Hybrid Polyoxotungstates as 2nd-Generation POM-Based Catalysts for Microwave-assisted H₂O₂ activation

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General Information. ^{183}W -NMR and ^{31}P -NMR were recorded with Bruker *Avance DRX 400* and Bruker *AV 300* instruments operating, respectively, at 16.67 and at 121.5 MHz. FT-IR were obtained on a Perkin Elmer *1600* instrument. GLC analyses were performed with a Shimadzu *GC-2010* instrument, equipped with flame ionisation detector and capillary column *Equity-5* (Supelco); $l=15\text{m}$, $\text{I.D.}=0.1\text{mm}$, $0.1\ \mu\text{m}$ film thickness. HPLC chromatograms were obtained by using a Shimadzu *LC-10 AT VP* pump, equipped with a Shimadzu *SPD-10 A VP* UV ($\lambda=242\text{nm}$) detector and a *Chiral Cell OD* (Dancel Chemical Industries) column. GLC-MS analyses were recorded by using a Agilent *GC 6850* coupled with a *5973* MS detector. ESI-MS (-) analyses were obtained on a Agilent *LC-MSD Trap SL* instrument. MW-lab-stations *Ethos 1600* (Milestone) or *Discover* (CEM) instruments were employed for MW assisted reactions. Kinetic fitting was performed with *Scientist* (Micromath) software.

Materials. Acetonitrile, 35% H_2O_2 , phenyl trichlorosilane, phenyl trimethoxysilane, 3-aminopropyl trimethoxysilane, methyl trichlorosilane, phenethyl trimethoxysilane, sodium metasilicate, sodium tungstate dihydrate, tetrabutylammonium bromide, phenyl phosphonic acid, phenyl phosphonyl chloride, R(-) and S(+)-1-aminoethyl phosphonic acids, were purchased from Sigma-Aldrich and used without further purification. 70% H_2O_2 was a Ausimont product.

POM synthesis and characterization. Hybrid polyoxotungstates were prepared from lacunary precursors,¹ following general literature procedures as described below.

Table 1S: Hybrid polyoxotungstates $[\text{G}_z\text{XW}_{12-n}\text{O}_{40-m}]^k$ used as catalysts for cyclooctene epoxidation with H_2O_2 .

catalyst	POM	G	hybrid POM
1	$\alpha\text{-PW}_{11}\text{O}_{39}^{7-}$	PhSi	$(\text{Bu}_4\text{N})_3[\alpha\text{-PW}_{11}\text{O}_{39}(\text{PhSi})_2\text{O}]$
2		PhPO	$(\text{Bu}_4\text{N})_2\text{H}[\alpha\text{-PW}_{11}\text{O}_{39}(\text{PhPO})_2]$
3	$\alpha\text{-SiW}_{11}\text{O}_{39}^{8-}$	PhSi	$(\text{Ph}_4\text{P})_4[\alpha\text{-SiW}_{11}\text{O}_{39}(\text{PhSi})_2\text{O}]$
4		PhPO	$(\text{Bu}_4\text{N})_3\text{H}[\alpha\text{-SiW}_{11}\text{O}_{39}(\text{PhPO})_2]$
5		MeSi	$(\text{Ph}_4\text{P})_4[\alpha\text{-SiW}_{11}\text{O}_{39}(\text{MeSi})_2\text{O}]$
6	$\gamma\text{-PW}_{10}\text{O}_{36}^{7-}$	PhSi	$(\text{Bu}_4\text{N})_3[(\gamma\text{-PW}_{10}\text{O}_{36})(\text{PhSiOH})_2]$
7	$\gamma\text{-SiW}_{10}\text{O}_{36}^{8-}$	PhSi	$(\text{Bu}_4\text{N})_3\text{H}[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{PhSi})_2\text{O}]$
8		PhPO	$(\text{Bu}_4\text{N})_3\text{K}[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{PhPO})_2]$
9		$\text{NH}_2(\text{CH}_2)_2\text{Si}$	$(\text{Bu}_4\text{N})_3\text{H}[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{NH}_2\text{PrSi})_2\text{O}]$
10		$\text{Ph}(\text{CH}_2)_2\text{Si}$	$(\text{Bu}_4\text{N})_3\text{H}[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{PhEtSi})_2\text{O}]$
11	$\alpha\text{-PW}_9\text{O}_{34}^{9-}$	PhSi	$(\text{Bu}_4\text{N})_3[\alpha\text{-A-PW}_9\text{O}_{34}(\text{PhSi})_3(\text{PhSiO}_3)]$
12		PhPO	$(\text{Bu}_4\text{N})_3\text{Na}_2[\alpha\text{-A-PW}_9\text{O}_{34}(\text{PhPO})_2]$
13	$\alpha\text{-SiW}_9\text{O}_{34}^{10-}$	PhSi	$(\text{Bu}_4\text{N})_4[\alpha\text{-A-SiW}_9\text{O}_{34}(\text{PhSi})_3(\text{PhSiO}_3)]$

