

REVIEW ARTICLE

Research progress in synthesis and catalysis of polyoxometalates*

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Received July 6, 2004; revised December 7, 2004

Abstract Recent progress in the synthetic chemistry and catalysis of polyoxometalates (POMs) is reviewed. The novel POMs and their derivatives emerging in nearly three years (2002–2004) are introduced, including POMs with novel structure, POMs-organic hybrid compounds and host-guest complexes. Our review is focused on the elaboration of POMs' supramolecular chemistry.

Keywords: polyoxometalates, hybrid, host-guest, structure, supramolecule, catalysis

Polyoxometalates (POMs) form a large class of metal oxide cluster type compounds. Their wealthy topology, physical and chemical properties have attracted increasing interests. In this paper, based on our group's research, we review the latest progress in the synthetic chemistry and catalysis of POMs and introduce some POMs with novel structure and their derivatives that emerged in 2002–2004. Most of the cited references come from those published in 2003.

Due to POMs' superior redox properties, photochemical response, conductivity, ionic charge, and ionic weights, POMs have many applications in different fields such as catalysis, medicine, coatings, analytical chemistry, processing radioactive waste, membranes, sensors, electrodes, capacitors, etc. There have been a number of high-level chemical reviews on POMs^[1–3]. Compared with these papers, we focus on the synthetic chemistry and catalysis of POMs. The latest progress in such two fields in nearly three years are particularly introduced. Emphasis is put on POMs' host-guest chemistry and supermolecular chemistry.

1 Research progress in the synthetic chemistry of POMs

1.1 POMs with novel structures

POMs comprise a structurally diverse family of

metal-oxygen clusters. The number and the species of POMs have been dramatically increasing. The discrete POMs and POMs linked by metal bridges are listed in Table 1. Waugh-type structure POMs usually refer to the heteropolyoxometalates with 1:9 ratio of center atom to coordination atoms. Recently, we have synthesized the first Waugh-type isopolyoxometalate $\text{Na}_4\text{M}_{10}\text{O}_{32} \cdot 8\text{H}_2\text{O}$ ^[4]. The anion is discrete, in which one molybdenum atom is center atom and the other nine molybdenum atoms are coordinate atoms; $[(\text{HPO}_4)_2\text{Mo}_{12}\text{S}_{12}\text{O}_{12}(\text{OH})_{14}(\text{H}_2\text{O})_2]^{6-}$ is dodecameric ring POMs that consist of twelve molybdenum atoms and two sulphur atoms^[5]. $[\epsilon\text{-PM}_{012}\text{O}_{36}(\text{OH})_4\{\text{La}(\text{H}_2\text{O})_4\}_4]^{5+}$ is the first Keggin cation, and four $\{\text{La}(\text{H}_2\text{O})_4\}^{3+}$ capping groups make this structure stabilize^[6]. In order to prevent the rapid aggregation of metal oxide, $[\text{H}_2\text{M}_{016}\text{O}_{52}]^{10-}$ was synthesized by “shrink wrapping”, which displays a low symmetry and high negative charge. Due to its high nucleophilicity, the anion can bind two divalent transition-metal ions to its framework and form $[\text{Fe}_2(\text{H}_2\text{O})_8\text{H}_2\text{M}_{016}\text{O}_{52}]^{6-}$ ^[7].

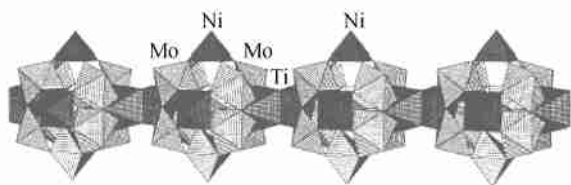
Discrete POMs can be linked by metal bridges for example, $[\text{YbAs}_2\text{W}_{20}\text{O}_{68}(\text{H}_2\text{O})_3]^{72-}$ is two lacunary Keggin moieties $(\text{AsW}_9\text{O}_{33})^{9-}$ connected by one $(\text{H}_2\text{O})\text{Yb}[\text{OW}(\text{H}_2\text{O})_2]$ fragment^[8]. $[(\text{NiOH})_2\text{M}_{010}\text{O}_{36}(\text{PO}_4)\text{Ti}_2]_n^{5n-}$ is a chain built from pseudo-Keggin clusters linked via Ti bridge (Fig. 1)^[9].

