

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

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A novel amphiphilic dipyridinium peroxo-phosphotungstate ion pair was developed as a selective and recyclable catalyst for the triphasic epoxidation of fatty acids and esters with hydrogen peroxide. The synthesis of the catalyst was studied extensively by solid and liquid phase <sup>31</sup>P nuclear magnetic resonance (NMR). The oxidation of vegetable oils is of prime importance for the production of lubricants, plasticizers, polymer stabilizers and other olefinic compounds. Based on the oxidizing activity of peroxophosphotungstates, we designed a lipophilic phase transfer agent that renders the active complex insoluble in the reaction media, without having to support it on a matrix. This affords a catalyst combining the activity of homogeneous catalysts and the recyclability of heterogeneous systems. We show that this catalyst is able to fully epoxidize methyl oleate with excellent selectivity, with a turnover frequency of 149 at 60 °C, and can be easily recycled, to reach a record turn over number of 1868. A larger scale experiment on 13 grams and a scope including linoleic and ricinoleic acids were also demonstrated. The catalyst also shows excellent activity and selectivity for the oxidative cleavage of methyl oleate and the oxidation of small olefins.

## Introduction

Biomass valorization constitutes a key instrument in the effort to mitigate global warming and its multiple environmental and economical consequences. Research in this area opens opportunities to address challenges such as the exploitation of non-edible resources and agricultural waste and transitioning out of fossil resources.<sup>1</sup> Among biomass sources, vegetable oils are the most important renewable raw material used in the chemical industry.<sup>2</sup> Vegetable oils consist of triglycerides with long lipophilic carbon chains, most of which feature one or several double bonds, depending on the oil source. These unsaturations can be oxidized to fabricate added-value products, such as epoxides, diols or carboxylic acids. Oxidized oil products are precursors for a variety of functional compounds such as lubricants, plasticizers, polymer stabilizers and other olefinic compounds.<sup>3</sup>

The most common industrial procedure to epoxidize oils is to use peroxyacids produced *in situ* from formic acid or acetic acid in the presence of hydrogen peroxide and sulfuric acid. While these reagents are cheap, they are used homogeneously

and are corrosive and toxic, requiring special equipment and safety measures. The oxidation with peroxyacids is also highly exothermic ( $\Delta H = 230 \text{ kJ.mol}^{-1}$ ),<sup>4</sup> which makes temperature control difficult at industrial scales and imposes a slow addition of hydrogen peroxide and catalyst with long cooling times to avoid a runaway reaction.<sup>4</sup> The addition of a strong mineral acid as co-catalyst also limits selectivity, since lowering the pH promoted the epoxide's ring-opening reaction *via* hydrolysis.<sup>5</sup>

In search for more sustainable approaches, peroxophosphotungstate catalysts were initially found to be active for the epoxidation of double bonds with hydrogen peroxide by Venturello *et al.*<sup>6, 7</sup> and triggered important research effort thereafter. To overcome the immiscibility of the oxidant (aqueous hydrogen peroxide) with the substrate (a fatty acid, ester or triglyceride), the active peroxophosphotungstate species ( $\text{PO}_4[\text{W}(\text{O})(\text{O}_2)_2]_4$ )<sup>3-</sup> trianion can be coupled with cationic phase transfer agents. This system prevents overheating hazards and efficiently affords epoxidized double bonds with higher selectivity and lower toxicity than peroxyacids. The oxidation method using peroxophosphotungstate species was further developed by Ishii *et al.* where they showed it can also be used to fully cleave double bonds into carboxylic acids and that phosphotungstic acid can be used as a convenient precursor to the active species.<sup>8</sup> However, this system is currently not economically viable compared to peroxyacids, because the catalyst is homogeneously dispersed and thus unrecoverable. Research has thus shifted towards creating recyclable catalysts that can be both cost-effective and efficient.

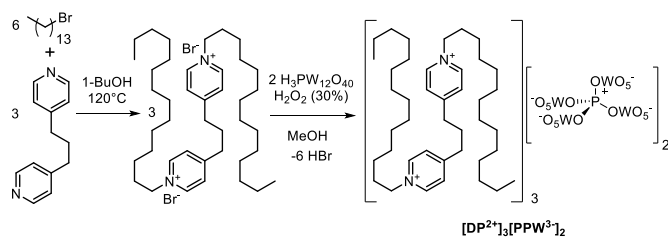
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Scheme 1: Synthetic procedure to access  $[\text{DP}^{2+}]_3[\text{PPW}^{3-}]_2$  catalyst.

