New progress of Keggin and Wells–Dawson type polyoxometalates catalyze acid and oxidative reactions

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Abstract

Polyoxometalates (abbreviated as POMs) are useful acids and oxidation catalysts in various reactions since its catalytic features can be controlled at a molecular level. This review summarizes some recent research progress in catalytic application of Keggin and Wells–Dawson type polyoxometalates. Particular attention is given to most developments of our recent studies on the use of POMs as heterogeneous and homogeneous catalysts for the selective oxidation and acid-catalyzed reactions.
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1. Introduction

Polyoxometalates (POMs) are metal-oxo anionic clusters whose chemical properties can be controlled by transition metal substitution and the countercation used. The number of publications and patents pertaining to POMs continues to grow. Among numerous applications of POMs, catalysis is by far the most important. Presently, over 80% of the patents concerning with POMs application is related to catalysis [1].

POMs have been found wide applications in many fields such as catalysis, medicine, magnetic properties, materials, surface chemistry and photochromism and electrochromism owing to the so-called "value-adding properties". Thus, on the one hand, combined with their ability to donate and accept electrons and their stability over a wide range of conditions, makes them attractive targets for catalysis; on the other hand, does them economically and environmentally attractive in both academic and industrial significance as useful acids and/or oxidation catalysts in various organic reactions since their catalytic features can be controlled at a molecular level [2–4]. In many cases,

molecular oxygen or H_2O_2 can be used as the oxidizing agent, which qualifies these as green reagents with POMs. Here we focus on catalytic application of POMs, particularly for some latest developments on the use of Keggin and Wells–Dawson type POMs as heterogeneous and homogeneous catalysts for the acid-catalyzed reactions and selective oxidation of hydrocarbons based on our group's research.

2. Properties and catalysis of polyoxometalates

2.1. Structure and feature

POMs are coordination compounds containing more than two metal atoms, which are generally formed from simple inorganic salts via condensation, and are anionic d^0 metal–oxygen clusters which consist of isopoly anions containing only one metal and heteropoly anions that are the larger, more studied and useful class of compounds. Two main types of structures of heteropolymetalate are shown in Fig. 1. Each black ball represents a metal atom in the center of the octahedron, and each corner represents an oxygen atom in the structure [5]. Heteropoly anions have central heteroatom(s), typically tetrahedral, about which the metal-oxo framework is built [6]. The major structure is known as the Keggin structure which is roughly spherical and
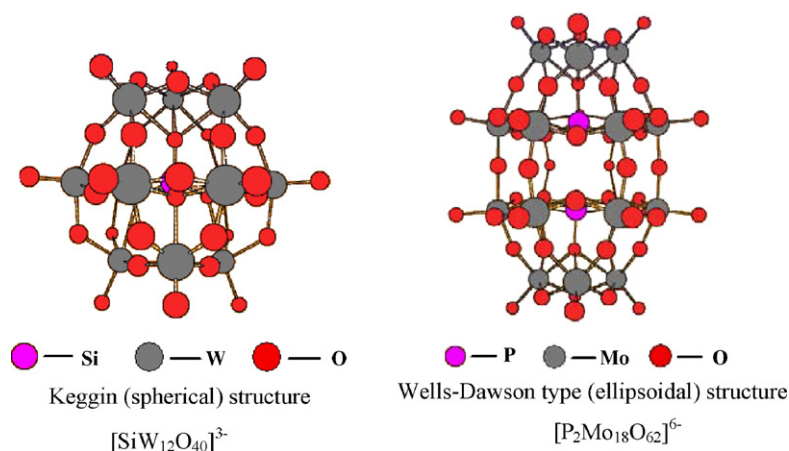
Fig. 1. The structure of Keggin and Wells–Dawson type anion [4].

gives a general formula of XM_{12}, where X is the heteroatom and M is the d^0 metal. Each corner of the heteroatom tetrahedron is associated with an M_3O_{13} unit. An anion $SiW_{12}O_{40}{}^{3-}$ (Fig. 1) can be obtained by acidifying the mixed solution of metasilicate and tungstate with a molar ratio of 1:12. The Si atom is called the heteroatom, while the W atoms are called the addenda atoms which are coordinated octahedrally by oxygen atoms and can be substituted by other metal atoms. Three WO_6 of octahedron unit form a triplet M_3O_{13} by sharing octahedral edges, and four such triplets share the octahedral vertexes and arrange tetrahedrally around the heteroatom Si, that is, the three-fold shared oxygen atoms in the triplet M_3O_{13} are coordinated to a Si atom, resulting in a Td symmetric polyoxometalate. In fact, more than 70 elements in the periodic table may act as the constituents of POMs.

Another structure is the Wells–Dawson type structure that is ellipsoidal, of formula X_2M_{18} [6,7]. This structure consists of two heteroatoms stacked one atop the other, and each end is composed of an M_3O_{13} cap, with two six-metal belts circling the molecule. Under basic conditions, the POM structure can lose an M=O unit and become what is known as a lacunary species. This species acts as a pentadentate ligand for transition metals that can be substituted into the POM structure. These metals (not d^0) are known as addenda atoms. POMs can be made to be mono-, di- and tri-lacunary. This allows the synthesis of a wide array of compounds. Lacunary species can share addenda atoms forming sandwich compounds, with a POM structure on the top and bottom joined by addenda transition metals.

