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Heteropolycompound-based catalysts: A blend of acid and oxidizing properties

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Abstract

This review reports some aspects of the synthesis, chemical–physical properties and reactivity of heteropolyoxometalates. Particular attention is given to most recent developments in the use of heteropolycompounds as heterogeneous and homogeneous catalysts for the selective oxidation of hydrocarbons. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

One of the areas of catalysis research which has been growing very rapidly in recent years is the study of the chemistry and reactivity of early-transition-metal-oxygen-anion clusters (more generally referred to as polyoxoanions or polyoxometalates). The reason for this is related essentially to two factors: (i) their versatility in composition and chemical–physical features, coupled with their relatively easy preparation, and (ii) the possibility, not often met in catalysis, of making an a priori design of the compound formulation, "tailoring" the composition so as to introduce those elements that are necessary to achieve defined properties.

These aspects have led to intense research activity for the application of polyoxometalates (well known by inorganic chemists for many decades) not only in the field of homogeneous and heterogeneous catalysis, but also in the fields of medicine (in anti-HIV chemotherapy), photochemistry, materials, and microdevice technology. The search for systems suitable for more and more sophisticated applications, i.e., those which are able to catalyze the transformation of complex multifunctional molecules, or to catalyze stereospecific reactions for the synthesis of medicines or of fine chemicals, can be potentially satisfied by engineering the molecular-type structure of these compounds. Another field in catalytic research where these compounds have recently attracted attention is the oxifunctionalization of the simplest but least reactive organic substrates, light paraffins. This comes from the awareness that activation of these molecules requires the co-operation of different functional properties (i.e., acid and redox properties), which can be found, if properly designed, in polyoxometalates.

Many reviews dealing with chemical–physical properties and activity of these compounds have been published since 1978 [1–21], which have been the

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source for the present article. The reader is referred to these reviews for a more complete analysis of the aspects of the polyoxometalates chemistry which are briefly described in this paper.

Since the design of polyoxometalates for catalytic applications is strictly related to the properties of metal oxoanions, the first part of this paper deals with the chemistry of isopolyanions and heteropolyanions in solution. The other sections deal with (i) the tuning of acid and redox properties of heteropolyanions, (ii) the methods of preparation, and (iii) their catalytic applications, both in homogeneous and heterogeneous reaction media.

2. The chemistry in solution of metallic polyoxoanions

2.1. Isopolyanions

The dissolution of metal ions M^{n+} in aqueous solution leads to the co-ordination of water molecules to the cation, with the formation of M–O bonds and ionization of the O–H bond. Dissociation of the proton is thus facilitated, and the higher the charge of the metal ion, the stronger is the acid which forms. The equilibria which develop can be represented as follows:

$$\mathrm{M}^{n+} + y\mathrm{H_2O} \rightleftarrows \mathrm{M}^{n+}(\mathrm{H_2O})_y \rightleftarrows \mathrm{M}^{(n-1)+}(\mathrm{H_2O})_{y-1}\mathrm{OH} + \mathrm{H}^+$$

$$\mathrm{M}^{(n-1)+}(\mathrm{H_2O})_{y-1}\mathrm{OH} \rightleftarrows \mathrm{O{=}M}^{(n-2)+}(\mathrm{H_2O})_{y-1} + \mathrm{H}^+$$

$$\mathrm{M}^{(n-1)+}(\mathrm{H_2O})_{y-1}\mathrm{OH} \rightleftarrows \mathrm{M}^{(n-2)+}(\mathrm{H_2O})_{y-2}(\mathrm{OH})_2 + \mathrm{H}^+$$

etc.

The nature of the ligand (water, hydroxo or oxo species), and the number of each ligand depends on the pH of the solution, and on the value of n.

Indeed, the monomeric complexes formed are not stable, and tend to dimerize through bridging hydroxo or oxo groups. Since the overall positive charge of the dimer is higher than the charge of the monomer, the dimer forms further hydroxo groups, and will continue the polymerization process until the electrostatic repulsion developed in edge-sharing polyhedra is too strong.

$$2\mathrm{M}^{(n-1)+}(\mathrm{H_2O})_{y-1}\mathrm{OH} \rightleftarrows \mathrm{M}^{(n-1)+} \times (\mathrm{H_2O})_{y-1}\mathrm{O}\,\mathrm{M}^{(n-1)+}(\mathrm{H_2O})_{y-1} + \mathrm{H_2O}$$

Metals in polyhedra may be connected via one or two M–O–M bridges, thus sharing edges of the co-ordination spheres.

The extent of polymerization is a function of the nature of the ligands on the metal ion: the higher the number of OH groups, the higher the tendency to polymerize. If the ligand is an oxo species O^{2-}, the tendency for polymerization is rather low. The metal ions with low charges (4+ or lower) will preferentially have water as the ligand or a low number of hydroxy ligands, and therefore will preferentially yield dimers or short-chain units. On the other hand, ions with greater positive charges (7+ and 8+) will form tetra-oxo species which do not polymerize like $\mathrm{Mn^{VII}O_4^-}$ and $\mathrm{Re^{VII}O_4^-}$, which are stable in the monomeric form.

For intermediate charges (5+ and 6+), complexes possess oxo O^{2-} ligands under basic conditions (and therefore prefer to remain as monomeric species), while under acidic conditions hydroxo species form tend to oligomerize forming the so-called *isopolyanions*. There exist, for these metal ions (Mo^{6+}, W^{6+}, $\mathrm{V}^{5+)}$), a large number of different isopolyanions depending on the conditions (pH, concentration of the solution). Another characteristic of polymeric species developed by these early transition metals is that the edge-sharing octahedra $\mathrm{MO_6}$ are arranged in such a way as to minimize the electrostatic repulsion between the metal ions. This aspect is of course more critical for these highly charged cations than for other cations. The best arrangement for three octahedra is that where the three metal cations form M–M–M angles of 60°, and this is indeed the unit found in many isopolymolybdates and isopolytungstates. The further addition of $\mathrm{MO_6}$ octahedra leads to the development of a complex anion with an approximately spherical shape. The limit in growth for the anion is dictated by the increasing electrostatic repulsion, i.e., by the M^{n+} characteristics as well as the pH of the solution.

