POLYOXOMETALATE SUPPORTED TRANSITION METAL COMPLEXES AND THEIR APPLICATIONS IN CATALYSIS

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APRIL 2022

POLYOXOMETALATE SUPPORTED TRANSITION METAL COMPLEXES AND THEIR APPLICATIONS IN CATALYSIS

A DISSERTATION REPORT

Submitted in Partial Fulfilment
Of
The Degree of M.Sc. (Analytical Chemistry)

By
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To the
School of Chemical Sciences
Goa University
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April 2022

CERTIFICATE

This is to certify that the dissertation entitled **“Polyoxometalate supported transition metal complexes and their applications in catalysis”** is bonafide work carried out by Ms. Dipti Dattaram Naik under my supervision in partial fulfilment of the requirement for the award of the degree of Master of Science in Chemistry at the School of Chemical Sciences, Goa University.

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STATEMENT

I hereby declare that the literature review and the matter presented in this dissertation entitled, '**Polyoxometalate supported transition metal complexes and their applications in catalysis**' has been carried out by me in School of Chemical Sciences, Goa University. The information derived from the literature has been duly acknowledged in the text and a list of references is provided.

Dipti D. Naik

ACKNOWLEDGEMENT

The literature review titled “Polyoxometalate supported transition metal complexes and their applications in catalysis” has been successfully completed under the guidance of **Dr. Savita A. Kundaikar** during the academic year 2021-2022 in the partial fulfilment of the requirements for the degree of Master of Science in Chemistry.

There is no good work done which comes without efforts; but those efforts cannot be obtained without proper guidance. So, in these few humble lines I take this opportunity to express my profound gratitude to the people who have made invaluable contribution during the course of completion of the literature review in time.

First of all I would like to thank my guide; **Dr. Savita A. Kundaikar** for giving me an opportunity to work under her guidance; for her patience and invaluable help and assistance during the course of work on this literature review. I am also very much grateful to our respected Dean **Dr. Vidhyadatta Verenkar** for his support and for providing us the opportunity to work in School of Chemical Sciences.

No acknowledgement would be complete without giving thanks to our Family and Friends. I would like to thank my parents for their support and people who helped me in the successful completion of my literature review.

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INTRODUCTION

Polyoxometalate (POM) is a polyatomic ion, usually an anion which consists of three or more transition metal oxyanions linked together by shared oxygen atoms to form closed 3-dimensional frameworks or it is an anionic aggregates of early transition metals (Mo^{VI}, W^{VI}, V^{V} etc.) and oxygen.

Polyoxometalates because of their potential applications in fields as diverse as catalysis[1], biochemical analysis[2,3], medicinal chemistry[4], and material science[5] have become a subject of general interest. The polyoxoanion – supported transition metal complexes is the important advance in polyoxometalate chemistry. Such metal oxide – based inorganic complexes provide new and exciting functional materials with an interesting optical, electronic, and magnetic properties and also serve as structural models for understanding the functions of oxide – supported catalysts. Mostly Keggin – type anions have been used to support inorganic complexes because the charge density of the Keggin – surface oxygen atoms can be increased either by reducing some of their metal centres (e.g., Mo^{VI} to Mo^{V}) or replacing higher – valent metal centers (e.g., replace Mo^{VI} with V^{IV}).[6]

In Polyoxometalate (henceforth called as POM) chemistry, a recent trend is the functionalization of the POM cluster anions, to explore more selective applications. Functionalization of a cluster anion in a broad sense can be discussed by three general categories:

i. Multidimensional inorganic organic hybrid materials that include porous structures.

ii. Replacement of MO_6 octahedra of the pertinent cluster anion with transition metal ions (known as substitution) resulting in a transition metal ion substituted lacunary POM cluster anion with higher negative charges (where M = addenda atoms, such as Mo, W, and V, etc.).

iii. Attachment of a transition metal complex (TMC) on the surface of a POM anion using coordinate covalent bonds (known as addition).[7]

In recent times, Category iii. has received considerable attention as far as new POM – based materials, having aesthetic supramolecular structures, are concerned.[7]

