Progress and challenges in polyoxometalate-based catalysis and catalytic materials chemistry

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Abstract

The impact of early transition-metal oxygen-anion cluster (polyoxometalate or "POM") geometric and electronic structural properties on POM-based catalysis is addressed. Three specific areas of general challenge in POM-based catalysis and catalytic materials are elaborated: (1) the role of ion pairing in catalyst stability, selectivity, and reactivity; (2) the presence of multiple reactive forms of the POMs and the interconvertability of these forms under turnover conditions; and (3) the impact of POM ground state and excited state electronic structure on turnover and selectivity. © 2006 Elsevier B.V. All rights reserved.

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There have been many recent reviews and two books on catalysis by transition-metal oxygen anion clusters (polyoxometalates or "POMs"). The subject matter in these publications tends to cover the same ground, typically a brief review of POM structures and properties followed by classes of reactions and brief discussion of selected processes. A few of these reviews go into a more detail and thus provide more insight than others [1–12]. In addition, several review volumes on POMs since 2000 have appeared and the subject matter in these has generally complemented that in the POM catalysis reviews [13–15]. Synthesis and structures have been the focus of nearly all the latter reviews [16]. One review specifically addressed fundamental reactivities of POMs [17]. This brief article, written in context with the other articles and reviews in this special issue of *Journal of Molecular Catalysis A: Chemical*, focuses on a few specific issues that the author believes are important intellectual and developmental challenges in POM-based catalysis. While these are based on our own research and observations over the last 23 years and a good deal of manuscript reviewing and journal editing in recent years, I fully appreciate that other practitioners in POM science and catalysis might highlight additional or other challenges. Importantly, there are many technical points I view as important that I do not address below for practical reasons including space.

The stability, combined with the extensively alterable molecular properties of POMs, including heteropoly acids (HPAs), make them attractive as catalysts. The ease of controlling acidity, reduction potential, solubility and most properties central to catalytic turnover has already led to the commercialization of several homogeneous or heterogeneous catalytic processes based on POMs. The ease of formulating these cluster molecules and their compatibility with nearly all other materials (supports, additives, solvents) is also a factor in their popularity as catalysts. Despite the current value and promise of POM-based catalysts and the application of a host of physical methods to characterize them, there remain myriad challenges and questions whose resolution would likely facilitate significant additional uses for POMs as catalysts. These uses may not be limited to the conventional ones: acids and oxidants in the production of commodity or specialty chemicals. POM systems might well find application in consumer products of many kinds that catalyze low-temperature dark air-based oxidation, in devices to cleanse/purify indoor environments or decontaminate chemical warfare agents, as photocatalysts for pollutant removal in several niches where TiO_2-based photocatalysts are used commercially now [18–20], and in other areas. These challenges and remaining questions in POM catalysis science combined with the promise and extraordinary diversity of POM-based systems partly explain the current research activity and define the promise of future work this broad area.

The community of investigators interested in POM catalysts, like most catalysis scientists and engineers in general, seek to understand the origins of and to optimize catalyst turnover rates,

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selectivities and stabilities. Simultaneously, they seek to develop new types of catalysts and occasionally seek catalysts to address problems in areas or fields where no catalysis-based solution currently exists.

Some general factors render progress in POM catalysis slow. First, any material that is isolated from a heterogeneous, and even more so a homogeneous catalytic process, is usually not a species involved directly in turnover (i.e. it does not lie on the catalytic reaction coordinate). It is generally a less active form and can represent a mechanistically misleading kinetic cul-de-sac. Second, the methods that provide the most insightful information about heterogeneous catalysts at the molecular level including the main stays of surface science such as Auger electron spectroscopy (AES), secondary ion mass spectrometry (SIMS), high resolution electron energy loss spectroscopy (HREELS), and more recently developed scanning probe microscopic and several other techniques, are not usually applicable to the compositionally complex and structurally non-uniform systems that are often the most successful heterogeneous POM catalysts [21–26]. Nonetheless, the classical techniques of differential scanning calorimetry (DSC) and selective chemosorption/desorption studies routinely provide information on the energetics of solid POMs including some mechanistically insightful heats of reaction. Vibrational spectroscopic methods (FT infrared and Raman, including surface enhanced Raman spectroscopy, SERS) [27], solid-state NMR [28], X-ray photoelectron spectroscopy (XPS), XANES and EXAFS [29], scanning probe microscopy (e.g. STM, AFM), X-ray diffraction (single crystal and powder) [30,31], and other experimental methods are now in standard use for characterizing the geometric and electronic structures of POM catalysts. Complementing this profusion of experimental efforts are density functional theory and *ab initio* quantum mechanical investigations of POM geometric and electronic structures and in some cases, reaction mechanisms [32–40]. The interplay and synergy between experimental and computational findings is substantial, and of course, getting better rapidly.

