Bio-inspired oxidations with polyoxometalate catalysts

Marcella Bonchio [a,*], Mauro Carraro [a], Andrea Sartorel [a],
Gianfranco Scorrano [a], Ulrich Kortz [b]

[a] *ITM-CNR, University of Padova, Department of Chemical Sciences, Via Marzolo 1, Padova 35131, Italy*
[b] *International University Bremen, School of Engineering and Science, P.O. Box 750 561, 28725 Bremen, Germany*

Abstract

Transition metal substituted polyoxometalates (TMS-POM) provide a redox-active metal center, (Fe, Ru, Mn or else), with a totally inorganic ligand system, featuring rigid polydentate binding sites, high electron-acceptor character, extreme robustness and interesting structural and coordination properties, in some cases, mimicking the coordination geometry of natural oxygenase enzymes. Their synthesis and reactivity can be promoted by microwave (MW) induced dielectric heating. In particular, MW irradiation induces a very efficient and selective hydrothermal synthesis of the diamagnetic, air-stable $[Ru^{II}(DMSO)PW_{11}O_{39}]^{5-}$. Its catalytic activity has been screened with shunt oxidants like $NaIO_4$ and $KHSO_5$ and $PyCl_2NO$. Under dioxygen and MW irradiation, $[Ru^{II}(DMSO)PW_{11}O_{39}]^{5-}$ catalyzes the oxidation of DMSO to $DMSO_2$ in water. Fe^{III}-POMs with nuclearities 1–4, namely $[\alpha\text{-}Fe(H_2O)SiW_{11}O_{39}]^{5-}$ ($FeSiW_{11}$), $[\gamma\text{-}Fe_2(H_2O)_2SiW_{10}O_{38}]^{6-}$ (Fe_2SiW_{10}), $[\alpha\text{-}Fe_3(H_2O)_3SiW_9O_{37}]^{7-}$ (Fe_3SiW_9) and $[\beta\text{-}Fe_4(H_2O)_{10}(XW_9O_{33})_2]^{n-}$ ($Fe_4X_2W_{18}$, $X = Se^{IV}$, Te^{IV}; As^{III}, Sb^{III}; $n = 4$, 6) were also found to catalyze the MW assisted cyclohexane oxygenation with high turnover frequencies. Preliminary results indicate that the Krebs-type Fe polyoxotungstates can also promote the oxidative cleavage of 3,5-ditert-butylcatechol with molecular oxygen.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Polyoxometalates; Aerobic oxidation; Ruthenium; Iron; Catalytic oxidation

1. Introduction

Polyoxometalates (POMs) are oxo-clusters of early transition metals in their highest oxidation state, namely Mo(VI), W(VI), V(V), etc. They are discrete, soluble multi-metal oxides characterized by a formidable structural variety with different chemical composition, anionic charge and counterions and by specific properties including: nano-sized dimensions, shape, charge density and surface reactivity [1–3]. These clusters retain a major appeal for oxidation catalysis because of their (i) inertness to thermal and oxidative degradation; (ii) tunable solubility by counterion metathesis (from water, to organic or perfluorinated media) [4]; (iii) polyelectrolyte behavior; (iv) photocatalytic activity [3]. Moreover, appropriate synthetic strategies can be exploited to generate catalyst diversity through substitution with hetero-transition metals and/or to obtain hybrids where the merging of organic and inorganic domains can be exploited to improve the catalyst performance and selectivity

[5,6]. This communication will focus on transition metal substituted polyoxometalates (TMSP) which display one or more redox-active metal center within a totally inorganic ligand system provided by the polyoxometalate framework [1–3]. Indeed, POM-based ligands feature rigid polydentate binding sites with unique electron-acceptor ability, extreme robustness and interesting structural and coordination properties. Worth of notice is that the coordination geometry of representative structural type POMs finds a close correspondence with the active site of natural oxygenase enzymes [7–9].

As highlighted in Fig. 1, Fe-substituted Keggin α-undeca- and γ-decatungstates [10,11] and the Krebs-type derivatives [12], may suggest a POM-based inorganic mimicry respectively of *heme*-Cytochrome P450, the $Fe_2(\mu\text{-}O)_2$ diamond core of methane monooxygenase (MMO) and the non-*heme* dioxygenase iron site with three exchangeable coordination positions [7–9]. Thus, a most desirable feature would be that such a structural diversity might pose the basis for a variety of catalytic functions paralleling the enzyme paradigm. A bio-inspired approach on the design and application of the POM-based catalysts has been proposed in the literature [13,14]. However few systematic investigation including detailed mechanistic studies

$[\alpha\text{-Fe}(H_2O)SiW_{11}O_{39}]^{5-}$ $[\gamma\text{-Fe}_2(H_2O)_2(SiW_{10}O_{36})]^{6-}$ $[\beta\text{-Fe}_4(H_2O)_{10}(AsW_9O_{33})_2]^{6-}$