* Supported by National Natural Science Foundation of China (Grant Nos. 20331010, 20271007 and 90406002)

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Table 1. POMs with novel structures

POMs	Structure	Ref.
Discrete POMs		
$\text{Na}_4\text{Mo}_{10}\text{O}_{32} \cdot 8\text{H}_2\text{O}$	The first Waugh-type isopolyoxometalate	[4]
$[\text{HPO}_4]_2\text{M}_{012}\text{Si}_{12}\text{O}_{12}(\text{OH})_{14}(\text{H}_2\text{O})_2]^{6-}$	A novel diphosphato anionic ring	[5]
$\text{Mn}_3[\text{Zr}(\text{H}_2\text{O})\text{CoW}_9\text{Mo}_2\text{O}_{39}] \cdot 21\text{H}_2\text{O}$	A poly coordination atomic POMs	[10]
$\text{H}_3[\text{Ga}(\text{H}_2\text{O})\text{ZrW}_{11}\text{O}_{39}] \cdot 14\text{H}_2\text{O}$	An undecatungstozircogallic POMs	[11]
$\text{K}_4\text{H}_2[\text{SiW}_7\text{Mo}_4\text{Co}(\text{H}_2\text{O})\text{O}_{39}] \cdot 22\text{H}_2\text{O}$	Tungstomolybdo silic complex with cobalt	[12]
POMs linked by inorganic metal bridges		
$[\text{YbAs}_2\text{W}_{20}\text{O}_{68}(\text{H}_2\text{O})_3]^{2-}$	Two lacunary Keggin structure linked by $(\text{H}_2\text{O})\text{Yb}[\text{OW}(\text{H}_2\text{O})_2]$	[8]
$\alpha\text{-}[\{\text{K}(\text{H}_2\text{O})_3\}_2\{\text{K}(\text{H}_2\text{O})_2\}(\text{Si}_2\text{W}_{18}\text{O}_{66})]^{13-}$	Two SiW_9 moieties bridged by K	[13]
$[\text{TiP}_2\text{W}_{15}\text{O}_{55}(\text{OH})_2]^{14-}$	Two $[\text{P}_2\text{W}_{15}\text{O}_{56}]^{12-}$ linked by Ti center	[14]
$\alpha\alpha\alpha\text{-H}_2\text{Na}_{14}[(\text{NaOH})_2\text{Fe}_2^{\text{III}}(\text{M}_2\text{W}_{15}\text{O}_{56})_2]$ (M = P or As)	Two $[\text{M}_2\text{W}_{15}\text{O}_{56}]^{12-}$ moieties linked by Na_2Fe_2 fragment	[15]
$[\text{P}_2\text{W}_{18}\text{Cd}_4(\text{H}_2\text{O})_2\text{O}_{68}]^{10-}$	Two $[\text{PW}_9\text{O}_{34}]^{9-}$ moieties linked by Cd_4O_{16} group	[16]
$(\alpha\text{-}1, 2, 3\text{-P}_2\text{W}_{15}\text{Ti}_3\text{O}_{62})_4$ $\{\mu_3\text{-Ti}(\text{OH})_3\}_4\text{Cl}\}^{45-}$	Tri-Ti ^{IV} -substituted Dawson substructures bridged by four $\text{Ti}(\text{OH})_3$ groups with one encapsulated Cl^- ion	[17]
$[(\text{NiOH})_2\text{M}_{010}\text{O}_{36}(\text{PO}_4)\text{Ti}_2]^{5n-}$	1D chain built from pseudo-Keggin cluster linked via Ti bridge	[9]
$[\text{H}_2\text{Si}_4\text{Nb}_{16}\text{O}_{56}]^{14-}$	1D chain built from $[\text{SiNb}_{12}\text{O}_{40}]^{16-}$ linked by $[\text{Ti}_2\text{O}_2]^{4+}$	[18]
$\{[\text{Cu}^{\text{II}}(\text{OH}_2)_4]_3(\text{OH})\}\text{PV}_2\text{M}_{010}\text{O}_{40}\}_n$	3D network built from mixed-addenda POM bridged by aquated $\text{Cu}(\text{II})$ units	[19]

Fig. 1. Chainlike structure of $[(\text{NiOH})_2\text{M}_{010}\text{O}_{36}(\text{PO}_4)\text{Ti}_2]^{5n-}$.

1.2 Inorganic-organic hybrid compounds based on POMs

The design, synthesis and structural characterization of POMs-organic hybrid compounds have established a new field of research in biology and material science. There are several strategies to obtain POMs-organic hybrid compounds. First of all, organic ligands can replace some fragment of POMs, for example, two tris (alkoxo) ligands can replace the six hydroxo groups in Anderson polyanions $[\text{H}_6\text{MMo}_6\text{O}_{24}]^{n-}$ (M = Mn, Fe) and $\{\text{MMo}_6\text{O}_{18}[(\text{OCH}_2)_3\text{CNH}_2]_2\}^{3-}$ can be obtained (Table 2 and Fig. 2)^[20]. Recently, Peng et al. have synthesized a series of covalently bonded inorganic-organic hybrid compound of POMs. The novel material includes hybrid molecular dumbbells in which two identical or different POM clusters are linked by a rigid conjugat-

ed organic rod, and the Mo-N π bond is delocalized into the organic conjugated π system (Fig. 3)^[21].