It is attractive that solid POMs have hierarchical structure (the example shown as Fig. 2) [8], which are important for the understanding of the heterogeneous POM catalysis process. The primary structure is the structure of heteropoly anion itself, i.e. the metal oxide cluster. The secondary structure is the three-dimensional arrangement consisting of polyanions, counter cations and additional molecules. The tertiary structure represents the manner in which the secondary structure assembles into solid particles and relates to properties such as particle size, surface area and pore structure.

2.2. Properties and catalysis

Based on POMs' hierarchical structure, it can be demonstrated that there are three completely different modes of catalysis for solid POMs: surface-type catalysis, pseudo-liquid bulk-type catalysis and bulk-type catalysis in the presence of electrons or protons (Fig. 3) [9]. Surface-type catalysis (a) is ordinary heterogeneous catalysis that takes place on the solid surface (two-dimensional reaction field on outer surface), (b and c) represent bulk-type catalysis where the reaction fields are three-dimensional in contrast to the surface-type catalysis. When the diffusion of reactant molecules in the solid (diffusion in the lattice rather than pores) is faster than the reaction, the solid bulk forms a pseudo-liquid phase in which catalytic reaction can proceed (Fig. 3 (b)). In the pseudo-liquid phase the catalysts appear as solids but behave like liquids (solvent). As the active sites in the solid bulk, e.g. protons, take part in catalysis, the very high catalytic activities are often observed in the bulk phase [9,10]. Due to the flexible nature of the solid structure of some POMs (variable secondary structure), reactant molecules having polarity or basicity are readily absorbed into the solid lattice (between the polyanions in the lattice, sometimes expanding the lattice) and react therein. In other words, the reaction field becomes three-dimensional like reactions in solution. Owing to this behaviour, POMs catalysts often exhibit high catalytic activities and unique selectivity [4].
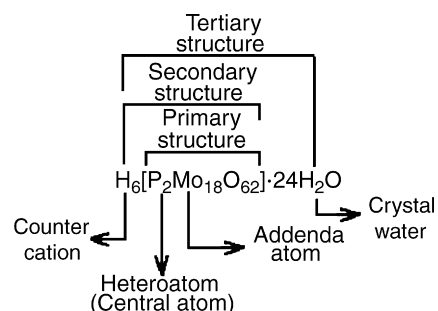

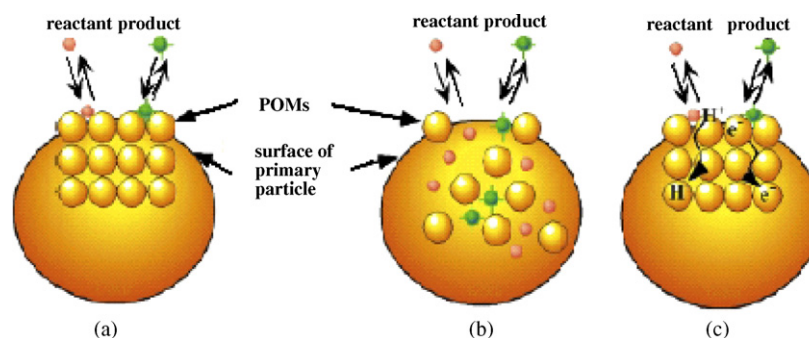Fig. 2. Primary, secondary and tertiary structure of Wells–Dawson POM.

Fig. 3. Three types of catalysis for solid POMs: (a) surface type; (b) pseudo-liquid bulk type (I); (c) bulk type (II).

Moreover, POMs have many "value-adding properties" [11], such as large size, high molecular mass, high anionic charge, discrete structure, discrete size (compared with the metallic oxides), strong electrolyte, easy solubility of acid forms in H_2O and in other oxygen-carrying solvents (ether, alcohols, ketones, etc.). It is these "value-adding properties" that make the POMs of considerable value in quite diverse disciplines of science and technology, e.g., catalysis, medicines and materials science. POMs' countercations may be exchanged by metathesis reactions that allows for the preparation of both inorganic and organic salts. Selection of different countercation makes the POM soluble in either water or organic phases [12]. Another characteristic is that the negatively charged oxygen atoms are polarized towards the positive metallic atoms on the interior of the structure. Therefore, the oxygen atoms are relatively inert, making them resistant to acidic or basic decomposition [13].

Polyoxometalates have several advantages as catalysts, which the most important are their multifunctionality and structural mobility. On the one hand, they have a very strong Brønsted acidity; on the other, they are efficient oxidants, exhibiting fast reversible multielectron redox transformations under mild conditions. Solid polyoxometalates possess a discrete ionic structure, comprising fairly mobile structural units-heteropoly anions and counteracations—unlike the network structure of, e.g., zeolites and metal oxides. The structure is frequently preserved upon substitution or oxidation/reduction and manifests itself to exhibit extremely high proton mobility and "pseudo-liquid phase" behavior. On top of that, many polyoxometalates have a very high solubility in polar solvents and fairly high thermal stability in the solid state.
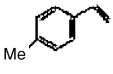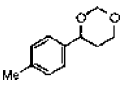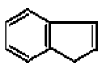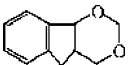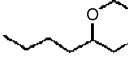
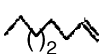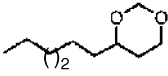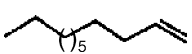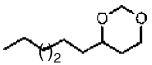Because of their unique properties, POMs are promising acid, redox and bifunctional catalysts. The catalytic reactions can be performed in homogeneous as well as in heterogenous (gas–solid, liquid–solid or biphasic liquid–liquid) systems. POMs are frequently used as model systems for fundamental research, providing unique opportunities for mechanistic studies on the molecular level. At the same time, they have become increasingly important for applied catalysis. Many POMs are able to activate molecular oxygen or hydrogen peroxide as reagents in oxidation reactions. The by-products formed from these reactions are water as opposed to organic compounds [14].