General procedure for the synthesis of hybrid POMs 6,7,9,10.^{2,3}

0.5 to 0.8 g of $[\text{XW}_{10}\text{O}_{36}]^{\text{k-}}$ as alkali metal salt were suspended in 10 mL of $\text{CH}_3\text{CN-H}_2\text{O}$ mixture with 3 equiv of $n\text{-Bu}_4\text{NBr}$ and $\text{RSi}(\text{OMe})_3$ (2 equiv). 6M HCl (6 equiv) was then added with vigorous stirring. The solution was stirred for 15 h and the soluble product was isolated by solvent evaporation, washed with water and diethyl ether.

FT-IR (KBr, $1200 < \text{cm}^{-1} < 600$): **[6]**. 1158(w), 1128(m), 1064(w), 1037(m), 978(sh), 952(s), 840(s), 738(s), 699(sh), 997(w).³ **[7]**. 1126(w), 1049(w), 1096(m), 964(m), 952(m), 902(s), 885(s), 844(sh), 820(s), 732(s), 670(sh), 650(w). **[9]**. 1384(m), 1102(w), 964(m), 944(m), 903(s), 885(s), 841(m), 820(s), 732(s, b), 667(w). **[10]**. 1174(w), 1153(w), 1100(w), 1029(w), 965(m), 903(s), 880(s), 820(m), 796(m), 770(m), 733(w), 669(w).²

General procedure for the synthesis of hybrid POMs 1,3,5.^{4,5}

0.5 to 0.8 g of $[\text{XW}_{11}\text{O}_{39}]^{\text{k-}}$ as $n\text{-Bu}_4\text{N}^+$ or Ph_4P^+ salt were dissolved in 10 mL of CH_3CN , and RSiCl_3 (2 equiv) was added. The solution was stirred for 15 h at room temperature and the product was isolated by solvent evaporation, washed with water and with diethyl ether.

FT-IR (KBr, $1200 < \text{cm}^{-1} < 600$): **[1]**. 1129(w), 1111(m), 1067(m), 1041(w), 1028(sh), 961(m), 867(s), 820(s,b), 761(m), 709(m). **[3]**. 1128(w), 1049(s), 1011(m), 997(w), 964(s), 950(m), 923(sh), 902(s), 884(sh), 855(m), 806(s), 756(m), 706(m). **[5]**. 1189(m), 1165(m), 1109(m), 1042(w), 998(m), 964(s), 947(m), 904(s), 882(sh), 849(m), 803(s), 746(m), 721(w), 688(w).

General procedure for the synthesis of hybrid POMs 11,13.^{6,7}

0.5 to 0.8 g of $[\text{XW}_9\text{O}_{34}]^{\text{k-}}$ as alkaline metal salt were suspended in 10 mL of CH_3CN , with $n\text{-Bu}_4\text{NBr}$ (3-4.5 equiv) and RSiCl_3 (2-4 equiv). The mixture was stirred for 24 h at 0°C , and the soluble product was isolated by solvent evaporation, washed with water and with diethyl ether.

FT-IR (KBr, $1200 < \text{cm}^{-1} < 600$): **[11]**. 1128(m), 1096(s), 1019(m), 964(s), 931(sh), 868(s), 846(s), 743(s), 702(m). **[13]**. 1130(m), 1056(m), 1028(w), 998 (w), 963(s), 908(s), 890(s), 823(m), 726(s), 699 (sh).

General procedure for the synthesis of hybrid POMs 2,4.^{8,9}

0.5 to 0.8 g of $[\text{XW}_{11}\text{O}_{39}]^{\text{k-}}$ as alkaline metal salt were suspended in 10 mL of CH_3CN with $n\text{-Bu}_4\text{NBr}$ (5-6 equiv). A CH_3CN solution of PhPOCl_2 (2 equiv) was slowly added. The solution was stirred for 48 h at room temperature, and the soluble product was isolated by solvent evaporation, washed with water and with diethyl ether.