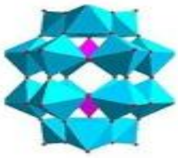
The introduction of the coordination complexes into the framework by covalently grafting the complex through the terminal or bridging oxygen atom(s) of the polyoxometalates is a recent modification to the polyoxometalates, taking into consideration the charge compensation or the structure direction, which are called polyoxometalate supported transition metal complexes (PSTMC's). This modification to the polyoxometalate enhances the potential applications of these hybrid PSTMC's in many diverse fields.[8]

Polyoxometalates are stable with respect to thermal and oxidative degradation. They can function as homogeneous as well as heterogeneous catalysts. A challenging goal of oxidation catalysis is the design of active, selective, and recyclable heterogeneous catalysts. Polyoxometalates or transition – metal oxoanion nanosized clusters have received increasing attention as oxidation catalysts because of their numerous advantageous properties, such as inorganic nature, thermodynamic stability to oxidation, hydrostability, tunability of redox and acid properties, and so on.[9]

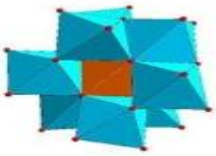
Various structure types of Polyoxometalates include:

Keggin

Anderson



Dawson



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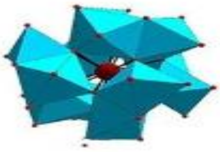

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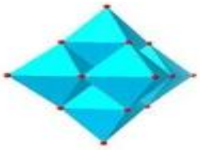


Lindqvist

The various development in POM studies took place which include discovery of giant wheel, Kepelarate, porous capsule type cluster. The mystery of molybdenum blue was solved.

LITERATURE REVIEW

Synthesis and structural features of polyoxometalates:

Table:

Sr. No.	Compound	Space group	Synthesis details/ conditions	POM cluster anion/ source/ acid (pH)	Applications	Reference
1.	$[2\text{-ampH}]_4[\{Zn(H_2O)_5\}Mo_7O_{24}].9H_2O$ where amp = aminopyridine	*Pnma*	Conventional wet synthesis at room temperature	$[Mo_7O_{24}]^{6-}$ / Sodium molybdate solution / HCl (pH 3-6)	-	7
2.	$[3\text{-ampH}]_4[\{Zn(3\text{-ampy})(H_2O)_4\}Mo_7O_{24}].4H_2O$	*Cc*	Conventional wet synthesis at room temperature	$[Mo_7O_{24}]^{6-}$/ Sodium molybdate solution / HCl (pH 3-6)	-	7
3.	$[3\text{-ampH}]_4[\{Co(3\text{-ampy})(H_2O)_4\}Mo_7O_{24}].4H_2O$	*Cc*	Conventional wet synthesis at room temperature	$[Mo_7O_{24}]^{6-}$/ Sodium molybdate solution / HCl (pH 3-6)	-	7
4.	$[2,3\text{-diampH}]_4[Co(H_2O)_6][Mo_7O_{24}].6H_2O$	*C2/c*	Conventional wet synthesis at room temperature	$[Mo_7O_{24}]^{6-}$/ Sodium molybdate solution / HCl (pH 3-6)	-	7
5.	$[2,3\text{-diampH}]_2[\{Zn(2,3\text{-diampH})_2(H_2O)_2\}Mo_8O_{27}].2H_2O$	*C2/c*	Conventional wet synthesis at room temperature	$[Mo_8O_{27}]^{6-}$ / Sodium molybdate solution / HCl (pH 3-6)	-	7
6.	$[Al(OH)_6Mo_6O_{18}\{Cu(phen)\}(H2O)_2\}_2][Al(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)Cl\}_2].5H_2O$	$P\bar{1}$	Wet synthesis/ aqueous organic – medium	$[Mo_6O_{18}]^{3-}$ / $AlCl_3$ in aqueous molybdate solution / conc. HCl (pH 2.6)	-	6

