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Recent Advances in Synthesis, Characterization, Structure and Applications of Polyoxometalates

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Abstract: Now a days polyoxometalates (POMs) become an interesting and attractive topic in the field of inorganic chemistry and has been reviewed extensively. Many useful information have been collected after intense and rigorous literature survey about recent advances in the development and application of polyoxometalate complexes in catalysis, material science to biology and medicines (as antibacterial, antitumour, antiviral). The present paper is a review on POM chemistry and gives an overall idea of recent trends in synthesis, characterization, structure, and applications of heteropoly acids and their salts.

Key Words: POM, antitumour, antibacterial, antiviral, catalysis, heteropoly acids.

I. INTRODUCTION

A. General Information

Polyoxometalates are nanosized anionic clusters of transition metals mainly Molybdenum(Mo), Tungsten (W), Vanadium (V),Tantalum(Ta), Niobium (Nb) etc and oxide ion. Thus, POMs are oligomeric aggregates of transition metal cation. They have diverse range of molecular structure and physicochemical properties [1].They have the ability to form different structures which ranges in nanometer to micrometer scale. Therefore, they have been utilized as building blocks in the formation of new materials [2,3]. Due to having structural diversity POM's have been noted for their catalytic [4-7] magnetic [8], biological [9-12] as anticancer, antibacterial, antiviral[13]and even insulin mimetic, supramolecular[14,15], electrochemical[16] and photophysical properties[17]. Most of the research done so far is on the synthesis and catalytic properties of Keggin $[XM_{12}O_{40}]^{-n}$ and Well Dawson $[X_2M_{18}O_{62}]^{-n}$ phases of POM. Keggin and Dawson type polyanions have proper and suitable vacancies so, they can linked using electrophiles to large aggregates and assemble themselves in a predictable manner to give higher dimensional POM framework[18]. Polyoxometalates are class of compounds based upon metal-oxide building blocks MO_x (x=5,6). They are characterized by a metallic center Msurrounded by atoms or group of atoms. Where M represents early transition metals in their high oxidation state for e.g.-Mo^{+6}, W^{+6}, V^{+5},Ta^{+5} and Nb+5 etc. Which can be partly substituted by other transition metal of 3d,4d and 5d block. Many transitional metal substituted POM have been reported till date[19-25]. In POM oxygen play a vital role as oxo ligand. In co-ordination chemistry an oxo ligand is an oxygen atom bound to one or more metal atoms or centers. Oxo ligands stabilize high oxidation state of a metal[26].POM's are generally highly negative because of having large no. of oxo ligands around the central metal atom. Apart from M and O other elements usually "X" can be part of the POM frame work. The "X" elements are called primary, central or hetero atom. Presence of the hetero atom in the polyanions cluster significantly affects their properties. Any atom can participate as "X" atom in the POM framework on the other hand "M" are called secondary, peripheral or addenda atoms, and only some elements are found. Who act as addenda atoms in such compounds. Because threre are certain criteria for being an addenda atom. Such as

1) high charge (+5 or +6)
2) small size
3) ionic radius $0.53A^o<<0.70A^o$
4) expandable co-ordination number from 4 to6.
5) Ability to form double bond with unshared oxygen atoms of MO_6 octahedra by pπ-dπ interaction. As the distance between addendum and oxygen bond decreases, the polarization increases that produces stronger ions in the induced dipole interaction[27].

B. Background and Developments

polyoxometalates have a rich background. Its discovery was arguably almost two century ago. Since its inception different scientists have nurtured the versatile aspects of POM to enrich our knowledge in this relatively unexplored field of solid state material chemistry. In 1826 J. J. Berzelius reported the first POM, the phosphomolyb date $[PMo_{12}O_{40}]^{-3}$. He noted that the reaction of ammonium molybdate with excess phosphoric acid gives a light yellow precipitate[28]. After the synthesis of first POM by Berzelius many leading scientists investigated these molybdates and tungsten based POM compounds in order to understand the composition and structure of materials. The structure of phosphomolybdate anion $[PMo_{12}O_{40}]^{-3}$ was established and reported by J.F.Keggin in 1933[29], which open the flood gate. Pope's group has reported a simple way to synthesized infinite number of 1D polyoxometalates by using lanthanides and actinide cations[30,31] and Muller's group has reported mixed valence polyoxomolybdates from "big wheel" [32-34]. In 1937 J.S.A nderson suggested the structure of a molybdenum containing POM. This structure was later confirmed by Evan's report of a hexamolybdotellurate , hence this type of POM is reffered as an Anderson-Evan or only an Anderson structure[35,36]. Large number of organic- inorganic hybrid materials based on oxometalates with 1D and 2D framework have been reported by Zubeita and co-worker [37].Many good examples of organic –inorganic hybrid compounds of polyoxometalates have been reported till date .Recently new phase of POM cluster having 1-D Keggin type architecture with inorganic- organic back bone has been synthesized by hydrothermal decarboxylation method. The one dimensional linear chain contain alternate inorganic $[SiW_{12}O_{40}]^{-4}$ and organic $[Cu(py)_2]^+$ clusters and both are co- ordinated with three and four copper ion[38]. After the synthesis of 1-D and 2-D polyoxometalate framework a new higher dimensional architecture POM $[Gd(H_2O)_3]_3[GdMo_{12}O_{42}].3H_2O$ [39]has been reported recently, in which gadulinium(III) is linked with the polyanion cluster of silverton type. Furthermore, the direct surface modification of POM molecular clusters is still a challenge. Thus, the concept of capped polyoxoanion clusters came in front, which is regarded as an important family in the field of modified POM. Many capped structures have been reported such as bi capped $[PMo^{V}{}_6Mo^{VI}{}_6O_{40}(V^{IV}O)_2]^{5-}$[40] , $[SiMo_{14}O_{44}]^{4-}$ [41]and $[As^{III}{}_2As^{V}Mo_8V^{IV}{}_4O_{40}]^{5-}$and tetracapped$[PMo^{VI}{}_5Mo^{V}{}_3V^{IV}{}_8O_{44}]^{6-}$ and $[PMo^{VI}{}_6Mo^{V}{}_2V^{IV}{}_8O_{44}]^{5-}$[42-48]. Polyoxometalates compounds with divalent cation of 3d transition metal as capping atoms have been scarcely reported[49]. Heteropolyoxoanion supported inorganic compounds are scarcely reported because it is difficult to find a suitable heteropolyoxometalates with sufficient charge density that can bind covalently to more than one chemical group.To our knowledge there are two strategies to increase surface charge density(i) by reducing central metal atom from their higher oxidation state to lower oxidation state or (ii) by replacing metal centers with lower valence metals[50]. The development of POM is based on the design and synthesis of new polyoxometalates with novel structure and properties. Recently porous POM based Metal-organic framework materials have been reported[51]. In 2015, progress in synthesis and application of polyoxometalates and nano gold hybrid material s have been discussed[52].

