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STUDY OF THE HETEROPOLY METAL OXIDE COMPLEXES: PRINCIPLE OF THEIR SYNTHESIS, STRUCTURE AND APPLICATIONS

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Abstract: The chemistry of polyoxometalates has been reviewed extensively. Much useful information about the synthesis, study of structures and various applications of heteropoly acids and their salts have been reported in the literature. Thus, POMs inorganic complexes composed of transitional metals mainly Mo, W and V.

The present review gives an introduction into the chemistry of these compounds and overviews of the principal studies of their catalytic effect on nitration of the phenols, acetylation of alcohols, phenols and their derivatives.

Key word: Eco-friendly catalysts, Heteropoly acids, Polyoxometalates

Introduction

Polyoxometalates are negatively charged aggregates of transition metals mainly vanadium, molybdenum, tungsten with oxygen. M.T.Pope[1] named these classes of compounds as heteroatomic oxometalates. These compounds are cluster type with metal- oxygen and metal- oxygen- metal linkages[2] with large number of lattice water in the interstitial position. Any element can be incorporated into the frame work of polyoxometalates. If heteropoly compounds are categorized as condensation heteroatomic inorganic polymers[3-4], then the repeating unit would be M_3O_{13} group where M=V, Nb, Ta, Mo and W. A classical heteropoly anion condenses numerous oxygen atoms, sometimes hydrogen atom and atoms of other elements in positive oxidation state. These complexes generally represent thermodynamically relatively stable arrangements, although especially in the case of polyoxotungstates. They characteristically maintain their identities in aqueous and non-aqueous solution as well as in ionic crystals. A heteropoly contains a high atomic proportion of one kind of atom in +ve oxidation state called addendum atom and much smaller proportion(s) of the other kind(s) of atom(s) in the positive oxidation state(s) known as heteroatom.V^{+5},Mo^{+6},W^{+6} function as addendum atom in a great many heteropoly anions. A few additional atoms in their highest oxidation states for eg Nb^{+5},Ta^{+5},Re^{+7},I^{+7} can less commonly acts as addenda atom. Over 60 other elements including non metal and transitional metals, can function as heteroatom. The atoms that can function as addenda atom are those that

1. Change their coordination with oxygen from 4 to 6 as they polymerize in the acidic solution,.
2. Have a high positive charge and are among the smaller atoms that fall within the radius for octahedral packing with oxygen.

The ability to act as addenda is enhanced if the atoms are able to form double bond with unshared oxygen of their MO_6 octahedra by Pπ-dπ interaction. The more the double bond shortens the addendum-oxygen distance, the greater is the polarization and the stronger is the ion in the induced dipole interaction[5].

Heteropoly complexes are generally strong oxidizing agent[6-7]. In the cases of complexes that do not contain any addenda that have just one unshared oxygen, reduction mainly disintegrates the complex forming species containing lower oxidation states of the addenda. The reduction products are characteristically deep blue in colour and comprise a very large group of complexes known as "heteroply blues"[8]. Further reduction of heteropoly blue complexes leads to formation of so called heteropoly brown anion. These are species that retain the gross structures of parent complexes but the addenda in some or all subunits (for M_3O_{13} group) are reduced by two electrons. The added electrons in heteropoly brown are not delocalized[9].

The application of POMs in the field of Chemical analysis, catalysis, material science, nuclear waste treatment and medicine are developed.

As inorganic pharmaceuticals are still rare compared to more common organic compounds, it draws the attention of the researchers outside the inorganic chemistry to study the biomedical applications[10-11] of POMs. However, there is still plenty of scope for further work in this field as many fundamental questions regarding the structural principles, mechanism of synthesis and reactivity of POMs remain unanswered..