7.	$[Cr(OH)_6Mo_6O_{18}\{Cu(phen)\}(H2O)_2\}_2][Cr(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)Cl\}_2].5H_2O$	$P\bar{1}$	Wet synthesis/ aqueous organic – medium	$[Mo_6O_{18}]^{3-}$ / $CrCl_3$ in aqueous sodium molybdate solution ($Na_2MoO_4.2H_2O$) / conc. HCl (pH 2.6)	-	6
8.	$[Mo_8O_{26}\{Cu_2(2,2'\text{-}bpy)_2(CH_3COO)_2H_2O\}_2].H_4Mo_8O_{26}.16H_2O$	-	Conventional wet synthesis at 70°C	$[Mo_8O_{26}]^{4-}$ / sodium molybdate, 2,2'-bipyridine, $Cu(NO_3)_2.6H_2O$ and CH_3COONa in aqueous acidic medium	Versatile heterogeneous electro – catalyst for water oxidation, proton reduction and hydrogen peroxide reduction	8
9.	$[PMo^{VI}_6Mo^{V}_2V^{IV}_8O_{44}\{Co(2,2'\text{-}bipy)_2(H_2O)\}_4][PMo^{VI}_4Mo^{V}_4V^{IV}_8O_{44}\{Co(2,2'\text{-}bipy)_2(H_2O)\}_2].4H_2O$	$P\bar{1}$	Synthesized in Teflon - lined autoclaves under autogenous pressure / Hydrothermal reactions	$[PMo^{VI}_4Mo^{V}_4V^{IV}_8O_{44}\{Co(2,2'\text{-}bipy)_2(H_2O)\}_2]^{3-}$ / mixture of NH_4VO_3, $Na_2Mo_4.2H_2O$, $CoCl_2.6H_2O$, 2,2'-bipy / H_3PO_3 (pH = 4.2)	-	10
10.	$[Cu^{I}(phen)_2]_4[PMo^{VI}_8V^{IV}_6O_{42}\{Cu^{I}(phen)\}_2].H_5O_2$	-	Synthesized in Teflon - lined autoclaves under autogenous pressure / Hydrothermal reactions	$[PMo^{VI}_8V^{IV}_6O_{42}\{Cu^{I}(phen)\}_2]^{5-}$ / mixture of NH_4VO_3, $Na_2Mo_4.2H_2O$, $CuCl_2.2H_2O$, 1,10-phen.H_2O / H_3PO_3 (pH = 4.4)	-	10
11.	$[Ni(phen)_3][PMo^{VI}_9Mo^{v}_3O_{40}\{Ni(phen)\}_2]$	-	Synthesized in Teflon - lined autoclaves under autogenous pressure / Hydrothermal reactions	$[PMo^{VI}_9Mo^{V}_3O_{40}\{Ni(phen)\}_2]^{2-}$ / mixture of $(NH_4)_6Mo_7O_{24}.4H_2O$, $NiCl_2.6H_2O$, 1,10-phen.H_2O / H_3PO_3 (pH = 3.8)	-	10
12.	$[Cu(dmbpy)]_2[SiW_{12}O_{40}].8H_2O$	-	Used Teflon-lined stainless steel reactor	Mixture of $Cu(NO_3)_2.3H_2O$, 4,4'-dimethyl-2,2'-bipyridyl and $H_4SiW_{12}O_{40}.xH_2O$	Anti-larvicidal activity, anticancer activity	11

