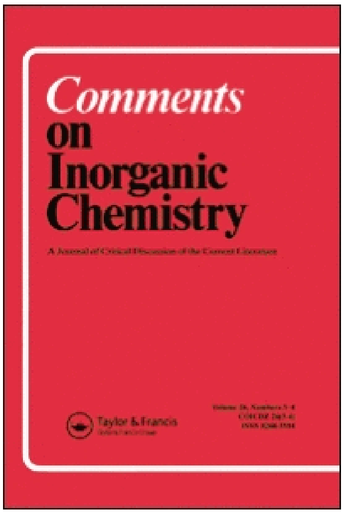

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Multifunctional Polyoxometalates as Catalysts for Environmentally Benign Processes

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Multifunctional Polyoxometalates as Catalysts for Environmentally Benign Processes

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In the face of declining natural resources and growing environmental deterioration, the coming generations of catalysts, and in particular oxidation catalysts, will need to address not only the conventional limitations of selectivity, rate and stability but also the emerging limitations imposed by the changing reality regarding resources and environment. An approach to develop flexible (modifiable) catalytic methodologies that addresses all these potential difficulties simultaneously will be presented. The use of multifunctional polyoxometalates as catalysts themselves or polyoxometalate fragments as catalytic components will be outlined.

Key Words: *environmentally benign catalysis, selective oxidation, aerobic oxidations, multifunctional polyoxometalates*

INTRODUCTION

Catalysis in abiological and biological systems alike has been and is conventionally driven by the need to simultaneously optimize three features of the catalyzed process—selectivity, rate, and sta-

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bility. The exhibition of higher selectivities, rates and stabilities in one industrial process facilitates economic advantage over competing processes just as the exhibition of these factors in biological systems provides an evolutionary advantage in the form of a more fit or biologically robust system. In addition, the catalytic processes of greatest value are those that will facilitate the economical use of dwindling natural resources and will be environmentally benign. The latter entails processes that utilize the least deleterious (toxic, carcinogenic, and biopersistent) solvents, reagents and conditions, and generate the least deleterious by-products and waste streams. Finally, there is always practical interest in catalytic systems that are highly flexible in formulation; that is, their structural, electronic, solubility and other properties pertinent to optimal turnover can be modified extensively to facilitate satisfactory operation under a range of conditions. In this Comment we present the general goals and limitations of homogeneous catalysis and catalytic processes with a focus on oxidative catalysis. We then outline the environmental considerations of most fundamental pertinence at the present. Finally, we describe multifaceted inorganic complexes and conditions that address sequentially all the key issues from selectivity to environmental compatibility.

Catalytic oxidation presents particularly vexing problems.[1-11] Few if any classes of catalyzed processes are more in demand and more difficult than selective oxidations. Better oxidation processes are needed in chemical synthesis on all scales from specialty (fine) to bulk chemicals and in a host of applications from fuel cell technology to microlithography. One general problem in selective catalytic oxidation is that while nearly all catalyzed processes of any significance are energetically favorable (usually exothermic), oxidations are particularly so. The driving force in organic oxidation reactions of all kinds, including oxidations by O_2 and other relatively weak oxidants, is substantial. This in turn dictates difficulties in achieving high selectivity. While high chemoselectivities are not too hard to achieve in many catalyzed processes, they are often quite hard to achieve in oxidations. More often than not the products of oxidations are more reactive than the substrates themselves, rendering it impossible to achieve high yields at high conversions of substrate without flow systems or other involved process engineering. For the most inert types of organic materials such as saturated hydrocarbons, the one pot catalytic oxidation almost always yields a cornucopia of products. Likewise the thermodynamic sledge hammer that is oxidation often militates against viable regioselectivities or stereoselectivities.