C. Classification and Structure

POMs are early transition metal oxide cluster polyanions. POMs have been classified on the basis of presence of atoms of different elements and their arrangement. Polyoxometalates are mainlyof two types.

1) *Isopolyoxometalates:* They are metal oxide framework without having any internal heteroatom. The general molecular formula for isopolyanion is $[M_a O_b]^{n-}$. Absence of heteroatom within the framework make them less stable than their heteropolyanions[53]. Apart from being unstable isopolyanion possess interesting physical properties like strongly basic oxygen surfaces and high charges , which make them an attractive building block unit[54].
2) *Heteropolyoxometalates:* They are clusters of metal-oxide that include one or more heteroatom of p, d, or f block element within their framework[55]. The general molecular formula is $[M_a X_c O_b]^{n-}$. In heteropoly compounds the hetero atom scan reside at surface (solvent accessible) or either buried (not solvent accessible) in the POM structure. Presence of heteroatom within their framework significantly enhances the structural stability and other properties of heteropolyanions. These are most explored set of POM clusters. Heteropolyanions are cluster compounds having M-O and M-O-M linkage[56] with large number of interstitial water molecules. heteropolyoxometalates have been categorized as condensation heteroatomic inorganic polymers[57-58], where the repeating is M_3O_{13} group (M=V, Nb, Mo, W and Ta). The structural and electronic properties of heteropoly compounds are easier to modify synthetically than those of the isopoly compounds. Heteropolyoxometelates have dominated the medically oriented research to date. Heteropolyanion condenses oxygen atoms and atoms of other elements in positive oxidation state. These compounds represent thermodynamically stable arrangement of atoms specially in the case of polytungstate. These compounds are stable in aqueous-non aqueous solutions as well as in ionic crystals. These compounds contain a high atomic proportion of one kind of atoms in positive oxidation state which is termed as addendum atom and a small proportion of another kind of atoms are present in heteropoly anion, known as hetero atoms or central atom. Many reports reveal that heteropolyanions are strong oxidizing agents[59-60] but reduction disintegrate the complexes that do not contain any addenda atom, that have just one unshared oxygen and form new species that contain lower oxidation state of the addenda atom. The product obtained by reduction of addenda atoms are deep blue in colour that comprise a large group of complexes termed as heteropoly blues[61].Their further reduction lead to the formation of another species called heteropoly brown anion. These

are the species that retain the gross structure of their parent complexes with reduced addenda atom by two electrons. In heteropoly brown the electrons present on addenda atoms are not delocalized[62].Polyoxometalates are formed by self assembly process[63-64] at a particular $p^{H.}$ Therefore, POM'S have high structural diversity. After the long period of invention of first POM , the structure was first time established by Keggin and after him so many scientists like Anderson, Evans, Well-Dawson, Waugh, Silverton etc have established various structures of POM.