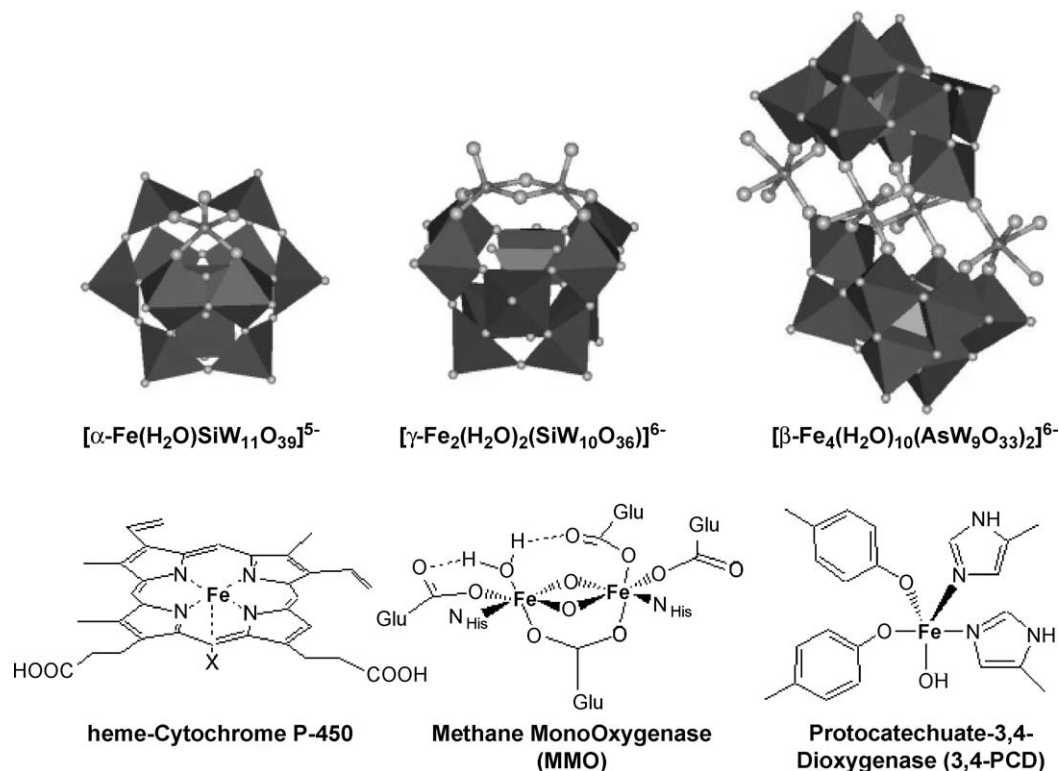heme-Cytochrome P-450   Methane MonoOxygenase (MMO)   Protocatechuate-3,4-Dioxygenase (3,4-PCD)

Fig. 1. Structures of representative Fe substituted polyoxotungstates as inorganic synzymes.

and structure–reactivity correlations are available. Moreover an appealing tool is the use of non-conventional activation techniques such as microwave (MW) irradiation [15]. The efficiency of microwave flash heating in accelerating organic transformations (reaction times reduced from days and hours to minutes and seconds) is well recognized [15]. Of particular interest is therefore the application of new microwave-assisted methodologies to high-speed metal catalyzed oxidations. In this respect, the use of robust polyanionic catalysts, especially in water as solvent, represent a specific advantage considering that polar and ionic conducting media lead to an extremely rapid in situ MW-induced heating, expected to produce an efficient thermal activation under controlled and safer conditions [15]. In the following paragraphs, we will address the effect of MW irradiation both in the synthesis of TMSP and in catalysis.

2. Experimental section

2.1. Materials

Hydrothermal synthesis of $Li_5Ru(DMSO)PW_{11}O_{39}$ was previously reported [16]. Iron substituted polyoxotungstates were prepared following literature procedures [10–12,17]. THA salts were obtained by cation exchange in water. $RuCl_3$ (Aldrich) was used as ruthenium source for the synthesis of $RuCl_2(DMSO)_4$. 3,3-DTBC (Aldrich, 99%) was recrystallized using n-hexane. Commercially available, reagent grade organic compounds used as oxidation substrates were used without additional purification.

2.2. Instrumentation

GC analyses were performed with a Hewlett Packard 5890 Series II instrument, equipped with flame ionisation detector and capillary column HP 5 (30 m; I.D. 0.32 mm; 0.25 μm film thickness, ^{31}P, ^{29}Si, ^{13}C, and ^{1}H NMR were obtained on a Bruker AV 300 instrument, equipped with a multinuclear probe spectra. ^{183}W and ^{99}Ru spectra were obtained on a Bruker Avance DRX 400 instrument, equipped with a standard (^{31}P–^{109}Ag) 10 mm broadband probe tuned below its specifications. MS (ESI) analyses were done with a Finnigan MAT LCQ instrument. FT-IR was recorded with a Perkin-Elmer 1600 series instrument. MW irradiation was performed inside the cavity of the MW Ethos-1600 labstation (Milestone).