A second generic and significant problem in homogeneous catalytic oxidation is the inherent thermodynamic instability of organic structure. One pervasive consequence of this is that if the oxidation catalyst has organic ligands, it will be susceptible, sooner or later, to irreversible oxidative degradation leading to loss of catalyst selectivity and/or activity. Some of the most successful homogeneous metal catalyzed oxidation reactions proceed with destruction of the organic ligands. Although this has not been economically prohibitive given the cost of the ligands, the products of the process and other factors, the formulation of catalysts that are impervious to oxidation is a desirable goal.

There are several generic types of mechanisms operable in metal-catalyzed oxidation reactions. Several reviews can be consulted for the details.[2,5-11] Despite the mechanistic diversity, oxidations of practical value or commercial interest generally fall into two categories, those that proceed by homolytic mechanisms and those that proceed by heterolytic mechanisms. The former mechanisms involve one-electron oxidation state changes at the metal and radical (often free radical) intermediates, while the latter mechanisms involve no oxidation state change or two-electron oxidation state change at the metal and do not involve radical intermediates. An example of a homogeneous metal-catalyzed oxidation process that is homolytic in nature is the oxidation of cyclohexane to adipic acid by O_2 catalyzed by Co complexes, long a mainstay at Dupont.[4,12] Examples of homogeneous metal catalyzed oxidation processes that are heterolytic in nature are the Halcon epoxidation process[4-6] and the mechanistically related Sharpless chiral epoxidation technology.[13-15] Both homolytic and heterolytic mechanisms are known for homogeneous metal catalyzed oxidations involving peroxygen compounds and other classes of oxidants.

ENVIRONMENTALLY AND ECONOMICALLY DESIRABLE CATALYSIS

1. General Considerations

The catalytic synthesis of organic materials and the implementation of catalytic processes in general now proceed in an environment that is significantly different from the one ten years ago. The environmental and consequent economic impact of processes are now major considerations. Social and political realities have sharpened focus on efficiency and environment. Some natural resources are more difficult to obtain and utilize at the same level of constraint as a few years ago. Not only is the climate with respect to environmental considerations changing but also the rate of change appears to be escalating. Now the ecological impact not only of the materials (reagents, solvents, etc.) themselves but also the design and formulation of the entire catalytic process are an issue. Processes that show an economy with respect to the process engineering and all the products are highly attractive.

A new thrust in the catalytic synthesis of fine chemicals and new materials that is picking up steam as a natural consequence of environmental considerations is the use of bioengineered bacteria and related methodologies.[16,17]

2. Oxidants

A few of the most desirable oxidants are listed in Table 1. The relevant criteria here are cost, % of active oxygen, and the toxicity and tractability of the reduced form of the oxidant and the oxidant derived by-products. The two most desirable oxidants are O_2 and H_2O_2. They are inexpensive and, in principle, environmentally "green." Unfortunately, they have more diverse chemistry than the other oxidants. They enter into more metal-catalyzed and uncatalyzed reactions, and their oxidation chemistry is harder to control relative to that of the other oxidants, with the possible exception of ozone.

3. Solvents

The desirability of solvents is dictated by environmental friendliness as well as cost. Based on these criteria, the most attractive

TABLE I

Representative or potential oxygen donor oxidants, DO.

DO	% Active Oxygen	By-product and Comments
O_2	100	None, provided reducing agent-free non-radical-chain aerobic oxygenation can be achieved—no commercially successful system yet exists.
H_2O_2	47	H_2O. Environmentally attractive.
O_3	33	O_2. Potentially environmentally attractive.
NaClO	21.6	NaCl. Although nontoxic, inorganic salt by-products are to be avoided in general. ClO^- can produce toxic and carcinogenic chlorocarbon by-products in some cases.
t-BuOOH	17.8	*t*-BuOH. Commercially important in catalyzed oxygenations.
$KHSO_5$	10.5	$KHSO_4$. Water compatible but generates marginally toxic salt.
C_6H_5IO	7.3	C_6H_5I. Metal catalyzed oxidations are often quite selective but cost is prohibitive.