3) *Keggin:* In 1826, the first α-Keggin anion i.e. ammonium phospho molybdate was reported by Berzelius. After the discovery of first POM, many researcher or scientist work to establish the structure of ammonium phospho molybdate. J. FKeggin[65] experimentally determined the structure of α Keggin anion $[PMo_{12}O_{40}]^{-3}$ in 1933, by using x-ray diffraction. Keggin structure is the most accepted structure of α Keggin anions. Keggin structure accounts for both hydrated and anhydrated form of α Keggin anions. The general molecular formula established for structure is $[XM_{12}O_{40}]^{-n}$. Where x= heteroatom, most commonly[P, Si, B etc], M is a addenda atom most commonly [Mo, V, W, Nb, Rb, Ta etc] and O represents oxygen atoms as oxoligand or bridging atom. Keggin structure is composed of one heteroatom surrounded by four oxygen atom to form a tetrahedron. The heteroatom is located at the centre of the cage formed by MO_6 octahedral units. They are linked to each other by neighboring oxygen atoms. The twelve addenda atoms are linked by total 24 bridging oxygen atoms. In 12 octahedra, the metal centres are arranged on a sphere almost at equidistant from each other in four M_3O_{13} units forming the complete structure . Keggin structure show tetrahedral symmetry. Keggin structured molecules are thermally stable. These kind of complexes can easily hydrate and dehydrate without any significant structural change. POM's having Keggin structure have an important place in the POM family. Because of having structural diversity and versatile electronic properties , a series of POM compounds of transition metal have been reported till date and the discovery is still in continuous. Keggin established the structure of $H_3[P\ W_{12}\ O_{40}].5H_2O$ that contains 12 WO_6 unit linked with edges and the corners are shared with PO_4 heteroatom that occupy the tetrahedral cavity or hole at the centre.
4) *Linqvist:* The structure of heptamolybdate $[Mo_7\ O_{24}]^{-6}$ was proposed by linqvist in 1950. After that in 1952 linqvist first reported $Na_7H\ [Nb_6\ O_{19}].16\ H_2O$ and later he also isolated the analogous tungsten $[W_6\ O_{19}]^{-2}$. linqvist structure consist of six MO_6 octahedral units. Each octahedral sharing four edges with neighbouring octahedral. The general molecular formula for Linqvist structure is $[M_6O_{19}]^{n-}$[69].
5) *Well-Dawson:* The structure of $[P_2W_{18}O_{62}]^{-6}$ complex was suggested by A.F.Wells in 1945[70], then 1952 T sigdinos[71] established the structure of Well's proposed molybdo complex. After that Dawson[72] determined the position of heteroatom by single crystal x-ray study. Therefore, this structure is known as Well-Dawson structure. It has been observed that the complex $[P_2W_{18}O_{60}]^{6-}$is made of two $[PW_9O_{34}]^{9-}$ because it showed one phosphorous NMR peak and two tungsten NMR peak with 1:2 ratio (i.e. 6 cap W and 12 belt W). the general formula of Dawson structure is $[X_2M_{18}O_{62}]^{-n}$. Dawson structure is closely related to Keggin structure , both have tetrahedrally co-ordinated heteroatm (such as P and Si).
6) *Waugh structure:* The first Waugh type isopolyoxometalate $Na_4Mo_{10}O_{32}$.$8H_2O$ was reported in 2003. Each 10 Mo^{VI} of the polyanion $[Mo_{10}O_{32}]^{4-}$ is co-ordinated with six oxygen atoms and exhibited distorted octahedral geometry. The general formula for Waugh type structure is $[XM_9O_{32}]^{-n}$.
7) *Dexter-Silverton structure:* The general molecular formula for silverton type is $[XM_{12}O_{42}]^{-n}$ .Its molecular formula is quite similar to Keggin type with two more oxygen atoms than keggin type structure.
8) *Preyssler type:* The Preyssler polyoxoanion consists of five PW_6 units. one PW_6 unit being composed of two groups of three corner sharing WO_6 octahedra, forming a crown and giving the structure an ellipsoid shape with aninternal fivefold symmetry axis. The molecular formula is $[X^{n+}\ P_5\ W_{30}O_{110}]^{(15-n)-}$ [74].
9) *Weakley –Yamase type:* The molecular formula of weakley –yamase type structure is $[XM_{10}O_{36}]^{n-}$.

From above details of different structures, central groups, basic building block units and molecular formula, the POMs are tabulated below:

TYPES	MOLECULAR FORMULA	BUILDING UNIT	TYPE OF SHARING	CENTRAL GROUPS
1.Keggin	$[XM_{12}O_{40}]^{-n}$	M_3O_{13}	Edge	XO_4
2.Anderson	$[XM_6O_{24}]^{-n}$	M_2O_{10}	Edge	XO_6
3. Linqvist	$[M_6O_{19}]^{n-}$	MO_6	Edge	XO_6
4.Dawson	$[X_2M_{18}O_{62}]^{-n}$	M_3O_{13}	Edge	XO_4

5.Waugh	$[XM_9O_{32}]^{-n}$	M_3O_{13}	Edge	XO_6
6.Silverton	$[XM_{12}O_{42}]^{-n}$	M_2O_9	Edge	XO_{12}
7.Preyssler type	$[X^{n+}P_5W_{30}O_{110}]^{(15-n)-}$	PW_6	Edge	WO_6
8.Weakley-Yamase type	$[XM_{10}O_{36}]^{n-}$	$M_{10}O_{36}$	Edge	XO_4

These are the eight classical structures of polyoxometalates. Before 1959, the x-ray crystallography studies of heteropoly complexes help to determine the position of heavier atoms. In 1959 the structure of $K_5\,[CoW_{12}O_{40}].2H_2O$ complex was determined by x-ray crystallography. It was the first structure that locate directly all the oxygen atoms in the heteropoly complex[75]. Simmon in 1962, proposed the heteropoly complexes that contain two different type of elements as heteroatom in the international conference of co-ordination chemistry[76]. The structure of this complex was given by Baker in 1966[77]. The complex was 11-tungsto silicate $[SiW_{12}O_{40}]^{4-}$. One of the W atom of this complex had been replaced by Co^{2+}.After Baker many leading scientists reported the preparation of large number of 11 and 17 tungs to and molybdo complexes with different heteroatom and various metal atom in lower valence state[78-81], which substituted W and Mo atom in the Keggin and Dawson structure. Extensive works on synthesis, structure and application of POM's have done in the period 1980-1990 and the structure of approx 190 POMs have been reported till date.

II. SYNTHESIS

The synthetic routes for preparation of new polyoxometalates are very simple and require small number of steps or even single step i.e. one pot synthesis. POMs are crystallizes by self assembly process and thus have a large range of structural diversiry. Various experimental variables control the synthesis of specific kind of POM. The factors on which synthesis of new POM crystals depend are (i) acidity of solution (P^H), (ii) concentration of metal oxide anion, (iii) types of heteroatom, (iv) ionic strength, (v) presence of additional ligands, (vi) temperature and pressure of the reaction and (vii) effect of counter ion and metal ion. The different synthetic strategies to produce new POMs till date are as follows:

