Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Aerobic Oxidation Catalyzed by Polyoxometalates Associated to an Artificial Reductase at Room Temperature and in Water

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Materials: All of the substrates, FMN (Flavin mononucleotide) and NADH were purchased from commercial suppliers and used as received. Deionized water was prepared using Elix® Advantage Water Purification System. The four POMs have been synthesized according to reported procedures (see main text).

Instrumentation: Gas chromatography analyses were performed by SHIMADZU GC-2010Plus. The sample was injected into Zebron ZB Semi Volatiles column (30 m x 0.25 mm x 0.25 mm). The applied GC method was: 100–130°C, 5°C min^{-1}, then 130–220°C, 50°C min^{-1}, then 220°C for 4 min. Injector and FID temperature was 300°C. All GC yields were calculated by applying calibration constants of acetophenone (standard), sulfoxide and sulfone derivative products that are shown in the Table S1 (ESI†). All ultraviolet-visible measurements were carried out in a Varian carry 300-bio ultraviolet-vis spectrophotometer in cuvettes equipped with septa for experiments under inert atmosphere. All data processing and Figures were done using OriginPro.

Synthesis of the modified polymer PEI$_{\text{guan-oct}}$: PEI$_{\text{guan-oct}}$ (14% guanidinium groups per monomer; 24% octyl groups per monomer) was synthesized from commercial multibranched PEI (25 kDa) dissolved in DMF to give final concentration of 400 mM. For the alkylation reaction, triethylamine (4 equiv. per 1-Iodooctane) was added to the PEI solution. After that, 1-iodooctane (0.4 equiv. per monomer) was added to the resulting mixture and the reaction was stirred for 3 hours at RT. For derivatization with guanidinium groups, 1-H-pyrazole-1-carboxamidin hydrochloride (0.3 equiv. per monomer) dissolved in 1 ml DMF was added slowly to the reaction after the addition of triethylamine (4 equiv. per praxadine). The corresponding solution was stirred vigorously for 3 days at room temperature. For purification, the crude reaction mixture was diluted (1:2) into hydrochloric acid (50 mM) and transferred to a dialysis tube (Spectra/Por membrane, MW cut-off 14,000). The resulting solution was dialysed under slow stirring against each of the following buffers for at least 2 hours: 20% EtOH in 50 mM HCl; 50 mM HCl; distilled water (twice); 50 mM NaOH (twice); and water (thrice).

Catalysis experiments: Aqueous solutions of polymer (2.5 mM in monomer), FMN (0.1 mM) and polyoxometalate (0.1 mM) were added to 1.5 mL tinted vial. The resulting solution was diluted with water to a final volume of 1 mL. Thioanisole derivatives (10 mM) and NADH (1 mM) were then added respectively. The vial was shaken vigorously and then left stirring for 24 h at room temperature under O_2 atmosphere (1 atm). For GC analysis, acetophenone was used as internal standard and the resulting solution was diluted with 8 mL acetonitrile, dried over Na_2SO_4 and filtered on a short silica column prior to injection in the GC.

Stability studies:

a) Isolation of the POM before the catalytic event: POM, PEI, FMN and NADH were dissolved in water at room temperature, and CsCl was added. The obtained precipitate was filtrated and washed 3-4 times with acetonitrile and the sample dried at 80°C for 5 hours.

b) Isolation of the POM after the catalytic event: POM, PEI, FMN and NADH were dissolved in water at room temperature and thioanisole and acetonitrile were added. The reaction mixture was stirred for 16 hours and CsCl was added. The obtained precipitate was filtrated and washed 3-4 times with acetonitrile and the sample dried at 80°C for 5 hours.

Zn_5W_9: POM: 11.0 mg (1.8 μmol), NADH: 11.76 mg (2 mM), FMN: 1.66 mL (0.2 mM), PEI: 316 μL (5 mM), water : 6.3 mL, thioanisole: 20 μL (19.5 mM), acetonitrile: 80 μL, CsCl: 20 mg.