Synthesis

Generally two types of polyoxometalates are distinguished as based on the chemical composition – Isopolyanions $[MmOy]^{-n}$ and heteropolyanions $[XxMmOy]^{-n}$ ($x \leq m$) where M is the addenda atom and X is the heteroatom also called central atom when located in the centre of the polyanion. Most common addenda atoms are molybdenum, tungsten, less frequently V and Nb or mixed of these elements in their highest oxidation state [d^o,d^1].Almost all elements in the periodic table can be incorporated in heteropoly anion. Mo^{VI} and W^{VI} are best polyoxometalates formers due to favorable combination of ionic radius, charge and accessibility of empty d orbitals for metal-oxygen π bond[12]. By 1908 approximately 750 heteropoly compounds have been reported and analysed by over 250 authors [13] .As a result of these efforts it had been widely noted that heteropoly species containing a 6:1 or 12:1 atomic ratio of addenda to heteroatom were the most common.

Transition metal cations are coordinated by aqua hydroxo (OH^-) or Oxo (O^{2-}) ligand in the aqueous solution. The acidity of a coordinated ligand parallels the metal cations. The higher the positive charge of the metal, the easier the proton on the ligand dissociate. Therefore, highly charged d^0 cations of group 5 and 6 (V^{5+},Mo^{+6} and W^{+6}) form stable complex with oxo ligands in aqueous alkaline solution(VO_4^{3-},MO_4^{2-} and WO_4^{2-}).A condensation reaction takes place forming M-O-M bridges on acidification[14-15].More condensed structures could be formed with more expanding coordination number. Thus the nature of the oxometalates depends on stoichiometry, solvent used, pH, temp, concentration etc. Many different POMs may be synthesized by systematic variation of these factors. The M-O bonds in POMs can be cleaved by the addition of base and many more lacunary compounds may be obtained by controlled degradation.

POMs are formed by self assembly process[16-17], typically in an acidic aqueous solution and can be isolated as solid with an appropriate counteraction e.g $–H^+$, alkali metal cations, NH_4^+ etc.

For the synthesis of polyoxometalates, the concentrations of the reactants are chosen in such a way by trial and error method so that the immediate precipitation may not occur. When a graph is plotted between the volumes of the heteroatomic solution added against the pH of the resulting solution, then a gradual fall in pH is observed initially but after some addition, the pH of the solution become constant. The constant plateau of the graph indicates the formation of some polymeric species may take place in the solution phase, the excess of H^+ ion added is being consumed in the formation of such species.

The close observation of the graph also indicates the exact volume of the solution containing reactants required for such type of condensation process to take place. Therefore from the pH studies, it can easily be predicted that the exact pH and exact concentration of the reactants to be taken for the preparation of a particularl heteropoly complex.

Common structures:

Among the different structures known for POMs, the following four structures are more common.

1. **Keggin structure**-(1933)[18] $[XM_{12}O_{40}]$-Four trimetallic M_3O_{13} groups are arranged around a central tetrahedron(XO_4).Each MO_6 octahedra is sharing two edges with other MO_6 and the four M_3O_{13} groups are attached to one another by corner sharing. The total assembly contains 40 close packed oxygen and a tetrahedral pocket in its centre for the heteroatom. Keggin discovered that the structure of the compound $H_3[PW_{12}O_{40}].5H_2O$ contained $12WO_6$ octahedra linked by the edge and the corner sharing with the heteroatom PO_4 occupying tetrahedral hole in the centre.

2. a.**Anderson**- The Anderson structures[19] (1937) consist of six coplanar MO_6 octahedra arranged in the ring sharing edges around the central heteroatom in $[XM_6O_{24}]^{-n}$. This leaves an octahedral pocket in the centre of the ring for the heteroatom(X).

   b.Anderson-Evans structure-The structure $[TeMo_6O_{24}]^{-6}$ proposed by Anderson went without experimental verification until 1948 when Evans [20-21] confirmed the structures by a single crystal X-ray determination of the position of the central heteroatom. This structure is now referred as Anderson Evans structure.

