Part I
Oxidation Reactions

1

Polyoxometalates as Homogeneous Oxidation Catalysts

Mauro Carraro, Andrea Sartorel, Masooma Ibrahim, Nadeen Nsouli, Claire Jahier, Sylvain Nlate, Ulrich Kortz, and Marcella Bonchio

1.1
Soluble Metal Oxides as Oxidation Catalysts

Polyoxometalates (POMs) are discrete multitransition metal oxides characterized by a formidable structural variety, resulting in different dimensions, shape, charge density, surface reactivity, and in a rich redox chemistry [1–7]. A first classification of POMs is based on the chemical composition of these species, essentially represented by two types of general formula [8]:

1) $[M_mO_y]^{p-}$ (isopolyanions)
2) $[X_xM_mO_y]^{q-}$ (heteropolyanions)

where M is the main transition metal constituent of the POM, O is the oxygen atom, and X can be a nonmetal of the p block or a different transition metal.

Most of POMs are based on edge- and corner-shared MO_6 octahedra, where M is an early transition metal in its highest oxidation state (V(V), Nb(V), Ta(V), Mo(VI), or W(VI)). Such metal ions exhibit dimensions (cationic radius) compatible with an octahedral coordination and possess empty d orbitals that allow the formation of terminal metal–oxygen double bonds, required to avoid the assembly of the octahedra into an extended material (as for most common metal oxides) [1, 2, 9, 10]. A recently discovered subclass of POMs based on noble metal ions comprises square-planar MO_4 addenda units (M = Pd(II) and Au(III)) [11–15].

Owing to their particular composition and electronic structure, POMs can be considered as discrete models of extended metal oxides. As for the latters, the doping process is a winning strategy to improve their catalytic behavior. Even if there are several examples concerning electrostatic interaction with different transition metal cations, the most stable coordination mode is on incorporation of the transition metal in the POM structure with the formation of *transition metals substituted polyoxometalates* (*TMSPs*).

TMSPs can be obtained by using vacant or ''lacunary'' polyanions, derived from the corresponding saturated POMs, through the formal loss of one or more MO_6 octahedral units, resulting from the hydrolytic cleavage of M–O bonds under
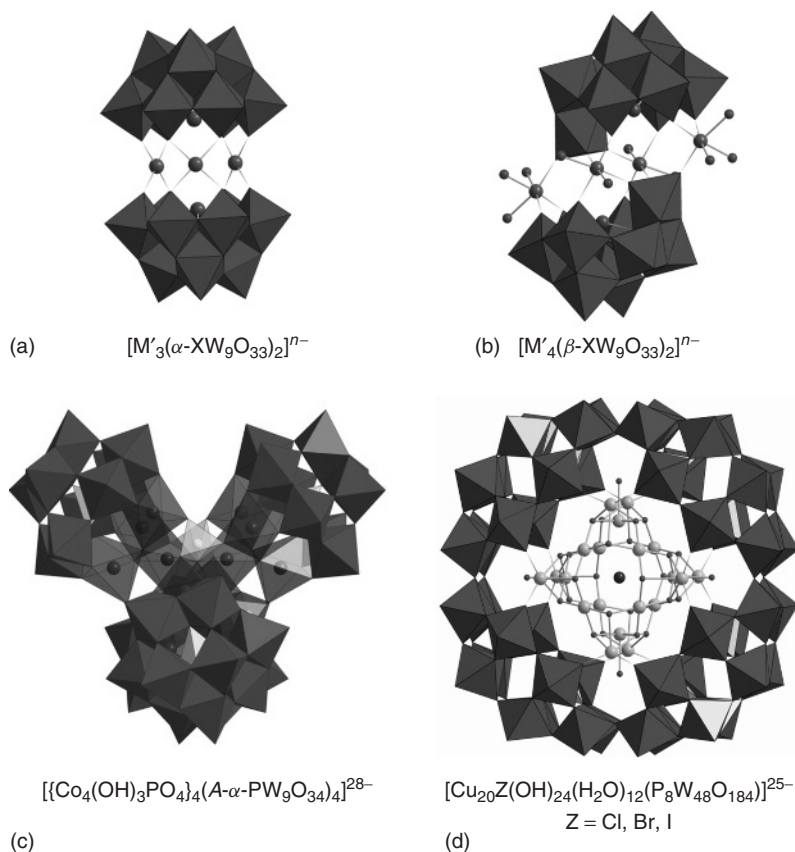
"In-pocket" coordination   "Out-of-pocket" coordination
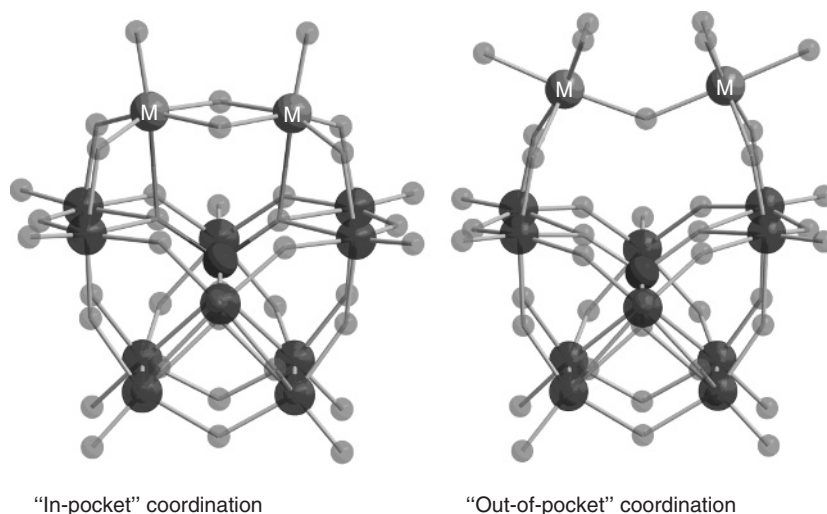
Figure 1.1 "In-pocket" and "out-of-pocket" structural motif involving the divacant $[SiW_{10}O_{36}]^{8-}$ unit and two transition metal ions M.

alkaline conditions [16]. Such polyanions feature reactive terminal, coordinatively unsaturated, oxygen atoms that surround the defect and form a "polydentate" site, able to coordinate to one or more redox-active transition metals M' as iron, manganese, cobalt, and ruthenium or different d^0 metal ions (zirconium, hafnium, and titanium). In some cases, one-pot synthesis of TMSPs can be achieved by using acidic/buffered solutions of suitable mononuclear precursors of both the transition metal and the POM itself.

Fundamental modes of binding include "in-pocket" coordination, where some addenda atoms are replaced by the same number of different transition metals, and "out-of-pocket" structural motif, with transition metals occupying a vacancy without being completely embedded (Figure 1.1). This latter coordination mode gives access to "sandwichlike" dimeric structures, where one or more transition metals bridge two vacant POM subunits, and to other bigger molecular architectures where clusters of four or more transition metals are stabilized by two or more vacant subunits (Figure 1.2) [17].