solvent is often water, followed by some hydrocarbons and then some oxygenated solvents of low toxicity (ethanol, methyl *t*-butyl ether, acetone, etc.). The least desirable solvents are those that are toxic, carcinogenic and quite persistent in the environment, particularly halocarbons and benzene. The obvious detraction of water as a solvent is that few organic compounds are soluble in water and few organic materials or surfaces are wet by water. The solubility can be addressed by using phase transfer catalysis, modifying the solubility of the substrate and/or the catalyst, running the reaction in a heterogeneous mode (substrate, oxidant, or catalyst is present as a solid), or just running the reaction in two phases with efficient mixing. The ideal catalyst would be active in water and would work under most or all of the above reaction conditions. It is noted that the low solubility of many organic reactants in water may limit the number of new compounds or materials that can be synthesized by enzyme systems in various formulations,[18] whole cells, fermentation, and emerging bioengineered approaches.[16,17] Nevertheless, the importance of all catalyst systems that function efficiently in water will doubtless grow in the future.

THE STEPWISE APPROACH TO IDEAL CATALYTIC SYSTEMS, ONES THAT ARE MODIFIABLE, SELECTIVE, STABLE, RESOURCE EFFICIENT AND ENVIRONMENTALLY BENIGN

Phase 1. Oxidatively Resistant Totally Inorganic Complexes for Catalytic Homogeneous Oxygenation

The first step to developing the ideal catalyst (selective, fast, stable, environmentally attractive, and modifiable) was to develop catalysts that simultaneously exhibited three features: (1) the ability to catalyze the oxidation including oxygenation (oxidation by oxygen transfer, Eq. (1)) of organic substrates (S) with oxygen donors (DO, Table I, vide supra), (2) deep kinetic if not thermodynamic stability with respect to oxidative degradation under turnover conditions, and (3) electronic and structural properties requisite for turnover that would be extensively modifiable by rational or defensible synthetic procedures.

$$\mathrm{DO} + \mathrm{S} \xrightarrow{\text{catalyst}} \mathrm{SO} + \mathrm{D} \qquad (1)$$

While a host of inorganic complexes in many categories have been reported to activate one or more of the common oxidants (Table I) or effect selective oxidation of organic substrates by one or more of these or other oxidants, effectively none prior to 1986 simultaneously exhibited all three of the above features. Several types of catalysts for homogeneous oxidation are commercially successful while falling far short of the ideal. Upon consideration of many classes of soluble inorganic complexes and other species we were led inexorably to consider d-electron transition-metal-substituted early transition metal oxygen anion clusters (henceforth polyoxometalates for convenience)[19-30] as the catalyst prototypes we had been seeking. The first class of these d-electron transition-