3. **Linqvist structure** (1952)[22] $[M_6O_{19}]^{-n}$ –It consist of an octahedral arrangement of six MO_6 octahedra. Each octahedral is sharing four edges with

neighbouring octahedral. This structure can be seen as fragment of a cubic closed packed metal oxide.

4. **Well Dawson structure** $(X_2M_{18}O_{62})^{-n}$ – A.F.Wells in 1945 suggested a detailed structure[23] of $[P_2W_{18}O_{62}]^{-6}$.In 1952, Tsigdinos[24] established the Well's proposed structures for the molybdo complex. In 1953, Dawson [25] determined the position of the heteroatom by single X-ray crystal study.This structure is referred as Well Dawson structure which is closely related as Keggin structure.

Prior to the 1959, all of the structural X-ray crystallography studies of heteropoly complexes determine only the position of the heavier atom. The X-ray crystal structure of $K_5[CoW_{12}O_{40}].20H_2O$ determine in 1959, was the first to locate directly all the oxygen atoms on the heteropoly complexes[26]. In 1962,Simmons reported the first heteropoly complexes containing two different elements as heteroatoms in the international conference on coordination chemistry[I.C.C.C][27]. The structure of this red complex was reported in 1966 by Baker.et.al [28]. It was 11-Tungsto- silicate where one W atom of the Keggin structure $[SiW_{12}O_{40}]^{4-}$ had been replaced by Co^{+2}.Thereafter Weakly, Mallick[29] Tournes [30] ,Puscaus [31] Souchay [32] and many others reported preparations of large number of 11-Tungsto,17-Tungsto,11-Molybdo, 17-Molybdo complexes with various central heteroatom and various lower valent octahedral metal atom substituted for W,Mo in a Keggin and Well Dawson structure.In 1980-90 extensive works have been done with expanding applications of polyoxometalates. By 1995, the structure of approx 180 POMS have been reported.

Applications:

An increasing number of potential applications for polyoxometalates continues to attract significant attention.

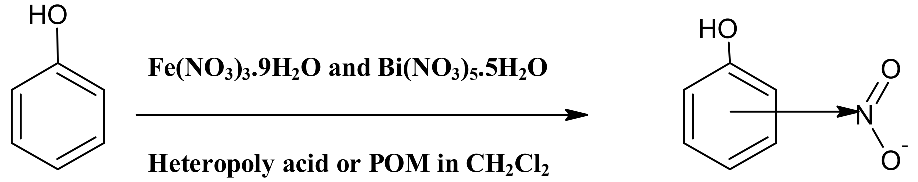
The applications of POMs are centered primarily on their redox properties, photochemical response, ionic charge, conductivity and ionic weights. The majority of the applications of POMs are found in the area of the catalysis. About 80-85% of the literature claims POMs for their catalytic activity. The remaining 15-20% of the application includes coating, membranes or thin films. These include corrosion, resistant and in conductive and non conductive polymers membranes and POMs as surface modifiers of substrate. POMs are also used as pigments, toners, wood pulp bleaching agent, reagent for chemical and biochemical analysis and for nuclear waste processing and some miscellaneous applications.

1. Heteropoly acids and polyoxometalates as catalysts

A series of eco friendly solid acid and their salts have been used as catalysts in many organic reactions particulary in nitration of phenols, acetylation of alcohols and phenols with acetic anhydride.The performance of different forms of heteropoly acids and POMs have been compared from their percentage yield.

Mononitration of phenol with metal nitrites[33]

The mononitration of phenols using $Fe(NO_3)_3.9H_2O$ and $Bi(NO_3)_5.H_2O$ in dichloromethane at room temperature are promoted with catalytic amount of heteropoly acids and polyoxometalates.