The nucleophilicity of vacant sites on the polyanions can be exploited to promote reactions with electrophilic organic moieties to give organic–inorganic hybrid complexes [22–25]. The covalent functionalization of a vacant polyoxoanion may impart a stabilization of the inorganic domain and generates tailored catalysts to be used in different media or for the preparation of hybrid materials [26–29].

Finally, the choice of a suitable counterion for such complexes allows their solubilization in a wide range of solvents: apolar organic solvents, by using highly lipophilic ammonium/phosphonium cations; polar organic solvents (acetonitrile, dimethylsulfoxide (DMSO)), with the tetrabutylammonium (TBA) cation; and water with alkali metals or protons as counterions.

(a) $[M'_3(\alpha\text{-}XW_9O_{33})_2]^{n-}$

(b) $[M'_4(\beta\text{-}XW_9O_{33})_2]^{n-}$

$[\{Co_4(OH)_3PO_4\}_4(A\text{-}\alpha\text{-}PW_9O_{34})_4]^{28-}$

(c)

$[Cu_{20}Z(OH)_{24}(H_2O)_{12}(P_8W_{48}O_{184})]^{25-}$

$Z = Cl, Br, I$

(d)

Figure 1.2 Some structural types of TMSPs, namely species with isolated transition metal ions, represented by the polyanions $[Pd_3(\alpha\text{-}SbW_9O_{33})_2]^{12-}$ (a) and $[Fe_4(H_2O)10(\beta\text{-}AsW_9O_{33})_2]^{6-}$ (b) [18, 19], and species with bridged transition metal ions, represented by the polyanions $[\{Co_4(OH)_3PO_4\}4(A\text{-}\alpha\text{-}PW_9O_{34})_4]^{28-}$ (c) and $[Cu_{20}Cl(OH)_{24}(H_2O)^{12}(P_8W_{48}O_{184})]^{25-}$ (d) [20, 21].

In the field of oxidation catalysis, the adoption of a totally inorganic ligand system derived from POMs represents a distinct advantage over coordination complexes displaying a set of organic ligands or organometallic moieties, because of their relevant stability under harsh oxidative conditions [30–32]. Oxidation reactions are traditionally performed using stoichiometric amounts of inorganic oxidants [33], whereas the design of robust inorganic catalysts featuring well-defined multinuclear active sites contributes to the development of sustainable and efficient oxidative processes with environmentally benign O_2 and H_2O_2. The occurrence of different transition metals within the POM structure generates the basis of their catalytic activity in oxidation reactions [34–36], since diverse oxidation mechanisms are accessible, including the formation of metal-peroxo and metal-oxene intermediates as well as thermal/photochemical activation (Figure 1.3).
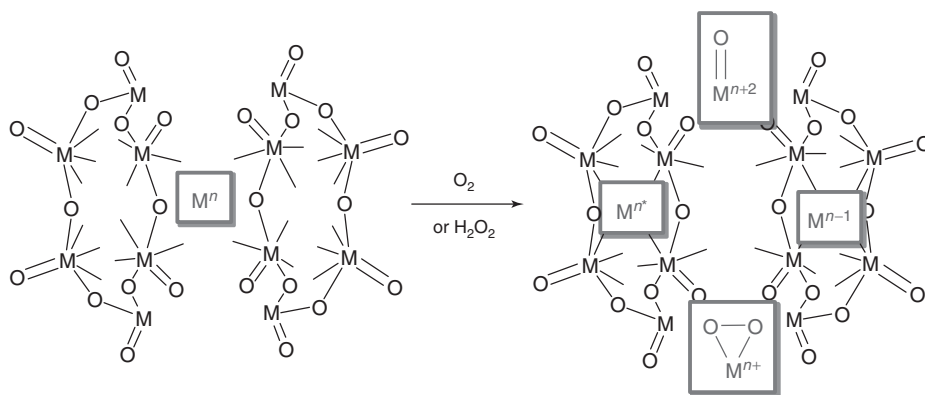
Figure 1.3 Activation modes occurring during oxidations with O_2 and H_2O_2.

In the next sections, some relevant and recent examples about the use of POMs in different oxidation processes are presented.

1.2
Homogeneous Oxidations with POMs Based Only on Mo(VI), W(VI), V(V) Addenda Ions

Dioxygen is the most attractive terminal oxidant, since it is cheap and abundant in the atmosphere. Moreover, it presents the highest active oxygen content with no harmful by-products. Several POMs have, thus, been used as catalysts to activate dioxygen through different approaches.

Keggin-type mixed-addenda heteropolyacids (HPAs) such as $H_{3+n}[PMo_{12-n}V_nO_{40}] \cdot nH_2O$ (HPA-n, with $n = 1, 2, 3$, etc.) act as electron-transfer oxidants [34, 37–39], and they have been used for the cleavage of *vic*-diols [40], α-hydroxyketones, and ketones [41]. As an example, regioselective cleavage of 2-hydroxycyclohexanone by HPA-2 gave adipic acid or its dimethyl ester as the major products (yields 80–90%) at 65 °C in aqueous acetic acid (in 3.5 h) or methanol (in 7 h), respectively [42].

HPAs have also been applied for the liquid-phase direct catalytic oxidation of benzene to phenol at room temperature. When using HPA-1 in glacial acetic acid, phenol was obtained with 26% yield and 91% selectivity in 100 min [43].

The possibility to undergo photoinduced multielectron transfers without changing their structure makes POMs very attractive for the photocatalytic oxidation of organic substrates in the presence of O_2 [44–51]. The general reaction mechanism involves (i) irradiation with wavelength <350–400 nm to promote a ligand-to-metal charge transfer (LMCT) transition, (ii) the oxidation of the organic substrate through hydrogen atom abstraction (or electron abstraction) to generate radical species, and (iii) the reaction between the reduced POM, (the *heteropolyblue* complex) [52–54] and dioxygen, to restore the initial form of the catalyst, while forming

reduced oxygenated species (superoxide radical and hydroxyl radical), which are also able to react with the substrate and the reaction intermediates. $[W_{10}O_{32}]^{4-}$ is the most investigated photoactive polyoxotungstate and it can be used in water, as sodium salt, to perform the oxidation of alcohols to their carbonyl compounds. In such conditions, however, an extensive overoxidation occurs at higher conversions [55, 56], owing to the production of highly reactive hydroxyl radicals OH · arising from solvent oxidation [57, 58]. In some cases, this strong oxidative capability has been applied for the mineralization of hydrosoluble pollutants [49]. Cation exchange allows its use in organic solvents: the tetrabutylammonium salt of $[W_{10}O_{32}]^{4-}$ has been mainly used in CH_3CN to oxidize aliphatic secondary alcohols and hydrocarbons [59, 60]. Cyclohexane has been oxidized to cyclic alcohols and ketones, depending on the O_2 pressure, whereas cyclohexene has been converted into the corresponding secondary hydroperoxide and α,β-unsaturated cycloketone [61]. Interestingly, the photocatalytic behavior of $[W_{10}O_{32}]^{4-}$ has been used to promote the formation of C-C bonds and alkane dehydrogenations through radical reactions in anaerobic conditions [62].