The requisite of an highly charged ion, however, is not sufficient to determine the type of polyanion developed in aqueous solution, and hence the chemistry in aqueous solution. Other important factors are the ion size and the π-acceptor properties. The ion size determines the co-ordination number adopted by the metal ion in oxides and in oxoanions; V^{5+}, Mo^{6+} and W^{6+} (metal ions which show the richest oxoanion chemistry in solution) adopt six-fold co-ordination in polyoxoanions (even though in oxides lower co-ordination are possible). The smaller Cr^{6+} ion, for instance, has a maximum co-ordination number of four. Even though a few isopolychromates are known (such as dichromate $Cr_2O_7^{2-}$, $Cr_3O_{10}^{2-}$ and $Cr_4O_{13}^{2-}$), these complexes are based on corner-sharing tetrahedra and, with the exception of dichromates, are not stable and undergo hydrolysis. On the other hand, effective ionic radii comparable to those of V^{5+}, Mo^{6+} and W^{6+} are exhibited by a number of post-transition elements such as Ge^{4+}, Sb^{5+} and Te^{6+}. These metal ions form polyoxoanions constituted of polymeric chains and networks of MO_6 octahedra, which however are very different from polytungstates, polymolybdates and polyvanadates (e.g., they do not have almost spherical shapes). This difference is due to the fact that in comparison with post-transition elements, the transition metal ions with their vacant d orbitals form stronger bonds with terminal oxygen and thus are characterized by a greater bond order. In this case, the reduced basicity of terminal O atoms, and consequently the lower charge density on the surface of the polyanion, minimizes further protonation and the tendency to continue polymerization. Under these conditions, the polyanion tends to arrange into almost spherical, discrete and compact entities characterized by high symmetry, where the electrostatic interactions are minimized. On the contrary, with post-transition elements the non-accessibility of vacant d-orbitals which may act as π-acceptors leads to the development of polyoxoanions constituted of infinite chains or networks of tetrahedra or octahedra, since there is no short M–O bond to terminate the polymerization.

V^{5+} oxide is amphoteric, and dissolves in alkali to yield the tetrahedral VO_4^{3-} anion, and in acid to yield the octahedral $VO_2(H_2O)_4^+$ cation. In aqueous solution many isopolyvanadates are formed, the relative amount of which is a function of the pH and concentrations. The prevailing polyanions are the di- and trivanadates, the cyclic tetramer and pentamer (solutions of metavanadates, such as NH_4VO_3, are indeed constituted of these polymeric species), and the decavanadates. Other isopolyvanadates are the hexavanadate $V_6O_{16}^{2-}$ and $V_5O_{14}^{3-}$. V^{4+} isopolyvanadates include $V_3O_7^{2-}$ and $V_{18}O_{42}^{12-}$. Mixed V^{4+}/V^{5+} anions also exist, such as $(V_3^{IV}V_7^{V}O_{26}H)^{4-}$ and $(V_6^{IV}V_{13}^{V}O_{40}H)^{8-}$.

Many different isopolymolybdates have been isolated. Mo^{6+} oxide is amphoteric, and in acid solution gives monomeric or dimeric species like $HMoO_3^+$, MoO_2^{2+}, and $HMo_2O_5^+$, where molybdenum has six ligands, the co-ordination sphere being completed by water molecules. In basic medium, the tetrahedral MoO_4^{2-} anion is formed, which however in water exhibits six-fold co-ordination, $MoO_2(H_2O)(OH)_3^-$. The progressive acidification of the MoO_4^{2-}-containing solution leads to the formation of different polymeric species such as $Mo_3O_{11}^{4-}$, $Mo_7O_{24}^{6-}$, $Mo_{10}O_{34}^{8-}$, $Mo_8O_{26}(OH)_2^{6-}$ (it can be isolated in two isomeric forms, α and β), $Mo_{36}O_{112}(H_2O)_{16}^{8-}$ and $Mo_{12}O_{41}^{10-}$. The heptamolybdate anion and the corresponding protonated forms $H_nMo_7O_{24}^{(6-n)-}$ are the predominant species in aqueous solutions at pH 3–5.

The isopolytungstates in aqueous solution can be classified into paratungstates, formed rapidly upon acidification of the WO_4^{2-} solution ($W_7O_{24}^{6-}$, $W_{12}O_{42}H_2^{6-}$, $W_4O_{16}^{8-}$), and metatungstate, $(H_2)W_{12}O_{40}^{6-}$, which is very stable, and can be isolated into two isomers, α and β. The structure of metatungstate is similar to that of Keggin heteropolyanions with the two protons which occupy the central tetrahedral site, i.e., the site normally occupied by the heteroatom. At strongly acidic pH, the decatungstate $W_{10}O_{32}^{4-}$, and the hexatungstate $W_6O_{19}^{2-}$ are the predominant species.

2.2. *Heteropolyanions*

Acidification of the Mo^{6+} or W^{6+} solutions in the presence of other anions leads to the incorporation of the latter anion (referred to as heteroatom) at the center of the polyanion, with formation of the so-called *heteropolyanions* (or heteropolyoxometalates, or heteropolycompounds, HPCs). Many different ions can be heteroatoms in HPCs: Be, B, Al, Si, Ge, Sn, P, Te, and all the first row transition elements. The heteroatom can adopt either tetrahedral or octahedral co-ordination. The atomic ratio between the atoms in peripheral position (otherwise referred to as addenda atoms) and the heteroatom can be 12, 11, 9 or 6.

The addenda atoms are organized in a structure around the heteroatom where usually MO_6 octahedra (but in some cases pentahedra or tetrahedra) share corners, edges and in some cases faces. The most commonly occurring octahedra are those which contain one terminal M=O oxo group and five bridging oxo M–O–M groups (type I octahedra); less common are those with two terminal oxo groups and four bridging oxo groups (type II octahedra).

There exists a large number of different HPCs, but the most important heteropolyoxometalates are classified as follows:

(1) *Keggin* HPCs, general formula $X^{n+}M_{12}O_{40}^{(8-n)-}$ (M/X=12). These are the most well known and studied compounds, also for catalytic applications, due to their easy preparation, relatively high thermal stability, and redox and acid properties. The heteroatom X (adopting tetrahedral co-ordination) is usually either P^{5+} or Si^{4+} (but also Co^{3+}, Ge^{4+} and many others have been reported to act as heteroatoms) and M is W^{6+} or Mo^{6+}:

$$PO_4^{3-} + 12MoO_4^{2-} + 27H^+ \rightarrow PMo_{12}O_{40}^{3-} + 3H^+ + 12H_2O$$

$$PO_4^{3-} + 12WO_4^{2-} + 27H^+ \rightarrow PW_{12}O_{40}^{3-} + 3H^+ + 12H_2O$$

Keggin compounds containing exclusively vanadium in the polyoxoanion have not been observed; however, the anion $PV_{14}O_{42}^{9-}$ has been isolated, which practically consists of a Keggin framework capped by two VO_5 trigonal bipyramids. Furthermore, mixed Keggin W/V and Mo/V-HPCs are frequently described in the literature. The structure of Keggin compounds, shown in Fig. 1(a), comprises four trigonal groups of edge-sharing MO_6 octahedra, each group sharing corners with neighboring groups and with the central tetrahedron (α structure). In each octahedron the metal is displaced towards the terminal oxygen atoms, like in isopolymetalates.