In past reports, the phase transfer agent was engineered so that the catalyst can be extracted,<sup>9</sup> or precipitated, either by cooling the medium,<sup>10</sup> or designing the catalyst to become insoluble once the hydrogen peroxide has been consumed.<sup>11, 12</sup> Cationic supports have been shown to make the catalytic complex heterogeneous, such as polymers derived from ionic liquids,<sup>13</sup> functionalized silica,<sup>14</sup> or even magnetic iron oxide nanoparticles coated with either cationic polymers<sup>15</sup> or functionalized silica.<sup>16, 17</sup> Another common method is to immobilize the neutral complex of peroxophosphotungstate and phase transfer agent into a solid matrix, such as mesoporous silica,<sup>18</sup> amphiphilic copolymers grafted onto silica,<sup>19</sup> metal-organic frameworks,<sup>20</sup> or metallic supports.<sup>21</sup>

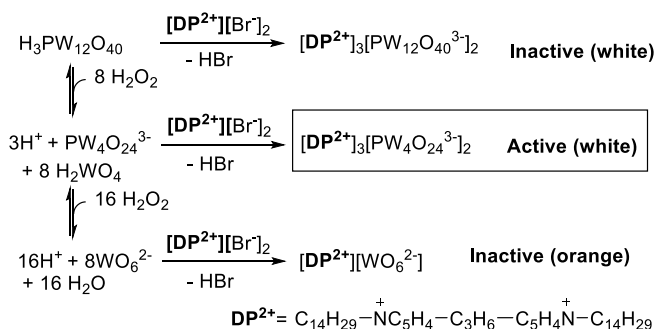
However, all the heterogeneous catalysts show reaction rates at least an order of magnitude lower than the best homogeneous counterparts (see Table S1). While direct comparisons are often not possible to make due to widely different conditions such as substrate scope, catalyst loading, temperature and solvent, it is still clear that heterogeneous systems are significantly less active. In order to be economically viable as a replacement of peroxyacids, both activity and recyclability need to be optimized.

Herein we report a novel catalytic system, using a dipyridinium dication ( $\text{DP}^{2+}$ ) as phase transfer agent paired with peroxophosphotungstate trianion ( $\text{PPW}^{3-}$ ), active for the oxidation of vegetable oils with hydrogen peroxide that bridges the gap between the homogeneous and heterogeneous systems. Our catalyst ( $[\text{DP}^{2+}]_3[\text{PPW}^{3-}]_2$ ) allows the reaction to function in a triphasic system – composed of an organic phase (the substrate), an aqueous phase (the oxidant) and a solid phase (the catalysts) – and shows reaction rates similar to reported homogeneous catalysts, while being easy to recycle through simple filtration and easy to synthesize from commercial reagents. The synthetic conditions for this well-defined complex were studied and characterization was performed by  $^{31}\text{P}$  magic angle spinning nuclear magnetic resonance ( $^{31}\text{P}$  MAS NMR) as well as scanning electron microscopy (SEM). Leaching during catalytic experiments was very limited as established by inductively coupled plasma mass spectrometry (ICP-MS) and a hot filtration test proved heterogeneous mechanism. Excellent results in terms of activity and selectivity were obtained for the epoxidation of methyl oleate, linoleic and ricinoleic acids, the oxidation of small alkenes to either the corresponding epoxide or diol and finally for the fully oxidative cleavage of methyl oleate. Recyclability of the system was also successfully tested.

## Results and Discussion

### Optimization of the Catalyst Synthesis

Our aim in this study was to design a cationic transfer agent able to form a complex with the active  $\text{PPW}^{3-}$ , while being insoluble in both the aqueous and the oil phase to achieve recovery. It should nonetheless retain enough hydrophilic interactions to regenerate the active peroxophosphotungstate species with hydrogen peroxide, enough lipophilic affinity to react with the substrate and cause limited leaching of the catalyst by ionic dissociation. Commercial ammonium and pyridinium surfactants are water soluble, and the catalytic complexes obtained using those phase transfer agents are thus homogeneous in the reaction mixture and not recyclable. Conversely, excessively lipophilic polymers have been found to fully deactivate the catalyst by preventing catalyst regeneration in the aqueous phase.<sup>13</sup> Indeed such supports typically rearrange to expose only their hydrophobic alkyl chains. We decided to use dicationic or tricationic surfactants, to optimize ion pairing with the catalyst. We initially explored the triammonium based on pentamethyldiethylenetriamine to match the charge of the phosphotungstate, but the resulting complex was very unstable and degraded quickly. After testing several diamines and dipyridines, we settled on using 4,4'-trimethylenedipyridine. Notably, it was found during its synthesis to be stable at least up to 120 °C and insoluble in water below 80 °C. A similar type of pyridinium was already proven to be very stable for supporting phosphotungstates by Yamada *et al.*<sup>22</sup> Sufficient lipophilicity was introduced by C14 carbon chains functionalization. Wu *et al.* showed that by increasing the length of the carbon chain on an alkylimidazolium, the activity towards the epoxidation of cyclohexene of the phosphotungstate-paired catalyst increased.<sup>11</sup> The synthesis of the dicationic phase transfer agent required only one step from commercially available substrates, followed by an ion exchange with  $\text{PPW}^{3-}$ , produced *in situ* by mixing phosphotungstic acid with excess hydrogen peroxide (scheme 1).

Scheme 2: Sequential oxidation of phosphotungstic acid by hydrogen peroxide and potential pairing with the amphiphilic dipyridinium ( $\text{DP}^{2+}$ ). Stoichiometry is not provided on the right end side of the scheme for clarity.