The decatungstate has been associated with different materials, so as to tune its selectivity toward different organic substrates: hydrophilic silica has been used to trap the decatungstate by a sol–gel procedure and oxidize alcohol to ketones and aldehydes [63], while hydrophobic mesoporous silica SBA-15 has been used as a support for the photocatalyst to oxidize aromatic and aliphatic hydrocarbons to the corresponding ketones in a CH_3CN/H_2O mixture [64].

The entrapping of decatungstate in polymeric membranes has also offered interesting perspectives to improve yield and selectivity of the reactions [56, 65–67].

Fluorinated media have conveniently been exploited in POM photocatalysis: besides the outstanding thermal and oxidative resistance, a preferential permeability of dioxygen can be obtained in fluorinated solvents [68]. The fluorophilic ${[CF_3(CF_2)_7CH_2CH_2CH_2]_3NCH_3}_4[W_{10}O_{32}]$ is soluble in fluorinated solvents as 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), and it has been used for ethylbenzene oxygenation at the benzylic carbon atom to obtain the corresponding hydroperoxide, alcohol, and ketone (56 : 23 : 21 product distribution), with turnover number (TON) = 580 [66].

Among oxygenation processes with *hydrogen peroxide*, those catalyzed by high valent d^0 transition metals are the most studied and selective [69]. The decomposition of hydrogen peroxide to form molecular oxygen is usually negligible, thus allowing a safely handling. In this respect, POMs are suitable candidates for the activation of hydrogen peroxide aimed at performing heterolytic oxidations.

The interaction between POMs and hydrogen peroxide has been investigated by many authors [70–77]. In some cases, alkylhydroperoxides have also been used [78].

Active peroxometal species have been prepared by employing polyoxoanions in phase-transfer conditions to perform selective epoxidations of olefins and benzyl alcohol oxidation [79–81]. Cetylpyridinium salts of polynuclear peroxometals have been used in biphasic conditions using chloroform as the solvent to obtain

the epoxidation of terminal and internal olefins and enols or the ketonization of secondary alcohols. The oxidative cleavage of *vic*-diols and carbon–carbon double bonds to carboxylic acids with H_2O_2 has been obtained under homogeneous conditions, using *tert*-butyl alcohol as the solvent [81]. In such conditions, the oxidant species in solution are dimeric peroxotungstate complexes such as $\{PO_4[WO(O_2)_2]_4\}^{3-}$ [82–85].

1.2.1
Oxidation with Hydrogen Peroxide by Peroxopolyoxotungstates-Dendrimers

Dendrimers and metallodendrimers are generating much attention for their potential applications in various areas [86–89]. The increasing use of these macromolecules in homogeneous catalysis is an emerging field, as they may allow the easy recovery of the catalysts after use, an essential feature for reaction efficiency, economy, and environmental concerns [90–93]. However, dendritic catalysts for oxidation reactions are relatively underrepresented [94–99], and only a few are based on POMs (DENDRIPOMs, dendritic polyoxometalates). The fixation of POM catalysts onto dendrimers is a very promising route, allowing to couple mechanistic knowledge and catalytic efficiency of the molecular POM unit, with the indispensable means of recovery and recycling. Two strategies can be used to incorporate POMs into the dendritic structure: covalent bonding or electrostatic interaction. In the first successful attempt to attach a POM anion to simple dendrimers, $[H_4P_2V_3W_{15}O_{62}]^{5-}$ was covalently bonded at the periphery of dendritic tetra-armed structure, and the DENDRIPOM hybrids were used as recoverable catalysts in the oxidation of tetrahydrothiophene to its sulfoxide by *t*-BuOOH or H_2O_2 [100]. On the basis of a similar approach, the synthesis of mannose- and ethoxyethanol-functionalized poly(amido)amine dendrimers bound to the $[H_4P_2V_3W_{15}O_{62}]^{5-}$ has also been reported [101].

A different class of DENDRIPOMs has been built by exploiting electrostatic interactions between dendrons and the heteropolytungstate $[(Mn(H_2O)_3)(SbW_9O_{33})_2]^{12-}$ [102].

A peroxophosphonatotungstate mixture has been prepared by *in situ* assembly of dendritic phosphonates with diperoxotungstates, efficiently exploited for the epoxidation of alkenes with hydrogen peroxide [103, 104].

Various dendritic ammonium structures with different sizes and end groups have been used as countercations for the trianionic $[PO_4\{WO(O_2)_2\}_4]^{3-}$, and their effects on the solubility, stability, and catalytic properties of the POM unit have been investigated. The heteropolyacid $H_3PW_{12}O_{40}$ decomposes in the presence of excess H_2O_2 to form the dinuclear peroxotungstate $[\{WO(O_2)_2(H_2O)\}_2O]^{2-}$ and the trianionic peroxophosphotungstate $[PO_4\{WO(O_2)_2\}_4]^{3-}$ [105–107]. The latter reacts selectively with the dendritic cations in a biphasic mixture of water and methylene chloride to give the DENDRIPOM hybrid, which contains the $[PO_4\{WO(O_2)_2\}_4]^{3-}$ core, in a very good yield. It has been demonstrated that the stability, catalytic efficiency, and recyclability of DENDRIPOMs largely depend on the location of the active species within the dendritic architecture that is used. Thus, three
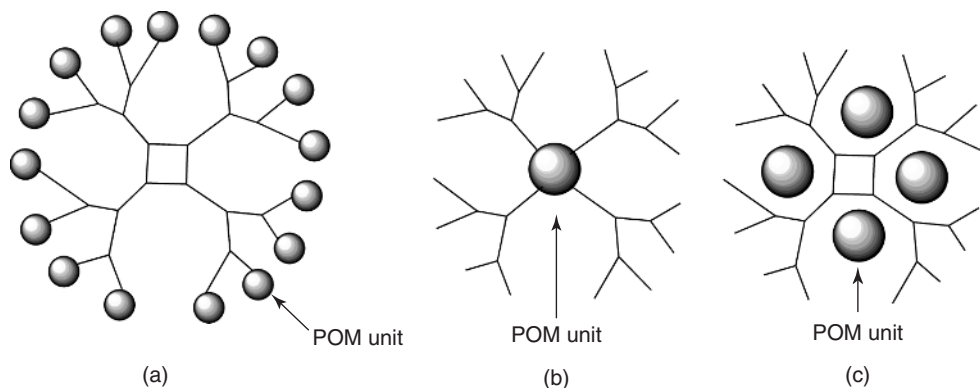
Figure 1.4 Schematic representation of different families of DENDRIPOMs (a) peripheral, (b) central, and (c) encapsulated catalytic domains.

families of dendritic POM hybrids built on the trianionic $[PO_4\{WO(O_2)_2\}_4]^{3-}$ have been studied [108–112]. In the first one, POM units are located at the dendrimer periphery (Figure 1.4a), whereas the POM unit represents the core of the dendrimer in the second family (Figure 1.4b) or it is encapsulated in the dendrimer cavities in the third example (Figure 1.4c).