13.	$[Ni^{II}(2,2'-bpy)_3]_3[\{Ni^{II}(2,2'-bpy)_2(H_2O)\}\{HCo^{II}W^{VI}_{12}O_{40}\}]_2.3H_2O$ where 2,2'-bpy = 2,2'-bipyridine	*C2/c*	Solvothermal method at 160°C	$[H(Co^{II}W_{12}O_{40}]^{5-}$ / $K_6[CoW_{12}O_{40}].6H_2O(CoW_{12})$ with $Ni(OAc)_2.4H_2O$ and 2,2'-bpy in an acidic aqueous medium	electrocatalysts for efficient water oxidation; Ni^{II} from the $\{Ni^{II}(2,2'-bpy)_2(H_2O)\}$ unit, acts as a catalytic active center	12
14.	$[XM^{III}(H_2O)W_{11}O_{39}]^{n-}$ (X = P, M = Fe or Mn; X = Si or B, M = Fe)	-	Iron and Manganese substituted polyoxotungstates were immobilized on triethylpropylammonium – functionalized silica	$[XW_{11}O_{39}]^{n-}$	Heterogeneous catalysts in the oxidation of cis-cyclooctene and cyclooctane at 80°C; can be reused several times without appreciable loss of catalytic activity	13
15.	$[PW_{11}O_{39}M(H_2O)]^{5-}$ where M = Ni^{2+}, Co^{2+}, Cu^{2+} or Zn^{2+}	-	Incipient wetness method	$[PW_{11}O_{39}]^{7-}$ / involves alkalization of an aqueous solution of $H_3PW_{12}O_{40}.23H_2O$ with aqueous $NaHCO_3$ solution upto pH 5.0 - 5.5	Efficient and recyclable catalysts for 2-(methylthio)-benzothiazole sulfoxidation to obtain a more biodegradable product	14
16.	$Na_{21}[NaFe_{15}(OH)_{12}(PO_4)_4(A\text{-}\alpha\text{-}SiW_9O_{34})_4].85H_2O$ $(Na_{21}\text{-}Fe_{15}P_4(SiW_9)_4)$	*Pmmn*	Synthesized using a facile one - pot, solution - based synthetic approach	$FeCl_2.4H_2O$, $Na_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}].18H_2O$, $Na_3PO_4.12H_2O$ and Na_2CO_3 / aqueous HCl (pH 8.0 - 9.0)	Catalyst for Visible - Light - Driven Generation of Hydrogen	15
17.	[2-ampH]4[{Co(H2O)5}Mo7O24]·9H2O	-	Synthesized according to literature procedure	Sodium molybdate and 2-aminopyridine	Helps in oxidation of styrene to benzaldehyde or benzoic acid	16
18.	$\{[Cu_{12}(pbtz)_2(Hpbtz)_2(OH)_4(H_2O)_{16}][Na(H_2O)P_5W_{30}O_{110}]\}\cdot16H_2O$	*C2/c*	Synthesized hydrothermally	$K_{12}.5Na_{1.5}[NaP_5W_{30}O_{110}]\cdot15H_2O$ and $CuCl_2\cdot2H_2O$	Show catalytic activity in cyanosilylation of aldehydes	17

19.	$[Na(H_2O)_5](NH_4)_7[P_2W_{15}O_{56}Co_3(H_2O)_3(OH)_3Mn(CO)_3]\cdot 19H_2O$	*I2/a*	Conventional aqueous solution method	$[P_2W_{15}O_{56}Co_3(H_2O)_3(OH)_3Mn(CO)_3]^{8-}$ / reaction of $[\alpha\text{-}P_2W_{15}O_{56}]^{12-}$ with $Co(OAc)_2\cdot 4H_2O$ and $Mn(CO)_5Br$ in acidic (pH6.0) solution	efficient catalyst in the cycloaddition of CO2 with epoxides	18
20.	$[Cu(2,2'\text{-bipy})][Cu(2,2'\text{-bipy})_2]_2[PMo_8V_6O_{42}]\cdot 1.5H_2O$	-	Hydrothermally synthesized	A mixture of $Na_2MoO_4\cdot 2H_2O$, NH_4VO_3, $CuSO_4\cdot 5H_2O$/ H_3PO_4 (pH=4)	Used in synthesis of dihydropyrimidinones	19

DISCUSSION

Polyoxometalate supported transition metal complex $[2\text{-ampH}]_4[\{Zn(H_2O)_5\}Mo_7O_{24}].9H_2O$ where amp = aminopyridine with space group *Pnma* was synthesized in simple one-pot wet synthesis (not under hydrothermal condition). The conventional wet synthesis was carried out at room temperature with $[Mo_7O_{24}]^{6-}$ as a POM cluster anion and sodium molybdate solution and HCl was used. The compound was isolated in an aqueous acidic medium (pH 3-6). When sodium molybdate was dissolved in an aqueous solution in the presence of 2-aminopyridine, the aminopyridine molecule formed weak complexes with transition metals and was readily labile in the presence of hydroxyl ligand during hydrolysis and condensation reactions took place to produce an -Mo-O-Mo-O-Mo- network leading to hepta- or octa-molybdate cluster anion. The compound was isolated at an ambient temperature and characterized by single crystal X-ray crystallography and additionally characterized by elemental analyses, infrared, thermogravimetric analysis/mass spectral studies.