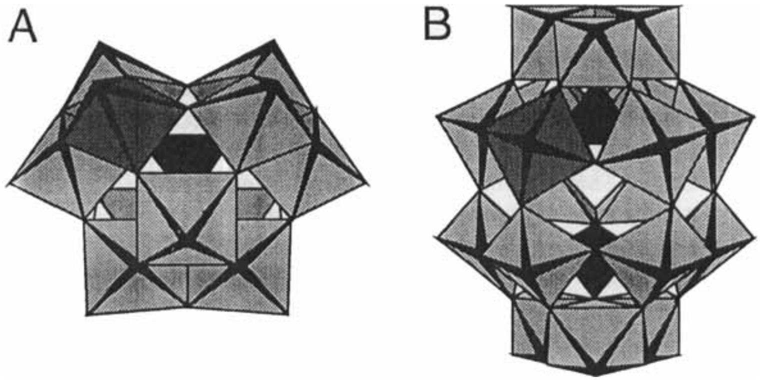

FIGURE 1 Illustrations in polyhedral notation of two common and readily accessible classes of TMSP complexes that can function as oxygenation catalysts: (A) the mono-substituted Keggin structure, $[(TM)XW_{11}O_{39}]^{x-}$, and (B) the mono-belt-substituted Wells–Dawson structure, α_1-$[(TM)P_2W_{17}O_{61}]^{x-}$, one of chiral TMSP complexes for potentially catalyzing asymmetric oxidation and oxygenation of organic substrates. In both figures, TM = d-electron transition metal ion that functions as the active site of the catalyst (e.g., Mn^{2+}, Fe^{2+}, Ru^{3+}, etc.). It is shaded more darkly than the other W(VI) ions. Also in both figures, X = the "heteroatom", one of many possible p or d block elements, resides in the internal coordination XO_4 tetrahedra. They are shaded the most darkly. In polyhedral notation, the vertices of the MO_6 or MO_4 polyhedra represent the nuclei of the oxygen atoms and the metal atoms are internal to the polyhedra and not directly visible.

metal-substituted polyoxometalate (TMSP) complexes is illustrated in Fig. 1A. Many features of these complexes parallel those of the most extensively investigated class of homogeneous oxygenation catalysts, the metalloporphyrins,[11] but do not have the Achilles' heel of oxidatively unstable organic structure exhibited by metalloporphyrins. Polyoxometalates are in many respects inorganic metalloporphyrin analogs.

Four attributes led us to examine TMSP complexes: (1) Polyoxometalates are profoundly resistant to oxidative degradation as their structural skeletons are usually constituted of d^O transition metal and oxide ions. (2) Several varieties of polyoxometalate defect structures are readily available which can function as multidentate ligands of d-electron transition metal ions, the "active sites" of the catalysts.[20] (3) In many cases, the polyoxometalate ligand systems in TMSP complexes can be reversibly reduced, increasing the possibility of facilitating multielectron activation processes. In addition, these ligand systems could also function, in principle, in several other capacities of potential interest in catalysis including the recognition, binding and activation of the oxidant and/or the substrate proximal to the d-electron transition metal "active site" prior to oxidation. (4) The polyoxometalates including the TMSP complexes can be rendered soluble in solvents ranging from water to hydrocarbons depending on the counterions and other properties of pertinence to catalysis.[28]

In 1986 it was first demonstrated that TMSP complexes could function as oxidatively resistant catalysts for the oxygenation of organic compounds (oxygenation of hydrocarbons by iodosylarenes).[31] The first complexes our group used in this capacity were readily available complexes of the monotransition metal-substituted Keggin class, $(TM)PW_{11}O_{39}^{5-}$, where TM = a divalent first row transition metal in this instance. This particular class of compounds was first reported over 3 decades earlier[32] and remains under continuing development. In 1984 Katsoulis and Pope had demonstrated that highly hydrophobic cations (i.e., the tetra-*n*-heptylammonium ion) could extract some types of TMSP complexes including those derived from the readily accessible Keggin structure (Fig. 1A) into hydrophobic solvents and these species could reversibly bind oxygen.[33] Since our initial report of oxygenation catalyzed by TMSP complexes, several research groups including ours have reported oxidations or oxygenations of five classes of compounds, including alkanes and alkenes, in several mono- and biphasic solvent systems, using 10 different oxidants catalyzed by many TMSP complexes of five or six structural types.[10,34–48] Despite the activity in TMSP-catalyzed oxidation and oxygenation from 1986 until the present, many of the fundamental energetic and mechanistic features in these catalytic processes that dictate selectivities and rates have yet to be elucidated in a satisfactorily quantitative manner. In addition, the applications of TMSP-catalyzed reactions in two areas of current and growing importance, asymmetric oxidations and oxidations involving environmentally optimal solvents (including water) and oxidants (O_2 or H_2O_2) have yet to be addressed to an appreciable extent.