Core-type DENDRIPOMs (Figure 1.4b) and encapsulated DENDRIPOMs (Figure 1.4c) were found to be more stable and more efficient catalysts in oxidation reactions than their homologs with POM units located at the periphery (Figure 1.4a).

Even if a negative dendritic effect, probably caused by the increased bulk around the catalytic center, has generally been observed on the reaction kinetics with DENDRIPOMs, the dendritic structure increases the stability of the POM unit, allowing oxidation of more challenging substrates, and facilitates the recovery and reutilization of the catalyst. The efficiency of DENDRIPOMs based on peroxophosphotungstate has been demonstrated in the oxidation of alkenes, sulfides, and alcohols to the corresponding epoxides, sulfoxides and/or sulfones, and ketones, in the presence of hydrogen peroxide, at 30 °C (Figure 1.5). These systems are easily recovered by precipitation, after each catalytic cycle, without any discernible loss of activity.

Recently, optically active DENDRIPOMs have been prepared by assembling chiral dendritic amines with achiral peroxophosphotungstate $[PO_4\{WO(O_2)_2\}_4]^{3-}$ in acidic medium [113, 114]. These compounds selectively oxidize sulfides to the corresponding sulfoxides with up to 14% enantiomeric excess (*ee*). Despite the modest *ee*, this work demonstrates chirality transfer to the POM unit in an asymmetric transformation. The chemo- and enantioselectivity of the POM unit are highly sensitive to the structure of the dendrimer. Interestingly, these chiral DENDRIPOMs can be recovered and reused. The appropriate design of chiral dendrimers from enantiopure amines with greater chiral induction potential,
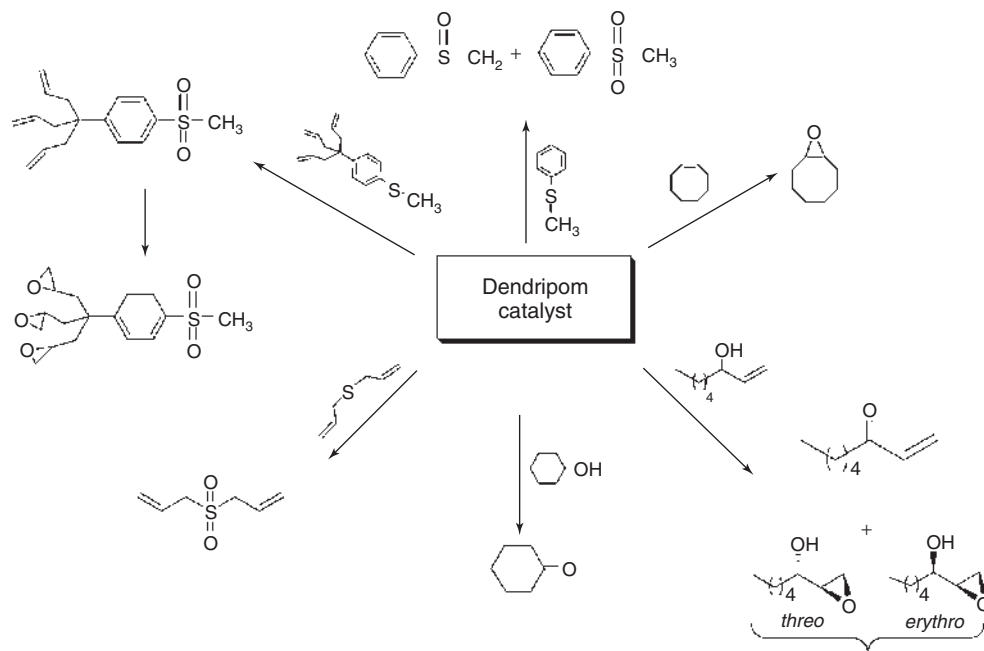
Figure 1.5 Reaction scope for the oxidation with DENDRIPOMs.

along with concomitant electrostatic and charge transfer interactions, will enable the increase of DENDRIPOMs enantioselectivity.

These findings highlight that some key parameters, important in catalysis, can be tuned by modifying the local environment of the polyanion. Hence, DENDRIPOMs represent a promising and elegant approach with respect to catalytic activity, selectivity (including enantioselectivity), and catalyst recovery.

1.2.2
Homogeneous Oxidation with Hydrogen Peroxide in the Presence of Vacant and Hybrid POMs

Promising catalysts for selective oxidations with hydrogen peroxide belong to the vacant polyoxotungstates family [115–118].

The divacant heteropolytungstate $(TBA)_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$ has been employed in CH_3CN to catalyze the oxidation of various substrates including olefins, allylic alcohols, and sulfides in the presence of 30% aqueous H_2O_2. Terminal olefins have been epoxidized with 90% yield in 10 h, while *cis*- and cyclic internal olefins have been oxidized in <6 h with yields up to 99% [119–121]. A high regioselectivity has been observed for the epoxidation of the less hindered, even if less nucleophilic, double bonds. This stable POM is a tetraprotonated species with two aquo ligands $W–(OH_2)$, a key feature for the formation of terminal peroxotungstate groups as active species [122–126].

Another important approach involving vacant POM-based catalysts is the use of hybrid complexes where the vacancy is completely or partially capped with an organic moiety. In this case, the merging of organic and inorganic domains may produce a functional synergistic effect with the ultimate scope to improve the catalytic performance. Chiral moieties have also been introduced on the surface to obtain C_2 symmetric complexes featuring induced optical activity [26].

Isostructural hybrid derivatives containing phenylsilanes or phenylphosphonates have been applied for the epoxidation of *cis*-cyclooctene in the presence of hydrogen peroxide [127]. The reactions have been performed under microwave (MW)-assisted conditions, since MW-induced dielectric heating may be efficiently exploited by the polycharged catalysts.

The catalyst behavior is strongly dependent on the structure/composition of the inorganic framework as well as on the nature of the organic moiety decorating the POM surface. Epoxidation yields ranged from 48 to 99% after 50 min of MW irradiation. In such conditions, the functionalization of the vacant site seems to inhibit the fast rearrangement of the POM structure, whereby nonfunctionalized vacant POMs evolve quickly to saturated Keggin derivatives.

Among the catalysts employed, the hybrid polyoxoanion $[(PhPO)_2SiW_{10}O_{36}]^{4-}$ has been used to perform the oxidation of several class of substrates in acetonitrile (Figure 1.6).
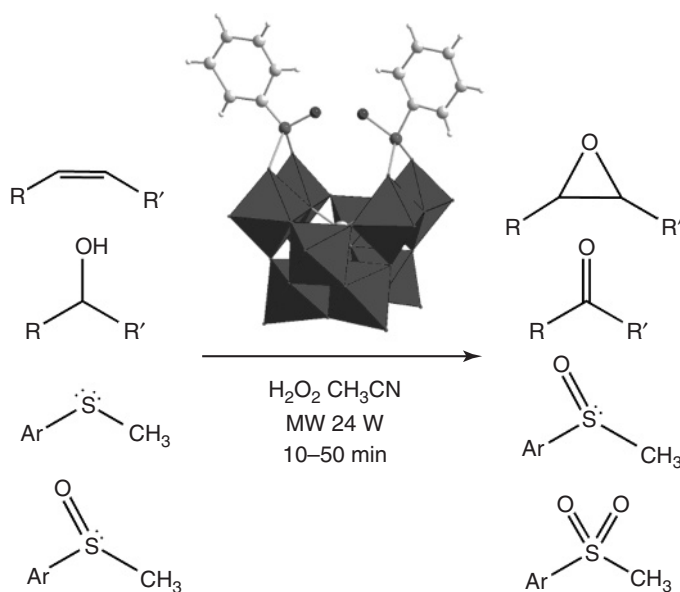
Figure 1.6 Combined polyhedral/ball-and-stick representation of $[(PhPO)_2SiW_{10}O_{36}]^{4-}$. The reaction scheme represents the oxidation of olefins, alcohols, sulfides and sulfoxides.