The oxidation of phosphotungstic acid into its activated peroxide prior to the ion exchange with 4,4'-trimethylenedipyridinium bromide was found to be crucial to obtaining an active catalyst. Although several reports in the literature showed that active catalysts can be obtained by

directly performing the ion exchange with  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ,<sup>11, 23</sup> or even mixing the surfactant and the phosphotungstate with the substrates *in situ*,<sup>24</sup> this scheme did not work in our hands using  $[\text{DP}^{2+}]$  as the phase transfer agent.

Table 1: Optimisation of catalyst synthetic conditions

Entry	Catalyst synthetic conditions			Methyl Oleate epoxidation conditions and results <sup>a</sup>					
	$\text{H}_2\text{O}_2 / \text{H}_3\text{PW}_{12}\text{O}_{40}$	$\text{DP}^{2+} / \text{H}_3\text{PW}_{12}\text{O}_{40}$	Solvent	Catalyst Loading (mol%)	Time (h)	Conversion	Epoxide Selectivity	TON	TOF ( $\text{h}^{-1}$ )
1	30:1	3:2	$\text{H}_2\text{O}^b$	1.1	4	99%	58%	89	22
2	30:1	3:2	$\text{CHCl}_3$	1.1	4	97%	58%	88	22
3	30:1	3:2	MeOH	1.1	4	98%	84%	88	22
4	200:1	3:2	MeOH	1.1	4	95%	99%	85	22
5 <sup>c</sup>	200:1	3:2	MeOH	1.1	2	71%	73%	64	32
6	200:1	5:1	MeOH	1.1	2	24%	96%	22	11
7	200:1	1:2	MeOH	0.22	4	88%	99%	400	100
8	200:1	1:2	$\text{H}_2\text{O}^*$	0.22	4	89%	95%	404	101
9	200:1	1:2	MeCN	0.22	3	98%	96%	447	149

<sup>a</sup> Conditions for the epoxidation of methyl oleate: 500 mg of methyl oleate (1 eq.), 222  $\mu\text{L}$  of  $\text{H}_2\text{O}_2$  30% (1.32 eq.). Heated to 60 °C. No solvent.

<sup>b</sup>  $\text{H}_2\text{O}$  needed to be heated above 80 °C to dissolve the dipyrindinium bromide.

<sup>c</sup> 50 mg of  $\text{H}_2\text{WO}_4$  were added to the epoxidation of methyl oleate

Both the synthesis of the active phosphotungstate catalytic species and the ion-pairing with phase transfer constitute a complex sequence of chemical equilibria and reactions (Scheme 2). It is generally accepted that the active species in the reaction is  $\text{PPW}^{3-}$ , i.e.  $(\text{PO}_4[\text{W}(\text{O})(\text{O}_2)_2]_4)^{3-}$ , as described by Venturello *et al.*<sup>6</sup> This species is obtained by the complete oxidation of phosphotungstic acid with hydrogen peroxide. It precipitates out of the aqueous phase when paired with a lipophilic transfer agent. However, this oxidation reaction also affords tungstic acid ( $\text{H}_2\text{WO}_4$ ), as a by-product which can be difficult to separate from the final product because they co-precipitate together under these conditions. Interestingly, it is also known that  $\text{H}_2\text{WO}_4$  can be further oxidized by  $\text{H}_2\text{O}_2$  to yield  $\text{H}_2\text{WO}_6$ , a strong acid which fully dissociates in water, and can pair with the cationic phase transfer agent.

In order to optimize production of the active catalyst,  $[\text{DP}^{2+}]_3[\text{PPW}^{3-}]_2$ , we explored several parameters: the ratio of hydrogen peroxide to phosphotungstic acid, the ratio of dipyrindinium to phosphotungstic acid, and the solvent used for synthesis. The catalysts obtained were evaluated for their activity in the epoxidation of methyl oleate using  $\text{H}_2\text{O}_2$  as oxidant at 60 °C with no solvent (table 1).

Catalysts prepared with 30 eq. of  $\text{H}_2\text{O}_2$  (Table 1, entries 1 to 3) were tested for the epoxidation of methyl oleate and afforded good conversions. However, poor epoxide selectivity was observed when using catalysts that were prepared in water or chloroform. We reasoned that the expected release of  $\text{H}_2\text{WO}_4$  under these conditions and its co-precipitation with the catalyst affected negatively the catalytic performances. Indeed, under catalytic epoxidation conditions where  $\text{H}_2\text{O}_2$  is in large excess compared to the catalyst (60 °C, 1.1mol% catalyst loading, 1.32 eq. of  $\text{H}_2\text{O}_2$ ),  $\text{H}_2\text{WO}_4$  readily oxidizes into  $\text{H}_2\text{WO}_6$ . This hypothesis was consistent with a measured pH between 0 and 1, indicative of the presence of the strong acid  $\text{H}_2\text{WO}_6$ .<sup>25</sup> It

is known that mineral acids catalyze the hydrolysis of epoxides, which is bound to adversely affect selectivity.