This structural arrangement leads to the formation of a spherical polyanion. Four kinds of oxygen atoms can be distinguished: the terminal oxygen O_t, which is $\sigma\pi$-bonded to the M atom, the oxygen bridging the edge-sharing octahedra O_e, the oxygen bridging the corner-sharing octahedra O_c, and the oxygen bridging the central heteroatom with the octahedra triads O_i.

There exist skeletal isomers (structures β, γ, δ and ε) of the Keggin α structure, where one or more of the edge-sharing groups of octahedra have been rotated by π/3. These structures are less stable than the α isomer, due to the increased electrostatic repulsion between neighboring M^{n+} atoms in adjacent MO_6 octahedra.

Another form of isomerism (positional isomerism) exists with the mixed addenda compounds, such as $PW_{12-x}V_xO_{40}^{(3+x)-}$, when x is higher than 1.

Lacunary Keggin compounds are formed by the removal of one MO_6 octahedron (stoichiometrically one MO unit is lost) from the Keggin anion with the formation of $XM_{11}O_{39}^{n-}$, and of other species as well. The formation of the lacunary compounds is obtained by raising the pH of the solution. The pH at which the Keggin structure is unstable, and is hydrolyzed with progressive loss of one or more MO entities, is a function of the HPC composition. The W_{12}-HPCs are more stable towards hydrolysis in aqueous solution

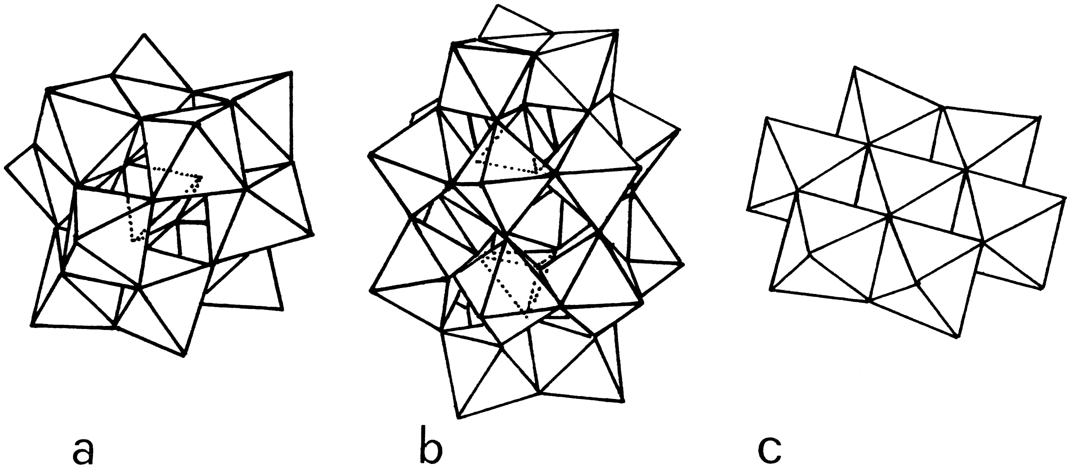

Fig. 1. The polyhedral representation of the primary structure of Keggin HPCs (a), of Wells–Dawson HPCs (b), and of Anderson HPCs (c).

than Mo_{12}-HPCs. The nature of the heteroatom also affects the stability towards hydrolysis, which in Mo_{12}-HPCs decreases in the order: Si>Ti>Ge>P>As. $SiW_{12}O_{40}^{4-}$ forms the lacunary compound at a pH higher than 5, while $PW_{12}O_{40}^{3-}$ is rapidly converted to its deficit derivative $PW_{11}O_{39}^{7-}$ already at a pH higher than 1.5–2, and to the $PW_9O_{32}^{5-}$ species at a pH higher than 7. $PMo_{12}O_{40}^{3-}$ hydrolyzes at a pH higher than 1–1.5. The $AsW_{12}O_{40}^{3-}$ compound is even less stable, and cannot be isolated in aqueous medium, since it is readily hydrolyzed. If another oxoanion is added to the solution containing the lacunary compound, the metal can be incorporated replacing the molybdenum which has been drawn away. In this way it is possible to synthesize mixed HPCs. This replacement is possible with V^{5+}, and also with many transition metal ions, even when they possess low charges such as Fe^{2+}, Ni^{2+}, and Co^{2+}. In this case, the electronic properties of these metals are such that they do not form short M=O bonds with terminal oxygen, and therefore the unshared ligand is either an OH group, or a neutral molecule (water). The possibility of introduction of these guest metal ions clearly indicates that the mixed HPCs are more stable at the given pH than the parent Mo_{12}- or W_{12}-HPCs (however, an increasing degree of replacement decreases the stability).

Table 1 summarizes the main P/Mo HPCS which are formed in solution as a function of the pH.

(2) *Wells–Dawson* HPCs, with general formula $X_2^{n+}M_{18}O_{62}^{(2n-16)-}$ (X is P^{5+}, S^{6+}, As^{5+}; M may be either W^{6+} or Mo^{6+}) (M/X=9). These HPCs are formed via dimerization of two α-PM_9O_{34} moieties (Fig. 1(b)), thus under conditions of pH at which the parent Keggin compound forms the corresponding trilacunary compound by the loss of MO groups.

$$2XMo_9O_{31}(H_2O)_3^{3-} \rightarrow X_2Mo_{18}O_{62}^{6-} + 6H_2O$$

Table 1
Main P/Mo HPCS in aqueous solution, and their pH of existence

P/Mo HPCS	pH of existence
$P_2Mo_5O_{23}^{6-}$, $HP_2Mo_5O_{23}^{5-}$, $H_2P_2Mo_5O_{23}^{4-}$	7.5–4.5
$PMo_9O_{31}OH(H_2O)_2^{4-}$, $PMo_9O_{31}(H_2O)_3^{3-}$	5.5–3.5
$PMo_{11}O_{39}^{7-}$, $HPMo_{11}O_{39}^{6-}$, $H_2PMo_{11}O_{39}^{5-}$	5–1.5
$PMo_{12}O_{40}^{3-}$	<1.5

Solutions of $X_2W_{18}O_{62}^{6-}$ are stable up to pH about 6. Above this pH, the anions are hydrolyzed into lacunary species.