The best performances have been observed for the oxidation of internal olefins, secondary benzylic alcohols, and organic sulfur compounds with >95% yield of H_2O_2 conversion after 10–50 min of MW irradiation.

The hybrid organic–inorganic catalytic complex $[(PhPO)_2SiW_{10}O_{36}]^{4-}$ has also been used in ionic liquids (ILs) [128]. The IL acts as a solvating/immobilization medium for the hybrid catalysts. The selective epoxidation of *cis*-cyclooctene, with quantitative conversion of H_2O_2 (up to >99%), has been achieved at 50 °C in hydrophobic ILs, such as $[bmim^+][(CF_3SO_2)_2N^-]$ and $[bmim^+][PF_6^-]$ in 45 and 90 min, respectively. A good recycling performance has been obtained after extraction of the products and vacuum dehydration (total TON = 500). The polyelectrolytic nature of the catalytic phase allows fast and selective MW-induced heating by ionic conduction mechanism, even at very low irradiation power (4–10 W). Under the conditions explored, quantitative epoxidation of *cis*-cyclooctene has been achieved in 1 min, with turnover frequency (TOF) $>200\,min^{-1}$, that is, 35 times higher than the reaction with conventional heating. About 99% selectivity has been obtained for the epoxidation of both internal and terminal olefins. Substituted olefins have been converted into the corresponding epoxides (>97% yield) in 15–60 min. High epoxide yields have also been achieved for 1-alkenes (up to 99% in 2–3 h).

1.3
Homogeneous Oxidations with TMS-POMs

Worth of note is that the coordination geometry of representative structural-type POMs finds a close correspondence with the active site of natural oxygenase enzymes. For example, Fe(III)-substituted POMs have attracted a great interest because of the well-recognized catalytic properties of iron both in biological and synthetic systems. Fe-substituted Keggin α-undeca- and γ-decatungstates $[\alpha\text{-}Fe(H_2O)SiW_{11}O_{39}]^{5-}$, $[\gamma\text{-}Fe_2(H_2O)_2SiW_{10}O_{38}]^{6-}$, and the Krebs-type derivatives $[\beta\text{-}Fe_4(H_2O)_{10}(XW_9O_{33})_2]^{n-}$ ($n = 4$ with X = Se(IV) or Te(IV); $n = 6$ with X = As(III) or Sb(III) have suggested a POM-based inorganic mimicry, respectively, of heme-Cytochrome P450, the $Fe_2(\mu\text{-}O)_2$ core of methane monooxygenase (MMO), and the nonheme dioxygenase iron site with three exchangeable coordination positions [129–131]. Their tetrahexylammonium (THA) salts have been used in 1,2-dichloroethane (DCE) as catalysts for hydrocarbon oxidation in the presence of *dioxygen*. Radical autooxidation of *cis*-cyclooctene has led to the formation of the epoxide as the main product, with selectivity up to 66% for olefin conversion in the range 30–78% after 300 h at 75 °C. MW-induced dielectric heating has been used to provide a rapid reaction protocol for screening the activity and selectivity of this class of catalysts. $[\alpha\text{-}Fe(H_2O)SiW_{11}O_{39}]^{5-}$ has been used to promote cyclohexane autooxidation, performing with more than 1100 TON in 250 min, yielding cyclohexylhydroperoxide (CHHP), cyclohexanol (A), and cyclohexanone (K), with 90–95% selectivity and product distribution CHHP:A:K 11 : 60 : 29 [132].

Iron-substituted Krebs-type POMs $[\beta\text{-Fe}_4(H_2O)_{10}(XW_9O_{33})_2]^{n-}$ can catalyze the oxidative cleavage of 3,5-di-*tert*-butylcatechol (DTBC) with molecular oxygen. Under controlled conditions, these polyanions display oxygenase activity: DTBC has been oxidized in wet tetrahydrofuran (THF), in the presence of a radical scavenger to inhibit free radical oxidation and polymerization pathways, to 3,5-di-*tert*-butyl-1-oxacyclohepta-3,5-diene-2,7-dione and 4,6-di-*tert*-butyl-1-oxacyclohepta-4,6-diene-2,3-dione, arising from intra- and extradiol cleavage mechanism, respectively [133].

Concerning the activation of *hydrogen peroxide* by TMSPs, different scenarios can be depicted. While isostructural TMSPs $(TBA)_n[PXW_{11}O_{39}]^{n-}$ ($n = 5$ with X = Ni(II), Co(II), Cu(II); $n = 4$ with X = Fe(III)) yield extensive decomposition of the oxidant or the formation of unidentified products [134], selective activation of H_2O_2 by different TMSPs may occur through the generation of metal-peroxo complexes with different coordination modes (η^2-O_2, μ-η^1:η^1-O_2, μ-η^1:η^2-O_2, μ-η^2:η^2-O_2, OOH, etc.). All these active oxygen species may play an important role in various oxidative transformations of organic substrates.

Interesting selectivities have been achieved by using POMs substituted with Lewis acids' metal ions (Al(III) [135], Zn(II) [136, 137]) for the oxidation of alcohols and enols to carboxyl derivatives.

$[ZnWM_2(H_2O)_2(ZnW_9O_{34})_2]^{n-}$, ($n = 12$ with M = Mn(II), Pd(II), Pt(II) or Zn(II); $n = 10$ with M = Ru(III) or Fe(III)), have shown to be very efficient for the diastereoselective epoxidation of chiral allyl alcohols in a biphasic system DCE/H_2O under mild conditions [138]. The Zn(II) derivative self-assembles in aqueous solution starting from simple precursors, and it has been used to oxidize different primary and secondary alcohols in water, within 7 h at 85 °C, with yields and selectivities up to 99% [139–141]. After cation exchange with $[(CF_3(CF_2)_7CH_2CH_2CH_2)_3NCH_3]^+$, the Mn(II)- and Zn(II)-substituted POMs have been used in biphasic systems containing fluorinated solvents for the epoxidation of olefins and alcohols/enols oxidation to the corresponding ketones, with yields and selectivities up to 99% in 8–13 h at 22–88 °C [142]. As in the case of other Sandwichlike complexes, the scarce dependence on the nature of the transition metal during the epoxidation of olefins and allyl alcohols has suggested the occurrence of peroxotungstic-active species [138, 143–146].