2.3. Catalytic oxidations

MW assisted oxidations were performed in water or in organic solvent, under dioxygen atmosphere, in a 10 ml closed teflon reactor (HPR-1000/10S, Milestone) equipped with temperature and pressure control units and irradiated inside the cavity of a MW Ethos-1600 labstation (Milestone). Oxidation of DMSO (27.5 mM) was performed in water in the presence of the tungstoruthenate catalyst (4.7 mM) under oxygen atmosphere and MW irradiation (initial power, 350 W; initial time, 2 min; final power, 300 W; T_{bulk}, 200 °C, reaction time, 180 min). Cyclohexane oxidation was performed in DCE (0.8 ml) with Fe-POM (0.75–0.19 μmol) and cyclohexane (0.98 ml), under dioxygen atmosphere, MW irradiation (at 240 W, T_{bulk} = 120 °C). The reactions were sampled

(50 μl) over time and analysed generally by ^{1}H NMR, GLC and GLC-MS. Conventionally heated oxidations were performed in thermostated reactors. Aerobic oxidation of 3,5-di-*tert*-butylcatechol (DTBC, 60 mM) was performed in mixed solvent THF:H$_2$O (98:2, 5 ml) in the presence of Fe-POMs (8 mM) and 3,5-di-*tert*-butyl-*p*-cresol (DTBC, 200 mM) under oxygen atmosphere (1 atm) at 25 °C. Products were identified by comparison with spectroscopic literature data and by comparison with authentic samples. Chemical yields and conversions were generally determined by quantitative GC analysis. Peroxide content was determined using the triphenylphosphine quencher method [18], carboxylic acids were revealed by silylation with BSTFA before GLC-MS analysis. Catalyst stabilities were assessed by FT-IR after precipitation from the reaction mixture and washing with diethyl ether.

3. Results and discussion

3.1. MW assisted synthesis and reactivity of [Ru^{II}(DMSO)PW$_{11}$O$_{39}$]$^{5-}$

Lacunary POMs with missing metallic addenda are key intermediates for the incorporation of hetero-transition metal cations [2]. In particular, Keggin-type undecatungstates of formula [XW$_{11}$O$_{39}$]$^{n-}$ (X = B, Si, Ge, P, As), represent a unique class of ligands. By providing a planar tetradentate binding site with a proximal axial coordination position, they have been considered as inorganic porphyrin analogs (Fig. 1) [19]. In the field of metal catalyzed oxidations, ruthenium porphyrins have proved to effect dioxygen activation [20], to react with N$_2$O [21], and to promote highly chemo- and stereoselective oxidative transformations in the presence of various oxygen donors [22].

Therefore, POMs derivatization with ruthenium is of great interest in the field of catalytic oxidations [14,23–25], and to this aim two different routes have been pursued: (i) ruthenium incorporation within the polyoxoanion framework, leading to Ru-substituted POMs; (ii) functionalization of the polyoxoanion surface leading to Ru-supported POMs [16,23–26]. The latter approach has been used for the synthesis of new organometallic species providing the ruthenium center with a hybrid set of ligands [23–25]. Despite their appealing potential, the synthesis of ruthenium substituted polyoxotungstates is not straightforward and high temperatures and prolonged reaction times are generally needed. Ruthenium precursors as RuCl$_3$·nH$_2$O, [Ru(H$_2$O)$_6$][C$_7$H$_7$SO$_3$]$_2$, Ru(acac)$_3$, and *cis*-Ru(DMSO)$_4$Cl$_2$ have been used under different experimental conditions [23–25]. In the most recent synthetic protocols, the reagent of choice has been the organometallic complex *cis*-Ru(DMSO)$_4$Cl$_2$ [24,25]. In particular, this latter has been employed for the metalation of the lacunary ligand [PW$_{11}$O$_{39}$]$^{7-}$ in water at 200 °C under MW irradiation [16]. The MW assisted hydrothermal process leads to the highly selective incorporation of a ruthenium atom into the polyoxometalate framework in 5–15 min (Scheme 1). The diamagnetic, air-stable, [Ru^{II}(DMSO)PW$_{11}$O$_{39}$]$^{5-}$ complex can be isolated, after purification on size exclusion and ion-exchange columns, as Li$^+$, Na$^+$ or K$^+$ salt, in 70–80% yields on a gram
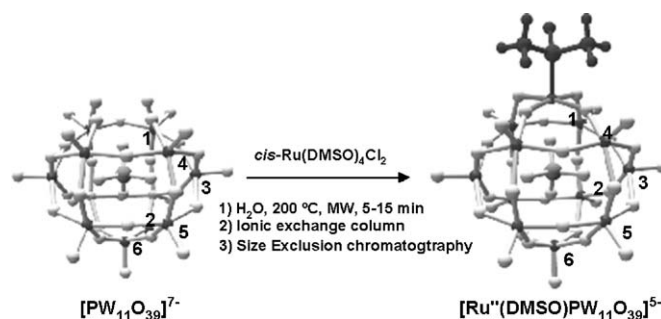
Scheme 1. Reagents and product of the MW assisted hydrothermal metalation. POM structures highlight the six non-equivalent W atoms of the ^{183}W-NMR spin systems.

scale. The progress and the selectivity of the POM metalation can be monitored by ^{183}W NMR given that the unreacted ligand and the tungstoruthenate complex give rise to two distinct sets of six resonances [16].