A. Hydrothermal process

The most simple, common and popular method for synthesis of new POM is hydrothermal method. Hydrothermal synthesis involves various techniques of crystallizing substances from high temperature aqueous solutions at high vapour pressures. The term hydrothermal comes from geological origin. Hydrothermal process can also be define as method of preparation of single crystals that depends on minerals solubility in hot water under high pressure condition. The growth of crystals is performed in an apparatus that consists a steel pressure vessel called an "autoclave". The nutrients are supplied in the autoclave along with water. Between the two opposite ends of the growth chamber a temperature gradient is maintained. The nutrient solute get dissolve at hotter end and it is deposited on a seed crystal , growing the desired crystal at the cooler end of the chamber. Hydrothermal method have large number of advantages over the other types of crystal growth processes like the ability to create crystalline phases which are not stable at the melting point. The materials which have a high vapour pressure near there melting points can also be grown by this hydrothermal method. Large, good quality crystals of POM can be obtained by controlling the composition of nutrient or starting material. The need of expensive autoclaves and the impossibility to obtain the crystal as it grows are the disadvantages of this method. Hydrothermal process is becoming more popular particularly in the synthesis of POM based co-ordination compounds. Large number of polyoxometalate complexes containing molybdenum/ tungsten has been synthesized by hydrothermal process. The first Keggin type POM was synthesized hydrothermally. After that large number of polyoxometalates have been reported till date, synthesized by hydrothermal method. In 2001, hydrothermal synthesis of three one dimensional heteropolytungstates formed by Keggin or Dawson units have been reported[82]. The three complexes are

$[Cu(en)_2(OH_2)]_2[H_2en][\{Cu(en)_2\}P_2CuW_{17}O_{61}].5H_2O$
$[Cu(en)_2(OH_2)]_2[Cu(en)_2]_{0.5}[H_2en]_{0.5}[\{Cu(en)_2\}P_2CuW_{17}O_{61}].5H_2O$
$[Co(dpa)_2(OH_2)_2]_2][Hdpa][PCoW_{11}O_{39}]$ (dpa=di-2-pyrudylamine)

Two dimensional POM frame work materials$[Co(en)_2][Co(bpy)_2]_2$-$[PMo^{VI}5Mo^{V}3V^{IV}{}_8O_{44}]4.5H_2O$ (en = ethylenediamine, bpy= 2,2A-bipyridine)[83] has been synthesized by hydrothermal method in 2002. After that three novel reduced and capped Keggin derivatives of polyoxometalates[84]

a)$[PMo^{VI}{}_6Mo^{V}{}_2V^{IV}{}_8O_{44}\{Co(2,2\text{-}bipy)_2(H_2O)\}_4]^{3+}$
b)$[PMo^{VI}{}_8V^{IV}{}_6O_{42}\{CuI(phen)\}_2]^{5-}$
c) $[PMo^{VI}{}_9Mo^{V}{}_3O_{40}]^{6-}$

decorated by transition metal complexes where hydrothermally synthesized, this was reported in November 2003.Further more in 2004 hydrothermal synthesis of one - dimensional polyoxometalates based composite compounds$[\{Ce(DMF)_4(H_2O)_3\}\{Ce(DMF)_4(H_2O)_4\}(P_2W_{18}O_{62})].H_2O$ (DMF =*N*,*N*dimethylformamide)and$[\{La(DMF)_6(H_2O)\}\{La(DMF)_{4.5}(H_2O)_{2.5}\}.\ (P_2W_{18}O_{62})]$[85]derive from Well- Dawsom sub unit have been reported. A unique and completely new 3D supramolecular array assembled by cross- link arrangement of 1D sandwich mixed molybdenum- vanadium polyoxometalate bridged co-ordination polymer chains have been reported in 2005 which have been synthesized by hydrothermal method[86]. Furthermore, hydrothermal synthesis , crystal structure and properties of 3D polyoxometalate $\{[Mo^{VI}{}_5Mo^{V}{}_3V^{IV}{}_8O_{40}(PO_4)][Ni(en)_2]\}[Ni(en)_2]_2 .\ 4H_2O$ [87]have been studied in march 2006. In the April of same year i.e. 2006 report of hydrothermal synthesis and crystal structure of two new polyoxometalate based charge transfer salts have come in front[88].

a) $[Hen]_2[H_2en][PMo^{VI}{}_{11}MoVO_{40}]\ \cdot 3.5H_2O$

b) and $[Hpy]_4[GeMo^{VI}{}_{12}O_{40}]\ \cdot 2H_2O$. Hydrothermal synthesis and characterization of Cu (II) substituted hexa tungstate and molybdate $Na_{10}[Cu^{II}W^{VI}{}_6O_{24}].22H_2O$ and $Na_{10}[Cu^{II}Mo^{VI}{}_6O_{24}].19H_2O$of Anderson type have been reported in march 2008[89]. The hydrothermal synthesis has become an important and successful technique for the preparation of modified polyoxometalate based inorganic- organic hybrid compounds. In 2009 copper Bis (triazole) co-ordination polymers were hydrothermally synthesized through use of the same Keggin polyoxometalate as template. A new organic- inorganic hybrid compound $[Zn(bpy)_3]_{1.5}[H_3W_{12}O_{40}Zn(bpy)_2(H_2O)]0.5H_2O$ (bpy = 2,2-bipyridine)[90] were synthesized and characterized in the same year. Keggin type vanadium containing polyoxometalate $[H_5PV_2Mo_{10}O_{40}]$ has been synthesized by hydrothermal process which has been reported in 2010 [91]. Furthermore in 2012 a keggin type polyoxometalate $[Cu(py)_2\ ][SiW_{12}O_{40}]$supported transition metal complex [92] has been synthesized by hydrothermal decarboxylation process. Yet another Co (II)-4f heterometallic – organic frameworks[93] synthesized hydrothermally were reported in the same year.