3. Acid-catalyzed reactions over Wells–Dawson type molybdovanadophosphoric heteropolyacids

Many researchers have reviewed the reactions catalyzed by heteropoly acids in both heterogeneous and homogeneous systems [2–3,15–18]. Our comprehensive review addresses mainly the advances in heterogeneous and homogeneous catalysis by Wells–Dawson type molybdovanadophosphoric heteropolyacids. POMs are strong Brønsted acid and most of them are stronger in acidity than the usual inorganic acids (HCl, H_2SO_4, HNO_3, HBr), even stronger than $HClO_4$ and CF_3SO_3H. This is of fundamental importance for POM application in acid catalysis. The difference in the acid strength between heteropolyacids and typical inorganic acids can be attributed to the fact that heteropoly anions are larger and more negative charge density of the POM (charge/number of atoms) than inorganic acids, so the strength of bonding between the proton and heteropoly anions should be lower, which implies that the dissociation constants should be lower compared to the usual acids. Moreover, the strength of the heteropoly acids relates more to negative charge density of the POM than solely the negative charge or solely the size. POMs show acidity as well as oxidative ability and can be profitably used in homogeneous, biphasic, or heterogeneous systems. Especially, Wells–Dawson type heteropolyacids possess super-acidity and a remarkable stability both in solution and in the solid state [19]. Many typical acid-catalyzed reactions, including tetrahydropyranylation of alcohols [20], acetolization, ketonilzation [21] and etherification [22] are all effective in the presence of a suitable Wells–Dawson type heteropoly acid catalyst.

Prins reaction with condensation of olefins with aldehydes as an important carbon–carbon bond forming reaction in organic synthesis is considered as one of the most straightforward method for the synthesis of 1,3-dioxanes, which are widely used in organic synthesis as solvents or intermediates [3]. Although Lewis acids as well as mineral acids can promote this transformation, most of them cause the corrosion of reaction equipment, use toxic reagents and also require prolonged reaction time and high-temperature reaction conditions resulting in low to moderate selectivity of products due to the polymerization of starting materials [15–18]. Prins cyclization of styrene with formaldehyde have been examined using Keggin-type HP as catalysts in aqueous solution, however, the conver-

Table 1
Efficiency of $H_8P_2Mo_{16}V_2O_{62}$ catalyzed synthesis of 1,3-dioxane derivatives in 1,2-dichloroethane[a]

Entry	Alkene	Product[b]	Reaction time (min)	Conversion of alkene (%)	Selectivity to 1,3-dioxane derivatives (%)
1			25	99.9	98.7
2			25	91.5	96.8
3			25	93.0	31.2
4			60	95.7	95.5
5			150	99.7	84.6[c]
6			150	99.6	45.0[c]
7			150	75.8	27.3[c]

[a] 1,2-Dichloroethane: 5 ml; olefins: 2 mmol; paraformaldehyde: 0.12 g; catalyst: 0.03 mmol; reaction time: 25 min.

[b] All products were characterized by mass spectroscopy.

[c] Reactions were carried out at 80 °C.

sion of styrene was only 29% at best with a difficulty of catalyst recycling due to the use of water as solvent (which has low volatility) [23]. Wells–Dawson type molybdovanadophosphoric heteropolyacids ($H_{6+n}P_2Mo_{18-n}V_nO_{62}$) ($n = 1$–2, 4) have been proved to be effective catalyst in the Prins cyclization alkenes and paraformaldehyde to produce corresponding 1,3-dioxane derivatives. Compared with conventional catalytic systems, the high-reaction rate, mild conditions and improved selectivity are the features obtained in our systems [24]. Moreover, various aliphatic linear olefins, which are considered to be inactive, also reacted well, indicating the wide scope of the substrates over $H_8P_2Mo_{16}V_2O_{62}$ catalytic system (Table 1). The experimental procedure is quite simple and convenient, and the reaction conditions are amenable to scale-up.

In our research result, the selectivity to 1,3-dioxolane reach to 93.3% with nearly complete conversion of epoxide and very high TOF ($1.1 \times 10^4 \, h^{-1}$) when Wells–Dawson type molybdovanadophosphoric heteropolyacids were used to catalyze cycloaddition of epoxides with carbonyl compound which is a subject of interest due to the importance of 1,3-dioxolanes as widely used protecting groups for diols and for carbohydrates and steroid chemistry. More investigation indicated various epoxides could be efficiently converted to 1,3-dioxolanes over $H_7P_2Mo_{17}VO_{62}$ catalyst within 5 min (Table 2), and the satisfactory results have been obtained in the reactions of different carbonyl compounds with 1,2-epoxypropane under same conditions.