The compounds 2-5 as listed in the table, $[3\text{-ampH}]_4[\{Zn(3\text{-ampy})(H_2O)_4\}Mo_7O_{24}].4H_2O$(2); $[3\text{-ampH}]_4[\{Co(3\text{-ampy})(H_2O)_4\}Mo_7O_{24}].4H_2O$(3); $[2,3\text{-diampH}]_4[Co(H_2O)_6][Mo_7O_{24}].6H_2O$(4); $[2,3\text{-diampH}]_2[\{Zn(2,3\text{-diampH})_2(H_2O)_2\}Mo_8O_{27}].2H_2O$(5), were synthesized in a similar way as compound 1 with conventional wet synthesis at room temperature using $[Mo_7O_{24}]^{6-}$ as a POM cluster anion for synthesizing compounds 2-4 and $[Mo_8O_{27}]^{6-}$ for compound 5. Compounds 2 and 3 crystallizes in a monoclinic system with space group Cc and both compounds 2 and

3 are isomorphous, and accordingly the unit cell volume, cell data, space group, number of lattice water molecules etc. of 2 and 3 are identical. They differ in their metal contents, that is, compound 3. $[3\text{-ampH}]_4[\{Co(3\text{-ampy})(H_2O)_4\}Mo_7O_{24}].4H_2O$ is cobalt analogue of zinc-containing compound 2. $[3\text{-ampH}]_4[\{Zn(3\text{-ampy})(H_2O)_4\}Mo_7O_{24}].4H_2O$. Compound 4 and compound 5 have similar space group i.e. C_2/c but the compound 5 uses $[Mo_8O_{27}]^{6-}$ POM cluster anion.[7]

The compound (6), $[Al(OH)_6Mo_6O_{18}\{Cu(phen)\}(H2O)_2\}_2][Al(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)Cl\}_2].5H_2O$ and (7) $[Cr(OH)_6Mo_6O_{18}\{Cu(phen)\}(H2O)_2\}_2][Cr(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)Cl\}_2].5H_2O$ was synthesized using simple wet synthesis. The synthesis was performed in a mixed aqueous-organic medium. For the synthesis of Anderson-type POM compounds, MCl3 (M = Al^{3+} and Cr^{3+}) in aqueous sodium molybdate solution was used to generate in situ Anderson-type heteropolyanion $[M(OH)_6Mo_6O_{18}]^{3-}$. $AlCl_3.6H_2O$ in aqueous molybdate solution was used for synthesis of compound 6 and $CrCl_3.6H_2O$ in aqueous solution of sodium molybdate ($Na_2MoO_4.2H_2O$) was used for compound 7 along with other reactants such as, copper nitrate, phenanthroline, and hydrochloric acid. POM cluster anion used was $[Mo_6O_{18}]^{3-}$ for both the compounds. Concentrated HCl solution was used to adjust the pH to 2.6. The two compounds were characterised by elemental analysis, EDAX, IR, diffuse reflectance, EPR, TGA, and single crystal X-ray diffraction.[6]

A polyoxometalate (POM) supported copper dimeric complex, $[Mo_8O_{26}\{Cu_2(2,2'\text{-bpy})_2(CH_3COO)_2H_2O\}_2].H_4Mo_8O_{26}.16H_2O$ was synthesized by the authors N. Tanmaya Kumar, Umashis Bhoi, Pragya Naulakha, and Samar K. Das using conventional wet synthesis at 70°C which include reactants such as sodium molybdate, 2,2'-bipyridine, $Cu(NO_3)_2.6H_2O$ and CH_3COONa in aqueous acidic medium using $[Mo_8O_{26}]^{4-}$ as a POM cluster anion. The compound was characterized using routine spectral techniques. One of the copper ions in each dimer is bonded to the POM anion from one side, whereas the other copper ion is bonded to a water molecule, hence acquiring a penta-coordinated square pyramidal structure around each copper center. This compound is found to function as a versatile heterogeneous electro-catalyst for water oxidation, proton reduction and hydrogen peroxide reduction.[8]