Co-precipitation of tungstic acid could be prevented entirely by adding a large excess of hydrogen peroxide (200:1) to the phosphotungstic acid prior to the addition of the phase transfer agent (Table 1, entries 4 to 9). This causes full oxidation of the by-product into  $\text{WO}_6^{2-}$  during catalyst synthesis. Yet, since  $\text{WO}_6^{2-}$  is an anion, it can also partially bind to the phase transfer agent and co precipitate with the desired catalyst. While this does not form adverse acid species, affecting catalyst selectivity, it does reduce its activity. Control experiments showed that directly using tungstic acid to form  $[\text{DP}^{2+}][\text{WO}_6^{2-}]$  yields an orange product that is inactive towards the epoxidation of methyl oleate (see supporting information). Separation of  $[\text{DP}^{2+}][\text{WO}_6^{2-}]$  from  $[\text{DP}^{2+}]_3[\text{PPW}^{3-}]_2$  was resolved by careful solvent selection as explained below. In further tests, a ratio of 200 for  $\text{H}_2\text{O}_2 / \text{H}_3\text{PW}_{12}\text{O}_{40}$  was selected. Next the impact of  $\text{DP}^{2+} / \text{H}_3\text{PW}_{12}\text{O}_{40}$  ratio on catalytic performance was studied, using catalyst color as an indication of purity (see supporting information).

The ratio of 3 to 2 was first tested as the “natural” choice to afford  $[\text{DP}^{2+}]_3[\text{PPW}^{3-}]_2$  as catalyst. When tested for epoxidation of methyl oleate, this catalyst afforded excellent conversion and selectivity of 95% and 99% respectively (Table 1, entry 4). Addition of  $\text{H}_2\text{WO}_4$  to the catalyst under these conditions confirmed its adverse effect on both fronts (Table 1, entry 5). When excess of the transfer agent was added (Table 1, entry 6), the conversion dropped to 24%, likely because the transfer agent could precipitate a large amount of the inactive  $\text{WO}_6^{2-}$  by-product, thus contaminating the catalyst. Interestingly, when using an excess of phosphotungstic acid starting material ( $\text{DP}^{2+} / \text{H}_3\text{PW}_{12}\text{O}_{40}$  ratio = 1:2, Table 1, entry 7), the catalytic activity was greatly enhanced and the catalyst loading could be reduced 5 fold, down from 1.1 mol% to 0.22 mol%. Under these conditions, excellent conversions and selectivity were obtained.

Finally, methanol, water and acetonitrile solvents were screened and acetonitrile was found to be the best system with 98% conversion and 96% selectivity after 3 hours at 60 °C (Table 1, entries 7-9). Under the latter conditions, TON and TOF could be greatly enhanced to 447 and 149 h<sup>-1</sup> respectively. Our experiments suggest that acetonitrile helps wash away the inactive, orange [DP<sup>2+</sup>][WO<sub>6</sub><sup>2-</sup>] by solubilizing this species. The effect of the solvent was studied with both liquid <sup>31</sup>P NMR (Fig. S1) prior to the ion exchange, and solid <sup>31</sup>P MAS NMR (Fig. S2) on the precipitated catalyst. The analysis showed that acetonitrile was the best solvent to promote the formation of highly peroxidized species, which is consistent with the higher activity observed.

### Characterization of the catalyst

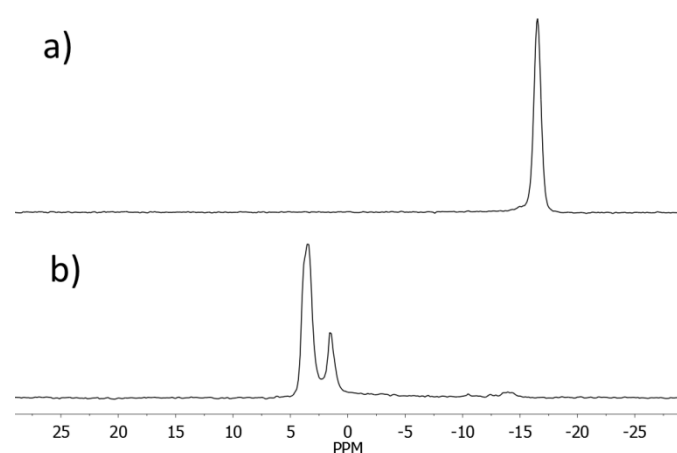


Fig. 1: <sup>31</sup>P MAS NMR spectra of a) [DP<sup>2+</sup>]<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub><sup>3-</sup>]<sub>2</sub>, b) [DP<sup>2+</sup>]<sub>3</sub>[PPW<sup>3-</sup>]<sub>2</sub> using conditions from Table 1 entry 9.