FT-IR (KBr, $1200 < \text{cm}^{-1} < 600$): **[2]**. 1137(w), 1117(m), 1105(w), 1079(w), 1064(w), 1044(m), 991(s), 881(s), 823(s), 785(s), 693(w). **[4]**. 1137(m), 1085(m), 1070(sh), 1041(w), 1009(w), 976(s), 914(s), 808(s), 735(sh), 693(sh), 648 (w).⁸

General procedure for the synthesis of hybrid POMs **8,12**.^{10,11}

0.5 to 0.8 g of $[\text{XW}_{12-n}\text{O}_{40-m}]^{k-}$ as alkaline metal salt were suspended in 10 mL of CH_3CN together with 3-3.5 equiv of $n\text{-Bu}_4\text{NBr}$, and $\text{PhPO}(\text{OH})_2$ (2 equiv) was added. 6M HCl (4 equiv) was slowly added while vigorously stirring. The solution was stirred for 15 h under reflux and the soluble product was isolated by solvent evaporation, washed with water and with diethyl ether.

FT-IR (KBr, $1200 < \text{cm}^{-1} < 600$): **[12]**. 1132(w), 1082(m), 1035(s), 1002(w), 976(s), 955(s), 876(s), 852(s), 817(s), 747(s), 687(sh), 667(w).¹⁰ **[8]**. 1196(w), 1137(w), 1049(w), 1008(w), 970(s), 943(s), 911(s), 884(s), 834(m), 796(m), 785(s), 752(s), 699(sh).¹¹ ESI-MS (-), ($\text{CH}_3\text{CN}/\text{H}_2\text{O}$): $m/z = 896.9$, $[\text{HSiW}_{10}\text{O}_{36}(\text{PhPO})_2]^{3-}$. $^{31}\text{P}\{-\text{H}\}$ NMR ($\text{CH}_3\text{CN}/\text{CD}_3\text{CN}$) δ : 18.68 ppm; ^{183}W -NMR ($\text{CH}_3\text{CN}/\text{CD}_3\text{CN}$) δ : -106.6 (2W, s), -114.4 (4W, s), -154.9 (4W, d, $J = 10.9$) ppm (Figure 1S);

Characterization of catalyst **[8]** recovered from the reaction mixture after MW irradiation provides the following spectra: FT-IR (KBr, $1200 < \text{cm}^{-1} < 600$): 1196(w), 1134(w), 1047(w), 1007(s), 970(s), 943(s), 911(s), 884(s), 834(m), 796 (sh), 785 (s), 752(s), 699(sh) (Figure 2S). ESI-MS (-): $m/z = 896.9$, $[\text{HSiW}_{10}\text{O}_{36}(\text{PhPO})_2]^{3-}$ (Figure 3S). After incubation with H_2O_2 (40 equiv) for a week: $^{31}\text{P}\{-\text{H}\}$ NMR δ : 18.70 ppm; ^{183}W -NMR δ : -108.0 (2W), -115.8 (4W) and -156.4 (4W, d, $J = 11.0$ Hz) ppm.

Figure 1S: ^{183}W -NMR spectrum of $[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{PhPO})_2]^{4-}$, TBA salt, in CH_3CN .

Figure 2S: FT-IR spectra of $[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{PhPO})_2]^{4-}$ before and after MW-assisted catalysis (50 min).

Figure 3S. ESI-MS of $[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{PhPO})_2]^{4-}$ recovered from the reaction mixture after MW-irradiation (25 min)

General oxidation procedure:

A CH₃CN solution (0.6 mL) containing POM (0.8-2.4 μmol) and 35 or 70 % H₂O₂ (0.1-0.3 mmol) was placed in a closed glass tube together with the substrate (0.5-1.5 mmol) (Caution: The uncontrolled heating of large amount of peroxides must be avoided. Care must be taken to avoid possible explosion). The reaction mixture was then exposed to MW irradiation in a Milestone *Ethos 1600 MW*-Labstation equipped with bulk temperature control *ATC-300* device, or in a CEM *Discover* instrument equipped with an IR temperature sensor, respectively with the following temperature programs: (i) initial ramp at 340 W for 3 min followed by maintenance at 240 W for 10, 25 or 50' at T_{bulk}=120 °C; (ii) 180 W for 50 min with T_{bulk}= 90-120 °C by cooling with compressed air. The reaction was monitored by withdrawing sample aliquots (20 μL), which were then diluted with a CH₂Cl₂ solution containing dodecane as internal standard, and analyzed by GLC. H₂O₂ consumption was verified by iodinated paper test. Formation of non-volatile products was monitored by GLC-MS analysis after silylation with BSTFA. Chalcone and cyclohexanone oxidation products were determined by ¹H-NMR on CD₃CN solutions. POM stabilities were assessed by comparison of their FT-IR spectra before the reaction and after it upon precipitation and washing with diethyl ether.