(3) *Anderson* HPCs, with general formula $XM_6O_{24}^{n-}$ (M/X=6) (X=Mn^{4+},Ni^{4+},Pt^{4+},Te^{6+}; M=Mo^{6+},W^{6+}). The structure is planar (Fig. 1(c)); each MoO_6 octahedron has two terminal oxygens (type II octahedra); the heteroatom X adopts the octahedral coordination. The anions can be protonated (the H atom is on the O atom directly attached to the heteroatom), like in $H_6CrMo_6O_{24}^{3-}$, $H_6NiW_6O_{24}^{4-}$ and $H_3PtW_6O_{24}^{5-}$. Anderson anions are usually obtained from aqueous solutions at pH 4–5.

The anions, together with their cations (protons or metal ions) and with water of crystallization (sometimes also organic molecules), form a three-dimensional structure, referred to as the secondary structure of the heteropolycompound. Molecules of water are arranged in such a way as to connect neighboring anions, through the formation of planar $(H_2O–H–OH_2)^+$ bridges, hydrogen bonded to O_t of the anions. With heating at high temperature the water molecules are lost, and the H^+ becomes directly attached to the O atoms of the neighboring Keggin units. In this case each proton migrates between four equivalent positions linking together the anions. This high delocalization makes this proton superacid.

There exist different types of secondary structures for Keggin heteropolyacids; e.g., the body-centered cubic lattice (which is the structure met in $H_3PW_{12}O_{40}·6H_2O$), and the face-centered cubic lattice (this structure is less compact than the previous one, and can accommodate up to 30 water molecules per anion, like in $H_3PW_{12}O_{40}·29H_2O$). Other lattices (triclinic, like in $H_3PW_{12}O_{40}·14H_2O$, rhombohedral, like in $H_3PW_{12}O_{40}·24H_2O$, etc.) may be formed by Keggin anions, depending on both the number of hydration water molecules and the anion charge.

The loss of these crystallization water molecules does not lead to the collapse of the structure. Different is the case for the constitutional water: protons that are directly linked to the oxygen atoms of the primary structure can be lost in the form of water by heat treatment, but this, in some cases, may lead to the destruction of the structure.

The loss of some of the crystallization water molecules can give rise to the formation of a porous structure and of materials with high surface area, analogous to what occurs in zeolites. However, unlike zeolite, the three-dimensional framework of HPCs is not rigid, and the surface area can be modified by changing the temperature and the water vapour pressure. In $H_3PMo_{12}O_{40}\cdot nH_2O$ (which has a very low surface area, 0.1 m^2/g), reversible dehydration can lead to a substantial increase in the surface area (over 10 m^2/g).

Different crystalline structures can be adopted by alkali metal salts of polyoxoanions, like in the corresponding acids. The salts are classified into two groups: A and B. Group A includes salts of small metal ions like Na^+, which behave like the acids. In fact, they are soluble in water, have low surface area (lower than 10 m^2/g) and are thermally unstable. Group B salts, including salts with larger cations such as NH_4^+, K^+ and Cs^+, are insoluble in water. The surface area of group B salts can be as high as 150–200 m^2/g, and microporosity is developed. Even though the presence of microporosity would seem to suggest that the high surface area is due to structural porosity (like in zeolites), it is generally believed that it is rather due to morphological features such as the development of very small crystallites.

Group B salts can be isolated directly from the aqueous solution, and used as solid catalysts. They are very stable, and some of them like $Cs_3PMo_{12}O_{40}$, can be heated up to the melting point without decomposition of the structure. This stability arises from the fact that large cations interact strongly with the anions, allowing a rigid structure to be maintained. Group B salts usually are much less hydrated than group A salts. In fact larger cations take up a large space between the anions, leaving little room for water molecules. Sometimes, with very large cations, it is not possible to fit enough cations in the lattice, and the charge balance is reached with hydrogen ions. This may explain why in some cases a residual proton acidity is left even when the precipitation of completely neutral salts is expected. In other cases, the acidity of these salts may arise from the partial hydrolysis of the cations themselves.

Polar molecules, like alcohols or amines, can penetrate the secondary structure and be retained in the bulk of heteropolyacids and group A salts, by replacement of water molecules or by expansion of the lattice, thus leading to swelling phenomena analogous to that occurring in clays. This state is called the "pseudo-liquid" phase; reactions which occur in this pseudo-solution are accelerated due to the participation of all bulk protons of the HPC.

3. The preparation of HPCs

The simplest way to prepare HPCs involves the acidification of an aqueous solution containing the oxoanions and the heteroatom:

$$12WO_4^{2-} + HPO_4^{2-} + 23H^+ \rightarrow PW_{12}O_{40}^{3-} + 12H_2O$$

Control of the pH and of X/M ratio is necessary in order to obtain the desired structure, i.e., the Keggin HPC, the Wells–Dawson HPC, the Anderson HPC, a lacunary compound or the desired specific isomer. Acidification is achieved by direct addition of a mineral acid. Isolation of the heteropolyacid can be obtained by the so-called "etherate method". If the aqueous acid solution is shaken with an excess of diethylether, three phases separate: an aqueous layer (which is drawn off, and treated again with ether to recover as much as possible of the HPC), an upper layer containing excess ether, and an intermediate heavy oily etherate, which contains a complex between the ether and the HPC (which also may contain water molecules). This etherate complex can be hydrolyzed by addition of a controlled amount of water; then the ether is removed, and the concentrated aqueous solution of the HPC is evaporated until crystallization occurs. Alternatively, the excess ether in the etherate complex is removed by evaporation, and the ether complex is thermally decomposed to yield the solid acid by drying at 80–100°C. The etherate method suffers from disadvantages due to the low yield generally achieved, and to the large amount of waste product formed.

The acid can be exchanged with other metal ions by dissolution in aqueous solutions and addition of the proper metal salt. If the salt or mixed acid/salt obtained is soluble, it has to be recovered by the evaporation of water.

Insoluble group B salts, can be directly precipitated from the acid solution through addition of the suitable metal salt, i.e., KNO_3 or KCl to precipitate the insoluble $K_3XM_{12}O_{40}$ salt.

4. Catalytic applications: The concept of intrinsic multifunctionality

The properties of HPCs make them rather unique compounds, and justify the great interest for the developments of applications in the field of homogeneous and heterogeneous catalysis. In fact, HPCs constitute an example of *intrinsic multifunctionality* which is not frequently met in materials used for catalytic applications. Multifunctional properties are useful in those reactions where different kinds of synthetic steps are needed. Examples are the reactions of reforming and isomerization of paraffins, which couple acid-type and dehydrogenation steps. In the latter cases, the necessary catalytic functions are provided by mixing different components, each one characterized by a specific property. HPCs, on the contrary, possess both acidic and oxidizing moieties in the same structure.