In the next sections, recent discoveries involving selected TMSP types and different fields of oxidation catalysis are described.

1.3.1
Peroxopolyoxometalates of Hf/Zr

The use of fourth or fifth group d^0 transition metal may be very useful to drive the formation of reactive peroxogroups on such metals. This could be particularly convenient to increase the selectivity through well-defined mechanistic pathways [147–149].

In this respect, fourth-group-based POMs have been suggested as molecular models for the well-known heterogeneous titanium silicalite catalyst (TS-1), with

major industrial appeal in the field of H_2O_2 activation and selective oxidations [150, 151].

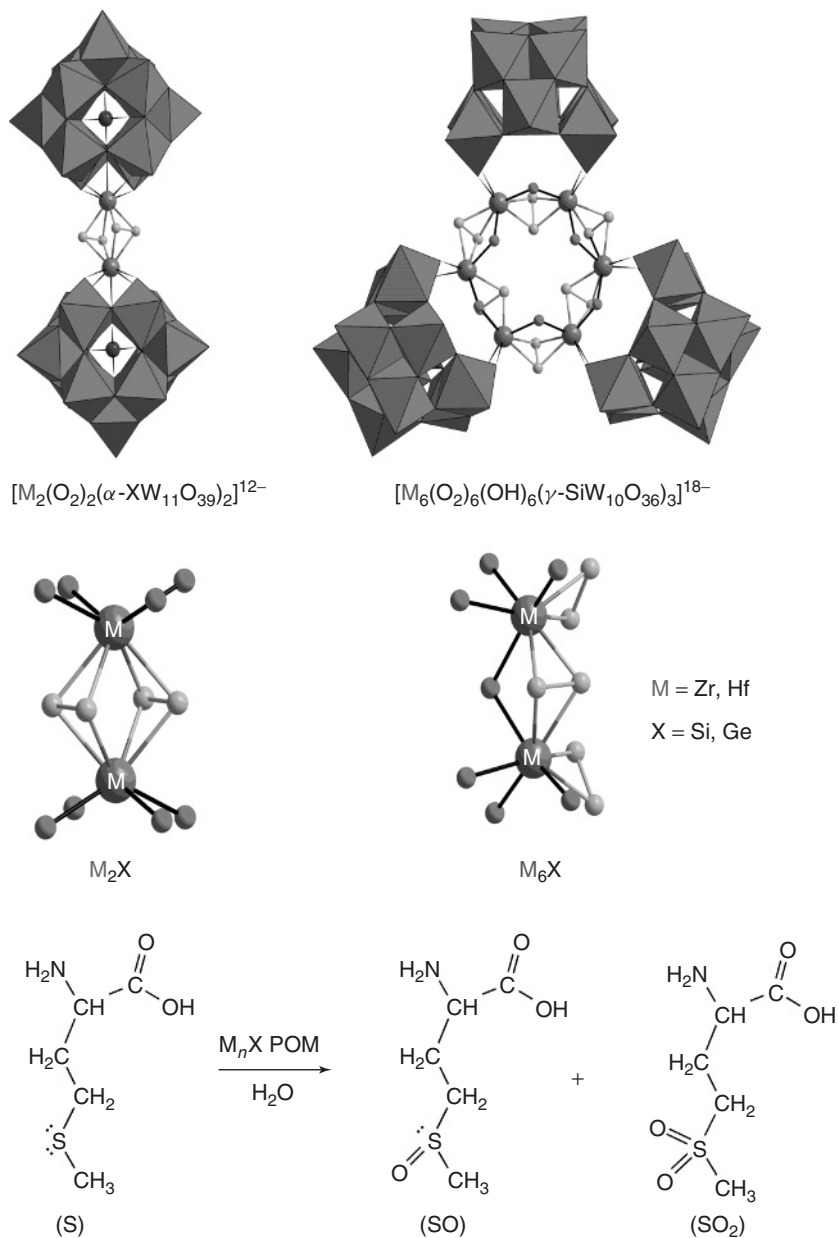Heteropolyoxotungstates incorporating Zr(IV) and Hf(IV) peroxides, $[M_2(O_2)_2(\alpha\text{-}XW_{11}O_{39})_2]^{12-}$ (M = Zr, X = Si (**Zr$_2$Si**), Ge (**Zr$_2$Ge**); M = Hf, X = Si (**Hf$_2$Si**)), and $[M_6(O_2)_6(OH)_6(\gamma\text{-}SiW_{10}O_{36})_3]^{18-}$ (M = Zr (**Zr$_6$Si**) or Hf (**Hf$_6$Si**)), are capable of oxygen transfer to suitable acceptors including sulfides and sulfoxides in water (Figure 1.7) [152, 153].

The reactivity of POMs **Zr$_2$Si**, **Zr$_2$Ge**, **Hf$_2$Si**, **Zr$_6$Si**, and **Hf$_6$Si** has been assessed for oxygen transfer to L-methionine (**S**) yielding the products, sulfoxide (**SO**) and sulfone (**SO$_2$**) via mono- and bis-oxygenation of the sulfur atom, respectively. Such a consecutive two-step process has been monitored with complementary ^{1}H-NMR and fast electrochemical scanning techniques, by following, respectively, the substrate/product time evolution or the fading of the peroxo-POM concentration on oxygen transfer. This combined screening strategy has allowed to match the diverse kinetic domains of the oxidation experiments, spanning from few seconds to hundred minutes, depending on the reactivity of these complexes. Under stoichiometric conditions, at neutral pH, they display a remarkable activity toward **S** oxidation, yielding quantitative oxygen transfer to the electron-rich sulfur atom, to give **SO** as the only product. In particular, sulfoxidation by polyanions **M$_2$X** is completed within seconds. In this chemistry, POMs **Zr$_2$Si**, **Zr$_2$Ge**, and **Hf$_2$Si** turn out to overarch the hexameric derivatives **Zr$_6$Si** and **Hf$_6$Si** by two orders of magnitude (Figure 1.7).

Analysis of oxygen transfer to **S** and **SO** ranks the POM performance in the range **Hf$_2$Si** $\sim$ **Zr$_2$Si**, $>$ **Zr$_2$Ge** $\gg$ **Zr$_6$Si** $\sim$ **Hf$_6$Si**. The superior reactivity of the bis-μ-η^2:η^2 peroxides **M$_2$X** is also apparent in the second oxidation, converting **SO** to **SO$_2$** [154].

The structural integrity of the POM scaffold, after oxygen transfer, has been confirmed for POMs **M$_2$X** by multiple techniques (FT-IR, UV–vis, and r-Raman analysis). Recharging experiments have demonstrated that these POMs can be reactivated on H_2O_2 addition, regenerating the active species, and used for multiturnover processes. Catalytic oxidations of **S** and **SO** have successfully been achieved (70–99% yield) in the presence of an excess of H_2O_2, with a reactivity order **Hf$_2$Si** $>$ **Zr$_2$Si** $>$ **Zr$_2$Ge** and up to 45 turnovers. Vice versa, spectroscopic analysis of spent **M$_6$Si** indicates a substantial modification of the POM features, and H_2O_2 recharge under catalytic conditions cannot be attributed to a well-identified reactive system.