It indicates our catalytic system has a good generality for the above-mentioned reactions. Short reaction time, simple work-up, mild reaction conditions and reliable reusability are the features obtained in the Wells–Dawson type heteropoly acids catalytic systems [25]. Moreover, we have found that $H_7P_2Mo_{17}VO_{62}$ is immiscible with reaction mixture and could be reused four times without visible loss of the activity in the reaction between 1,2-epoxypropane and acetone with 99.0% of conversion of 1,2-epoxypropane and 90.4% of selectivity to 2,2,4-trimethyl-1,3-dioxolane, simply by filtering the catalyst, washing with acetone, drying and immediately reusing. Therefore, this catalyst can be used as a stable and recyclable catalyst, not only for the possibility to perform environmentally benign synthesis, but also for the good yields, accompanied by excellent selectivity that can be achieved.

As to the alkylation of phenol with t-butyl alcohol reaction, the known catalytic systems include Lewis acids, Brønsted acids [28], montmorillonite [29], metal oxide [30–31], aluminum salt catalyst [32], cation-exchange resin [33,34], zeolites [35,36], molecular sieves [29], supercritical or near-critical water [37] and ionic liquids [38]. Although cation-exchange resin catalysts have some advantages over other catalysts such as no equipment corrosion and no pollution of the environment, they still possess lots of disadvantages. Cation-exchange resin catalysts involve a tedious work-up and thus cannot be used at higher temperatures. The activity and product selectivity of cation-exchange resin catalysts are not up to the mark [33,34]. Ionic liquid, [b_{mim}]PF$_6$ can also catalyze this transformation [38], but the active center was demonstrated to be HF derived from the decomposition of [PF$_6$] in the presence of water.

Table 2
Reaction of epoxides and acetone over $H_7P_2Mo_{17}VO_{62}$

Entry	Epoxides	Conversion (%)	Products	Selectivity (%)	TOF (h)
1	(structure)	~100	(structure)	93.3	~12000
2	(structure)	99.6	(structure)	96.1	11952
3	(structure)	99.2	(structure)	92.7	11904
4	(structure)	99.5	(structure)	90.4	11940
5	(structure)	99.7	(structure)	92.6	11964
6	(structure)	99.0	(structure)	91.3	11880
7	(structure)	99.8	(structure)	94.0	11976
8	(structure)	99.4	(structure)	95.6	11928
9[a]	(structure)	94	(structure)	–	376
10[b]	(structure)	95	(structure)	–	10

[a] Result reported in Ref. [26] using $K_5CoW_{12}O_{40}\cdot 3H_2O$ as catalyst.
[b] Result reported in Ref. [27] using $(NH_4)_8[CeW_{10}O_{36}]\cdot 20H_2O$ as catalyst.

It is interesting that $H_7P_2Mo_{17}VO_{62}$ was also found to be a suitable catalyst for the reaction with high conversion and excellent selectivity (Fig. 4) [39]. It can be seen that a 91.2% conversion of phenol was obtained in the first 4 h. When reaction time was extended, both the conversion of phenol and the selectivity to 2,4-DTBP was decreased. Thus, the suitable reaction time could be 4 h for the $H_7P_2Mo_{17}VO_{62}$ catalyzed alkylation between phenol and TBA.

It is worthy to be noted that $H_7P_2Mo_{17}VO_{62}$ has a potential application in the production and the experimental procedure is quite simple and convenient, indicating the probability of the reaction conditions are amenable to scale-up.

For the distinction between Wells–Dawson type and Keggin-type heteropolyacids in above transformatins, it potentially is resulted by the fact that Wells–Dawson type heteropolyacids are amorphous in homogeneous solution due to the ellipsidal shape of the polyanion, whereas Keggin-type polyanions, having spherical shape, are crystalline (bcc structure) [40]. As a result, the former is easy to adsorb polar molecules, such as formaldehyde, and forms active pseudo-liquid that allows the reactions to take place at the surface and solid bulk of the heteropoly anion, but the latter are much less active [40].

4. Epoxidation of alkenes over Keggin-type polyoxometalates

Polyoxometalates, as the effective catalysts for epoxidation, have drawn wide attention in the last two decades [41–57]. The most significant developments in this field were the research of groups of Venturello and Ishii. In 1983, Venturello et al. [45–47] discovered that the complex consisting of tungstate and phosphate can catalyze the epoxidation of different alkenes with dilute H_2O_2 solution (15%) as oxidant. In 1988, Ishii et al. [48] reported that the system composed of $H_3PW_{12}O_{40}$ and cetylpyridinium chloride can catalyze epoxidation of alkenes with commercially available H_2O_2 solution (35%) as oxidant. In recent years, the epoxidation mechanism on these catalysts has been investigated by many groups [49–54]. It has been proved that $\{PO_4[WO(O_2)_2]_4\}^{3-}$ is the active species in the olefin epoxidation in the Venturello–Ishii system. Heteropolyacids with the Keggin structure, $H_3PW_{12}O_{40}$, are degraded in the presence of excess H_2O_2 to form peroxo species $\{PO_4[WO(O_2)_2]_4\}^{3-}$ and $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$, which are the true catalytic active intermediate.