MW irradiation induces a remarkable acceleration as compared to conventional heating performed at 100 °C for 48 h. In fact, despite the prolonged heating, the conventional reaction occurs only to a 50% extent (Fig. 2) while the MW assisted metalation results in the formation of the expected product, as the only detected species in solution, after just 15 min.

Experimental and computational studies addressing the structure of the metalated complex, indicate that ruthenium is coordinated to the four lacunary oxygens of the phosphotungstate ligand and to the sulfur atom of one terminal DMSO molecule [16,27]. The problem with respect to catalytic applications is that bound DMSO ligands are very inert and provide a strong stabilization of the Ru(II) center thus preventing its oxidation to high valent Ru-oxo intermediates. In particular the title catalyst displays a remarkable stability in water, under O$_2$ atmosphere, at room temperature. In this respect, activation of the ruthenium center should involve either the substitution of the DMSO ligand and/or high temperature conditions [24,25]. In first instance, the behavior of [Ru^{II}(DMSO)PW$_{11}$O$_{39}$]$^{5-}$ in catalytic oxidation has been examined in the presence of "shunt" oxidants, including 2,6-dichloro pyridine *N*-oxide (PyCl$_2$NO), which has proved to be highly efficient in porphyrin-based systems [28]. Inspection of Table 1 results show that oxidation turnover can be obtained with sodium periodate (NaIO$_4$) and potassium monopersulfate (KHSO$_5$) as tested in the oxidation of two model hydrocarbons, cyclooctene and adamantane, respectively. No reaction is observed with the heteroaromatic *N*-oxide, PyCl$_2$NO [29]. Of particular interest is the ruthenium promoted cleavage of the olefinic double bond with NaIO$_4$, which can be also performed in water, with no need of organic solvent or phase transfer agent, and leads to substrate quantitative conversion in 4 h at 50 °C, suberic acid being the major product formed (84% yield) [16]. In analogous conditions cyclohexene yields adipic acid (90% yield). In the hydroxylation of adamantane, the title catalyst exhibits the high selectivity for the tertiary C–H functionalization, typical of high valent ruthenium-oxo species. Under turnover conditions the DMSO ligand is oxidized to dimethylsulfone (DMSO$_2$). The lack of reactivity found with PyCl$_2$NO is likely associated to the strong binding of the DMSO ligand
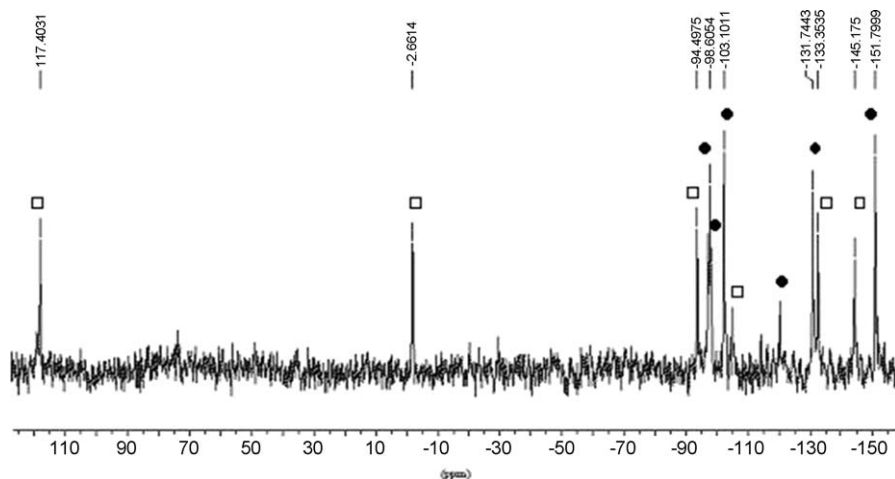
Fig. 2. ^{183}W-NMR spectrum of the reaction mixture after 48 h at 100 °C under conventional heating showing signals of unreacted $[PW_{11}O_{39}]^{7-}$ (full circles) and of $[Ru^{II}(DMSO)PW_{11}O_{39}]^{5-}$ (empty squares).

Table 1
Catalytic oxidation of model hydrocarbons by $[Ru^{II}(DMSO)PW_{11}O_{39}]^{5-}$ with different oxidants[a]

Substrate (M)	Oxidant (M)	Time (h)	Conversion (%)[b]	Main products (%)[c]
Cyclooctene (0.1)	PyCl$_2$NO (0.1)	18	0	–
	NaIO$_4$ (0.4)	22	95	Suberic acid (80)
Adamantane (0.1)	PyCl$_2$NO (0.1)	30	0	–
	KHSO$_5$ (0.4)[d]	24	60	1-adamantanol (30), 1-chloroadamantane (20)[e]

[a] In all reactions: catalyst (0.005 M) in H$_2$0:1,2-dichloroethane biphasic medium with nBu$_4$N$^+$HSO$_4$$^-$ (0.05 M) as phase transfer agent, room temperature. Reactions with PyCl$_2$NO were performed in 1,2-dichloroethane.