B. Microwave method

Conventional heating works by means of a heated surface which in turn heats the reaction vessel. It involves the use of a furnace or oil bath. It heats the wall of reactor by convection or conduction and thus the sample takes much longer time to achieve the target temperature. While microwave irradiation method is able to heat the target compounds without heating the entire furnace or oil bath, which saves time and energy. it provides energy efficient internal heating by direct coupling of microwave energy with dipoles or ions present in the reaction mixturte. Even thin objects are also sufficiently heated throughout their volume (instead of its outer surface only) by microwave heating. However design of most microwave ovens show uneven absorption by the object being heated because the microwave field is not uniform and localized super heating occurs. Microwave volumetric heating overcomes the problem of uneven absorption by applying an intense uniform microwave field. Different compounds convert the microwave radiation to heat by different amount. This allows selective heating, some parts are heated more quickly and some are slowly. The microwave heating have many advantages over conventional heating. These are (a) accelerate reaction rate (b) milder conditions (c) higher chemical yield (d) different reaction selectivity's (e) lower energy usage (f) safety under high temperature and pressure (g) excellent parameter control (h) continuous power output and many more. Microwave synthesis is applicable in both organic and inorganic field. polyoxometalate clusters. A solid state eco friendly silver/nickel substituted salt of phosphomolybdate has been reported. Recently in 2015, Microwave assisted synthesis of a mono organo imido functionalized $[Mo_6\ O_{18}\ NC(OCH_2\ )_3\ MnMo_6\ O_{18}(OCH_2)_3CNH_2]^{5-}$Anderson type polyoxometalate has been reported[94].

C. Ionothermal process

Ionothermal method is an another synthetic method for the synthesis of solid material with novel morphologies or improved properties. The ionothermal synthesis uses ionic liquids which function simultaneously as solvent, potential templates and structure directing agent in the formation of solid inorganic materials. The ionothermal process resembles with hydrothermal process where the solvent is water. Ionic liquids are non volatile, non flammable, wide range of working temperature and thermally stable . These properties of ionic liquids make possibilities of the reaction to take place in an open reactor. The term ionothermal comes from the reaction that take place in ionic liquids at high temperature with ambient pressures. Thus, this method avoid high pressure which is required by many other synthetic methologies and safety problems related to high pressure. The morphology and growth of material depend on the ionic liquid precursors (ligands) used. Ionothermal method has recently employed in the field of POM synthesis . Three novel polyoxometalates （POMs） 1.$[Emim]8Na_9[WFe_9(\mu 3O)_3(\mu 2OH)_6O\ 4H_2O(SiW_9O_{34})_3]\cdot 7H_2O$ 2.$[EMIM]_4[SiW_{12}\ O_{40}]$ and $[EMIM]_6\ [P_2\ W_{18}\ O_{62}]\cdot 4H_2O$ have been reported synthesized by ionothermal method with ionic liquid Emim Br (Emim =

1ethyl3methylimidazolium)as solvent in 2010 and a high nuclearity transition metal substituted polyoxometalate anion connected by [WFe_9] cluster core has been reported synthesized by this process[95].A new sandwich type phosphotungstate compound, $H_3(Emim)_7[Ni_4(Mim)_2(PW_9O_{34})_2]\cdot 4H_2O$ has been synthesized using 1ethyl-3-methylimidazolium bromide ([Emim]Br) as ionic liquids (ILs)[96].

D. Sol-gel method

The sol- gel process is a synthetic method for producing solid materials from small molecules. This method is useful for the fabrication of metal oxide. The process convert the monomers into colloidal solution which acts as precursor to form integrated network of either discrete particles or polymers. This chemical procedure involves formation of gel like biphasic system gradually that contain both a liquid and solid phase. In the colloidal state the volume fraction of particle may be so low that a significant amount of fluid need to be removed initially to recognize the gel like property. This can be done by simple methods like allow time for sedimentation and pour off the extra liquid or by centrifugation. The remaining solvent can be removed by drying process. Morphology of final materials depends on the structural changes occur during the different phases of processing. Very few compounds based on polyoxometalates have been synthesized by sol-gel method up to date. In 2000, a new hybrid covalent networks based on poly(ethyl methacrylate) cross linked by heteropolyanions have been synthesized by sol gel method[97]. Microporous Keggin type polyoxometalate materials were synthesized by incorporating $H_3\,PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ and into a silica matrix via sol gel process have been reported in November 2000[98]. In 2009, a polyoxometalate- zirconia (POM/ZrO_2) nanocomposite was prepared by sol-gel technique involving the hydrolysis of zirconium(IV) n-butoxide, $Zr(n\text{-}OBu)_4$. It is green and recyclable photocatalyst used for efficient and selective aerobic oxidation of alcohol into aldehydes and ketones[99].

E. Electrochemically assisted laser ablation method:

This method of synthesis is very simple, catalyst free and green. This process require an ambient environment for the synthesis of noble metal nanoparticles. Nanoparticles are produced by condensation of a plasma plume formed by the laser ablation of bulk metal plate dipped in a liquid solution. Laser ablation technique form stable nanoparticles in water, in organic solvents, ionic solutions and other reactive solution that contains interesting ions). POM's synthesized by this method are simple as they contain two different metals and insoluble in water. In 2011, fabrication of $Cu_3\,(OH)_2\,(MoO_4)_2$ nano rods by electrochemically asiisted laser ablation technique have been repoted[100]. For this synthesis molybdenum was used as solid target for laser ablation in liquid copper electrodes for electrochemical reaction and water as solvent. Another well defined $Cu_3Mo_2O_9$ nanorods were obtained by annealing the $Cu_3\,(OH)_2\,(MoO_4)_2$ nanostructures at 500 °C .

F. Flow method

This is the latest method for preparation of polyoxometalate aggregates. In this method we get a stationary kinetic state molybdenum-blue cycle, packed up with MO_{36} guest to give host-guest complex[101]. some reported complexes prepared by this method are

sodium 11-vanadonickelocuprate(II)[102].Tetra methyl ammonium11- vanadonickelocuprate(II)[102]Potassium 11-vanadonickelocuprate(II)[102]Cetyltrimethyl ammonium POM $(C_{19}H_{42}N)_4H_3(PW_{11}O_{39})$[103]

III. CHARACTERIZATION

The percentage composition, molecular formula, structure and morphology of newly synthesized polyoxometalate compounds are established by different chemical and modern instrumental techniques. These are described below

A. ICP

The basic elemental analysis of polyoxometalate solid materials is done by inductively coupled plasmaatomic emission spectroscopy (ICPAES). After analysis of ICP data , the composition of different elements present in the POM framework can be determine .