Since the catalyst was designed to be heterogeneous, it could not be dissolved in any common solvents for traditional analysis and characterization was performed by <sup>31</sup>P MAS NMR. As a standard for comparison, the inactive species [DP<sup>2+</sup>]<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub><sup>3-</sup>]<sub>2</sub> was synthesized by simple ion exchange. It presented a chemical shift of -16.6 ppm, which is very similar to the chemical shift of phosphotungstic acid in water, -15.2 ppm (Fig. 1a). The <sup>31</sup>P MAS NMR spectrum of [DP<sup>2+</sup>]<sub>3</sub>[PPW<sup>3-</sup>]<sub>2</sub> synthesized under the conditions of Table 1, entry 9, reveals two peaks at 3.5 ppm and 1.5 ppm (Fig. 1b). The chemical shift of PW<sub>4</sub>O<sub>24</sub><sup>3-</sup> species has been reported in the region between 0 and 1 ppm and is known to change when using different cationic surfactants.<sup>26</sup> Also, Duncan *et al.* had shown that by varying amounts of H<sub>2</sub>O<sub>2</sub>, peaks in the region -15 to 5 ppm could be observed by <sup>31</sup>P NMR, attributed to fully or partially peroxidized species en route to PW<sub>4</sub>O<sub>24</sub><sup>3-</sup>, but no formal characterization was reported.<sup>26</sup> This led us to believe that the peaks observed for our catalyst belong to either PW<sub>4</sub>O<sub>24</sub><sup>3-</sup> or highly peroxidized intermediates. However, despite exploring several reaction conditions and solvents, precipitated [DP<sup>2+</sup>]<sub>3</sub>[PPW<sup>3-</sup>]<sub>2</sub> always presented itself as a mixture of several compounds in the 0-5 ppm region by <sup>31</sup>P MAS NMR (see Fig S2). These results are in agreement with reports by Kozhevnikov *et al.* that showed activity towards the epoxidation of oleic acid with a mixture of

phosphotungstate intermediates, as ascribed by <sup>31</sup>P NMR, suggesting that the Venturello anion may not be the only active species.<sup>25</sup>

The morphology of the catalyst was studied by SEM. The catalyst arranges itself in the shape of rectangular prisms with varying length between 2 and 50 μm, as well as width and height roughly between 0.5 and 5 μm. Some amorphous regions could also be observed, which is consistent with the <sup>31</sup>P MAS NMR study, revealing the fact the catalysts are present as a mixture of closely related compounds (see Fig. S3).

### Catalytic results

With an optimized catalyst synthesis in hand, we turned to catalytic reaction optimization. Epoxidation of methyl oleate was tested under neat conditions and with solvents (Table 2). In all cases but with methanol, the reaction took place in a triphasic mixture of solid catalyst and two immiscible liquid phases: the aqueous phase containing hydrogen peroxide, and the organic phase containing methyl oleate. By design, the [DP<sup>2+</sup>]<sub>3</sub>[PPW<sup>3-</sup>]<sub>2</sub> catalyst possesses amphiphilic properties, with lipophilic long chains on the cation, combined to the hydrophilic properties of the peroxophosphotungstate moiety. Under neat conditions, good conversion (84%) with perfect selectivity was obtained at room temperature with 1 mol% of catalyst loading, while a fivefold loading reduction gave an excellent result of 98% conversion with 96% selectivity at 60 °C (entries 1 and 2). Overall, we observed that selectivity was perfect until 90% conversion, at which point, traces of the corresponding diols, hydroxyketones, aldehydes and carboxylic acids could be observed and selectivity dropped. Selectivity continued to drop if the reaction was left running past full conversion, as epoxides can slowly hydrolyse under these conditions.

Table 2: Epoxidation of methyl oleate

Entry	Catalyst Loading (mol%)	Solvent (1 mL)	Time (h)	Temp (°C)	Conversion (%)	Selectivity (%)
1	1	neat	4	21	84%	100%
2	0.22	neat	3	60	98%	96%
3	0.22	Heptane	3	60	70%	100%
4	0.22	EtOAc	3	60	64%	100%
5	0.22	MeOH	3	60	96%	68%
6	0.22	MeCN	3	60	91%	98%
7	0.22	CHCl <sub>3</sub>	3	60	87%	100%
8 <sup>a</sup>	0.22	neat	2	60	93%	98%
9 <sup>b</sup>	0.22	neat	3	60	2%	100%

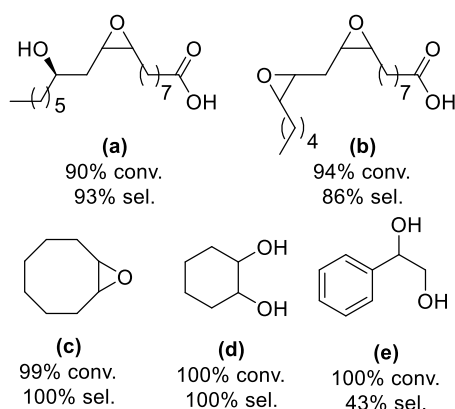
Conditions for the epoxidation of methyl oleate: 500 mg of methyl oleate (1 eq.), 222 μL of H<sub>2</sub>O<sub>2</sub> 30% (1.32 eq.). Time and catalyst loading varied depending on activity observed.

<sup>a</sup> Scaled up to 13.2 g of methyl oleate (1 eq.), 5.9 mL of  $\text{H}_2\text{O}_2$  30% (1.32 eq.) and 200 mg of catalyst (0.0022 eq.)

<sup>b</sup> Control test using  $[\text{DP}^{2+}]_3[\text{PW}_{12}\text{O}_{40}^{3-}]_2$  as catalyst.