[b] % of substrate conversion.

[c] % yield based on substrate conversion.

[d] Added in four portions over 4 h.

[e] Adamantanone and 2-chloroadamantane are also formed in ca. 10% overall yield.

which prevents the coordination of the heteroaromatic N-oxide to the ruthenium center, and therefore the formation of the active metal oxidant in solution [28].

In order to provide a highly efficient thermal activation, catalytic oxygenation by $[Ru^{II}(DMSO)PW_{11}O_{39}]^{5-}$ has been performed with the assistance of MW irradiation. To this aim, water can be considered the solvent of choice due to the high efficiency in the MW absorbance thus inducing strong dielectric heating [15].

Under MW assistance, Li$_5$Ru^{II}(DMSO)PW$_{11}$O$_{39}$ catalyzes the selective oxygen transfer to DMSO in water leading to the quantitative production of DMSO$_2$. The reaction is carried out in acetate buffer solution (pH 4.8), requires oxygen atmosphere and MW induced dielectric heating (T_{bulk} = 200 °C). Oxidation turnover is obtained in the presence of DMSO excess. Under the condition adopted the resting state of the catalyst is a paramagnetic Ru(III) complex which retains the α-Keggin structure of the POM ligand as confirmed by IR spectroscopy and ESI-MS studies. While a detailed analysis of the dioxygen activation mechanism will be reported in due course, it is important to anticipate that ^{18}O incorporation (>60%) in DMSO$_2$ occurs when the oxidation is run in enriched H$_2$O^{18}. This evidence speaks in favor of the involvement of a high valent Ru-oxo species which undergoes oxygen atom exchange with the solvent prior to oxygen transfer to substrate. The occurrence of

high valent "oxene" intermediate in the realm of TMSP catalysts has been recently assessed through computational methods [30]. Indeed, the involvement of a Ru(III)–Ru(V) manifold for oxygen transfer in water has been demonstrated in the electrolytic oxygenation of DMSO catalyzed by Ru^{III}(H$_2$O)PW$_{11}$O$_{39}$$^{4-}$ as reported by Pope and Rong according to Scheme 2 [26].

3.2. Iron substituted polyoxotungstates as oxygenation catalysts

Metalation of lacunary polyoxotungstates is the way to Fe^{III}-POMs with nuclearities 1–4, namely $[α-Fe(H_2O)SiW_{11}O_{39}]^{5-}$ (FeSiW$_{11}$), $[γ-Fe_2(H_2O)_2SiW_{10}O_{38}]^{6-}$ (Fe$_2$SiW$_{10}$), $[α-Fe_3(H_2O)_3SiW_9O_{37}]^{7-}$ (Fe$_3$SiW$_9$) and [β-Fe$_4$
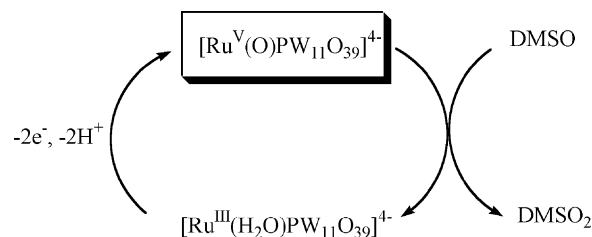
Scheme 2. Electrolytic oxygenation of DMSO catalyzed by Ru^{III}(H$_2$O)PW$_{11}$O$_{39}$$^{4-}$.
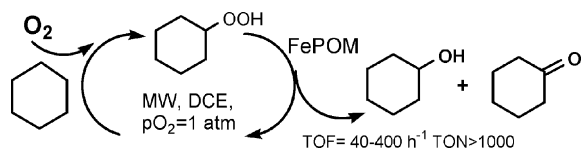
Scheme 3. MW assisted cyclohexane oxygenation by FePOMs.

Fig. 3. kinetics of the MW assisted cyclohexane oxygenation by $FeSiW_{11}$ (graph A) and $Fe_4As_2W_{18}$ (graph B).

$(H_2O)_{10}(XW_9O_{33})_2]^{n-}$ ($Fe_4X_2W_{18}$, $X = Se^{IV}$, Te^{IV}; As^{III}, Sb^{III}; $n = 4$, 6) [10–12,17]. These complexes, as tetrahexylammonium (THA) salts, have been used in 1,2-dichloroethane (DCE) as catalysts for hydrocarbon oxygenation [31]. Catalytic aerobic oxygenation at low dioxygen pressure is generally plagued by a prolonged reaction time, associated to the presence of a marked induction time and low turnover frequencies (TOFs). MW induced dielectric heating, provides a rapid reaction protocol for screening the activity and selectivity of this class of catalysts. Under the conditions explored (Scheme 3), cyclohexane oxygenation occurs with conversion of up to 3% in 250 min, yielding cyclohexylhydroperoxide (CHHP), cyclohexanol (A) and cyclohexanone (K) with 90–95% selectivity [32], total turnover number >1000, and TOFs in the range 40–400 h^{-1} [31].