This multifunctional feature can be useful for those hydrocarbon transformations that require both functions. The oxidation of saturated organic substrates constitutes an example, and indeed in most recent years HPCs have been studied as either homogeneous or heterogeneous catalysts for the oxifunctionalization of light paraffins. Most successful catalytic systems developed in recent years for the selective oxidation of paraffins (i.e., V/P/O, V/Mg/O, which activate and oxidize hydrocarbons through a completely heterogeneous mechanism), join together specific oxidation properties and acid (or basic) functions. Acid properties are necessary for the heterolytic activation of the C–H bond in paraffins. In addition, acid properties favor the desorption of acid products (such as the methacrylic acid formed in the oxidation of isobutane), thus hindering the unselective consecutive heterogeneous reactions of combustion, or may also favor the formation of intermediate complexes with a basic nature.

4.1. The tuning of HPCs redox properties

HPCs are multielectron oxidants, and the mechanism of reduction of Keggin HPCs involves the transfer of as many as six electrons to the unit without collapse of the structure. The reduction increases the basicity, and can be accompanied by the protonation of the compound:

$$\mathrm{PMo_{12}O_{40}^{3-}} + a\mathrm{e^-} + b\mathrm{H^+} \rightleftarrows \mathrm{PMo_a^{V}Mo_{12-a}^{VI}O_{40-b}} \times \mathrm{(OH)}_b^{(3+b-a)-}$$

Mixed valence complexes are characterized by an intense blue colour (*heteropolyblues*) which is caused by intervalence transitions. These complexes are characterized by the same structure as the parent oxidized compounds.

The redox properties of HPCs are a function of the nature of the metal atoms in the primary structure (addenda atoms) and of both the heteroatom and the counterions.

The oxidation potential decreases in the order HPC-V/Mo>HPC-Mo>HPC-W, which means that the vanadium-containing HPCs are the strongest oxidants. This order is the same as that observed for the corresponding monomeric species, $\mathrm{VO_3^-}>\mathrm{MoO_4^{2-}}>\mathrm{WO_4^{2-}}$. The replacement of one or more molybdenum atoms in the primary structure of Keggin HPC-Mo for vanadium leads to an enhancement of the oxidation potential of the HPC due to the vanadium reducibility. In fact the redox reactions:

$$\mathrm{H_{3+n}PMo_{12-n}V_nO_{40}} + a\mathrm{e^-} + a\mathrm{H^+} \rightarrow \mathrm{H_{3+n+a}PMo_{12-n}V_{n-a}^{V}V_a^{IV}O_{40}}$$

$$\mathrm{H_{3+n+a}PMo_{12-n}V_{n-a}^{V}V_a^{IV}O_{40}} + a/4\,\mathrm{O_2} \rightarrow \mathrm{H_{3+n}PMo_{12-n}V_nO_{40}} + a/2\,\mathrm{H_2O}$$

are thermodynamically favored (*redox reversibility*) in aqueous media with a wide variety of organic substrates acting as electron-donors (reducing agents), and this allows these complexes to be used as homogeneous catalysts for oxidation with molecular oxygen. This property arises from the fact that the oxidation potential of these mixed complexes at pH 1 is approximately 0.68–0.71 V, that is higher than potentials of many organic substrates (with respect to which they can act as oxidizing agents), and lower than the potential of dioxygen (1.23 V), so that the latter can act as oxidizing agent towards the reduced HPC. This property is exhibited by mixed-ligand Keggin HPCs (HPC-Mo/V, HPC-W/V, HPC-Mo/W), while it is not shown by HPCs with only one type of oxometal (HPC-Mo and HPC-W). It is worth mentioning that however these less reactive complexes can be used efficiently as oxidation catalysts under more severe conditions, that is higher temperature (as in gas-phase applications), under which redox reversibility is achieved.

The nature of the heteroatom affects the overall charge of the polyanion; e.g., an increase in the charge leads to a decrease in the oxidation potential for the W^{6+}/W^{5+} couple in:

$$\begin{aligned}&P^{V}W_{12}O_{40}^{3-} > Si^{IV}W_{12}O_{40}^{4-} \approx Ge^{IV}W_{12}O_{40}^{4-}\\ &\quad > B^{III}W_{12}O_{40}^{5-} \approx Fe^{III}W_{12}O_{40}^{5-} > H_2W_{12}O_{40}^{6-}\\ &\quad \approx Co^{II}W_{12}O_{40}^{6-} > Cu^{I}W_{12}O_{40}^{7-}.\end{aligned}$$

Also the effect of the counterion can be significant. When the cation is easily reducible, the redox properties of the HPC is parallel to those of the cation. When the cation is not reducible (alkali metals), the reducibility of the metal in the primary structure is nevertheless affected by the nature of the cation. In particular, there exists a relationship between structural stability and reducibility. For instance, the very stable $K_3PMo_{12}O_{40}$ shows a lower rate of reduction than the less stable $H_3PMo_{12}O_{40}$, indicating that molybdenum is less reducible.

4.2. The tuning of HPCs acid properties

The acid–base properties of HPCs can be modified by the choice of the heteroatom, of the oxometal in the primary structure, and of the cation.

The acidity may be generated by protons which act as counterions in heteropolyacids (i.e., in $H_3PW_{12}O_{40}$), and in mixed acidic salts (for instance, in $K_xH_{3-x}PW_{12}O_{40}$), or by protons which develop by other phenomena such as (i) the dissociation of water coordinated to metal cations, analogous to what occurs in zeolites $[Mg(H_2O)_n^{2+} \rightarrow Mg(OH)(H_2O)_{n-1}^{+} + H^{+}]$, (ii) the protons formed by the reduction of metal ions or of the metal in the primary structure $[Cu^{2+} + 1/2\,H_2 \rightarrow Cu^{+1} + H^{+};\ H_3PMo_{12}O_{40} + 1/2\,H_2 \rightarrow H_4PMo^{V}Mo_{11}O_{40}]$.

The bridging oxygen atoms, which have a higher electron density than the terminal oxygen atoms, are the predominant protonation sites in solution. In solid HPCs, the protons link the neighboring units, and the more accessible terminal oxygens also can be protonated. However, it is generally accepted that also in solid anhydrous HPCs the three protons acting as counterions of the framework charge are located on the bridging oxygen atoms.