Using a solvent affected both conversion and selectivity. Lipophilic solvents (heptane, EtOAc and  $\text{CHCl}_3$ , entries 3-5) gave lower conversions likely because greater dilution in the oil limited the catalysis rate. Acetonitrile mixed with the aqueous phase (entry 6) and gave results more similar to neat conditions with 91% conversion and 98% selectivity. Among the solvents tested, methanol was the only one able to dissolve both the aqueous and the organic phases into a single phase, thus allowing good mass transfer to reach 96% conversion. However, this solvent also facilitated the hydrolysis of the epoxide to form the diol, which reduces selectivity to 68% (entry 7). The catalyst  $[\text{DP}^{2+}]_3[\text{PPW}^{3-}]_2$  was also tested on a larger scale, showing excellent conversion of 93% and full selectivity upon epoxidizing 13 grams of methyl oleate (entry 8). A control experiment using the precursor  $[\text{DP}^{2+}]_3[\text{PW}_{12}\text{O}_{40}^{3-}]_2$  showed almost no activity (entry 9), revealing the importance to pre-peroxidize the catalyst prior to cation exchange (scheme 2).

In an effort to expand the scope of the reaction, the epoxidation of two fatty acids, linoleic acid and ricinoleic acid, was tested with  $[\text{DP}^{2+}]_3[\text{PPW}^{3-}]_2$  and proceeded with good conversions and selectivities (Scheme 3).



Scheme 3: Oxidation of alkenes with 0.22 mol% of  $[\text{DP}^{2+}]_3[\text{PPW}^{3-}]_2$  as catalyst at 60 °C with no solvent. Conditions used for ricinoleic acid: 1h, 1.32 eq.  $\text{H}_2\text{O}_2$ . Linoleic acid: 2h, 2.2 eq.  $\text{H}_2\text{O}_2$ . Cyclohexene, cyclooctene and styrene: 3h, 1.32 eq.  $\text{H}_2\text{O}_2$ .

Cyclohexene, cyclooctene and styrene were also tested to verify if the catalyst, designed for large lipophilic substrates, would also epoxidize small alkenes effectively. Cyclooctene, in particular, is a commonly used substrate for epoxidation in the literature of phosphotungstate catalysts.<sup>11, 13-16, 19-21, 23, 24, 27</sup> The conversion and selectivity for the epoxidation of cyclooctene were in fact better than those obtained for methyl oleate, as shown in Scheme 3. 1,2-epoxycyclooctene was obtained with full selectivity and 99% conversion in 3 h at 60 °C with 0.22 mol% of catalyst, which gives a TOF of 150  $\text{h}^{-1}$ . To the best of our knowledge, this is the highest reported TOF for heterogeneous tungsten catalysts. Cyclohexene afforded full selectivity towards the diol instead of the epoxide, since 1,2-epoxycyclohexene quickly hydrolysed in the presence of

$[\text{DP}^{2+}]_3[\text{PPW}^{3-}]_2$ , even at room temperature. Styrene was found to be too reactive for this catalyst, leading to a complex mixture of aldehydes, carboxylic acids and styrene glycol.

A hot filtration test was carried out with methyl oleate as substrate to confirm the heterogeneous nature of the catalyst. In a standard epoxidation method, the solution was filtered after 30 minutes of reaction at 60 °C, which showed 40.6% yield by GC-MS. The filtrate was stirred at 60 °C for 12 hours with an additional 1.32 Eq. of  $\text{H}_2\text{O}_2$  and a virtually unchanged yield of 42.4% was then measured. These results confirm that  $[\text{DP}^{2+}]_3[\text{PPW}^{3-}]_2$  operates as a heterogeneous catalyst.

Recycling tests were performed by diluting the mixture at the end of the reaction with ethyl acetate, centrifuging and removing both aqueous and organic supernatants with a pipette. The addition of organic solvent was necessary to remove the product due to the high viscosity of the epoxidized methyl oleate at room temperature. The solid catalyst remained in the flask and was dried with air for 1 minute before reuse. When using 1mol% catalyst loading, the catalyst performed very well over 5 cycles, with conversions ranging from 98.6 to 100 % and selectivity remaining stable (Fig. 2), thus affording a recyclable system. When employing the optimized loading of 0.22mol%, a decrease in catalytic activity was observed after three cycles (See supporting information, table S2). Pushing to 5 cycles under these conditions allowed achieving a record cumulated turnover number (TON) of 1868. The highest number of turnovers to date for Venturello-type catalyst was reported by Khlebnikova *et al.*<sup>28</sup>, with a value of 940 turnovers for a homogeneous catalysis loaded at 0.01mol%. The highest number of recycling cycles to date was reported by Chen *et al.*<sup>10</sup> where 17 cycles at 3% catalyst loading amounted to 560 turnovers.