In all cases, several lines of evidence delineate a radical chain mechanism, namely (i) a biphasic kinetic trace, indicating an autocatalytic behavior; (ii) accumulation of the autoxidation product CHHP; (iii) fast initiation by *tert*-butyl hydroperoxide (TBHP); (iv) inhibition by the radical scavenger 3,5-di-*tert*-butyl-4-hydroxytoluene (BHT). The severe mechanistic complexity associated with metal-mediated radical chain oxidations, hampers a clear-cut elucidation of the catalyst role and its involvement in homolytic and/or heterolytic mechanistic pathways. However, a key point is that both conversion and selectivity of the oxidation show a marked dependence on the nature of Fe-POM catalyst (Table 2). In particular POMs with higher iron nuclearity, lead to an increase in CHHP accumulation and in ketone selectivity (cfr entry 1 with entries 2–7 in Table 2). This observation emerges also from inspection of the oxidation kinetics obtained with catalysts $FeSiW_{11}$ and $Fe_4As_2W_{18}$ (Fig. 3). Both features are consistent with a depressed peroxide decomposition via homolytic pathways, favoring heterolytic ketonization. This latter is likely to involve peroxometal intermediates, whose nature and stability may depend on the structural

Table 2
MW assisted cyclohexane oxygenation by Fe^{III}-POM catalysts[a]

#	Catalyst[a]	Conversion (%)[b]	Selectivity[c] CHHP:A:K
1	$FeSiW_{11}$	1.42	6:67:28
2	Fe_2SiW_{10}	0.54	73:7:20
3	Fe_3SiW_9	0.37	76:6:18
4	$Fe_4Se_2W_{18}$	0.30	88:0:12
5	$Fe_4Te_2W_{18}$	0.51	66:25:9
6	$Fe_4Sb_2W_{18}$	0.57	45:35:20
7	$Fe_4As_2W_{18}$	0.96	49:33:18

[a] DCE 0.8 ml, cyclohexane 9.1 mmol, catalyst 0.75 μmol, O_2 1 atm, $T = 120\,°C$, MW irradiation at 240 W for 150 min.
[b] % of substrate conversion.
[c] % Product distribution.
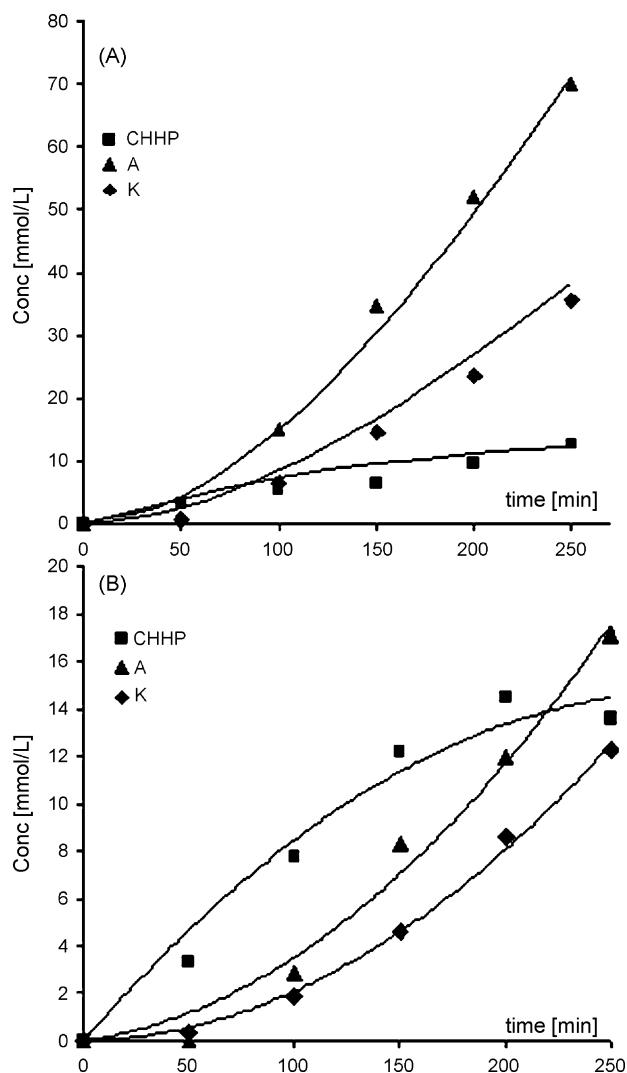
arrangement of the iron moiety and on the POM tungsten framework [33].