Phenol **Nitrophenol**

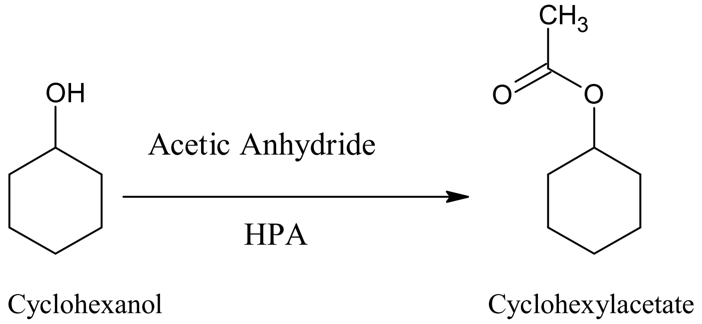
Table 1a: Effect of Keggin type heteropoly acids and POMs on the mononitration of phenols by $Fe(NO_3)_3.9H_2O$.

Entry	Catalysts	Time (h)	Product(%)		
			Ortho	Para	Meta
1	No catalysts	1	68.5	30.5	1.0
2	$H_3[PW_{12}O_{40}]$	1	66.2	33.8	-
3	$H_3[PMo_{12}O_{40}]$	1	53.4	46.6	-
4	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	1	71.9	28.3	-
5	$(NH_4)_2HPW_{12}O_{40}$	1	61.0	49.0	-

Table 1b: Effect of HPAs and POMs on the mononitration of phenols by Bi $(NO_3)_3.5H_2O$.

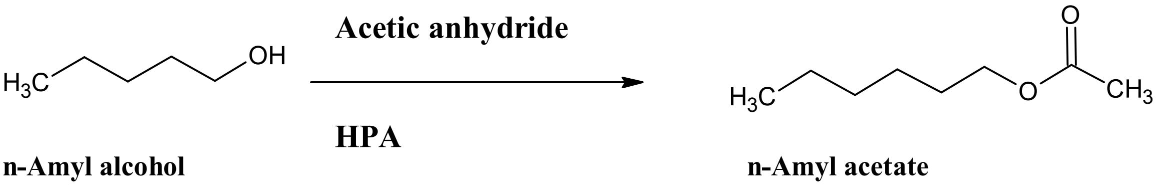
Entry	Catalysts	Time (h)	Product (%)		
			Ortho	Para	Meta
1	No catalysts	1	64.6	32.8	-
2	$H_3[PW_{12}O_{40}]$	1	51.3	48.1	-
3	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	1	54.2	38.4	-

Table 1c: Effect of Keggin type heteropoly acids on acetylation of cyclo alcohols in acetic anhydride[34].



Entry	Catalysts	Time (Min)	Yield (%)
1	$H_5[PMo_{10}V_2O_{40}]$	30	95
2	$H_4[PMo_{11}VO_{40}]$	30	92
3	$H_4[SiMo_{12}O_{40}]$	30	90
4	$H_3[PMo_{12}O_{40}]$	30	94
5	$HNa_2[PW_{12}O_{40}]$	30	90

Table 1d: Effect of heteropoly acids and POMs on acetylation of n-alcohol in acetic anhydride



Entry	Catalysts	Time (Min)	Yield (%)
1	$H_5[PMo_{10}V_2O_{40}]$	30	91
2	$H_4[PMo_{11}VO_{40}]$	30	91
3	$H_4[SiMo_{12}O_{40}]$	30	91
4	$H_3[PMo_{12}O_{40}]$	30	93
5	$HNa_2[PW_{12}O_{40}]$	30	88

Table 1e: Effect of HPAs as catalysts on acetylation of phenols and their derivatives in acetic anhydride

Entry	Substrate	Product	$H_5[PMo_{10}V_2O_{40}]$ Time(Min)/ Yield %	$H_4[PMo_{11}VO_{40}]$ Time(Min)/ Yield %	$H_4[SiMo_{12}O_{40}]$ Time(Min)/ Yield %	$H_3[PMo_{12}O_{40}]$ Time(Min)/ Yield %	$HNa_2[PW_{12}O_{40}]$ Time(Min)/ Yield %
1.	Phenol	Phenyl acetate	10/95	35/95	180/95	35/95	60/95
2.	p-cresol	p-cresyl acetate	10/91	20/91	180/91	15/91	30/91
3.	4 -Nitro phenol	4 -Nitro Phenyl acetate	15/89	40/89	210/89	40/89	45/89

2. Polyoxometalates as materials:

POMs represent a very significant use to build polynuclear and supramolecular structures with collective properties.