Kinetic analysis of methyl *p*-tolylsulfide oxidation by [γ-SiW₁₀O₃₆(PhPO)₂]⁴⁻

The consecutive oxidation of methyl *p*-tolylsulfide to sulfoxide and sulfone (equation 1S) was conducted at 50°C in CH₃CN (0.6 mL) with initial methyl *p*-tolylsulfide: 0.5 mmol, [γ-SiW₁₀O₃₆(PhPO)₂]⁴⁻ (0.8 μmol) and H₂O₂ (1.36 mmol). The reaction progress was monitored by GLC on quenched sample aliquots (20 μL) (Figure 4S). Pseudo-first order rate constants were obtained by fitting of the kinetic curves with *Scientist* (Micromath) software.

Figure 4S.: methyl *p*-tolylsulfide oxidation kinetic. ♦= methyl *p*-tolylsulfide; ■: methyl *p*-tolylsulfoxide ▲: methyl *p*-tolylsulfone. $k_S=2.5 \cdot 10^{-3} \text{ s}^{-1}$, $k_{SO}=2.4 \cdot 10^{-4} \text{ s}^{-1}$.

LFER studies (Tables 2S-5S)

Hammett correlations were obtained under MW irradiation or with conventional heating (25 °C), by performing the competitive oxidation of thioanisoles or methyl phenylsulfoxides (0.25 mmol) with equimolar *p*X-substituted terms, in the presence of H₂O₂ (0.1 mmol) and $[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{PhPO})_2]^{4-}$ (0.8 μmol) in CH₃CN (0.6 mL).

Table 2S: Hammett substituent effect in the oxidation of *p*-substituted thioanisoles by $[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{PhPO})_2]^{4-}$ at 25°C ($\rho=+-0.54$, $R^2=0.971$).

X	σ^+	$\log(k_X/k_H)$
MeO	-0.78	$4.0 \cdot 10^{-1}$
Me	-0.30	$2.8 \cdot 10^{-1}$
H	0	0
Cl	0.11	$-4.7 \cdot 10^{-2}$
CF ₃	0.53	$-3.3 \cdot 10^{-1}$
CN	0.71	$-3.7 \cdot 10^{-1}$
NO ₂	0.81	$-3.8 \cdot 10^{-1}$

Table 3S: Hammett substituent effect in the MW-assisted oxidation of *p*-substituted thioanisoles by $[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{PhPO})_2]^{4-}$ at $T_{\text{bulk}} = 120^\circ\text{C}$ ($\rho = -0.38$, $R^2 = 0.994$).

X	σ^+	$\log(k_X/k_H)$
MeO	-0.78	$2.6 \cdot 10^{-1}$
Me	-0.30	$1.1 \cdot 10^{-1}$
H	0	0
Cl	0.11	$-5.9 \cdot 10^{-2}$
CF ₃	0.53	$-2.4 \cdot 10^{-1}$
CN	0.71	$-2.8 \cdot 10^{-1}$
NO ₂	0.81	$-3.3 \cdot 10^{-1}$

Table 4S: Hammett substituent effect in the oxidation of *p*-substituted methyl phenylsulfoxides by $[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{PhPO})_2]^{4-}$ at 25°C (ρ , $\sigma < 0 = -0.55$, $R^2 = 0.952$; ρ , $\sigma > 0 = 0.21$, $R^2 = 0.988$).

X	σ	$\log(k_X/k_H)$
(Me) ₂ N	-0.87	$4.5 \cdot 10^{-1}$
MeO	-0.27	$2.1 \cdot 10^{-1}$
Me	-0.17	$1.2 \cdot 10^{-1}$
H	0	0
Cl	0.23	$5.6 \cdot 10^{-2}$
CF ₃	0.54	$1.1 \cdot 10^{-1}$

Table 5S: Hammett substituent effect in the MW-assisted oxidation of *p*-substituted methyl phenylsulfoxides by $[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{PhPO})_2]^{4-}$ at $T_{\text{bulk}} = 120^\circ\text{C}$ (ρ , $\sigma < 0 = -0.58$, $R^2 = 0.987$; ρ , $\sigma > 0 = 0.18$, $R^2 = 0.935$).