In spite of some encouraging results the quest for synthetic oxygenases in the field of POMs appears a formidable challenge. The possibility to access a library of isostructural POM-based catalysts represent a unique tool for structure–reactivity correlations in order to address both the reaction mechanism and the structural/electronic requirements of the active catalysts. In this context the very large family of Krebs-type isostructural polyoxotungstates (almost 20 species including Fe^{III} derivatives) represented by the formula $[\beta-M_4(H_2O)_{10}(XW_9O_{33})_2]^{n-}$ ($n = 6$, $X = As^{III}$, Sb^{III}, $M = Fe^{III}$ and Cr^{III}; $n = 4$, $X = Se^{IV}$, Te^{IV}, $M = Fe^{III}$ and Cr^{III}; $n = 8$, $X = Se^{IV}$, Te^{IV}, $M = Mn^{II}$, Co^{II}, Ni^{II}, Zn^{II}, Cd^{II} and Hg^{II}), see structure in Fig. 1, can be considered an ideal catalyst pool [12]. Most noticeably, such complexes display four highly accessible transition metal ions, featuring at least two coordination positions available for both substrate and oxygen binding. Thus, considering the coordination geometry of the catalytic center, these complexes have been screened

Scheme 4. Aerobic oxidation of 3,5-diterbutylcatechol (DTBC) catalyzed by Fe-POMs.

for catechol oxidative cleavage, performed with high efficiency and selectivity by non-heme iron-dioxygenase enzymes [8]. Preliminary studies indicate that, iron substituted polyoxotungstates with Krebs structure $[\beta\text{-Fe}_4(H_2O)_{10}(XW_9O_{33})_2]^{n-}$ ($Fe_4X_2W_{18}$), catalyze the oxidative cleavage of 3,5-di-*tert*-butylcatechol (DTBC) with molecular oxygen (Scheme 4).

Under the condition explored, oxidative cleavage account for ca. 25% of substrate conversion, leading to products deriving both from intra- and extra-diol cleavage selectivity, respectively, 3,5-di-*tert*-butyl-1-oxacyclohepta-3,5-diene-2,7-dione (muconic acid anhydride, 3,5-DTBA) and 4,6-di-*tert*-butyl-1-oxacyclohepta-4,6-diene-2,3-dione (2,3-dione) [8]. The reaction has been performed in the presence of 3,5-di-*tert*-butyl-*p*-cresol (BHT) as radical scavenger to inhibit substrate autoxidation responsible for the formation of 3,5-di-*tert*-butyl-1,2-benzoquinone (3,5-DTBQ), a major side-product. The observed reactivity is ascribable to the two iron(III) centers having three binding sites available for both substrate and dioxygen coordination. In fact, isostructural complexes incorporating Mn^{II}, Co^{II}, Ni^{II}, Cr^{III}, Cu^{II}, Cd^{II} are inactive, and so are other iron substituted complexes, namely $[\alpha\text{-Fe}(H_2O)SiW_{11}O_{39}]^{5-}$ ($FeSiW_{11}$) and $[\gamma\text{-Fe}_2(H_2O)_2SiW_{10}O_{38}]^{6-}$ (Fe_2SiW_{10}), in which the iron center does not display the opportune coordination geometry. The system displays an interesting reactivity also in aqueous media thus potential applications for wastewater treatment and the oxidative degradation of water-soluble aromatic pollutants may be envisaged. This reaction establishes a new mimicry of the catechol dioxygenase enzymes with an all-inorganic class of catalysts.

4. Conclusions

The quest for efficient oxygenation systems represents a major objective in catalysis. In particular, there is a call for a high turnover, highly stable catalytic system capable of reacting with O_2 to effect substrate oxygenation and performing ideally in water under mild or controlled thermal activation. In this respect, the use of MW induced flash-activation fits well with the polyanionic, inorganic nature of POM-based oxidation catalysts. High performance and peak efficiencies can be achieved both in the synthesis and in turnover regimes. Our results contribute to the search for non-traditional processes, featuring competitive productivity rates with MW technology. On the other end, they validate a foreseen mechanistic variety within the realm of the so-called "inorganic synzymes" and set the basis for a detailed investigation to address powerful structure–reactivity correlations.

Acknowledgements

References

[1] M.T. Pope, Heteropoly and Isopoly Oxometalates, Springer-Verlag, New York, 1983.

[2] In: C.L. Hill (Ed.), "Polyoxometalates" Special Issue, Chem. Rev. 98 (1998) 1–387;
C.L. Hill, C.M. Prosser-McCharta, Coord. Chem. Rev. 143 (1995) 407.

[3] M.T. Pope, A Müller Polyoxometalate Chemistry. From Topology Via Self-assembly to Applications, Kluwer Academic Publishers, Dordrecht, The Netherlands, 2002.

[4] M. Vazylyev, D. Sloboda-Rozner, A. Haimov, G. Maayan, R. Neumann, Top. Catal. 34 (2005) 93.

[5] M. Bonchio, M. Carraro, G. Scorrano, A. Bagno, Adv. Synth. Catal. 346 (2004) 648.

[6] A. Bagno, M. Bonchio, Angew. Chem. Int. Engl. Ed. 44 (2005) 2023.