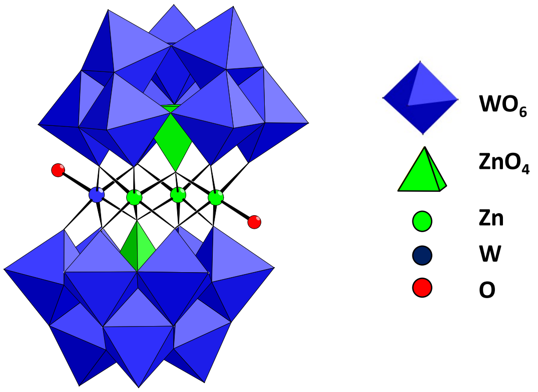
PMo_{12} : POM: 8.5 mg (3.6 μmol), NADH: 23.52 mg (4 mM), FMN: 3.32 mL (0.4 mM), PEI: 632 μL (10 mM), water: 4.3 mL, thioanisole: 40 μL (39 mM), acetonitrile: 60 μL, CsCl: 40 mg.

PMo_{12}V: POM: 10.8 mg (5.4 μmol), NADH: 35.3 mg (6 mM), FMN: 5 mL (0.6 mM), PEI: 948 μL (15 mM), water: 2.4 mL, thioanisole: 60 μL (58.5 mM), acetonitrile: 40 μL, CsCl: 60 mg.

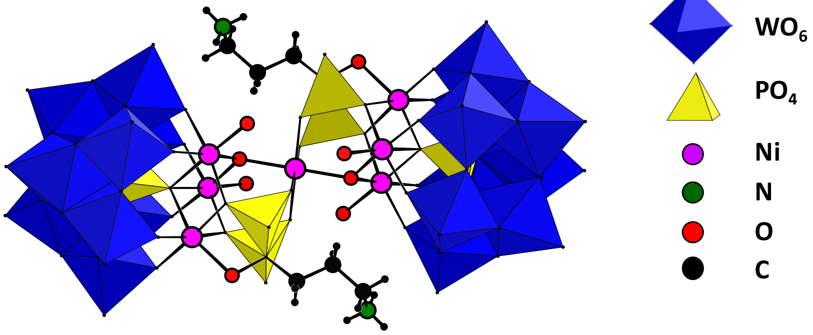
Ni_7W_{18}: POM: 11.6 mg (1.8 μmol), NADH: 11.76 mg (2 mM), FMN: 1.66 mL (0.2 mM), PEI: 316 μL (5 mM), water: 6.3 mL, thioanisole: 20 μL (19.5 mM), acetonitrile: 80 μL, CsCl: 20 mg.

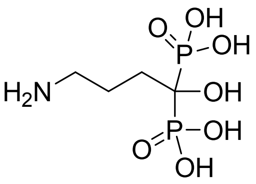
Products	**$K_{(sulfoxide\ or\ sulfone)}$**
Acetophenone	$1.89131.10^{13}$
Methyl phenyl sulfoxide	$1.86843.10^{13}$
Methyl phenyl sulfone	$1.95029.10^{13}$
Methyl-p-tolyl-sulfoxide	$1.96969.10^{13}$
Methyl-4-bromo-sulfoxide	$1.94442.10^{13}$
Methyl-4-methoxy-sulfoxide	$2.06919.10^{13}$

Table S1. Calibration constants (K) of acetophenone, sulfoxide and sulfone derivatives.



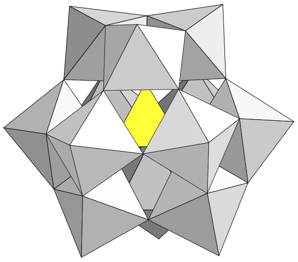
$[(ZnW_9O_{34})_2WZn_3(H_2O)_2]^{12-}$ (**Zn_5W_{19}**)



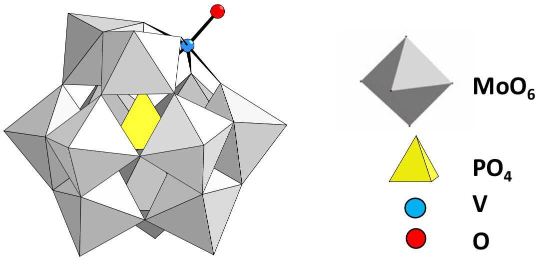


$[\{(PW_9O_{34})Ni_3(OH)(H_2O)_2(Ale)\}_2Ni]^{14-}$ (Ale = alendronate = $O_3PC(O)(C_3H_6NH_3)PO_3$) (**Ni_7W_{18}**)

Alendronic acid



$[PMo_{12}O_{40}]^{3-}$ (**PMo_{12}**)



$[PMo_{11}VO_{40}]^{4-}$ (**$PMo_{11}V$**)

Figure S1. Mixed ball-and-stick and polyhedral representation of the POMs studied as catalysts. For **$PMo_{11}V$**, the heterometals are disordered over the twelve positions of the Keggin ion.