3. Energy storage applications:

The reversible electrochemistry, light weight and polymeric nature made them very promising materials in thin, plastic energy storage devices like rechargeable batteries.

4. Biological and medical activities:

a.Antiviral activity:

Silicotungstic acid are recognized as inhibitor[35] and led to a systematic study of the antiviral activity. Ex- $(NH_4)_{19}[Sb_9W_{12}O_{86}]$[36]

b.Antitumoral activities:

$(NH_3Pr)_6[Mo_7O_{24}]$ is investigated which significantly supresses the tumor growth in mice[37]. Further, the effectiveness of $(NH_3Pr)_6[Mo_7O_{24}]$ against the progressive growth of the human cancer[38]. $(NH_4)_6[Mo_6O_{24}]$ and $K_6[Mo_7O_{24}]$ also show sarcoma inhibiting activity. This shows that the antitumor activity is associated with polyoxomolybdate anion.

c.Antibacterial activities:

Now a days antibiotics are ineffective as the bacteria are resistant to drugs. Bacteria produce beta lactam ring of the anti biotics. Bacteria are developing resistant against these antibiotics by modifying their penicillium binding protein. In 1993, Tajima reported the effect of the mixture of tungstate and phosphate in combination with beta-lactum antibiotics[39]. He discovered that a factor greatly enhanced he antibacterial effect of the drug in MRSA (Methicillin-Resistant-Staphylococcus Aureus) strains. Besides polytungstate, Yamase also reported an anti bacterial effect of polyoxovanadates against six strains of penicillin resistant Streptococcus pneumonia.[40]

5. Corrosion resistant coating:

Chromates, Phosphate or Silicates are used to combat corrosion of metal surface. Polyoxometalates replaced the toxic inhibitors. Oxometalates accept electrons without major changes of their structures and form insoluble salts with large cations. These properties make them attractive as oxidizing and film forming corrosion inhibitors.

Examples:

$[C_{16}H_{33}N(CH_3)_3]_xH_{4-x}SiMo_{12}O_{40}$ - Corrosion resistant coating and primers[41]

$[C_{16}H_{33}N(CH_3)_3]_xH_{4-x}SiW_{12}O_{40}$

$Na_5H_2PV_6Mo_6O_{42}$ - Corrosion inhibitor for mild steel [42].

$(NH_4)10H_2W_{12}O_{42}(NH_4)6P_2W_{12}O_{62}$-Corrosion inhibitor of Al alloys[43]

6. POMS as additives in organic matrixes

POMs are incorporated in organic non conductive matrixes to form composite materials Like the inorganic matrixes, organic resins such as alkyl resins have been claimed as a carriers of POM acids and antistatic[44] film formers. Composite films of polyvinylalcohol and POM acids are described by lazareva [45].

POMs also act as conductive filters[46] and hardeners[47].

7. Dyes/Pigments/Inks

The polyoxometalates are able to form stable precipitates with cationic dyes which results in their use as pigments, dyes and inks[48]. Hair[49] described dye poly (ethylene glycol)-heteropolyanion compositions suitable for use in ink jet printer applications. The composition of complexes of the Keggin type acids with dyes and their use in colorant formation of acidic fibres such as polyesters and polyacrylonitriles is described by Clarke[50].