As shown in the above table, the synthesis of compound $[PMo^{VI}_6Mo^{V}_2V^{IV}_8O_{44}\{Co(2,2'\text{-bipy})_2(H_2O)\}_4][PMo^{VI}_4Mo^{V}_4V^{IV}_8O_{44}\{Co(2,2'\text{-bipy})_2(H_2O)\}_2].4H_2O$ was carried out hydrothermally in Teflon-lined autoclaves under autogenous pressure. The POM cluster anion was $[PMo^{VI}_4Mo^{V}_4V^{IV}_8O_{44}\{Co(2,2'\text{-bipy})_2(H_2O)\}_2]^{3-}$. The reaction was carried out using mixture of NH_4VO_3, $Na_2Mo_4.2H_2O$, $CoCl_2.6H_2O$, 2,2'-bipy and H_3PO_3 was used to adjust the pH = 4.2.[10]

The compound (10), $[Cu^I(phen)_2]_4[PMo^{VI}_8V^{IV}_6O_{42}\{Cu^I(phen)\}_2].H_5O_2$ was synthesized in a hydrothermally under autogenous pressure in Teflon-lined autoclaves. It consist of $[PMo^{VI}_8V^{IV}_6O_{42}\{Cu^I(phen)\}_2]^{5-}$ as a POM cluster anion. Reactants used in synthesis are mixture of NH_4VO_3, $Na_2Mo_4.2H_2O$, $CuCl_2.2H_2O$, 1,10-phen.H_2O and H_3PO_3 to adjust pH to 4.4.[10]

The compound (11), $[Ni(phen)_3][PMo^{VI}_9Mo^{V}_3O_{40}\{Ni(phen)\}_2]$ was synthesized in a similar way to compound 9 and 10 with $[PMo^{VI}_9Mo^{V}_3O_{40}\{Ni(phen)\}_2]^{2-}$ POM cluster anion and mixture of $(NH_4)_6Mo_7O_{24}.4H_2O$, $NiCl_2.6H_2O$, 1,10-phen.H_2O and pH was adjusted to 3.8 with H_3PO_3.[10]

During the synthesis of the compound 12, $[Cu(dmbpy)]_2[SiW_{12}O_{40}].8H_2O$, the reactions were carried out in Teflon – lined stainless steel reactor. It was synthesized with a good yield in a one-pot reaction. Reactants used were mixture of $Cu(NO_3)_2.3H_2O$, 4,4'-dimethyl-2,2'-bipyridyl and $H_4SiW_{12}O_{40}.xH_2O$. The compound was investigated for its biological applications such as Anti-larvicidal activity, and anticancer activity.[11]

Solvothermal method at 160°C was used for synthesizing the compound $[Ni^{II}(2,2'\text{-}bpy)_3]_3[\{Ni^{II}(2,2'\text{-}bpy)_2(H_2O)\}\{HCo^{II}W^{VI}_{12}O_{40}\}]_2.3H_2O$ where 2,2'-bpy = 2,2'-bipyridine with a space group of C_2/c. The reaction was carried out along with a POM cluster anion $[H(Co^{II}W_{12}O_{40}]^{5-}$ and reactants $K_6[CoW_{12}O_{40}].6H_2O(CoW_{12})$ with $Ni(OAc)_2.4H_2O$ and 2,2'-bpy in an acidic aqueous medium. Ni^{II} from the $\{Ni^{II}(2,2'\text{-}bpy)_2(H_2O)\}$ unit, attached to POM cluster acts as a catalytic active center and the Compound have the potential to act as electrocatalysts for efficient water oxidation.[12]

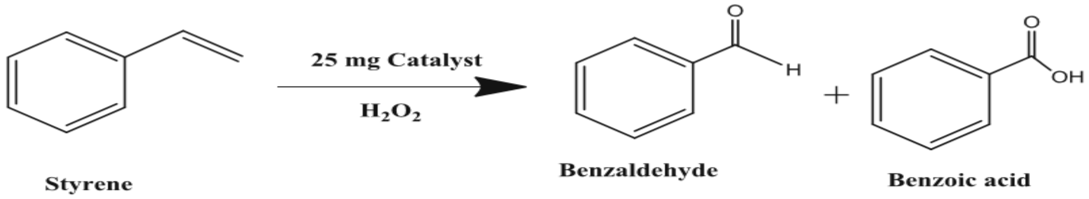
In the synthesis of compound, $[XM^{III}(H_2O)W_{11}O_{39}]^{n-}$ (X = P, M = Fe or Mn; X = Si or B, M = Fe), iron and manganese substituted polyoxotungstates were immobilized on triethylpropylammonium – functionalized silica. POM cluster anion is $[XW_{11}O_{39}]^{n-}$. It is used as a heterogeneous catalysts in the oxidation of cis-cyclooctene and cyclooctane at 80°C and can be reused several times without appreciable loss of catalytic activity.[13]