We first systematically studied the cyclohexene epoxidation by anhydrous urea-hydrogen peroxide adduct (UHP)
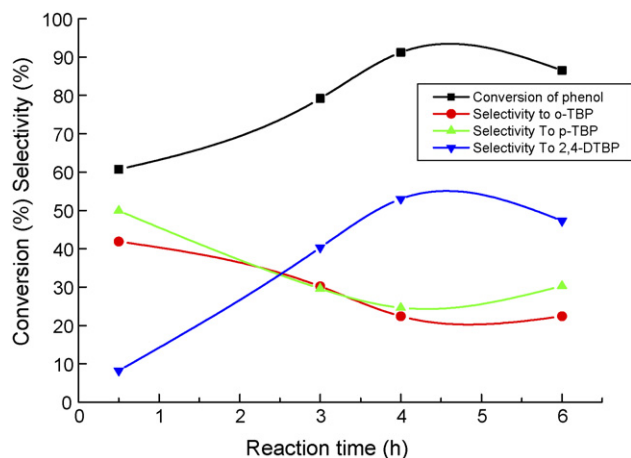

Fig. 4. Phenol conversion and product selectivity vs. reaction time. Conditions: phenol:TBA (1:2) mol ratio; 80 °C, 0.03 mol $H_7P_2Mo_{17}VO_{62}$ (20 mmol phenol).

over a series Keggin-type heteropoly compounds using ace-tonitrile as an alternative solvent [58]. Among a series of Keggin-type POMs, tris(cetylpyridinium)12-tungstophosphate $((CPB)_3[PW_{12}O_{40}])$ showed the highest activity, a 80% conversion of cyclohexene and 97% selectivity for cyclohexene oxide could be achieved in the UHP/CH_3CN system. The reaction of UHP with $(CPB)_3[PW_{12}O_{40}]$ has been studied by UV–vis and ^{31}P NMR spectroscopy, which has revealed that the Keggin-type heteropoly compounds $(CPB)_3[PW_{12}O_{40}]$ is degraded in the presence of excess UHP to form a considerable amount of phosphorus-containing species.

Here, we observed complex time-dependent distribution of polytungstophosphate where the particular distribution depends on the ratio $[UHP]_0/(CPB)_3[PW_{12}O_{40}]_0$. An exemplary experiment using ^{31}P NMR spectra is illustrated in Fig. 5. In this study $(CPB)_3[PW_{12}O_{40}]$ was incubated with the indicated number of UHP equivalents, then the two solids mixture were dissolved in 5 ml N,N-dimethylformamide (DMF) at room temperature. When no UHP was added to $(CPB)_3[PW_{12}O_{40}]$, the ^{31}P NMR spectra showed only one peak at -14.68 ppm, which is attributed to $[PW_{12}O_{40}]^{3-}$ [57]. The addition of UHP leads initially to the gradual conversion of $(CPB)_3[PW_{12}O_{40}]$ to a number of unidentified species (Fig. 5(b–d)). After adding 40 equiv. of UHP (b), two new signals appeared: one is at 0.920 ppm, and the other is at 1.290 ppm. But the peak intensity of $[PW_{12}O_{40}]^{3-}$ (-14.68 ppm) is much stronger than that of the two new bands, implying that the structure of $(CPB)_3[PW_{12}O_{40}]$ is still kept and hardly degraded. For the 50 equiv. of UHP (c), the signal of $[\{W(=O)(O_2)_2\}_4(\mu\text{-}PO_4)]^{3-}$ (2.54 ppm) appears along with two other phosphorus-containing species with ^{31}P NMR
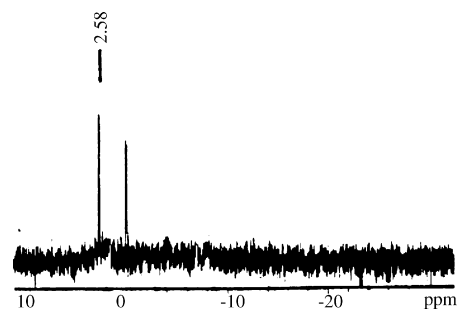
Fig. 6. ^{31}PNMR spectrum of a DMF solution of $(Bu_4N)_3[\{W(=O)(O_2)_2\}_4(\mu\text{-}PO_4)]$. Spectra are referenced to 85% H_3PO_4 as an external standard, 380 scans. The sum of the NMR data acquisition time and the incubation period was 180 min.

resonances at 1.06 and -14.14 ppm, respectively. The latter is attributed to $[PW_{12}O_{40}]^{3-}$, but the peak intensity is weaker than the case b. After the addition of 400 equiv. of UHP (d), there altogether appear six lines in the ^{31}P NMR spectra pattern. The line at 2.60 ppm is attributed to $[\{W(=O)(O_2)_2\}_4(\mu\text{-}PO_4)]^{3-}$, and the signal of $(CPB)_3[PW_{12}O_{40}]$ (-14.22 ppm) has become very weak, suggesting that it has degraded nearly completely. Other five signals in the -8.00 to 1.20 ppm region can be attributed to phosphorous-containing species, which are probably intermediates during the degradation process in the presence of excess UHP.