In the area of asymmetric oxidation or oxygenation, there are several classes of TMSP complexes that are inherently chiral and several are not hard to obtain in a pure but racemic form. One example of a readily accessible racemic TMSP complex is shown in Fig. 1B. The practical limitations here are that the resolution of the enantiomers of chiral TMSP complexes including the belt- or α_1-substituted Wells–Dawson complex (Fig. 1B) have not yet been satisfactorily worked out, and more significantly, many chiral TMSP complexes will doubtless exhibit enantiomeric excesses (ee's) well below the 85+% level of serious interest to pharmaceutical and other industries seeking chiral organic compounds. It has been the conventional wisdom for some time that at least 3 points of attachment between the prochiral substrates and the chiral reagents are needed for the exhibition of high ee's.[49] Also, effective enantiomerically differentiating transition states are pocket like, that is, there is considerable steric bulk on more than two sides of the transition state complex. Although most families of TMSP complexes, including the family of complexes modeled by Fig. 1B, do not exhibit these features proximal to the transition metal active sites, some TMSP complexes do to some extent. No research whatsoever has been done thus far on the systematic synthesis of chiral TMSP complexes using chiral templates, counter cations, solvents, or other chiral auxiliaries.

Phase 2. Selective Catalytic Homogeneous Oxidation Under Environmentally Desirable Conditions With Economically Attractive Reagents

As articulated above, the most desirable catalytic system would be selective, rapid, stable and function in water. If the catalyzed process were an oxidation, then either dioxygen or hydrogen peroxide would be the choice for the terminal oxidant. TMSP complexes of various kinds could probably fill this tall order under limited experimental conditions but the data are not yet available. Although Katsoulis and Pope reported the reversible binding of dioxygen[33] and the oxidation of phenols,[40] the role(s) of TMSP complexes in autoxidation and the usual O_2-based organic oxidation processes has yet to be addressed. Hydrogen peroxide, on the other hand, is the one oxidant that clearly facilitates the solvolytic decomposition of some polyoxometalate complexes. Indeed the Ishii[50-53] chemistry, a fairly new commercial homogeneous selective catalytic epoxidation of terminal alkenes by H_2O_2, mechanistically related to the Venturello[54–56] chemistry, involves the degradation of a Keggin complex pre-catalyst, $PW_{12}O_{40}^{3-}$, into peroxopolytungstates under the two-phase and phase transfer conditions of reaction. A few classes of polyoxometalates seem to be quite impervious to peroxolytic degradation.[10,57] Studies on various TMSP prototypes that facilitate selective oxidation by H_2O_2 are under development in various laboratories.

A complementary approach that fulfills all the above criteria involves the aerobic oxidation of a range of organic substrates (S) catalyzed by certain classes of polyoxometalates, P_{ox} (Eq. (2)). Long before our group began any research on polyoxometalates, Pope pointed out that polyoxometalates composed primarily of MO_6 octahedra with one terminal and five bridging oxo groups (Type I octahedra) were readily and reversibly reduced while polyoxometalates composed primarily of MO_6 octahedra with two terminal and four bridging oxo groups (Type II octahedra) were not readily and reversibly reduced.[20] The majority of polyoxometalates structurally characterized thus far have many or exclusively Type I MO_6 octahedra. One example, metatungstate ($H_2W_{12}O_{40}^{6-}$) is a complex of the Keggin structure (Fig. 1A) with two constitutional hydrogen atoms in place of a large heteroatom in the central T_d cavity, and can be reduced by 32 electrons without major structural perturbation.[58] Consistent with these points is the fact that a large number of polyoxometalates should be capable of Eqs. (2)–(4).