The reaction scope has been extended to secondary alcohols leading to the corresponding carbonyl compounds with yields up to 99% after 50 min under MW irradiation ($T_{bulk} = 90\,^{\circ}$C). Density functional theory (DFT) calculations have revealed that polyanions **Zr$_2$Si**, **Zr$_2$Ge**, and **Hf$_2$Si** feature high-energy peroxo-HOMOs (highest occupied molecular orbitals), and a remarkable electron density localized on the peroxo-sites, as indicated by the calculated map of the electrostatic potential (MEP). This evidence suggests that the overall description of the oxygen transfer mechanism should include possible protonation equilibria in water, favored for peroxo-POMs **M$_2$X**.

$[M_2(O_2)_2(\alpha\text{-}XW_{11}O_{39})_2]^{12-}$ $[M_6(O_2)_6(OH)_6(\gamma\text{-}SiW_{10}O_{36})_3]^{18-}$

M = Zr, Hf

X = Si, Ge

M₂X   M₆X

(S)   (SO)   (SO₂)

Figure 1.7 Combined polyhedral/ball-and-stick representation of $[\{M(O_2)(\alpha\text{-}XW_{11}O_{39})\}_2]^{12-}$ (M = Zr, X = Si (**Zr₂Si**), Ge (**Zr₂Ge**); M = Hf, X = Si (**Hf₂Si**)) and of $[M_6(O_2)_6(OH)_6(\gamma\text{-}SiW_{10}O_{36})_3]^{18-}$ (M = Zr (**Zr₆Si**) or Hf (**Hf₆Si**)). Particulars of the peroxo-butterfly-active species are also depicted. The reaction scheme represents the oxygen transfer to L-methionine (**S**) to give DL-methionine sulfoxide (**SO**) and methionine sulfone (**SO₂**).

$[Pd(II)_{13}As(V)_8O_{34}(OH)_6]^{8-}$ (**Pd$_{13}$**) $[Pd_{15}P_{10}O_{50}]^{20-}$ (**Pd$_{15}$**)
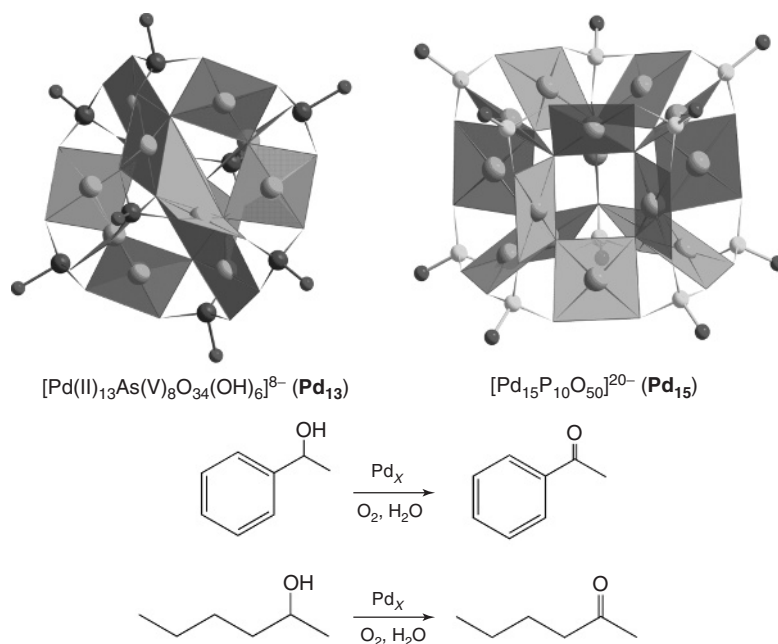
Figure 1.8 Combined polyhedral/ball-and-stick representation of some polyoxopalladates, and the corresponding alcohol oxidation scheme.

Dendritic POMs based on zirconium-substituted polytungstates have been synthesized by coupling of the zirconium-peroxo tungstosilicate **Zr$_2$Si** with ammonium dendrons via electrostatic bonding [155]. Contrary to its potassium salt, the dendritic counterparts are soluble in common organic solvents, an important feature for the use of DENDRIPOMs in homogeneous catalysis. These DENDRIPOMs are stable, efficient, recoverable, and reusable catalysts for the oxidation of sulfides in aqueous/CDCl$_3$ biphasic media, with hydrogen peroxide as the oxidant, in contrast to their nondendritic *n*-butyl ammonium counterpart. As mentioned for peroxophosphotungstate DENDRIPOMs, the reaction kinetics and selectivity of zirconium-substituted polytungstates-based DENDRIPOMs are influenced by the structure of the countercation used.

1.3.2
Aerobic Oxidations with Polyoxopalladates

The synthesis of nanostructured materials is an area with a great potential [156], due to their high surface-to-volume ratio. In particular, palladium-oxide-based nanomaterials are a current research topic owing to their important catalytic properties. However, only a few (and rather complex) synthetic methods for the preparation of such materials are known [157–159]. Recently discovered heteropoly-palladates $[Pd(II)_{13}As(V)_8O_{34}(OH)_6]^{8-}$ (**Pd$_{13}$**) and $[Pd_{0.4}Na_{0.6}Pd_{15}P_{10}O_{50}H_{6.6}]^{12-}$

(Pd_{15}) can be prepared using a simple one-pot self-assembly reaction. They display well-defined structure and composition and large surface-to-volume ratio, which make them attractive for application as homogeneous catalysts [11, 12]. On the other hand, these palladates might be anchored on a support in a highly dispersed form, resulting in a heterogeneous catalyst [160]. Owing to their molecular nature, they might thus be useful as novel precursors for the design of nanocatalysts, with atomic or molecular level tailoring.

The polyoxopalladates(II) Pd_x have been documented as catalysts for the aerobic oxidation of alcohols in water [11, 12]. Noteworthy, sustainable methodologies employing air as oxidant have been developed [161, 162].

In initial experiments, benzyl alcohol was studied as a key example of a primary alcohol. Its oxidation in the presence of Pd_{13} was conducted at $100\,°C$ and 30 bar pressure (2.1 bar oxygen partial pressure). A 54% benzaldehyde yield was achieved after 12 h together with 11% benzoic acid. The consecutive oxidation of benzaldehyde could not be inhibited by the addition of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as radical inhibitor. However, when performing the reaction in a shorter time frame and using oxygen-enriched air, no overoxidation to benzoic acid occurred. In this case, 100% selectivity to benzaldehyde was realized, with a 49% yield of benzaldehyde after 5 h and a TON of 49 (based on total Pd). Under similar conditions, albeit using a cosolvent, a less reactive secondary alcohol (2-hexanol) has also been oxidized. A TON of 10 (based on total Pd) of 2-hexanone after 5 h has been observed.