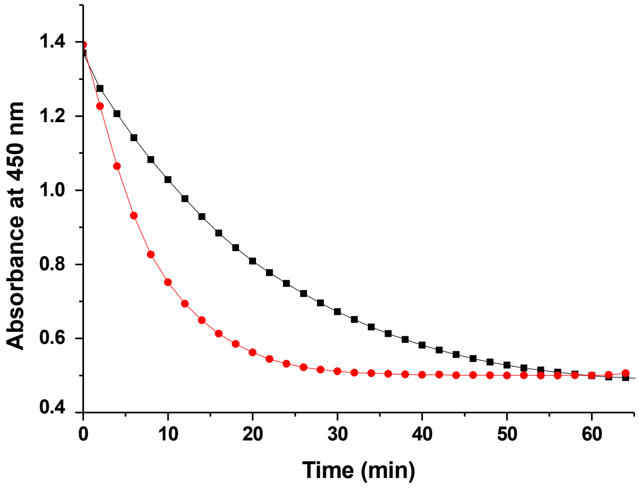


Figure S2. Time course for the reduction of FMN (0.1 mM) by NADH (1 mM) in deoxygenated water in absence (black squares) or in presence (red circles) of $PEI_{guan\text{-}oct}$ (2.5 mM in monomer).

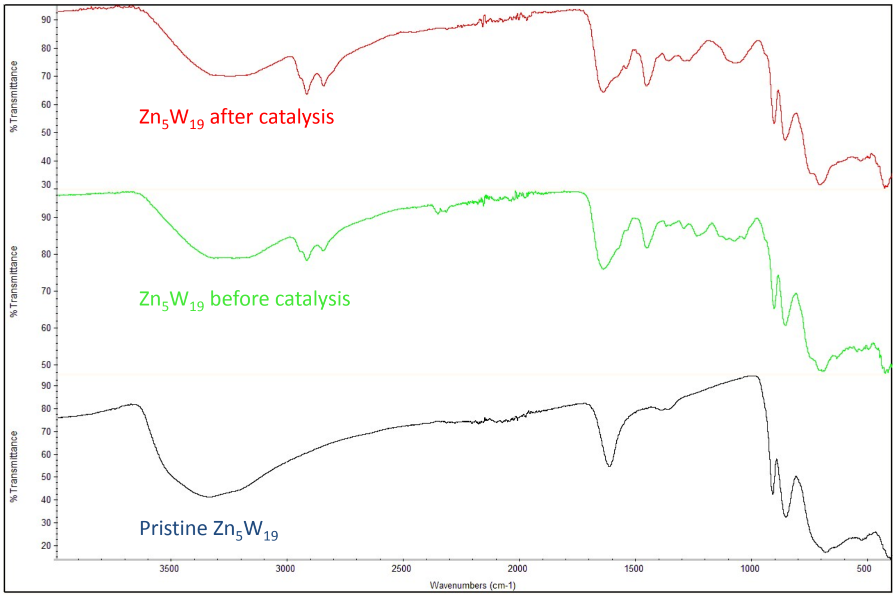


Figure S3. IR spectra of pristine $\mathbf{Zn_5W_{19}}$ (black line), $\mathbf{Zn_5W_{19}}$ isolated from the catalytic medium before the catalytic event (green line) and $\mathbf{Zn_5W_{19}}$ isolated from the catalytic medium after the catalytic event (red line). For the spectra related to the POMs isolated before and after the catalytic event, the bands in the 1200 - 1500 cm^{-1} range are due to the C-N, N-H, C-C and C-H vibrations characterizing the co-precipitated polymer. See experimental section for details.