$$S + 1/2\ O_2 \xrightarrow{P_{ox}\ \text{(catalyst)}} S_{ox} \qquad (2)$$

$$S + P_{ox} \longrightarrow S_{ox} + P_{red} \qquad (3)$$

$$P_{red} + 1/2\ O_2 \longrightarrow P_{ox} \qquad (4)$$

In fact, it has now been demonstrated that many classes of polyoxometalates do indeed catalyze this type of process via the two general steps indicated, direct oxidation of the substrate by the resting and oxidized form of the complex, Eq. (3), followed by reoxidation of the reduced form of the complex, P_{red}, by a suitable terminal oxidant such as O_2. As the reduced polyoxometalate reoxidation, Eq. (4), can be readily separated in space and/or in time from the substrate oxidation, Eq. (3), the usual capture of O_2 by intermediate radicals that propagate radical chain autoxidation is totally avoided. The selectivity is dictated in large part by the characteristics of the oxidized polyoxometalate, P_{ox}, which directly interacts with and oxidizes the substrate, and not the organoperoxy radical, ROO·, that oxidizes the substrate and dominates the selectivity in most O_2 based industrial oxidation processes. Furthermore, unlike the organoperoxy radical, a single species whose selectivity and reactivity controlling properties are not alterable, the oxidized polyoxometalate, P_{ox}, could be one of a host of complexes varying in ground state redox potential, molecular shape, molecular charge, and other properties that typically affect and collectively control the observed selectivity and reactivity of the complex.

Matveev and co-workers illustrated that some strongly oxidizing polyoxometalates could reoxidize Pd(0) produced in the oxidation of a wide variety of organic substrates by Pd(II) salts. The reduced polyoxometalates could then be reoxidized by O_2.[25,26] The net reaction was the catalyzed aerobic oxidation in Eq. (5).

$$S + 1/2\ O_2 \xrightarrow[P_{ox}\ \text{(co-catalyst)}]{\text{Pd(II) (catalyst)}} S_{ox} \tag{5}$$

In the pioneering research of the Matveev group on Eq. (5), the polyoxometalates were not involved in the actual substrate transformation, i.e., they did not oxidize or interact with the substrate directly. They were added to the systems to facilitate reoxidation of the reduced form of the Pd, the true catalyst.[25,26]

In 1989 we demonstrated that strongly oxidizing polyoxometalate complexes such as $H_5PV_2Mo_{10}O_{40}$ could catalyze the oxidation of thioethers, RSR′, with extraordinarily high (>99%) selectivity, by the widely used commercial oxidant *t*-butylhydroperoxide (TBHP, Table I).[59] In these processes, the polyoxometalate complex was the actual oxidant of the substrate and TBHP, which could be present in the same reaction, functioned solely to reoxidize the reduced form of the polyoxometalate. In other words, Eqs. (2)–(4) were demonstrated using TBHP as the terminal oxidant in place of O_2. The background direct uncatalyzed oxidation of RSR′ by TBHP was at least two orders of magnitude slower and less selective than the polyoxometalate catalyzed reaction. Also in 1989 Brégeault and co-workers demonstrated that the same polyoxometalate, $H_5PV_2Mo_{10}O_{40}$, could catalyze the selective aerobic oxidative cleavage of some ketones.[60,61] R. Neumann and co-workers have demonstrated that $H_5PV_2Mo_{10}O_{40}$ catalyzes the oxidation of amines, some alcohols, some alkylaromatic hydrocarbons and bromide by Eqs. (2)–(4).[62–64] We present here two projects that extend this chemistry to potentially useful applications.

In the last year, our laboratory in collaboration with Dr. I. Weinstock of the U.S.D.A. Forest Products Laboratory in Madison, Wisconsin, established that wood pulp could be selectively bleached, a key process in the manufacture of paper, via Eqs. (2)–(4). Wood pulp consists principally of two complex biopolymers, the structural polysaccharide cellulose, which imparts most of the texture and physical strength to pulp fibers, and residual lignin. Lignin, a polymer of electron rich methoxylated phenol and benzyl alcohol and ether functions, imparts most of the color to wood pulp.[66] The purpose of the wood pulp bleaching process is to selectively remove the colored lignin while minimally degrading the cellulose. In the United States and many countries, this is done by the use of chlorine or chlorine-derived oxidants. While chlorine-based bleaching is quite selective it produces chlorocarbon by-products, nearly all of which are carcinogenic to varying degrees. One class of chlorocarbon by-products produced in small to trace quantities during wood pulp bleaching is the dioxins, an extraordinarily toxic and carcinogenic class of compounds that continue to be of major concern societally, politically and economically.