X	σ	$\log(k_X/k_H)$
(Me) ₂ N	-0.87	$5.0 \cdot 10^{-1}$
MeO	-0.27	$1.7 \cdot 10^{-1}$
Me	-0.17	$5.5 \cdot 10^{-2}$
H	0	0
Cl	0.23	$5.1 \cdot 10^{-2}$
CF ₃	0.54	$1.1 \cdot 10^{-1}$
NO ₂	0.78	$1.4 \cdot 10^{-1}$

Determination of the substrate kinetic order for the oxidation of methyl *p*-tolylsulfoxide by $[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{PhPO})_2]^{4-}$. Initial oxidation rates (R_0) were obtained by monitoring the reaction kinetics with $^1\text{H-NMR}$ at room temperature. Initial sulfoxide concentration was varied in the range $[\text{methyl } p\text{-tolylsulfoxide}]_0 = 0.013\text{--}0.57\text{ M}$, in the presence of $[\text{POM}] = 1.36\text{ mM}$ and $[\text{H}_2\text{O}_2]_0 = 0.167\text{ M}$, in CD_3CN (0.5 mL) (Table 6S).

Table 6S: Dependence of the initial oxidation rate on the substrate concentration. In all experiments: $[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{PhPO})_2]^{4-}$ 0.68 μmol and H_2O_2 83.5 μmol , in 0.5 mL CD_3CN , $T = 25^\circ\text{C}$.

$[\text{methyl } p\text{-tolylsulfoxide}]_0, \text{ M}$	$R_0, \text{ M/s}$
$1.3 \cdot 10^{-2}$	$8.5 \cdot 10^{-8}$
$8.8 \cdot 10^{-2}$	$2.0 \cdot 10^{-6}$
$1.6 \cdot 10^{-1}$	$3.2 \cdot 10^{-6}$
$3.2 \cdot 10^{-1}$	$3.3 \cdot 10^{-6}$
$5.7 \cdot 10^{-1}$	$3.9 \cdot 10^{-6}$

Figure 5S : Dependence of the initial rate (R_0) on the initial concentration of methyl *p*-tolylsulfoxide.

Interpolation of kinetic data according to a Michaelis-Menten saturation kinetic $\text{Rate} = (R_{\text{max}} \cdot [\text{Sub}]) / (K_{\text{M}} + [\text{Sub}])$, yields the following parameters: $R_{\text{max}} = 4.7 \cdot 10^{-6}\text{ M/s}$; $K_{\text{M}} = 0.11$.

Competitive experiments with 2-hexene isomers. Selectivity experiments on *cis/trans* olefins were set up at 35°C , with *cis*-2-hexene (0.75 mmol) and *trans*-2-hexene (0.75 mmol), 70 % H_2O_2 (0.3 mmol) and $[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{PhPO})_2]^{4-}$ (2.4 μmol) in CH_3CN (0.6 mL). Reaction samples were analysed by GLC.

Stereoselective oxidation of methyl *p*-tolylsulfide with chiral 1-aminoethylphosphonic acid-POM derivatives. Enantiomeric POM hybrids were obtained as described for catalyst **8**,¹¹ by using R(-) or S(+) 1-aminoethylphosphonic acids. The attachment of the chiral organic moiety on the POM surface was assessed by ³¹P-{H}NMR and FT-IR, showing the occurrence of a functionalized decatungstosilicate. ³¹P-{H}NMR (CH₃CN\CD₃CN) δ: -14.7 ppm; FT-IR, KBr, (1200<cm⁻¹<600): 1151(s), 1107(s), 1004(m), 963(s), 925(s), 904(s), 881(s), 784(s,b), 663(s).

The asymmetric oxidation of methyl *p*-tolylsulfide (14.2 μmol) was performed in CH₃CN (0.5 mL) with the chiral POM (22 mg) and 35 % H₂O₂ (14.2 μmol) for 72 h at -10 °C. Reaction samples were analysed by GLC and by chiral HPLC using hexane : isopropanol = 9:1 as eluent.

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