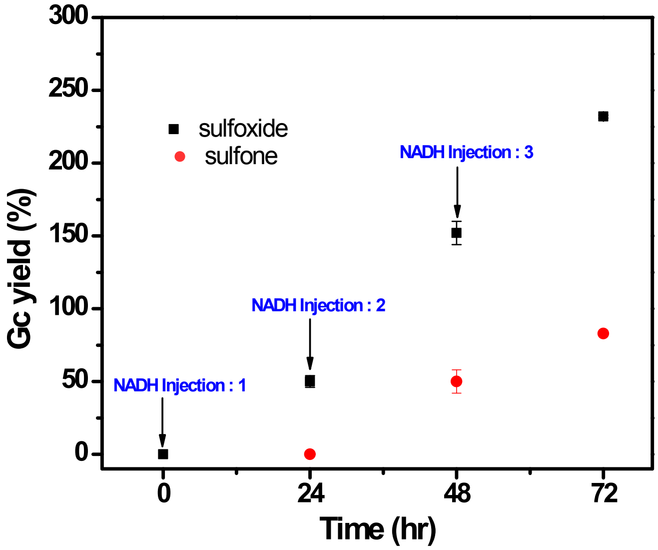


Figure S4. Sulfoxide and sulfone formed after three successive additions of NADH (1 μmol) to a solution of **Zn_5W_{19}** (0.1 mM), FMN (0.1 mM), and thioanisole (10 mM) in 1 mL of water.

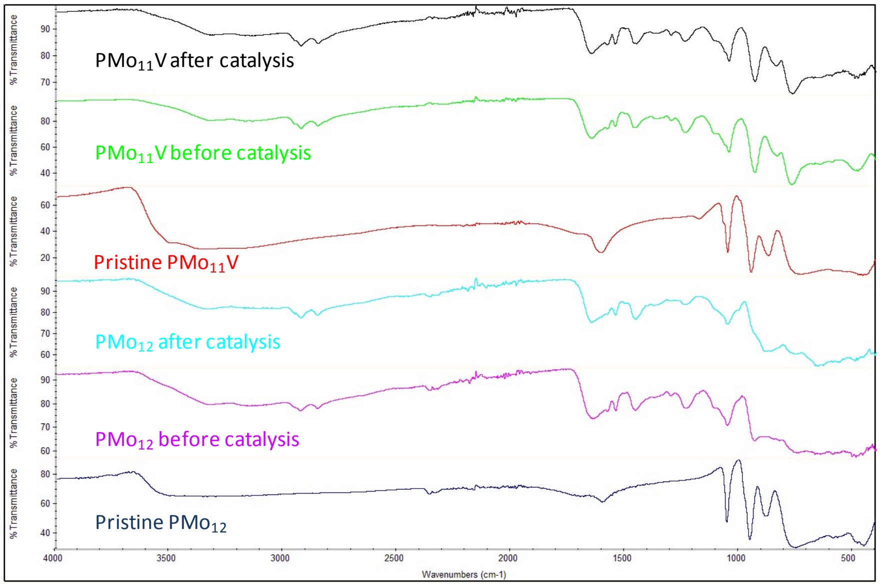


Figure S5. IR spectra of pristine **PMo_{12}** and **$PMo_{11}V$** (dark blue and red lines, respectively) **PMo_{12}** and **$PMo_{11}V$** isolated from the catalytic medium before the catalytic event (pink and green lines respectively) and **PMo_{12}** and **$PMo_{11}V$** isolated from the catalytic medium after the catalytic event (cyan and black lines, respectively). For the spectra related to the POMs isolated before and after the catalytic event, the bands in the 1200 - 1500 cm^{-1} range are due to the C-N, N-H, C-C and C-H vibrations characterizing the co-precipitated polymer. See experimental section for details.

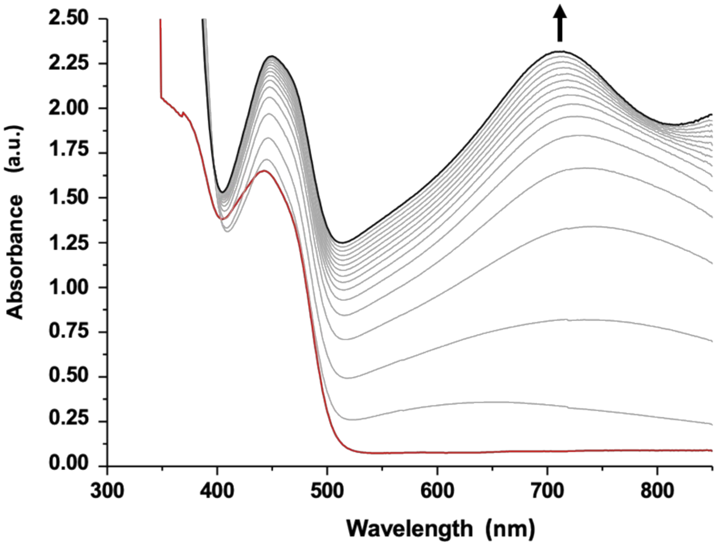


Figure S6. UV-Visible spectra of aqueous solutions of (a) **PMo$_{11}$V** (0.1 mM) and FMN (0.1 mM) followed for 30 min. after addition of NADH (1 mM) under anaerobic conditions.