B. XRD

Powder X-Ray Diffraction analysis provide information regarding crystallinity, chemical composition and crystal structure of the POM materials. The particle size can be calculated by using scherrer equation, $D=K\lambda\ /\ \beta Cos\theta$; where D= Particle size, K= Crystallite constant,λ= Wave length of radiation and β=Full width half maximum (FWHM). X-ray diffraction pattern helps in the identification of structure of newly synthesize POM, For example diffraction at $2\theta = 9^o$ is a typical feature of Keggin type POM.

C. IR

The nature of bonding between the atoms of different element present in polyoxometalate compounds are ascertain by IR spectroscopic studies. The bonding between addenda atoms ,hetero atoms, and oxygen atoms within the cluster of POM's are determine after analysis of IR data. The IR band in between 1090-1060 cm^{-1} shows (V-O) stretching vibration and broader band at 810-780 cm^{-1} shows (V-O-V) vibration. A small and sharp band within 572-520 cm^{-1} range indicates Cu-O bonds in the compound. The band within 987-940 cm^{-1} shows Ni-O stretching bond. A wider band in the range of 3461-3425cm^{-1} indicates water molecules as lattice.

D. SEM

Micro structural features can be studied by scanning electron microscope. Study of surface morphology, texture, chemical composition and crystal structure of polyoxometalates can be done by examine the SEM images. It utilizes beam of high energy electron which produces different types of signals at the surface of solid samples.

E. TGA/DTA

Thermogravimetric is type of thermal analysis which examines the mass change of a sample as a function of temperature in the scanning mode and as a function of time in the isothermal mode. Thermo gravimetric analysis is mainly used to determine the composition of materials and its thermal stability. From TGA/DTA analytical data the number of water molecules present in different position within the POM clusters can be calculated. The molecular weights of different type of POM's are determine by cryoscopic method in order to establish the molecular formula.

IV. APPLICATIONS OF POM

Primarily the application of POMs was centered on redox properties, ionic charge, conductivity, photochemical responses and ionic weights. Now a day's Polyoxometalates chemistry continues its development as pure chemical science and also with many new dimensions in a multi disciplinary context. Furthermore, spontaneous self organization of POM provides a wide range of versatile structure and their applications in different field[104]. Due to their simple synthesis procedure and thermal stability, polyoxometalates are often used as catalyst. In the beginning $H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$, $H_4SiMo_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ were used as starting material for many applications. These are consider to have strong acidity compare to the conventional inorganic acid[105]. The corresponding POM anions have weak basicity, which make them softer material and thus they are easy to handle without any hazardous effect, unlike the inorganic acids[106-107].

Since the addenda atom of POMs are in their highest oxidation state therefore most of the POM complexes exhibit fast reversible redox transformation in mild conditions. Lanthanide containing POMs function as efficient lewis acids[108]. Photochemical reduction of POM compounds with water as electron donor has also been reported. They function as photocatalyst[109].

POMs are soluble in many polar and polar organic solvents due to their interaction with most solutions, via hydrogen bonding, electrostatic forces and covalent and non- covalent interactions[110]. They are oxidatively and thermally stable than other organometallic complexes.

A large percentage (about 80-85%) of patents and literature related to POMs show their catalytic property. Thus majority of the application of POMs and POM based compounds are found in the area of catalysis and the rest 20-25% includes other application of POMs, which include coating, membranes, thin films, corrosion resistant, as conductive and non conductive polymers membranes and as surface modifiers of substrates. POMs have many other applications like they are used as toners, wood pulp bleaching, pigments, reagent for chemical and bio- chemical analysis, in the processing of nuclear waste and many more.

A. POMs/HPAs as homogenous and heterogenous catalyst

Several reports exist related to homogenous and heterogeneous catalytic properties of POM. HPAs are proton acids that incorporate polyoxometalate anions with metal oxygen octahedral as basic building unit. The first well characterized member of this family is Keggin heteropoly anion represented by general formula $[X_2\ M_{12}\ O_{40}\ ]^{-n}$ where, X= hetero atom (most commonly silicon and phosphorous), M= metal ion or addenda atom (commonly W^{6+} and Mo^{6+}). The M can be replaced by other metal ions and n= negative charge of the cluster. Thus by changing the metal ion wide range of polyoxometalates with different physical and chemical properties can be obtained. Many other POM complexes like Dawson, Keggin Dawson lacunary anions and their transitional metal complexes are often use as catalyst. But among the wide range of POMs, Keggin based polyoxometalates are most widely used catalyst in different catalytic processes. They can be use as oxidation catalyst for alkanes, alkenes, aldehydes, sulphides to alcohol, ketones, allylic ketones, alcohol, allylic alcohol, epoxides, and sulphoxides[111].POMs based on molybdenum and tungsten are good acid and redox catalyst. The catalytic property of POM can be amplified in presence of organic derivatives as solvent and inorganic anions.

A series of eco-friendly POMs have been synthesized and applied as catalysts in various organic reactions, particularly in acetylation of alcohols and phenols with acetic anhydride[112], nitration of phenols[113]. A heterogenous catalyst $(NH_4)_5 H_6PV_8Mo_4O_{40}/C$ have been used as catalys in the oxidation of allylic and benzylic alcohols to carbonyl compounds[114]. The use of $H_4[Si W_{12}O_{40}]/Ru$ as catalyst for the rapid conversion of cellulose to sugar alcohol at 81% yield for C_4 to C_6 derivatives have been reported which opened the door towards novel catalytic application of POM based clusters[115].Another catalytic application of POM based clusters have been reported by Mizuno . $TBA_4[\gamma\text{-}HPV_2W_{10}O_{40}]$ (TBA= tetra-n- butylammonium) have been used for H_2O_2 based oxidative bromination of alkanes, alkenes and aromatic compounds[116]. Recently a new Cu containing phosphotungtic $[Cu_2PW_{11}O_{39}]^{5-}$ POM-MOF has been reported. This catalyst has been used for the detoxification of various sulphur compounds[117].