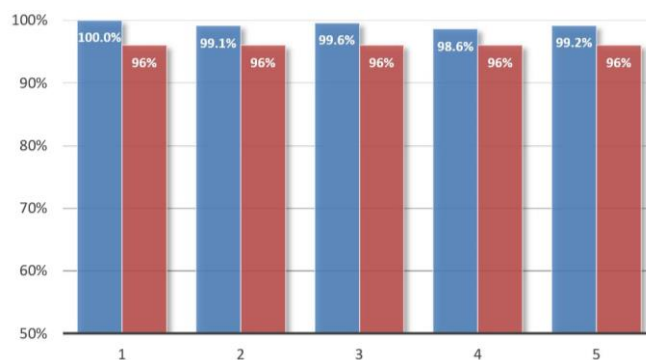


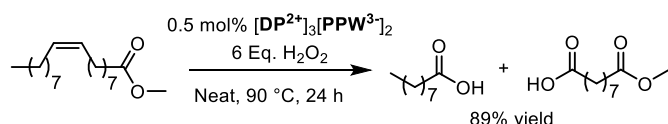
Fig. 2: Conversion (blue, left bars) and selectivity (red, right bars) towards methyl 9,10-epoxystearate obtained as a function of cycle number for the epoxidation of methyl oleate with recycled  $[\text{DP}^{2+}]_3[\text{PPW}^{3-}]_2$  catalyst. Catalytic conditions: 1h, 60 °C, 1mol% catalyst loading.

In order to study the stability of the catalyst, a leaching study was conducted. After filtering the solid catalyst, the aqueous filtrate from the 13 gram scale experiment was analysed by ICP-MS (using conditions of Table 2, entry 8). A limited leaching of 2.8% was measured. The product was recovered without contamination from the organic phase.

Previous reports by Duncan *et al.*<sup>26</sup> on quaternary ammonium paired peroxophosphotungstates investigated degradation of the Venturello catalyst. In their case, it was

reported that the catalyst degraded after approximately 500 turnovers. Here  $[\text{DP}^{2+}]_3[\text{PPW}^{3-}]_2$  starts to deactivate noticeably after 1300 turnovers (see Table S2). Additional experiments were performed by preheating  $[\text{DP}^{2+}]_3[\text{PPW}^{3-}]_2$  for 24 hours with methyl oleate at 60 °C before adding hydrogen peroxide, in order to exclude thermal degradation. The epoxide yield and selectivity were unchanged compared to the fresh batch of catalyst.

Homogeneous Venturello-type catalysts have also been reported to cleave double bonds of fatty acids/esters and small organic molecules in order to form the corresponding carboxylic acids,<sup>8, 28, 29</sup> but no heterogeneous systems had proven successful for this reaction on the fatty molecules. The cleavage requires higher temperatures to promote the hydrolysis of the epoxide and a longer reaction time (Scheme 4). Since  $[\text{DP}^{2+}]_3[\text{PPW}^{3-}]_2$  showed comparable activity for the epoxidation of methyl oleate to homogeneous systems, we tested the oxidative cleavage as well. Catalyst loading had to be increased to 0.5 mol% to support the four oxidation steps involved in the cleavage.<sup>29</sup> The catalyst successfully cleaved methyl oleate into its two corresponding carboxylic acids with a yield of 89% at 90 °C for 24 hours. The reaction afforded no side product, and no sign of transesterification or saponification was observed.



Scheme 4: Cleavage of methyl oleate with  $[\text{DP}^{2+}]_3[\text{PPW}^{3-}]_2$  as catalyst.

## Conclusion

We have produced an active heterogeneous catalyst for the oxidation of olefins and vegetable oils, which is selective, recyclable and easy to synthesize. This phosphotungsten catalyst was rendered insoluble by tuning the lipophilicity and charge of the counter-cation, instead of supporting it to a solid structure. We optimized the synthetic conditions to access the catalyst and used liquid and solid state  $^{31}\text{P}$  MAS NMR to support our findings. The resulting catalyst has shown excellent activity and selectivity for the epoxidation of methyl oleate, linoleic acid, ricinoleic acid and cyclooctene. It afforded cleanly diols with other small alkenes. At last, changing the conditions gave access to excellent yields for the full oxidative cleavage of methyl oleate. It was also recyclable by simple centrifugation, at least 5 times. Very limited leaching was measured, while a large-scale experiment of 13 mg was successfully performed. In short, we have discovered a new counter anion providing excellent activity, selectivity, recyclability and versatility in alkene and unsaturated oil oxidation.

## Experimental section

All chemicals used were analytical grade except otherwise noted. Chemicals were all bought from Sigma Aldrich and used

as received. Phosphotungstic acid hydrate water content was determined by thermogravimetric analysis (TGA).  $^1\text{H}$ -NMR spectra were measured with a 500 MHz Bruker AVIIHD spectrometer at ambient temperature in  $\text{D}_2\text{O}$ , MeOD or  $\text{CDCl}_3$  using TMS as internal reference.  $^{31}\text{P}$  MAS NMR spectra were measured in a 400 MHz Varian VNMRs in 4 mm zirconia rotors spinning at 13 kHz at 25 °C using  $(\text{NH}_4)_2\text{HPO}_4$  as reference. Tungsten leaching was measured using a Thermo Scientific iCAP Q ICP-MS. Water content of phosphotungstic acid hydrate was determined with a TGA Q500 instrument under  $\text{N}_2$  at a rate of 10 °C/min. GC-MS spectra were measured using an Agilent 7890A gas chromatography connected to an Agilent 5975C MS instrument with triple-axis detector. The column used is an HP-5MS UI (length: 30m, diameter 0.25 mm, film of 0.25  $\mu\text{m}$ ). SEM analysis was performed with a FEI Inspect F-50 FE-SEM.