All heteropolyacids are strong acids, much stronger than mineral acids, and are completely dissociated in aqueous solutions; in organic solvents they are dissociated in part. This strong acidity can be attributed to the delocalization of surface charge density throughout the large sized polyanion, leading to a weak interaction between the protons and the anion. Also solid HPCs are stronger than conventional solid acids, such as SiO_2–Al_2O_3 or HY zeolites. The order of acid strength is the same as that observed in solution. Usually, the activity in acid-catalyzed reactions also follows this order.

The acid strength can be expressed by the Hammett acidity function H_0:

$$H_0 = pK_{BH^+} - \log([BH^+]/[B]),$$

where [B] is the concentration of the indicator B, $[BH^+]$ is the concentration of the conjugated acid, and K_{BH^+} is the equilibrium constant for the reaction:

$$BH^+ \rightarrow B + H^+$$

The H_0 value of 100% H_2SO_4 (-11.94) is taken as a reference number, since acids with values lower than -12 are classified as superacids. Superacids with H_0 values of -20 (that is 10^8 times stronger than 100% H_2SO_4), such as HSO_3F–SbF_5, are able to protonate methane. The values of the Hammett function for a number of solid acids, including $H_3PW_{12}O_{40}$, are compared in Table 2.

The extraordinarily high acidity of HPCs (which according to this scale can be classified as superacid compounds) has led to increasing interest in the possibility of using them as alternative catalysts for acid-catalyzed transformations which employ environmentally unfriendly homogeneous liquid acids (HF,

Table 2
Hammett function for some solid acid catalysts

Solid acid	$-H_0$
Nafion	12
$H_3PW_{12}O_{40}$	13.2
$AlCl_3$–$CuCl_2$	13.7
SbF_5/SiO_2–Al_2O_3	13.7
SO_4^{2-}/TiO_2	14.5
SO_4^{2-}/ZrO_2	16.1

$AlCl_3$ or H_2SO_4), such as alkylation and acylation processes. On the other hand, a very high acidity may be responsible for undesired side-reactions, and for quick deactivation phenomena due to the formation of heavy by-products. One way to control the acid properties is through partial neutralization of the protons. This can be achieved by exchanging the acid form with a suitable metal ion (i.e., an alkali or alkaline earth salt). In this way it is possible to decrease the number of protons in the compound.

Also Lewis acidity of metal cations can contribute to the generation of the acid properties of these compounds. A correlation exists between the activity in acid-catalyzed reactions and the electronegativity of the counterion. In neutral salts, the acidity as determined by the amount of irreversibly adsorbed NH_3 at 200°C increases from Cs^+, Na^+ (the least electronegative cations) to Mn^{2+}, Ni^{2+}, Cu^{2+} (intermediate electronegativity), up to the most electronegative Fe^{3+} and Bi^{3+}.

On the other hand, the acid strength is affected by the nature of the metals in the primary structure. The acid strength in acetone solution follows the order:

$$H_3PW_{12}O_{40} > H_4PVW_{11}O_{40} > H_4SiW_{12}O_{40} \approx H_3PMo_{12}O_{40} > H_5PV_2Mo_{10}O_{40} > H_4SiMo_{12}O_{40}.$$

The catalytic activity of solid HPCs in heterogeneous acid-catalyzed transformations is similar since it follows the order:

$$H_3PW_{12}O_{40} > H_4SiW_{12}O_{40} \approx H_3PMo_{12}O_{40} > H_4SiMo_{12}O_{40}.$$

5. The use of HPCs as homogeneous catalysts

5.1. *Acid-catalyzed reactions*

Today, the commercial use of HPCs for acid-catalyzed transformations is limited to the hydration of propene, *n*-butene and isobutene, and for the synthesis of polyoxytetramethyleneglycol (PTMG) from tetrahydrofuran. New applications are currently being studied:

1. in the refinery industry for applications which require superacids (such as skeletal isomerization of *n*-paraffins and isobutane alkylation with C_3–C_4 olefins);
2. in the petrochemical industry for the alkylation of aromatics with olefins. These applications are being studied for both homogeneous and heterogeneous systems;
3. in the synthesis of fine chemicals (Beckmann rearrangement, Prins reaction, acylations, condensation reactions in the multistep synthesis of vitamins E and C, esterification of aromatic acids, hydration or dehydration of complex unsaturated molecules).

5.2. *Oxidation with* O_2

Usually, in the oxidation of organic substrates catalyzed by HPCs which use molecular oxygen as the oxidizing agent, the mechanism is redox-type, where the substrate is stoichiometrically oxidized by the HPC, and the original oxidation state of the latter is restored by dioxygen. The two steps can be carried out either simultaneously in the same reactor or separately in two reactors. HPCs-based systems usually consist of the phosphomolybdate anion where molybdenum is in part replaced by vanadium. A HPC-based catalyst (the $PMo_{12-x}V_xO_{40}^{n-}/Pd^{2+}$ system) is active for the oxidation of ethylene to acetaldehyde, as an alternative to the Wacker catalyst ($PdCl_2/CuCl_2$). The advantage lies in the fact that the HPC-based system can operate even in the absence of chloride. In this way, a less corrosive reaction medium is obtained, and in addition there is no formation of chlorinated compounds that constitute a waste stream of the industrial process. The system operates very efficiently due to the redox properties of vanadium when it is in the Keggin framework. In fact, vanadium acts as the reoxidizing species for Pd^0, which is reduced after the oxidation step.

Other reactions which are studied include:

- oxidation of alcohols to ketones;
- oxidative dehydrogenation of dienes to aromatics;
- oxidation of amines;
- epoxidation of olefins (cyclohexene);
- Baeyer–Villiger oxidation of cyclic ketones;
- oxidation of aldehydes to acids;
- oxidation of alkylbenzenes to the corresponding aldehydes;

- oxidative bromination of arenes (use of $Br^{-}+O_2$ instead of Br_2);
- oxidative coupling of arenes;
- acetoxylation of arenes;
- oxidation of benzene to phenol;
- oxidation of phenols to quinones;
- oxidation of isobutane to *t*-butyl alcohol;
- oxidation of propane to isopropyl alcohol and acetone.

In some cases, however (as in the oxidation of light paraffins under pressure), it is likely that the true operating mechanism is a radical-initiated auto-oxidation.