Similar results have been obtained with Pd_{15}. After 5 h of reaction, 42% of benzyl alcohol has been converted selectively to benzaldehyde. 2-Hexanol has been oxidized under the same reaction conditions ($100\,°C$, 50 bar): with TON $= 8$ in 5 h.

These results indicate that palladates can be used as stable catalysts to perform green alcohol oxidations using dioxygen as oxidant and water as solvent.
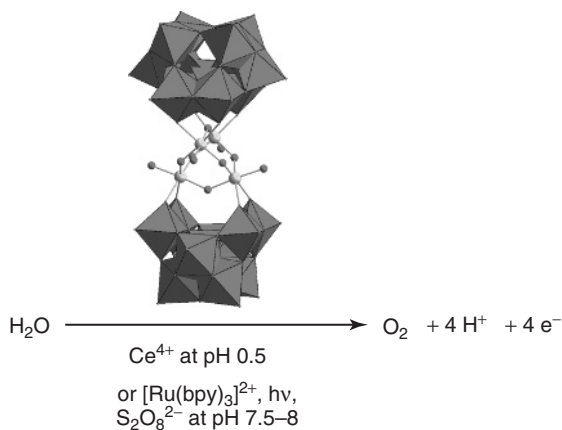
1.3.3
TMSPs as Oxygen-Evolving Catalysts

POMs have recently emerged as a promising class of catalysts to perform water oxidation [163–167].

An efficient light-driven catalytic splitting of water into molecular oxygen and hydrogen ($2H_2O \rightarrow O_2 + 2H_2$) represents one of the most ambitious research goals for the development of systems able to convert an ubiquitous energy source such as solar energy into chemical energy [168]. In this process, H_2O provides a total of four electrons per mole by the oxidative half reaction ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$; $E^0 = 1.23\,V$ vs NHE (normal hydrogen electrode)), required to accomplish the photosynthetic process.

In green plants and some bacteria, water oxidation occurs at the heart of the photosystem II (PSII) enzyme, featuring a polynuclear metal-oxo cluster with four manganese and one calcium atom held together by oxygen bridges ($CaMn_4O_x$) [169]. The multitransition metal catalytic core characterized by

$$H_2O \xrightarrow{\phantom{Ce^{4+} \text{ at pH 0.5}}} O_2 \quad + 4\,H^+ \quad + 4\,e^-$$

Ce^{4+} at pH 0.5

or [Ru(bpy)$_3$]$^{2+}$, hν,
S$_2$O$_8$$^{2-}$ at pH 7.5–8

Figure 1.9 Combined polyhedral/ball-and-stick representation of **Ru$_4$SiW$_{10}$**. The reaction scheme represents water oxidation by using Ce(IV) or [Ru(bpy)$_3$]$^{3+}$, formed *in situ*.

multiple-μ-hydroxo/oxo-bridging units seems to be a key feature to efficiently master the four-electron/four-proton mechanism through sequential redox steps.

The oxygen-evolving tetraruthenium POM [Ru(IV)$_4$(μ-OH)$_2$(μ-O)$_4$(H$_2$O)$_4$ (γ-SiW$_{10}$O$_{36}$)$_2$]$^{10-}$ (**Ru$_4$SiW$_{10}$**) is constituted by two staggered [γ-SiW$_{10}$O$_{36}$]$^{8-}$ units that coordinate an adamantanelike tatraruthenium-oxo core, which displays strict analogies with the tetramanganese oxygen-evolving site of PSII [164, 165]. Indeed, in both cases, four redox-active transition metals, coordinating a water molecule as the terminal ligand, are connected through μ-oxo or μ-hydroxo bridges.

This POM seems to undergo consecutive single proton-coupled electron transfers, finally yielding a high valent intermediate, responsible for oxygen production in a single four-electron step [170].

Homogeneous water oxidation catalysis by **Ru$_4$SiW$_{10}$** occurs in the presence of Ce(IV) as a sacrificial oxidant, with remarkably high TOF (0.125 s^{-1}) (Figure 1.9) [164]. With [Ru(bpy)$_3$]$^{3+}$ as sacrificial oxidant, a TOF of 0.45–0.60 s^{-1} has been obtained [165].

In the light-driven water oxidation catalyzed by **Ru$_4$SiW$_{10}$**, [Ru(bpy)$_3$]$^{2+}$ has been used as the photosensitizer with persulfate as sacrificial acceptor in phosphate buffer [171]. With this system, up to 350 turnovers and an initial TOF of 8×10^{-2} s^{-1} have been obtained. Such good performance has been ascribed to fast reaction kinetics of the electron transfer from the catalyst to the photogenerated oxidant [172].

[Ru{(μ-dpp)Ru(bpy)$_2$}$_3$]$^{8+}$ has been used as sensitizer with enhanced absorption toward the solar emission spectrum: the time profile of oxygen evolution during continuous irradiation of a phosphate-buffered solution (pH = 7.2) containing [Ru{(μ-dpp)Ru(bpy)$_2$}$_3$]$^{8+}$, **Ru$_4$SiW$_{10}$** and persulfate, is represented by linear kinetics, maintained up to circa 80% reaction within the overall experimental time

(180 min), achieving 80 turnovers with an initial TOF of 8×10^{-3} s^{-1}. In this time frame, the O$_2$ evolution accounts for a persulfate conversion higher than 90%. In this case, a top-record quantum yield for oxygen production of 0.3 was calculated by irradiating at 550 nm [173].

The unique mechanistic and stability features of **Ru$_4$SiW$_{10}$** were exploited to prepare a very stable, efficient, and nanostructured oxygen-evolving anode on assembly of the POM cluster on a conductive bed of carbon nanotubes functionalized with polycationic dendrimeric chains. In this case, an appreciable catalytic current with a remarkable TOF (36 h^{-1}) was observed beginning at overpotential $\eta = 0.35$ V and reached a peak performance of 306 h^{-1} at $\eta = 0.60$ V. Carbon nanotubes have also shown to be superior in comparison to amorphous carbon solid support [174, 175].

1.4
Conclusions

Owing to their remarkable oxidative stability, oxidation catalysis by POMs continues to be a timely field of investigation. The possibility to tune their composition at the molecular level offers the advantage of controlling fundamental properties of interest for selective oxidations. Steric hindrance, redox potential, single-site activation via coordination/Lewis acid catalysis are instrumental to direct the chemo- and regioselectivity required for the processing of polyfunctional substrates. In addition, the easy access to a large structural/compositional variety of POMs, combined with their unique molecular nature, offers straightforward tools for mechanistic investigation under turnover regime, with the possibility to trace fundamental structure–activity descriptors, validated by computational studies.

The association with organic ligands and cations, including dendrimeric polycations, is a powerful tool to broad the range of applications and to improve technological issues, such as immobilization and recovery, of the catalytic processes.

In conclusion, the use of POM catalysts, along with benign oxidants, represents a true possibility for the development of novel and selective synthetic procedures. Noble-metal-based POMs are expected to further broaden this field of applications.

Finally, water splitting for sustainable hydrogen production and energy applications represents a challenging frontier in TMSP-based catalysis, nowadays attracting great attention.

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