With this wealth of methodology, why do so many challenges and so much unrealized promise exist in POM catalysis science? Part of the answer derives from the intrinsic diversity of POMs: few studies by one group can be compared quantitatively with those of other groups, or even by the same group conducted earlier, because the POM catalytic system of focus (the polyanion structure and composition, the counter cations, the ionic strength and pH for aqueous solution studies, solvent, and other parameters) has rarely been held constant from study to study. Another reason why more progress has not been made is that many studies have not provided critical, fully elaborated discussions of rigorous complete experiments. The physical and mechanistic aspects of the catalytic reactions are often treated at a superficial level. Unfortunately, such studies typically leave more questions about the chemistry unanswered than answered.

One specific issue that pervades all POM-based catalysis is the role of the counter cations necessarily associated with the polyanions [41,42]. While scores of X-ray diffraction studies (powder and occasionally single crystal) locate these cations, and calculations often provide support for these structural assignments, it is not a trivial exercise to infer the role(s) of the counterions in catalytic turnover. It is difficult to assess the thermodynamic properties (substrate–POM surface associations and others) and kinetic properties (activation parameters, etc.) in POM-catalyzed processes from X-ray structures and computational work based on these structures, particularly for catalytic processes involving solvated polyanion surfaces (heterogeneous catalysis in the liquid phase or homogeneous catalysis). As noted above, isolated and thus thoroughly characterized species are rarely the key intermediates in catalytic turnover. In addition, it has not feasible to provide sophisticated solvation models of POM catalyst surfaces with current computational methods and computing power.

Classic studies establish that ion pairing of salts in most if not all non-polar organic media is pervasive [43–45], and many studies have sought to put ion pairing and its impact on reactivity on a solid intellectual basis [42,46–50]. Furthermore, there are studies that quantify the significant influence of ion pairing on ground state POM reduction potentials and the consequent impact of this on rates of POM reduction [51–53]. Since POM reduction is involved in nearly all POM-based catalytic oxidations, ion pairing is clearly of importance in at least oxidation catalysis. Ion pairing must impact the reduction potentials of POM-excited states as well as POM ground states [54,55]. Since nearly all POM photocatalysis involves initial photoreduction of the POMs [56–68], then for the many POM photocatalysis studies in organic media, frequently acetonitrile (more than 50 publications) where some POM-counterion pairing is likely operable, ion pairing is doubtless important in catalytic turnover. Given all these points, it is noteworthy and telling that ion pairing in POM-based catalytic oxidation processes has rarely been quantified and has frequently been ignored. While considerable data indirectly probe ion pairing in heterogeneous heteropoly acid-catalyzed processes, more research addressing the impact in counterions on the selectivities and rates in POM-catalyzed processes is warranted. Studies that provide useful information under turnover conditions (the "*in situ*" methods) would be particularly insightful.

The stability of heteropoly acid catalysts is also well known to depend in part on the presence of any non-proton counterions [5,8,69,70]. For example many studies on the heteropolyanion, $[PW_{12}O_{40}]^{3-}$ alone, confirm that the temperature of decomposition varies over a wide range as the counterions are changed. It is reasonable that the thermal stability of all POMs depends to some extent on the counterions and on the structural and energetic aspects of ion pairing. Because stability as noted above is a central goal of catalytic development, ion pairing plays a role here. Additional studies that quantify the thermodynamic (ΔG°, ΔH° and ΔS°) and kinetic (A, E_a, $\Delta G^{\ddagger}$, etc.) features of POM thermal decomposition as a function of the counterions (size, charge, shape, etc.), solid-state structure, and composition of the interface with the catalytic medium are needed.

A second issue that is common in POM-based catalysis is the presence of multiple reactive forms of the POMs and the interconvertability of these forms under turnover conditions. This phenomenon is more common in homogeneous catalysis than heterogeneous catalysis, but can be operable in the latter.