5.3. *Oxidation with* H_2O_2 *or with organic peroxides*

A large number of reactions have been studied using HPCs as the catalysts, and either hydrogen peroxide or organic peroxides as the oxidizing agent, either in a homogeneous system or in two-phase systems (phase-transfer catalysis):

- oxidation of allyl alcohol to glycerol;
- epoxidation of cyclohexene, and of other olefins as well;
- oxidation of cyclopentene to glutaraldehyde;
- oxidative cleavage of olefins and vic-diols;
- oxidation of alcohols to ketones;
- oxidation of aliphatic and aromatic amines;
- oxidation of benzene to phenol;
- oxidation of phenols to quinones;
- hydroxylation of arenes and phenols;
- oxidation of cyclohexane to cyclohexanone/cyclohexanol.

The HPC is generally considered to be the precursor of the true active species; the latter can be a peroxopolyoxometalate species, such as $PW_4O_{24}^{3-}$, which includes the $WO(\mu\text{-}O_2)(O_2)$ moiety.

Epoxidation reactions (the most interesting potential application from an industrial point of view) are generally carried out with mixed organic/water solvents, at acidic pH (2–4) and moderate temperatures, with phase-transfer catalysis. High selectivities can be achieved, except with epoxides of lower alkenes which are soluble in the aqueous phase and therefore undergo consecutive ring-opening reactions.

The most studied iso- and heteropolycompounds for this kind of reaction are those based on tunsgten, due to the property of this metal in the formation of peroxo species. The tungsten in the primary structure has often been partially replaced with other transition metal ions in the search for more active and more selective systems, i.e., for catalysts able to oxygenate the organic substrate with specificity, and which do not catalyze the parallel decomposition of hydrogen peroxide.

6. The use of HPCs as heterogeneous catalysts

6.1. *Acid-catalyzed reactions*

Solid HPCs in the acid form are more efficient catalysts than conventional solid acids. The ability to absorb large amounts of polar molecules in the bulk, coupled with high proton mobility, leads to a high catalytic efficiency for liquid-phase reactions. This behavior favors the reaction kinetics and the participation of all structural protons in the reaction. This high activity allows operation to be carried out at milder conditions than with other solid acids, and this is particularly useful for the synthesis of thermolabile organic substances in the fine chemical industry. In addition, one of the major challenges is the development of a solid acid active enough to catalyze reactions of great interest for the refinery industry, such as skeletal isomerization of linear paraffins and alkylation of isobutane with olefins.

Reactions which are currently under study and employ HPCs as solid catalysts are the following:

- hydration/dehydration of olefins;
- conversion of methanol to hydrocarbons;
- alkylation of benzene with olefins;
- skeletal isomerization of *n*-paraffins over Pd or Pt-containing HPCs.

6.2. *Gas-phase oxidation*

The oxidation of methacrolein to methacrylic acid is the only industrial application of HPCs as oxidation catalyst. P/Mo-based Keggin-type HPCs are claimed, which also contain vanadium as a mixed addenda atom, and are further doped with Cu and alkali metal ions in cationic positions. The effect of the cations is two-fold: (i) an increase in the structural stability and (ii) a better control of the oxidation properties of the compound.

Reactions which have been claimed where HPCs are used as gas-phase oxidation catalysts are the following:

- ammoxidation of isobutene to methacrylonitrile;
- oxidation of butenes and *n*-butane to maleic anhydride;
- oxidation of crotonaldehyde to furan;
- oxidation of acrolein to acrylic acid;
- oxidehydrogenation of isobutyric acid to methacrylic acid;
- oxidation of propane to acrylic acid;
- oxidation of isobutane to methacrylic acid;
- oxidehydrogenation of light paraffins to olefins.

There is a great interest for the use of HPCs as catalysts for the oxidative functionalization of light paraffins, because the proper combination of acid and oxidizing properties may lead to the development of active and selective catalysts. On the other hand, the high temperatures which are usually necessary to activate light paraffins may lead to the structural decomposition of the HPCs, with a loss of the unique properties of the compound and worsening of the catalytic performance. Therefore, it is necessary to use stable group B salts, which on the other hand, are less reactive. Alternatively, it is possible to:

1. Operate in the liquid phase at high pressure and moderate temperature.
2. Use supported HPCs, in order to obtain better spreading of the active phases (i.e., increase the specific surface area of the active compound). A problem may arise due to the strong chemical interaction that develops between the support and the HPC, which can lead to the destruction of the compound itself. Less reactive supports such as silica are therefore needed.
3. Improve at the same time the structural stability of the HPC and its oxidation potential, by using group B salts and by adding transition metal ions which are known to enhance the oxidation potential of the oxometal, such as low-valence early transition metal ions in the cationic position of the HPC, or vanadium as a mixed addenda oxometal.

In gas-phase oxidations usually water is also added in the stream. This guarantees stable catalytic performance and higher activity, likely because the presence of water can favor the surface reconstruction of the heteropolyacid even under conditions at which it would usually decompose. In addition, water may favor the desorption of the products, saving them from unselective consecutive combustion.

7. Some recent developments in catalytic applications of HPCs for the oxidation of organic substrates

It is undoubtedly in the field of oxidation catalysis that HPCs have been more widely studied. We shall summarize here some of the most significant achievements recently reported, where HPCs are used as catalytic systems for oxidative transformations of interest for the petrochemical industry. More complete analysis are reported in reviews specifically devoted to catalytic applications of HPCs [3,6,10,14–17,19,21,22].

7.1. Liquid-phase and gas-phase oxidation of light alkanes

Keggin-type and Wells–Dawson HPCs have been claimed to be active and selective in the following reactions of alkane transformation:

1. Oxidehydrogenation of C_2–C_4 paraffins to the corresponding olefins [23–25];
2. Oxidation of propane to acrylic acid and of isobutane to methacrylic acid in the gas phase [26–31];
3. Oxidation of alkanes and of cycloalkanes to alcohols and ketones in the liquid phase by dioxygen or by other oxygen donors [32,33].

HPCs possess those features which are needed to activate and functionalize a saturated organic substrate. However, the main problem concerns the stability of these compounds under the reaction conditions which are necessary to activate the paraffin. It was found that the addition of controlled amounts of antimony ions to ammonium salts of P/Mo Keggin-type HPCs allows the thermal structural stability of these materials to be significantly improved [34]. This made it possible to apply HPCs as catalysts in reactions which necessitate high temperatures, such as the oxidehydrogenation of ethane [25]. On the other hand, this problem is less dramatic when stable potassium salts of P/W Keggin-type or Wells–Dawson-type HPCs are used [23,24]. The latter systems were found to be particularly active and selective in the oxidehydrogenation of isobutane to isobutene. It has been proposed that the good catalytic performance origins from the peculiar radicalic reaction mechanism, which probably begins on the catalyst surface and is then transferred into the gas phase [23].