One direct response and potential solution to this pervasive problem is to use polyoxometalates to catalyze the selective oxidation of wood pulp, Eq. (2), via Eqs. (3) and (4) using either H_2O_2 or O_2 as the terminal oxidant. The key is that the ground state redox potentials and other features of the polyoxometalate catalyst, P_{ox} in Eqs. (2)–(4), can be fine-tuned so that only the more readily oxidized lignin is oxidatively degraded and the less readily oxidized cellulose is not badly damaged. One beauty is that a host of polyoxometalate complexes capable of oxidizing lignin can be reoxidized by H_2O_2 and more slowly by O_2. Versatility in

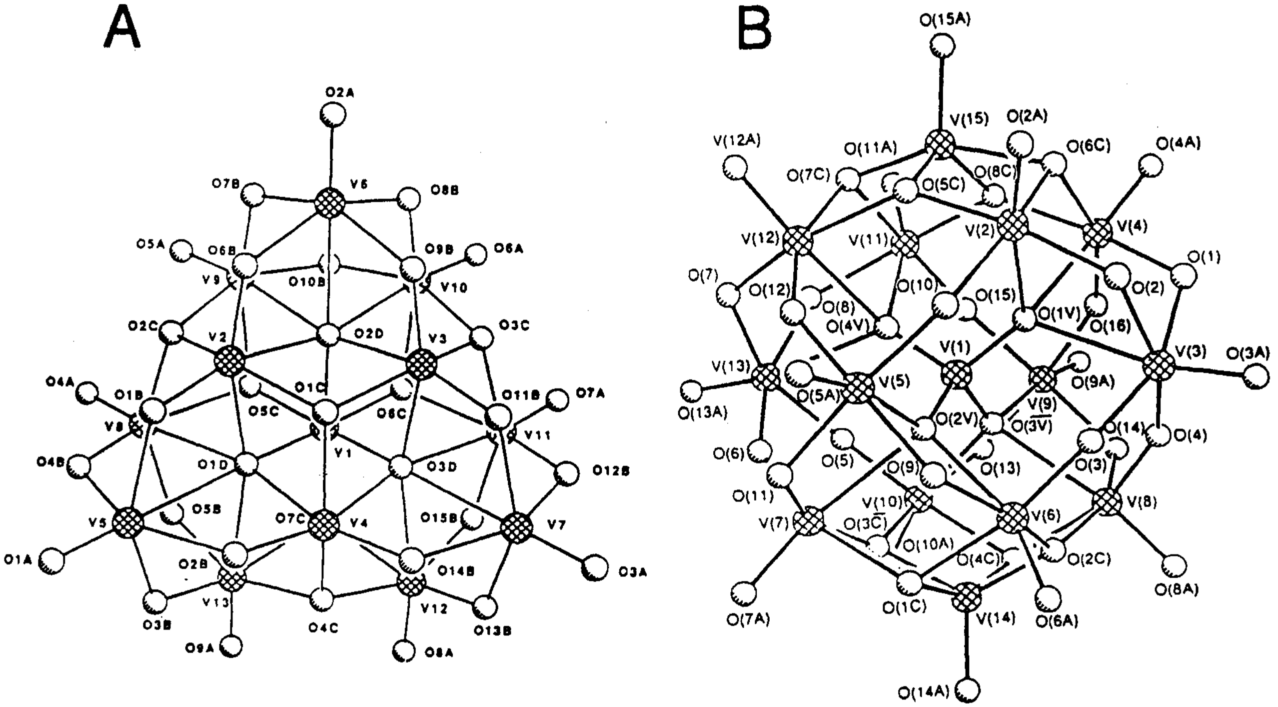

FIGURE 2 ORTEP plots of two recently prepared isopolyvanadates with all vanadium atoms in the V(V) oxidation state. (A) $V_{13}O_{34}^{3-}$; (B) $V_{15}O_{42}^{9-}$ (Refs. 68 and 69).

this catalytic approach derives in part from the fact that not only can different polyoxometalate structures of the strongly oxidizing polyoxometalate forming elements such as V(V) now be prepared, but also the ground state potentials and other features affecting reactivity including protonation state and counter cations can be controlled and altered to a considerable degree. The number of structurally diverse polyoxovanadates alone that might be useful in this type of catalysis has been growing rapidly. Of the 25 or so new polyoxovanadates synthesized and structurally characterized in the last 4 or 5 years, three new ones are in the fully oxidized state (all vanadium atoms in the V(V) oxidation state, d^{0}): $V_{12}O_{32}^{4-}$,[67] $V_{13}O_{34}^{3-}$,[68] and $V_{15}O_{42}^{9-}$.[69] Structures of the last two are given in Fig. 2.

