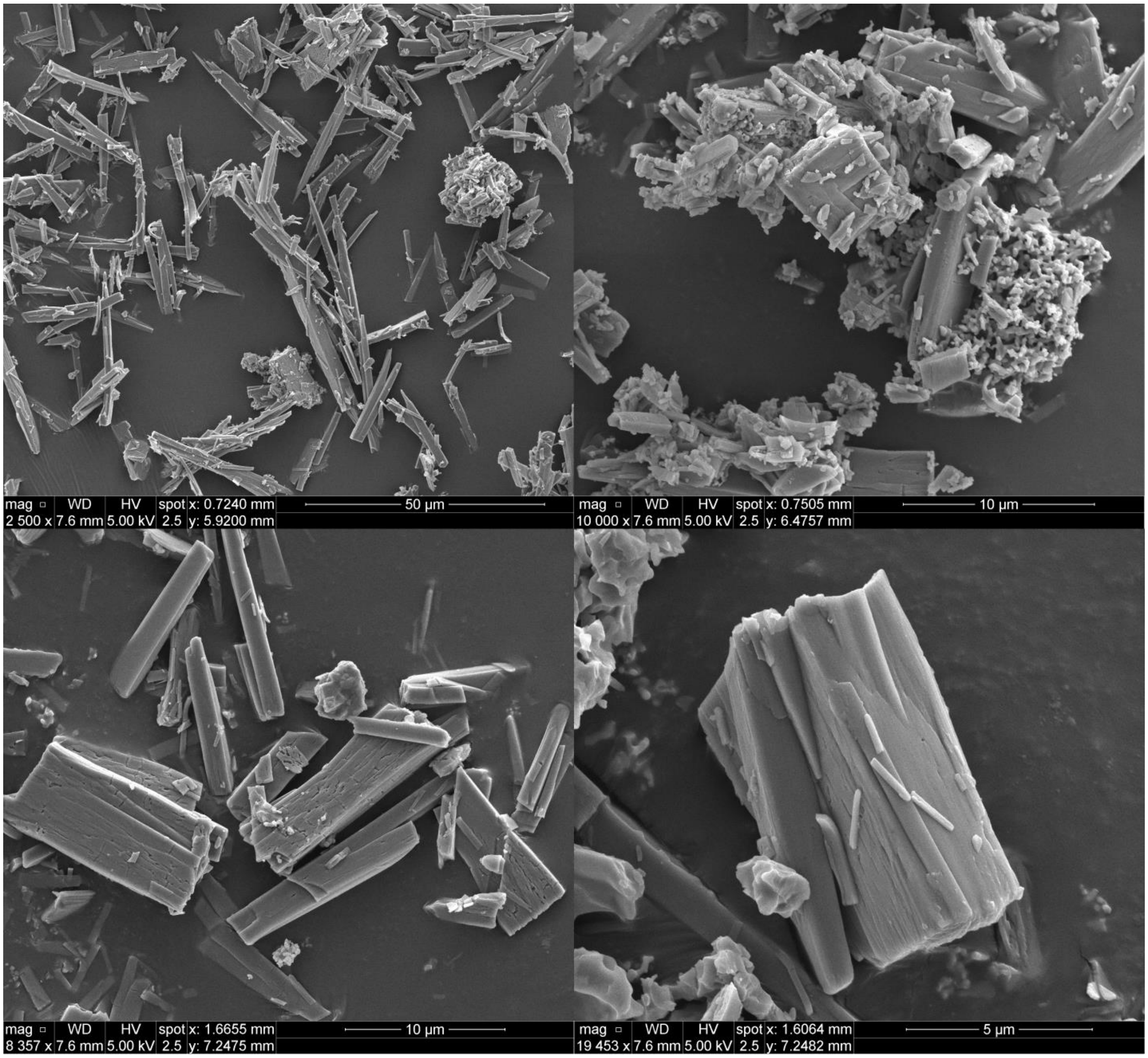

Fig. S3: SEM pictures of ([**DP^{2+}**]$_3$[**PPW^{3-}**]$_2$) as synthesized using conditions from Table 1 entry 9.

From the SEM pictures, it can be observed that the product has two distinct regions. The majority of the sample observed arranged itself in the shape of rectangular prisms, which range between 1 µm and 50 µm in length, with height and width between 0.5 and 5 µm. These slabs agglomerate at random while retaining their shape. The second region observed is an amorphous agglomeration with no determined size or shape, which appears to be the result of particle growth in random directions, and is consistent with the ^{31}P MAS NMR analysis that shows the product is not a single pure compound, but a mixture.

Catalyst recovery and recycling

Fig S4: Picture of a typical catalytic test for the epoxidation of methyl oleate (water and EtOAc added to increase the volumes of each phase for clarity). The catalyst ([**DP^{2+}**]$_3$[**PPW^{3-}**]$_2$) floats between the organic phase (top) and the aqueous phase (bottom).

The catalyst ([**DP^{2+}**]$_3$[**PPW^{3-}**]$_2$) was designed to be immiscible in both the organic and the inorganic phases, as can be clearly seen in fig 3. In order to recycle the catalyst, we tested a few strategies. Simple filtration allowed to recover clean product, but made catalyst recovery largely inefficient. Given the small amounts of catalyst used for most experiments (7.6 mg of catalyst for a 0.22mol% test), we turned to centrifugation which allowed to have the solid catalyst adhere strongly to the bottom of the flask, while both liquid phases could be removed with a pipette.

Recycling tests using 1mol% catalysts allowed for efficient recycling and high activity and selectivity upon 5 cycles. When 0.022mol% was used the catalyst activity dropped after 3 cycles. The low loading, however, allowed after 5 cycles to achieve a high cumulated TON of 1868 (Table S2). Specifically, significant loss of activity was observed after TON exceeded 1300. This drop is not consistent with loss of catalyst as a leaching of 5.3% in tungsten was measured in the larger scale experiment (Table 2, entry 8). Thermal degradation was ruled out as a cause of degradation by pre-heating the catalyst for 24 hours, after which the catalyst showed normal activity. Therefore the loss of catalytic activity appears to correlate with catalyst degradation after extensive number of cycles.

Table S2: High TON recyclings.

Cycle	Conversion	Selectivity	Accumulated TON	Accumulated TOF
1	98%	96%	446	149
2	97%	96%	886	148
3	92%	98%	1304	145
4	71%	100%	1626	135
5	53%	100%	1868	125

Reaction Conditions: 500 mg of methyl oleate (1 eq.), 7.6 mg of [**DP^{2+}**]$_3$[**PPW^{3-}**]$_2$ (0.0022 eq.), 222 µL H_2O_2 30% (1.32 eq.). Reaction is heated to 60 °C and stirred for 3 hours at this temperature.

Recycling conditions: The reaction mixture was diluted with 10 mL of ethyl acetate, centrifuged, and both liquid phases removed with a pipette. The solid catalyst remaining in the flask was dried with air for 1 minute.

References

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