[7] B.J. Wallar, J.D. Lipscomb, Chem. Rev. 96 (1996) 2625.

[8] M. Costas, M.P. Mehn, M.P. Jensen, L. Que Jr., Chem. Rev. 104 (2004) 939.

[9] T.J. McMurry, J.T. Groves, in: P.R. Ortiz de Montellano (Ed.), Metalloporphyrin Models for Cytochrome P-450, Plenum Press, New York, 1986.

[10] F. Zonnevijlle, C.M. Tourné, G.F. Tourné, Inorg. Chem. 21 (1982) 2751.

[11] C. Nozaki, I. Kiyoto, Y. Minai, M. Misono, N. Mizuno, Inorg. Chem. 38 (1999) 5724.

[12] U. Kortz, M.G. Savelieff, B.S. Bassil, B. Keita, L. Nadjo, Inorg. Chem. 41 (2002) 783–789.

[13] C. Nozaki, M. Misono, N. Mizuno, Chem. Lett. 27 (1998) 1263;
Y. Nishiyama, Y. Nakagawa, N. Mizuno, Angew. Chem. Int. Ed. 40 (2001) 3639;
N. Mizuno, M. Hashimoto, Y. Sumida, Y. Nakagawa, K. Kamata, Polyoxometalate Chemistry for Nano-Composite Design, Kluwer Academic/Plenum, New York, 2002, p. 197.

[14] R. Neumann, M. Dahan, Nature 388 (1997) 353;
R. Neumann, M. Dahan, J. Am. Chem. Soc. 120 (1998) 11969.

[15] M. Larhed, C. Moberg, A. Hallberg, Acc. Chem. Res. 35 (2002) 717;
A. Loupy, CR Chimie 7 (2004) 103;
C.O. Kappe, Angew. Chem. Int. Ed. 43 (2004) 6250;
A. de la Hoz, A. Diaz-Ortiz, A. Moreno, Chem. Soc. Rev. 34 (2005) 164.

[16] A. Bagno, M. Bonchio, A. Sartorel, G. Scorrano, Eur. J. Inorg. Chem. (2000) 17.

[17] J. Liu, F. Ortéga, P. Sethuraman, D.E. Katsoulis, C.E. Costello, M.T. Pope, J. Chem. Soc. Dalton Trans. (1992) 1901.

[18] G.B. Shul'pin, CR Chimie 6 (2003) 163.

[19] L.C.W. Baker, J.S. Figgis, J. Am. Chem. Soc. 92 (1970) 3794;
C.L. Hill, R.B. Brown, J. Am. Chem. Soc. 108 (1986) 536.

[20] J.T. Groves, R. Quinn, J. Am. Chem. Soc. 107 (1985) 5790.

[21] J.T. Groves, J.S. Roman, J. Am. Chem. Soc. 117 (1995) 5594.

[22] T. Naota, H. Takaya, S.-I. Murahashi, Chem. Rev. 98 (1998) 2599.

[23] L.-H. Bi, U. Kortz, M.H. Dickman, B. Keita, L. Nadjo, Inorg. Chem. 44 (2005) 7485.

[24] L.H. Bi, F. Hussain, U. Kortz, M. Sadakane, M.H. Dickman, Chem. Commun. (2004) 1420;
Li-H Bi, U. Kortz, B. Keita, L. Nadjo, Dalton Trans. (2004), 3184 (and references therein).

[25] V. Artero, D. Laurencin, R. Villanneau, R. Thouvenot, P. Herson, P. Gouzerh, A. Proust, Inorg. Chem. 44 (2005) 2826.

[26] C. Rong, M.T. Pope, J. Am. Chem. Soc. 114 (1992) 2932.

[27] A. Bagno, M. Bonchio, Eur. J. Inorg. Chem. (2002) 1475;
A. Bagno, M. Bonchio, A. Sartorel, G. Scorrano, ChemPhysChem 4 (2003) 517;
A. Bagno, M. Bonchio, Magn. Res. Chem. 42 (2004) 79.

[28] J.T. Groves, M. Bonchio, T. Carofiglio, K. Shalyaev, J. Am. Chem. Soc. 118 (1996) 8961;
T. Shingaki, K. Miura, T. Higuchi, M. Hirobe, T. Nagano, Chem. Commun. (1997) 861 (and references therein.);
A. Berkessel, P. Kaiser, J. Lex Chem. Eur. J. 9 (2003) 4746.

[29] M. Bonchio, G. Scorrano, P. Toniolo, A. Proust, V. Artero, V. Conte, Adv. Synth. Catal. (2002) 841.

[30] S.P. de Visser, D. Kumar, R. Neumann, S. Shaik, Angew. Chem. Int. Ed. 43 (2004) 5661.

[31] M. Bonchio, M. Carraro, G. Scorrano, U. Kortz, Adv. Synth. Catal. (in press).

[32] Carboxylic acids were mainly observed as overoxidation products.

[33] J.D. Chen, J. Dakka, R.A. Sheldon, Appl. Catal. A-Gen. 108 (1994) L1.