In order to examine where the active species of $[\{W(=O)(O_2)_2\}_4(\mu\text{-}PO_4)]^{3-}$ locate in the ^{31}P NMR spectra pattern, $(BuN)_3[\{W(=O)(O_2)_2\}_4(\mu\text{-}PO_4)]$ in DMF was measured by ^{31}P NMR. As shown in Fig. 6, only one signal at 2.58 ppm
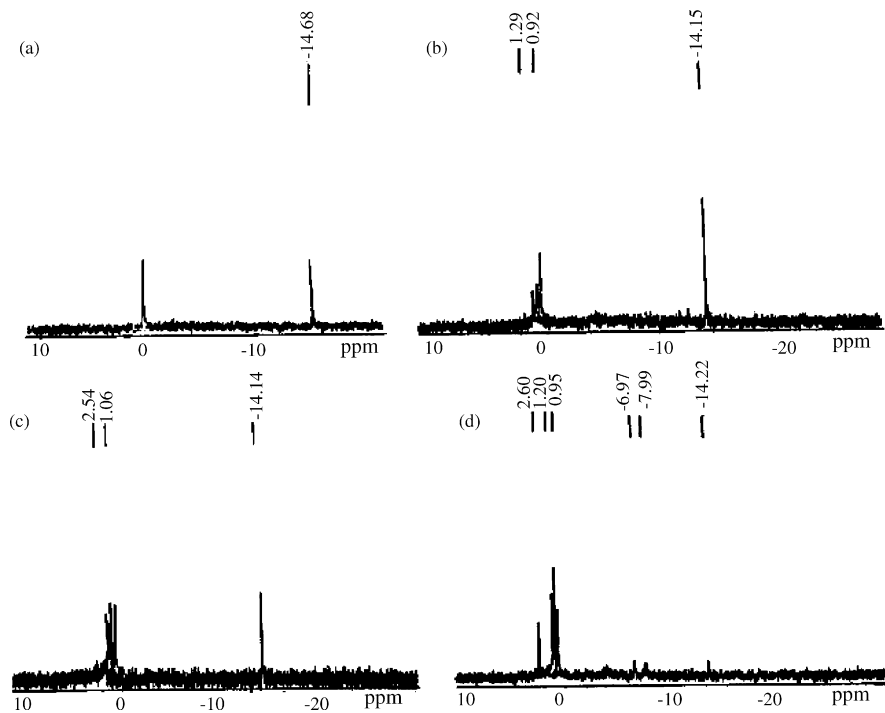

Fig. 5. ^{31}P NMR spectra of a DMF solution of $(CPB)_3[PW_{12}O_{40}]$ reacted with n equivalents of urea-hydrogen peroxide adduct (UHP), where $n = $ (a) 0, (b) 40, (c) 50, (d) 400. Spectra are referenced to 85% H_3PO_4 as an external standard, 380 scans. The sum of the NMR data acquisition time and the incubation period for each sample was constant in all cases (180 min).

Table 3
Epoxidation of cyclopentene catalyzed by heteropoly acids combined with CPB[a]

Entry	Catalyst	Conversion (mol%)	Selectivity (mol%)	Yields (mol%)
1	$H_3PMo_{12}O_{40}$	3.7	Trace	Trace
2	$H_3PMo_{11}W_1O_{40}$	24.1	83.2	20.0
3	$H_3PMo_{10}W_2O_{40}$	59.8	59.5	35.6
4	$H_3PMo_9W_3O_{40}$	49.5	62.3	30.8
5	$H_3PMo_8W_4O_{40}$	38.4	90.6	34.8
6	$H_3PMo_7W_5O_{40}$	63.2	76.0	48.0
7	$H_3PMo_6W_6O_{40}$	60.2	95.5	57.5
8	$H_3PMo_5W_7O_{40}$	66.6	79.8	53.1
9	$H_3PMo_4W_8O_{40}$	48.8	88.3	43.1
10	$H_3PMo_3W_9O_{40}$	51.2	71.9	36.8
11	$H_3PMo_2W_{10}O_{40}$	57.9	71.9	41.6
12	$H_3PMo_1W_{11}O_{40}$	38.0	62.9	23.9
13	$H_3PW_{12}O_{40}$	27.0	43.6	11.8

[a] Reaction conditions: 3 mmol cyclopentene; 0.75 mmol hydrogen peroxide; 0.015 mmol of catalyst (0.5 mol%); 0.045 mmol cetylpyridinium bromide; 3 ml acetonitrile; 0.52 mmol of n-butyl ether as an internal standard; reaction temperature: 60 °C; reaction time: 3.5 h.

is observed, proving that the signal of around 2.50 ppm is the characteristic peak of the active species of $[\{W(=O)(O_2)_2\}_4(\mu\text{-}PO_4)]^{3-}$.

We found that the epoxidation was more efficiently catalyzed by $H_3PMo_{12-n}W_nO_{40}$ ($n = 1$–11) than that by $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ (Table 3) [59], when $H_3PMo_{12-n}W_nO_{40}$ ($n = 0$–12) combined with cetylpyridinium bromide (abbreviated CPB) as a phase transfer reagent and with 50 equivalence of H_2O_2 solution (30%) was used to catalyze epoxidation of cyclopentene in acetonitrile. Among 13 heteropoly acids
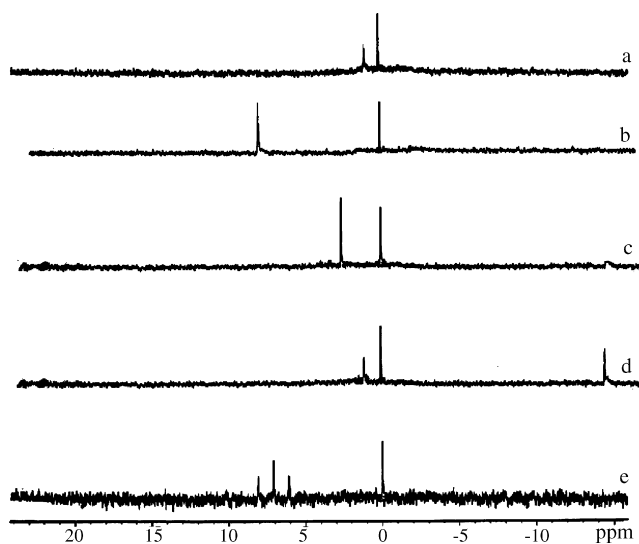