Incipient wetness method is used for the synthesis of the compound, $[PW_{11}O_{39}M(H_2O)]^{5-}$ where M = Ni^{2+}, Co^{2+}, Cu^{2+} or Zn^{2+} which involves alkalization of an aqueous solution of $H_3PW_{12}O_{40}.23H_2O$ with aqueous $NaHCO_3$ solution upto pH

5.0 - 5.5 with polyoxometalate cluster anion $[PW_{11}O_{39}]^{7-}$. The compound was found to be efficient and recyclable catalysts for 2-(methylthio)-benzothiazole sulfoxidation in order to obtain a more biodegradable product than the corresponding substrate.[14]

$Na_{21}[NaFe_{15}(OH)_{12}(PO_4)_4(A\text{-}\alpha\text{-}SiW_9O_{34})_4].85H_2O$ ($Na_{21}\text{-}Fe_{15}P_4(SiW_9)_4$) with space group *Pmmn* was synthesized using a facile one-pot, solution-based synthetic approach. The reactants used were $FeCl_2.4H_2O$, $Na_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}].18H_2O$, $Na_3PO_4.12H_2O$ and Na_2CO_3 and aqueous HCl for pH 8.0 - 9.0 adjustment. This compound is used as a catalyst for Visible - Light - Driven Generation of Hydrogen.[15]

[2-ampH]4[{Co(H2O)5}Mo7O24]·9H2O was synthesized according to literature procedure using Sodium molybdate and 2-aminopyridine. It Helps in the oxidation of styrene to benzaldehyde or benzoic acid. This catalyst is efficient to be reused again for three times with similar percentage of conversion.[16]



Scheme 1. Oxidation of styrene leading to benzaldehyde and benzoic acid using heptamolybdate coordinated transition metal complex as a catalyst.

$\{[Cu_{12}(pbtz)_2(Hpbtz)_2(OH)_4(H_2O)_{16}][Na(H_2O)P_5W_{30}O_{110}]\}\cdot 16H_2O$ has been synthesized hydrothermally with $K_{12}.5Na_{1.5}[NaP_5W_{30}O_{110}]\cdot 15H_2O$ and $CuCl_2\cdot 2H_2O$. It is used as an acid catalyst for the cyanosilylation of carbonyl compounds.[17]

The compound 19, $[Na(H_2O)_5](NH_4)_7[P_2W_{15}O_{56}Co_3(H_2O)_3(OH)_3Mn(CO)_3]\cdot 19H_2O$ with space group *I2/a* has been successfully synthesized using $[P_2W_{15}O_{56}Co_3(H_2O)_3(OH)_3Mn(CO)_3]^{8-}$ as cluster ion by conventional aqueous solution method. It was prepared by reaction of $[\alpha\text{-}P_2W_{15}O_{56}]^{12-}$ with $Co(OAc)_2\cdot 4H_2O$ and $Mn(CO)_5Br$ in a slightly acidic (pH6.0) solution.[18] Compound 20 has been used in synthesis of dihydropyrimidinones.[19]

POMs applications are centered primarily on their redox properties, photochemical response, ionic charge, conductivity, and ionic weights. POM's are used as electrolytic capacitors, primers, and for corrosion resistant coatings and so on.[20]

CONCLUSION

Polyoxometalates are large anionic metal clusters formed mainly by transition metals and oxygen atoms. They can adopt a variety of spatial structures. In this literature review we can see that Polyoxometalate supported transition metal complexes were synthesized using different methods and approaches. They have various applications in catalysis as well as in other fields. Polyoxometalates or transition – metal oxoanion nanosized clusters have received increasing attention as oxidation catalysts because of their numerous advantageous properties. Polyoxometalates can function as homogeneous as well as heterogeneous catalysts.

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