The fluidity ("pseudo-liquid phase") of some POM-based heterogeneous catalysis could facilitate rearrangements and isomerizations in the polyanion units under turnover conditions [71,72]. The core concern is that POMs with different numbers of proton or cation counterions are distinct species and frequently have different activities in acid or oxidation catalysis. This makes establishment of precise reaction mechanisms quite difficult. The vanadium-substituted polymolybdates, the single most studied class of homogeneous POM oxidation catalysis, are a case in point. They also provide one reference for the interconvertability of these structures in solution and to some extent the distinct properties of closely related interconvertable isomers. They are also the class of POMs whose speciation chemistry in water (pH and ionic strength dependences of the different positional and compositional isomers) has been the most thoroughly investigated [73–77]. Many studies have documented that the various isomers of these complexes including the five positional isomers of $[PV_2Mo_{10}O_{40}]^{5-}$, the single most studied POM in homogeneous catalysis [3,4,78–90], interconvert even in organic solvents. Polytungstates are significantly less labile than polymolybdates or polyvanadates but can also certainly isomerize readily in the appropriate pH ranges in water at ambient temperature [17,91]. The phenomenon of having multiple POM isomers simultaneously present and catalytically competent makes the quantitative and species-specific interpretation of reactivity (principally kinetic) data problematic at best. Use of the most non-polar solvents such as toluene (although reactivity of the benzylic hydrogens can be a problem in catalytic oxidations using the popular aromatic solvents with such hydrogens) might slow isomerization and rearrangement of the polyanions units to the point where the structural integrities of even the highly labile polyvanadomolybdates would be maintained during catalytic turnover.

A third specific area of challenge in POM catalysis is to better understand the electronic structures of POMs in their oxidized and reduced (particularly one- and two-electron-reduced) ground states and excited states and the relationships between these states and the rates of several fundamental processes. The potentials and reactivities of these forms in key competing processes dictate much of POM-based redox catalysis and most of POM-based photochemistry. Extensive product, spectroscopic and kinetic studies have clarified that the key substrate oxidation–POM reduction step involves atom transfer (AT) in nearly all reactions where C–H bond cleavage is observed [59,61,92,93], but electron transfer (ET) can be operable with other substrates [68,94]. Time resolved and steady state kinetics measurements have largely clarified the excited state properties of at least decatungstate [54,65–67,95–98]. These definitive studies, often necessarily conducted using simpler anaerobic conditions, facilitate elucidation of some POM-based photocatalytic processes under the more mechanistically complicated but potentially useful aerobic conditions.

The electron donor–acceptor character in POM electronic absorption spectra and photocatalysis has been noted and quantified in some systems, but key questions remain in this area. One of these is whether the shifts in POM electronic absorption and the nearly identical photoredox action spectra induced by several types of organic molecules [95,96,99–101] are intramolecular or intermolecular in nature. In other words, do these spectral shifts result from medium affects on the intramolecular oxygen-to-metal charge transfer bands (the regular electronic absorption bands) of the POM or do they result from an intermolecular electron transfer from the proximal organic molecules to the POM (or both). The origin and degree of these medium-induced spectral (absorption and photochemical action) shifts are not of trivial consequence because the quantum yields for photo-oxidation of organic materials by POMs, at least for decatungstate, the most studied POM in photochemical research, and the common Keggin and Wells-Dawson heteropoly compounds, is high wherever the complexes absorb light. Thus the ability to move the absorption and photochemical action spectra to the visible could lead to robust assemblies for the conversion of considerable sunlight into chemical energy, an issue of growing concern in 2006 given the current skyrocketing price of fossil fuels.

Also at the fundamental level, the roles of electron delocalization in the excited or ground states of reduced POMs on electron transfer rates are not clear. Among existing ambiguities are the size of the Jahn Teller effects in these reduced polyanions and to extent to which these impact Marcus theory reorganization energies and other parameters.

There has been significant recent progress in developing heterogeneous and consequently more useful POM-based photocatalysts, and articles in this issue elaborate some significant findings. Clearly additional challenges in supported POM photochemistry remain including the roles of supports on quenching of excited states, facilitation of electron transfer, and, for potential solar fuels applications, the storage of electrons transferring from POM excited state(s).

In closing, a few fundamental and practical issues in POM catalysis have been noted in this brief article, but there are a host of others of some consequence. Given this fact and the extraordinary recent development of a wide range of physical methods to probe geometric and electronic structural properties, the future for research on POM catalytic systems is ripe with possibility.

Acknowledgements

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