Fig. 7. ^{31}P NMR spectra of a DMF solution of various catalysts: (a) $H_3PMo_6W_6O_{40}$ + CPB; (b) $(Bu_4N)_3\{PO_4[MoO(O_2)_2]_4\}$; (c) $(CTP)_3\{PO_4[WO(O_2)_2]_4\}$; (d) $H_3PW_{12}O_{40}$ + CPB + H_2O_2 ($H_2O_2/HPA = 50$); (e) $H_3PMo_6W_6O_{40}$ + CPB + H_2O_2 ($H_2O_2/HPA = 50$). Spectra are referenced to 85% H_3PO_4 as an external standard, 380 scans. The sum of the NMR data acquisition time and the incubation period for each sample was constant in all cases.

investigated, catalyst of $H_3PMo_6W_6O_{40}$ showed the highest activity. At first sight, the poor reactivity of $H_3PW_{12}O_{40}$/CPB system compared with $H_3PMo_{12-n}W_nO_{40}$ ($n = 1$–11)/CPB system is difficult to understand. In an attempt to interpret these results, we characterized the fresh catalysts and the catalysts under reaction condition by UV–vis, FT-IR and ^{31}P NMR spectroscopy. It was found that the Keggin-type $H_3PMo_6W_6O_{40}$ is degraded completely in the presence of 50 equivalence of H_2O_2 to form $[(PO_4)\{Mo_{4-x}W_xO_{20}\}]^{3-}$ ($x = 0$–4). Just these peroxo molybdotungstophosphate species efficiently catalyzed the alkene epoxidation in the $H_3PMo_6W_6O_{40}$/CPB/H_2O_2/CH_3CN system. Under the same reaction conditions, $H_3PW_{12}O_{40}$ is hardly degraded and no $\{PO_4[WO(O_2)_2]_4\}^{3-}$ is detected by ^{31}P NMR (see Fig. 7).

5. Alcohol oxidation over mono-substituted Keggin-polyoxometalate complexes

The most effective catalysts with hydrogen peroxide as the oxidant are early transition metal ions with a d^0 configuration, e.g., Mo (VI), W (VI) and Re (VII), which operate via a peroxometal mechanism. Early transition metal ions in high oxidation states, on the other hand, are poor catalysts for H_2O_2 decomposition. Several molybdenum- and tungsten-based catalysts, e.g., Na_2WO_4, Na_2MoO_4 [41,60–62] and peroxo complexes of Mo and W [63] were reported to be effective in the oxidation of alcohols with H_2O_2. Similarly, ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ in combination with a phase transfer catalyst and co-catalyst [(n-C_4H_9)_4NCl, and a base (K_2CO_3)], catalyzed the selective oxidation of secondary alcohols with H_2O_2 [64]. Recently, Noyori and co-workers [61] have achieved substantial improvements in the sodium tungstate-based, biphasic system first described by the group of Di Furia and Modena. By employing a phase transfer agent containing a lipophilic cation and bisulfate as the anion, e.g. [CH_3(n-C_8H_{17})_3N] HSO_4, they obtained a highly active catalyst that is effective under solvent-free conditions and with only 1.1 equivalents of H_2O_2. By this token, molybdenum- and tungsten-containing heteropoly anions are also effective catalysts for alcohols oxidations with H_2O_2 [65–67]. Over the past decade these polyoxometalates have awoken interest for catalytic oxidations, as they are inherently stable to oxidation. As concerns oxidation with hydrogen peroxide, most of the research described has been using the Keggin compounds $PW_{12}O_{40}$ or $PMo_{12}O_{40}$, as catalysts. There is, however, now ample evidence, that in almost all cases these polyoxometalates are reduced to simpler peroxophosphometalates, $(PO_4[Mo(O_2)_2]_4)^{3-}$, which are in fact the active catalysts. An especially interesting subclass of polyoxometalates which are "sandwich" type compounds where one or perhaps more of the addenda are substituted by lower valent transition metals such as manganese (II), cobalt (II), iron (II), and ruthenium (II), has been shown to be efficient for catalytic oxygen-transfer reactions [68–72], e.g. $[Fe(II)_4(PW_9O_{34})_2]^{10-}$ for alkene epoxidation in monophasic systems[73], whereas $[WZnMn(II)_2(ZnW_9O_{34})_2]^{2-}$ was found to be highly active (thousands of turnovers) in biphasic alkene epoxidation and alcohol oxidation with H_2O_2 [74,75].