The interest in isobutane transformation to methacrolein and methacrylic acid, as alternatives to the commercial acetone–cyanohydrin process, dates back to the 80's, when companies from Japan began issuing a large number of patents on the application of HPCs for this reaction [35]. Interest was also given to the selective oxidation of propane, which might become economically convenient with respect to the current multistep process starting from propylene provided good yields to the desired product were achieved. However, only in recent years papers have appeared in open literature describing the reactivity of HPCs in these oxidative transformations [26–31].

Key aspects of these catalytic applications of HPCs are the following:

1. The possibility of improving the activity of P/Mo-HPCS by the addition of di/trivalent transition metal ions (Cu^{2+}, Fe^{3+}, Ni^{2+}) in the secondary framework of the compound. The partial hydrolysis of these cations (in the same way as it occurs in zeolites) and the Lewis character of some of these ions also contribute in affecting the acid properties of the compounds; acidity plays a fundamental role in the activation of the C–H bond in paraffins [17].
2. Operation must be carried out under fuel-rich conditions (large excess of isobutane with respect to molecular oxygen), since a much higher selectivity can be achieved with respect to operation under fuel-lean conditions. This effect is related to the redox properties of Mo^{VI}, and to the oxidation state of molybdenum under reaction conditions, which is a function of reaction conditions. Average oxidation states lower than VI make the reaction more selective [31], since the parallel and consecutive reactions of combustion become slower.

HPCs have also been claimed as catalysts for the liquid-phase oxidation of light alkanes under a pressure of molecular oxygen [32]. Catalysts were prepared from the trilacunary P/W complexes by inserting Fe or Ni ions; three metal centers were claimed to be incorporated in the anion. Isopropyl alcohol and tert-butyl alcohol were obtained with high selectivity from propane and isobutane, respectively. It is possible that the mechanism involves the generation of the corresponding alkylhydroperoxide, followed by a classical radical-chain mechanism.

7.2. *Epoxidation of olefins*

Epoxidation of olefins has been studied in the liquid phase, either in homogeneous phase, or in two-phase systems, or with heterogeneous supported catalysts. Most work has been done with homogeneous transition-metal-substituted HPCs (i.e., containing Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}). Keggin-type and Wells–Dawson-type HPCs have been used by several groups as catalysts for double bonds epoxidation, and have been claimed to activate oxygen donors and to catalyze oxo transfer reactions [36–41]. Organic cations are used as the counterion for the Keggin anion, in order to increase the solubility of the complexes in the organic solvent. C_6–C_{18} tetraalkylammonium or cetylpyridinium cations-containing complexes are employed as phase-transfer catalysts.

Different kinds of oxidizing agents have been used, such as H_2O_2, $NaIO_4$, NaClO, PhIO, alkylhydroperoxides, or even molecular oxygen, but in the presence of an aldehyde (typically, isobutyraldehyde, which is oxidized to the corresponding peracid, thus generating in situ the oxidizing agent). Model unsaturated substrates employed range from cycloolefins, to stilbene, to linear olefins.

Many doubts exist on the nature of the active sites, which might possibly originate from the HPC decomposition.

A few examples have also been reported which make use of supported catalytic systems; for instance, the results achieved with alumina-supported

$H_3PW_{12}O_{40}$ in cycloolefins epoxidation are very good, expecially in terms of selectivity to the epoxide [42]. Also in this case, however, the real active site is likely a partially or totally decomposed HPC.

7.3. Hydroxylation of aromatic organic substrates

Hydroxylation of aromatic organic substrates has been studied in the liquid phase, i.e. of benzene to phenol and of phenol to hydroquinone and pyrocatechol, with H_2O_2.

Dissolved $PMo_{12-x}V_xO^{(3+x)-}$ compounds have been used in benzene hydroxylation, at pH conditions at which the compounds were claimed to be structurally intact. A vanadium peroxo species was proposed to be the active site. Selectivity to phenol (on benzene basis) was total, while yield (on H_2O_2 basis) was higher than 90% [43,44].

In diphenol hydroxylation, one advantage of HPCs-based catalyst is indeed given by the possibility of affecting the diphenols ratio (ortho/pyro) by changing the catalyst composition, thus making it possible to meet the market's requirements. In fact, when $(Cpyr)_4PMo_{11}VO_{40}$ soluble complexes were used as the catalysts, the predominant product was hydroquinone, while with $(Cpyr)_4PW_{11}VO_{40}$ complexes, the prevailing product was catechol [45].

8. Conclusions: Can HPC-based catalysts really be designed a priori?

As mentioned in Section 1, the reason for the deep interest in the use of these materials for catalytic applications derives from their properties, i.e., (i) solubility in aqueous and organic media for many HPCs, acids or salts, (ii) intrinsic multifunctionality, (iii) strong acidity and (iv) tuneable redox properties. All these potential advantages are really exploitable provided they can be effectively used for the design of a suitable catalytic composition. Indeed, the most important restriction to the design potential of these compounds is the limited thermal structural stability of most of them, and the fact that the most active compounds (for both oxidizing and acid-type reactions) are usually the least stable. This considerably limits the use of these materials for heterogeneous gas-phase applications. Other disadvantages are their high costs, which would suggest the use of diluted or supported HPCs, and the fact that the high reactivity of these compounds often leads to a chemical interaction with the support (above all when the latter is highly hydroxylated), with the destruction of the structure of the HPC and loss of its peculiar properties.

Nonetheless, it is possible to give some general rules that can be helpful in the design of a HPC-based catalysts:

1. If an acid catalyst is needed, it is necessary to prepare a W-based HPC in the acid form, and possibly modify the acidity by partial exchange of protons with alkali or alkaline earth metal ions.
2. If a homogeneous oxidation catalyst is needed, it is necessary to prepare a Mo-based HPC (if a reaction of oxygen insertion via a classic redox mechanism is to be carried out), either acid or salt, and to tune the redox properties by partial replacement of molybdenum with other transition metal ions (typically vanadium but also other transition metal ions). This usually leads to an increase in the oxidizing properties of the compound (i.e., increased turnover number). In liquid-phase oxidations where peroxides are used as the oxidizing agent, the W-based HPCs are the most efficient.
3. If a gas phase, heterogeneous oxidation catalyst is needed, preparation of a group B salt of a Mo-based HPC or of a W-based HPC is preferred; it is also possible to modify the oxidizing properties by replacing part of the cations with other transition metal ions (Fe, Co, Ni). The partial replacement of molybdenum or tungsten with other metal ions (mixed addenda compounds) leads to thermally unstable compounds, except in the case where the metal is vanadium.

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