### Synthesis of 4,4'-(trimethylene)bis(1-tetradecylpyridinium) dibromide $\text{C}_{41}\text{H}_{72}\text{N}_2\text{Br}_2$

4,4'-Trimethylenedipyridinium (3.9652 g, 20 mmol, 1 eq.) and 1-bromotetradecane (16.6368 g, 60 mmol, 3 eq.) were dissolved in 1-butanol (40 mL) and stirred at 120 °C for 48 h. The product was precipitated by diluting in ethyl acetate, then filtered and washed with pentane. The solid was then recrystallized in water, filtered and washed with acetone. 11.5482 g of a white solid was recovered (77% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 0.89 (t, 6H,  $\text{CH}_3$ ), 1.25 (m, 44H,  $\text{CH}_2$ ), 2.00 (m, 4H,  $\text{CH}_2$ ), 2.33 (q, 2H,  $\text{CH}_2$ ), 3.12 (t, 4H, Pyr- $\text{CH}_2$ ), 4.76 (4H,  $\text{N}^+-\text{CH}_2$ ), 8.18 (d, 4H, CH), 9.02 (d, 4H,  $\text{N}^+-\text{CH}$ ).  $m/z$  = 296.28560

### Synthesis of catalyst $(\text{C}_{41}\text{H}_{72}\text{N}_2)_3(\text{PW}_4\text{O}_{24})_2$

Phosphotungstic acid hydrate ( $\text{H}_3\text{PW}_4\text{O}_{24} \cdot 16\text{H}_2\text{O}$ ) (2.496 g, 0.80 mmol, 2 eq.) is dissolved in 15.9 mL  $\text{H}_2\text{O}_2$  30% (159 mmol, 200 eq.) and stirred at room temperature for 10 minutes, then the solution is diluted with 15 mL of acetonitrile. A solution of 4,4'-(trimethylene)bis(1-tetradecylpyridinium) dibromide (300 mg, 0.40 mmol, 1 eq.) in 50 mL of acetonitrile is slowly added drop by drop to the first solution, during which the product precipitates in solution. The mixture is stirred for 2 h at room temperature. The solid is filtered and washed with 20 mL of water and then 20 mL of acetonitrile. 465 mg recovered (86% yield).  $^{31}\text{P}$  MAS NMR (400 MHz, 13 kHz spinning,  $(\text{NH}_4)_2\text{HPO}_4$  as chemical shift reference at 0 ppm)  $\delta$  (ppm) = 3.47 (s), 1.51 (s).

### Catalytic epoxidation of methyl oleate

Methyl oleate (500 mg, 1.69 mmol, 1 eq.),  $(\text{C}_{41}\text{H}_{72}\text{N}_2)_3(\text{PW}_4\text{O}_{24})_2$  (7.6 mg, 0.0037 mmol) and  $\text{H}_2\text{O}_2$  30% (222  $\mu\text{L}$ , 2.23 mmol, 1.32 eq.) were added to a 20 mL flask and heated to 60 °C under vigorous stirring for 3 h. After the reaction, the mixture was filtered to remove the catalyst. The organic phase was analyzed by GC-MS and  $^1\text{H}$  NMR.

### Catalyst recycling method

Methyl oleate (500 mg, 1.69 mmol, 1 eq.),  $(\text{C}_{41}\text{H}_{72}\text{N}_2)_3(\text{PW}_4\text{O}_{24})_2$  (34.4 mg, 0.0168 mmol, 0.01 eq.) and  $\text{H}_2\text{O}_2$  30% (222  $\mu\text{L}$ , 2.23 mmol, 1.32 eq.) were added to a 20 mL flask and heated to 60



°C under vigorous stirring for 2 h. After the reaction, the mixture was diluted with 10 mL of ethyl acetate and centrifuged at 8000 rpm for 20 minutes. Then both the organic and aqueous supernatants were removed with a pipette. The organic phase was filtered using a filter paper and analyzed by GC-MS. The solid remaining in the flask was dried with air for 1 minute, then reused.

### Catalytic cleavage of methyl oleate

Methyl oleate (500 mg, 1.69 mmol, 1 eq.),  $(C_{41}H_{72}N_2)_3(PW_4O_{24})_2$  (17.2 mg, 0.0084 mmol, 0.005 eq.) and  $H_2O_2$  30% (1.01 mL, 10.12 mmol, 6 eq.) were added to a 20 mL flask and heated to 90 °C under vigorous stirring for 24 h. After the reaction, the organic phase was diluted with 10 mL of ethyl acetate and filtered to remove the catalyst. The aqueous phase was saturated with NaCl and the product was extracted three times with 10 mL ethyl acetate, dried with  $MgSO_4$  and filtered. The organic phase was analyzed by GC-MS.

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### Graphical abstract