8. Recording material:

The POM acids of Mo and W are claimed to be photosensitive by Lyman in 1961[51].He showed that a photographic process could be built on photosensitive systems composed of POM acids and organic reducing agents. Salts of laking cationic dyes with heteropoly acids of W and Mo that contained P, Si, V, Co, Al, Mn or Cr were used to produce pigments with λ_{Max} >700nm that were markable by semiconductor lasers[52].

9. Electrophotography toners

The POMs and their salts primarily with organic cations have been claimed to function either as the active ingredient in photochromic coatings or as a charge control agents in toners.

Averbach[53] claimed the Keggin type POMs together with reducing agents such as phenyl glycolic and a binder such as poly (Vinyl alcohol) as the active ingredients in photochromic coating related to the production of images.

10. Membrane Sensors

The ionic conductivity of POMs, their capability to form a plethora of salts with any cations and their ability to undergo redox processes under mild conditions make them highly applicable in membranes based devices and sensors.The most common use of these membranes are in selective electrode,in gas detection apparatus,in solid state electrochromic devices and in liquid and solid electrolytic device.

11. Capacitors:

Oxometalates have been claimed as electrolytes for capacitors(solid and solution).[54] Alwitt showed that the electrolytic capacitors which consisted essentially of salts of $H_4SiM(=Mo,W)_{12}O_{40}$ in polar organic solvent such as DMF had lower dissipative factors at low temperature then conventional electrolyte such as salts of organic acids,borates or borate complexes[55].

12. Wood pulp Bleaching:

The chlorine is used commonly for bleaching of wood pulp to remove the residual lignin and to brighten the pulp by degradation or removal of any chromophores. The chromophores and residual lignin to form chlorinated aromatics and dioxins which pose serious threat to the environment. Weinstock [56] reported the use of $H_5PMoV_2O_{40}$ offer a safer alternative to elemental chlorine.Later on Paren established a process for the delignification of pulp based on peroxide and/or peracids in the presence of water soluble salts of elements in group 4,5 and 6 and atleast one heteroatom such as Si,P or B capable of forming heteropoly acids.

13. Protein Precipitation agents:

POMs are used as precipitating agents for proteins[57]. $H_3PW_{12}O_{40}$ is the most common agent. The phosphomolybdic acid and phosphotungstic acid are used as protein precipitators in wine and cheddar type cheese respectively.

14. Staining agent:

POMs are well recognized and established as staining agents[58]. Yamashita[59] demonstrated the use of $H_3PW_{12}O_{40}$ as a staining agent of formalin fixed paraffin-embedded clinical samples for enhancement of immuno reactivity with the microwave method.

15. Processing of radio active waste:

Cesium ions are extracted from active aqueous waste by utilizing heteropoly acids and macrocyclic crown ethers as demonstrated by Blasius[60]. Deicke[61] claimed a method of separation of Cs^+ from radioactive waste by precipitation with $H_3PM(=Mo,W)_{12}O_{40}$ followed by NH_4OH treatment to dissolve the precipitate and subjecting it to an electric field. Later on Pfrepper[62] described the recovery of Cs as Cs molybdate from Cs-POM salts after heat treatment with SrCO3 at 750°C for 30 min.

16. Sorbent of gases:

Keggin type polyxoxmetalates have been proved to be used as solvent of flue gases (NOx, SO_2 and CO_2)[63]. $H_3PM(=Mo,W)_{12}O_{40}$ is used as catalysts for the decomposition of highly toxic organic compounds in gases from incineration of municipal refuse[64]. $H_3PMo_6W_6O_{40}$ acts as bed for the purification of vent air from odorous components[65]. Keggin type acids also act as absorbents for H_2S.

Conclusion

The literature survey indicates that the utilization of Keggin type POMs continues to grow in many areas in addition to the tradition area of the catalysis. The thermal stability of POMs is one of the important properties in their applications over comparable materials. The most important areas of their applications are donor technology, in isopolyoxometalates, film formation technology, in electrode modification technology. However, the comparative studies with existing commercial system, the need exists for better characterization of the system used in POM- based applications.

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