Table 4
Selective oxidation of alcohol with aqueous hydrogen peroxide by $SiW_{11}Zn$[a]

Substrates	Effective conversion of H_2O_2 (%)	Alcohols conversion (%)	Product selectivity (%)	TON
Benzyl alcohol[b]	99	100	Benzoic acid (100)	544 (250[d])
4-Bromo-benzyl alcohol[b]	99	100	4-Bromo-benzoic acid (100)	366
4-Nitrobenzyl alcohol[b]	99	100	4-Nitrobenzoic acid (100)	417
1-Phenyethanol[c]	99	100	Acetophenone (100)	471 (250[d])
Ethanol	91	77	Acetaldehyde (7), acetic acid (93)	942
1-Pentanol	89	58	Pentanal (8), pentanaonic acid (92)	340 (165[d])
Propan-2-ol	99	96	Acetone (95)	830 (233[d])
2-Butanol	99	98	2-Butanone (100)	
2-Pentanol	99	100	2-Pentanone (100)	577 (235[d])
2-Hexanol	99	100	2-Hexanone (100)	697
2-Octanol	86	91	2-Octanone (100)	356 (228[d])
2-Ethyl-1,3-hexanediol	99	100	2-Ethyl-1-hydroxy-3-hexanone (93), butanoic acid (7)	398 (250[d])
2,2,4-Trimethyl-1,3-pentanediol	99	100	2,2,4-Trimethyl-1-hydroxy 3-pentanone (97)	385
Cyclohexanol	99	100	Cyclohexanone (100)	600 (250[d])
	96	98[e]		
Cyclooctanol	99	100[f]	Cyclooctanone (100)	479
	76	95[g]		(238[d])
	85	78[h]		195
	93	93[i]		233
2-Cyclohexen-1-ol	99	100	2-Cyclohexen-1-one (100)	638
1-Octen-3-ol	99	100	1-Octen-3-one (100)	488
Menthol	99	99	Menthone (100)	401
Borneol	99	100	Camphor (100)	406

[a] Reaction condition: 2 ml substrates; 0.1 g of catalyst; 4 ml H_2O_2 (30%); temperature 363 K; reaction time: 9 h; 10 ml water.
[b] Two millilitres substrates; 0.1 g of catalyst; 2 ml H_2O_2 (30%); reaction time: 2 h.
[c] Two millilitres substrates; 0.1 g of catalyst; 3 ml H_2O_2 (30%); reaction time: 7 h.
[d] Calculated from Ref. [77].
[e] The fifth run.
[f] $SiW_{11}Zn$ as catalyst.
[g] Na_{12}-$[WZnZn_2(H_2O)_2(ZnW_9O_{34})_2]$ as catalyst.
[h] $Q_3PW_{12}O_{40}$ as catalyst (Q = cetylpyridinium).
[i] $Q_3[PO_4(W(O)(O_2)_2)_4]$ as catalyst. The remaining H_2O_2 after reaction was estimated by titration with KI solution.

Although these "sandwich" type compounds are active in above reaction systems, they almost need noxious organic solvents.

We reported the oxidation of alcohols with aqueous hydrogen peroxide using a mono-substituted Keggin-polyoxometalate [76], $Na_6[SiW_{11}ZnH_2O_{40}]\cdot12H_2O$, as catalyst in biphasic system without the use of organic solvent. Primary alcohols, for instance, ethanol, 1-pentanol, benzyl alcohol, are all worked well under our conditions, but the formation of corresponding carboxylic acids was proved to be the predominant reaction, and only slight amount of corresponding aldehydes was detected after reaction. Secondary alcohol, such as 2-pentanol, 2-hexanol and cyclooctanol, were converted to corresponding ketones with H_2O_2 using $SiW_{11}Zn$ as catalyst in a short period with excellent conversions and good selectivity. Secondary allylic alcohols such as 2-cyclohexen-1-ol, 1-octene-3-ol also could be oxidized effectively to the corresponding β-unsaturated ketones. This biphasic system with $SiW_{11}Zn$ permits extensive recycling of the catalyst without significant loss in activity. Due to a very easy separation of product and catalyst as well as the simplicity of the process, tremendous energy and cost saving has been achieved (Table 4).

Polyoxometalate is also an efficient oxidation catalyst for hydroxylation phenol. We reported that a Cu-SiW_{12} catalyst, synthesized by the reaction of the $H_4SiW_{12}O_{40}\cdot nH_2O$ with Cu^{2+} is an efficient catalyst for the hydroxylation phenol with hydrogen peroxide in aqueous solution. The maximal conversion of phenol is ca. 39%, which is much higher than the results in acetonitrile reported previously. At meantime, the decomposition of H_2O_2 was slow for the catalyst and the efficiency of H_2O_2 is relatively higher [78].

6. Prospect

Catalysis with heteropoly acids and related polyoxometalate systems is a field of growing importance. Because of their unique physicochemical properties, POMs can be widely used in homogeneous, biphasic and heterogeneous systems. In many cases, POMs provide higher activity and selectivity and allowing for cleaner processing compared to conventional catalysts. From above discussion, it can be seen that POMs catalysis is a rapidly expanding field. Some of the more successful systems described show very high activity and selectivity. With the development of the synthetic chemistry of POMs, more

and more POMs with novel structures will be produced. If the structure, composition and stability of polyanions are properly controlled, POMs catalysts will find much wider practical applications. In liquid-phase oxidation reaction, POMs can be applied either as stoichiometric oxidants or as catalysts in conjuction with environmentally friendly oxidants as O_2 and H_2O_2. The use of a variety of multicomponent redox systems based on POMs greatly extends the scope of possible oxidations. However, for these potentially promising reactions to be used in practice, complete recovery and recycling of POMs catalysts will be required. Detailed knowledge of mechanisms of catalysis by polyoxometalates is needed for the catalyst design and scale-up.

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