Polyoxometalate containing functional materials are applicable in removal of dye. $H_4SiW_{12}O_{40}$ and $Na_2HPW_{12}O_{40}$, a homogenous catalyst have been used to degrade acid dye.

Many organic- inorganic hybrid POM compounds function as heterogeneous catalyst. Some metal-organic co-ordination networks have been used as heterogeneous catalyst in de-sulfurization of fossil fuels. Furthermore, during photo induced decomposition of organic pollutants POM based solid materials play an important role as environmental catalyst.

A magnetic nanoparticle supported POM has been reported which is applicable as heterogeneous catalyst for solvent free synthesis of α-aminophosphonates[118].

B. *Biological and medicinal application:*

In biological and pharmacological field, polyoxometalates play an important role as antiviral, antibacterial, anticancer and even insulin mimetic material. These properties of POM is most probably depends upon interaction of POM with bio macromolecules like proteins.

1) *Antiviral activity:* In 1971, Raynaud et al. noted that polytungstosilicate heteropoly compounds inhibited murine leukemia sarcoma (MLSV). Prior to 1990, he observed that polytungstosilicate heteropoly compounds showed good inhibitory activity with low cytotoxicity against several viruses[119-123]. Example of some POM as antiviral,$[A\text{-}\alpha\text{-}SiNb_3W_9O_{40}]^{7-}$[124-125], $[SiTaW_{11}O_{40}]^{5-}$, $[SiNbW_{11}O_{40}]^{5-}$ etc.[126]
2) *Anticancer activity:* The first report of POM antitumoral activity was the tumor growth inhibition exhibited by $[NH_3Pr]_6[Mo_7O_{24}]$ on CD-1 mice[127]. Further more its effectiveness was observed against the growth of the human cancer. After that Mukherjee[128] reported a combination of $H_3[PW_{12}O_{40}]$, $H_3[PMo_{12}O_{40}]$ and caffeine (PTMC) used on patients suffering from carcinoma of the intestinal tract. some poly molybdate anions [129]have also been reported showing sarcoma inhibiting activity. Ex- $(NH_4)_6[Mo_6O_{24}]$ and $K_6[Mo_7O_{24}]$.
3) *)Antibacterial activity:* Studies show that POM's also have considerable antibacterial property. In 1993, Tajima[130] reported effect ofthe mixture of tungstate and phosphatein combination with β-lactum antibiotics. Antibacterial effect of polyoxovanadates against 6 strains of penicillin resistant streptococcus pneumonia have also been reported by Yamase[131]. Two kinds of multilayer films based on Keggin polyoxometalates $\alpha\text{-}[SiW_{12}O_{40}]4-/\alpha\text{-}[PMo_{12}O_{40}]^{3-}$ and methylene blue have been reported which shows a distinct antibacterial effect against Escherichia coli[132].

C. *POMs in protein crystallization*

Success of crystallization does not depend only on protein properties but it also strongly influenced by other auxiliaries. Due to having diverse range of structure, shape and size POMs promote protein crystallization process.POM functions as a potential additive in protein crystallization. correct choice of appropriate POM is very important for crystallization of protein. Example of POMs commonly used are $[P_2W_{18}O_{62}]^{6-}$ and $[Mo_3O_{14}]^{10-}$[133] .

D. *As corrosion resistant:*

Most commonly used corrosion resistant materials are chromates, phosphates and silicates but their environmental toxicity limits their applicability. Hence, nontoxic POM based materials as anticorrosion agents are highly recommended. POM can accept electrons without any major changes in their structure. Thus, it forms anticorrosion POM film.

Examples:

$[PMo_{12}O_{40}]^{3-}$ acts as an inhibitor of iron dissolution.[135]
$H_{12}P_3Mo_{18}V_7O_{85}$ as corrosion resistant for titanium alloy and stainless steel.[136-137]
$PMo_{12}O_{40}^{3-}$ efficient in inhibiting the oxidative degradation of metal iron.[138]
$(NH4)_{10}H_2W_{12}O_{42}(NH4)_6P_2W_{12}O_{62}$ as corrosion inhibitor of Al alloy.[139]
$Na_5H_2PV_6Mo_6O_{42}$ as Corrosion inhibitor for mild steel.[140]

E. Waste water decontamination:

Industries produce harmful chemical wastes which accumulate in environmental system and cause dangerous problems for aquatic and non aquatic organism. Thus, it is important for the industries to isolate harmful chemicals from wastes before discharging into the environment[141] . Polyoxometallates play an important role in dye, pesticides, toxic cationic and anionic decontamination.
Examples
$[PW_{12}O_{40}]^{3-}$, $[SiW_{12}O_{40}]^{4-}$ and $[PMo_{18}O_{62}]^{6-}$ as photo catalyst in the recovery of copper[144].

F. processing of radioactive wastes

Radioactive wastes have unstable nuclei. Their nuclei decay to emit ionizing radiation energy, which are harmful for human and environment[145-147]. POMs can form stable complexes with radioactive elements and can be separated. Pope et al. reported crypto hydration of uranium (IV) by $[P_5W_{30}O_{110}]^{5-}$to form a stable crystal compound $(NH_4)_{11}[U(OH_2)P_5W_{30}O_{110}].12H_2O$[148]. separation and safe disposal of long lived Np-237 isotopes has also been studied. The neptunyl ion (NpO_2^{+}) react with POMs and form stable complex [Na2(NpO2)2(A-PW9O34)214-], which can be readily extracted into an organic solvent[149].