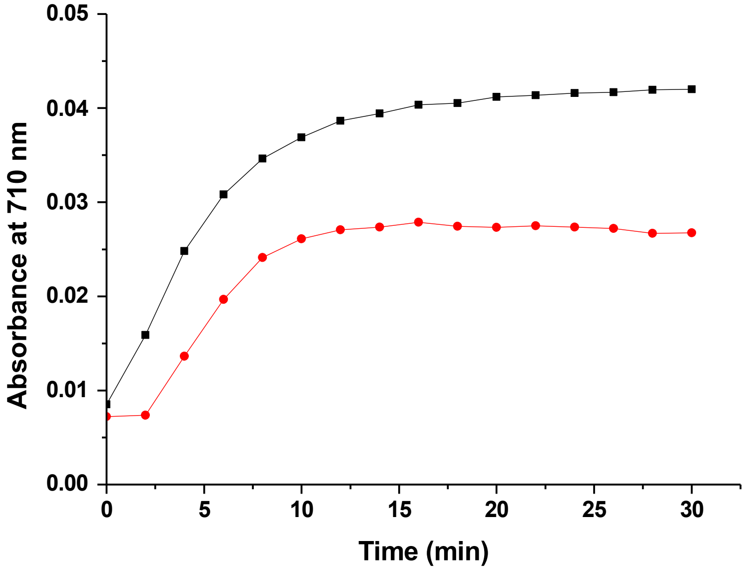


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Figure S7. Time course for the reduction of **PMo$_{12}$** (0.01 mM) upon addition of NADH (0.1 mM) in the presence of FMN (0.01 mM) and PEI$_{com}$ (0.25 mM) (red circles) or in the presence of FMN (0.01 mM) and PEI$_{guan\text{-}oct}$ (0.25 mM) (black squares). Because of solubility issues in the presence of polymers, these experiments were realized at lower concentration compared to catalysis conditions.

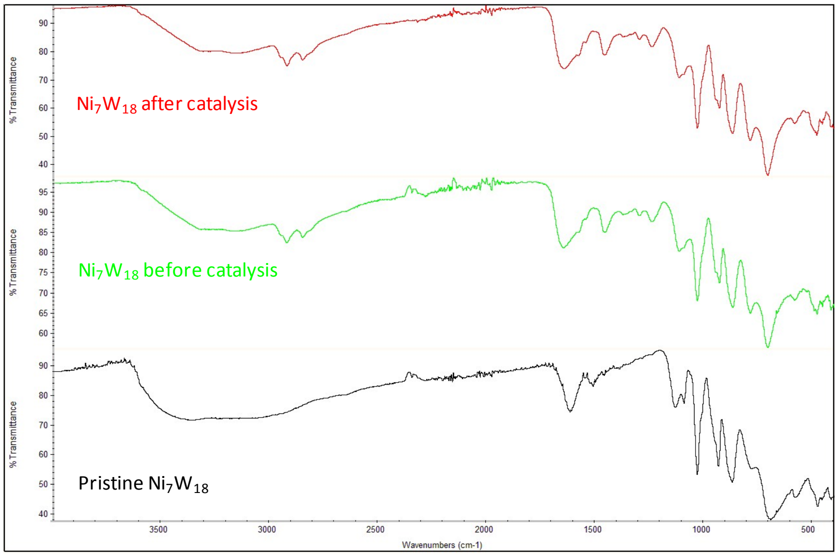

Figure S8. IR spectra of pristine **Ni_7W_{18}** (black line), **Ni_7W_{18}** isolated from the catalytic medium before the catalytic event (green line) and **Ni_7W_{18}** isolated from the catalytic medium after the catalytic event (red line). For the spectra related to the POMs isolated before and after the catalytic event, the bands in the 1200 - 1500 cm^{-1} range are due to the C-N, N-H, C-C and C-H vibrations characterizing the co-precipitated polymer. See experimental section for details.