The second application of the two-step oxidations by O_2 (or H_2O_2) catalyzed by polyoxometalates, Eqs. (2)–(4), involves the oxidation of H_2S to S_8 by O_2, Eq. (6).

$$H_2S + 1/2\ O_2 \xrightarrow{P_{OX}\ \text{(catalyst)}} 1/8\ S_8 + H_2O \qquad (6)$$

H_2S is a toxic pollutant in several catalytic waste streams and its discharge into the environment is to be avoided. The uncatalyzed oxidation is far too slow to be effective. At present, chelated iron, such as iron EDTA complexes, and related compounds are used to catalyze Eq. (6), but the organic EDTA ligands succumb to oxidative degradation thus terminating catalysis. We have recently demonstrated that a number of polyoxometalates catalyze Eq. (6) and some may have the oxidative and hydrolytic stability, tractability and low cost to be attractive for this application.[70]

Although some solid work on the mechanisms of Eqs. (3) and (4) for a number of systems has been reported, more research needs to be done before this chemistry is sufficiently delineated that it can be optimally tailored for the host of applications to which it might ultimately be applicable. While the mechanism of Eq. (3), direct oxidation of some substrates by oxidized polyoxometalates, has been addressed in some detail for a few substrates it has not been for many others. Likewise the mechanism of reduced polyoxometalate reoxidation by the oxidant of primary economic and environmental interest, O_2, Eq. (4), has been experimentally addressed in a few systems but more definitive work needs to be done here before the diversity and some of the details of this generic process are fully appreciated. Dioxygen has been known to reoxidize reduced polyoxometalates since the early work of Papaconstantinou.[71] Very recently Papaconstantinou studied the mechanism of Eq. (4) for reduced heteropolytungstic acids in aqueous media but did not specifically infer the nature of the first step in this process.[72] Also very recently, Neumann and co-workers concluded from ^{18}O isotopic labeling experiments that the reduced form of $[H_5PV_2Mo_{10}O_{40}]^{5-}$ was reoxidized by direct replacement of the polyoxometalate oxygen atoms with oxygen from O_2.[73] Recently our group has examined the reoxidation of several reduced polyoxometalates by O_2 using ^{17}O NMR and other methods and found that an outer sphere mechanism is a common if not dominant mechanism for this general reaction.[74] The collective research in this area by several groups should soon provide a fairly good picture of the mechanistic diversity and details of Eq. (4).

Phase 3. Inorganic Catalysts That Self-Assemble Under Turnover Conditions

One future concept to explore in context with effective and environmentally benign catalysis involves the demonstration that some catalysts are not only in deep kinetic minima but are thermodynamically stable under turnover conditions. The isolation of an intact catalyst after a large number of turnovers coupled with documentation of the stability of the catalyst under redox conditions thermodynamically well beyond those encountered under turnover conditions is a strong and practical measure of stability, but it does not establish the thermodynamic stability of the catalyst under turnover conditions. The next step in defining an absolute scale of stability and one approaching an assessment of the true thermodynamic stability would involve a catalyst that not only has the attributes above (isolable intact after reaction and no sign of decomposition under redox conditions beyond those involved in the catalysis), but also one that will actually self-assemble under turnover conditions. It is likely that self-assembly will be important not only in addressing selectivity in catalytic transformations involving organic and biological substrates but also in the formation of more robust and versatile catalysts.

Acknowledgments

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