G. Toxic gas sequestration

Flue gases from industries is the main sources of increased CO_2 , SO_2 , NO_2 and CH_4 in the atmosphere, which not only increasing the temperature of the earth but these gases have highly toxic effects on organism. POM based materials play significant role in avoiding production of these toxic gases. POMs are used as wet chemical adsorbents to extract CO_2 from flue gas.
Examples:
CO_2 from flue gas.[150]
$[H_4PMo_{10}V_2O_{40}]^{-}$ /SiO_2 as catalyst to convert methane to methanol[151].
$[(C_{38}H_{80}N)_9LaW_{10}O_{36}]$ used for desulfurization[152-153].

H. POM as addititve in sol-gel inorganic/organic matrix

POMs are used as an additive in inorganic and organic matrixes. POMs anion such as $[PW_{12}O_{40}]^{3-}$, $[SiW_{12}O_{40}]^{4-}$ and $[W_{10}O_{32}]^{4-}$are trapped into gel matrixes and produces conductive materials with electrochromic and photochromic properties[154].

I. Pigments/ Dyes/ Inks

Many patents have been reported related to the formation of stable precipitates of Polyoxometalates with cationic dyes and their use as pigments, dyes and inks[155-167]. Combination of (polyethylene glycol) and heteropoly anion is suitable for use in ink jet printer[168]. Clarke[169] described in his patent that combination of Keggin type complex acids with large number of basic dyes provides a composite material which is use in colarant formulations for acidic fibres for e.g. polyacrylonitriles and polyesters.
Polyoxometalate complexes with tri or tetra cationic polymethinine dyes are useful colarants for pigmenting, printing inks, paints and plastics[170].

J. Recording materials

Lyman in 1960 claimed in patent that POM acids of Mo and W are photosensitive. He presented that photographic process could be built on photosensitive systems composed of POM acids and organic reducing agents[171-172].
Some patents also claimed, use of cationic dyes-POM complexes for recording purposes. Cationic dyes with heteropoly acids of Mo and W that contained P, Si, V, Co, Mn, Al, or Cr were use to produce pigments with λ_{max} > 7oonm that were markable by semiconductor lasers[173].
The complex $H_4SiW_{12}O_{40}$ was use for improving the color –forming sensitivity and lowering the color forming temperature of formulated films of vinyl chloride-vinyl acetate polymers[174].

K. Toners (Eectrophotography)

Polyoxometalate patents related to the field of electrophotography (copiers) are good in numbers. POMs and their salts with organic cations were used either as the active ingredients in photochromic coatings or as charge control agents in toner.Keggin type POMs together with reducing agent and binder such as PVC have been used in the production of images as claimed by Avebach[175-176].

L. Bleaching of wood pulp:

Wood pulp bleaching is a process which involves removal of residual lignin and to brighten the pulp either by degradation or by removal of chromophore. Most commonly chlorine was use for bleaching of wood pulp, but it forms chlorinated aromatics and dioxins which poses dangerous effects to the environment.

Polyoxometalates become a safe alternative to the elemental chlorine. Weinstock[177]reported the use of $H_5PMo_{10}V_2O_{40}$for wood pulp bleaching. After that an another process for delignification of pulp based on peroxides and per acids in presence of water soluble salts of group 4, 5, and 6and at least one heteroatom like Si, P, or B capable of forming heteropolyacids[178-179]. Furthermore, Kaneda claimed use of thiourea with peroxides in presence of $K_2HPW_{12}O_{40}$ for the bleaching of paper pulp[180].

M. Capacitor

polyoxometalates and their corresponding heteropoly acids have been claimed as electrolytes for capacitor[181-186]. Electrolytic capacitors which consist salts of $H_4SiM_{12}O_{40}$ (M=Mo, W) in organic solvents like DMF show lesser dissipative factor at low temperature and the capacitors also maintained good reliability at high temperature operation up to 150 °C.

N. Analysis

Mo and Whave the ability to form POM's with almost all the elements of periodic table, many of which exhibit spectroscopic features. Thus, offer a new way or opportunity to the chemist to develop a methodology for the determination of heteroatom elements and also for discrete compounds. No. of elemental analysis methods have been generated by using POM chemistry[187-198].

A process has been develop for the removal of silica from water by addition of isopoly molybdate or tungstate under acidic condition to produce HPA which can be re precipitate and remove[199].

O. Sensor, Membrane

Sensing is one of the key topics in current science and technology. POMs shows high ionic conductivity , capable to form plethora of salts with any cation and also under mild condition they have the ability to undergo redox processes. These properties of POMs make them applicable for building membrane based devices and sensors. Most commonly use in gas detection devices, solid state electro chromic devices, in selective electrode and in solid and liquid electrolytic cells.

P. Staining agent

POMs have well recognized staning ability[200-206]. use of 1% $H_3PW_{12}O_{40}$ on SEM samples of lipid membranes and proteins that improve the adhesion between materials and the hydrophobic grids[201]. $H_3PW_{12}O_{40}$ as a staining agent of formalin-fixed paraffin-embedded clinical samples[202].

V. CONCLUSION

Polyoxometalate chemistry is found to be an interesting topic and have attracted attention of many researchers due to having wide range of structure, thermal and hydrolytic stability, high polarity and magnetic properties . Some new type of molecular structured POMs have been introduced into the POM family like Weakley-Yamase and Preysslers type compounds. It can be seen that the utilization of polyoxometalates are tremendously increasing day by day specially in the field of material science and medicines. POMs are found to be environment friendly and recyclable compound. It can also be seen that the synthetic strategies are also changing depending upon their requirement and use.

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