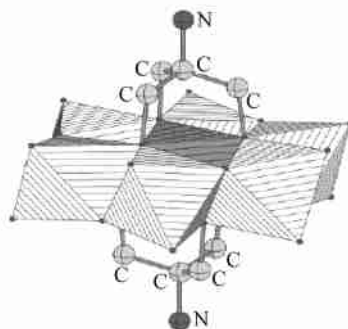
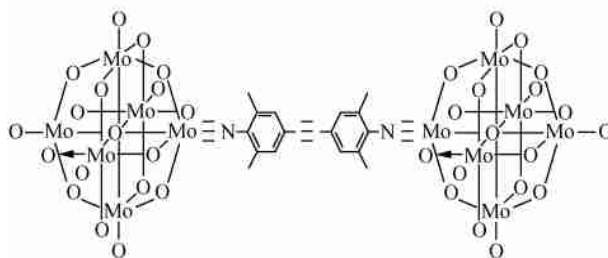
Fig. 2. Structure of $\{\text{MMo}_6\text{O}_{18}[(\text{OCH}_2)_3\text{CNH}_2]_2\}^{3-}$.

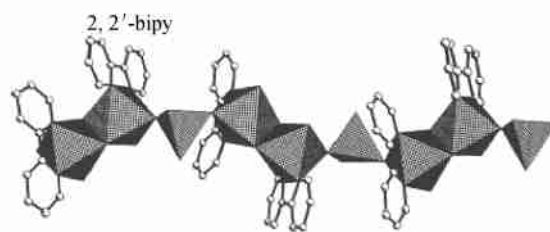
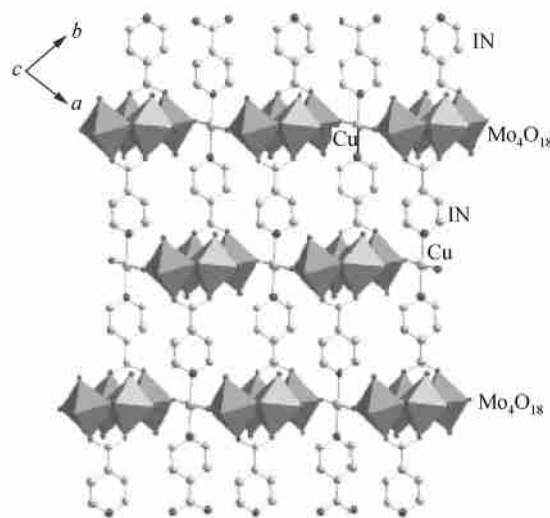
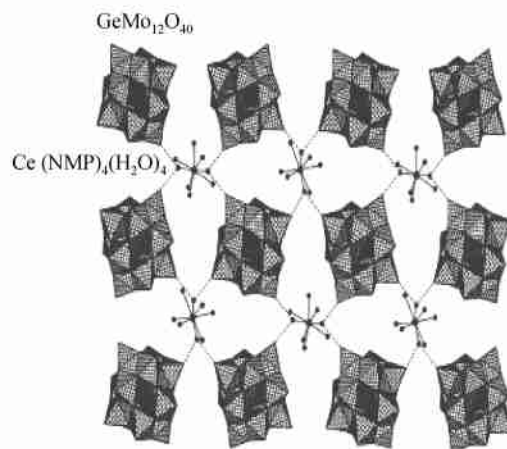
Fig. 3. Hybrid dumbbells with two POMs linked through a conjugated organic rod.

Table 2. POMs-based inorganic-organic hybrid compounds

Inorganic-organic hybrid compounds	Ref.
Some fragment in POMs replaced by organic ligands	
[MM ₆ O ₁₈ (OCH ₂) ₃ CNH ₂] ₂ ³⁻ (M = Mn ^{III} , Fe ^{III})	[20]
[MM ₆ O ₁₈ (OCH ₂) ₃ CR] ₂ ³⁻ (R = CH ₃ , NO ₂ , CH ₂ OH)	[22]
[P ₂ W ₁₇ O ₆₁ {Sn(CH ₂) ₂ CO ₂ H}] ⁷⁻	[23]
[Mo ₆ O ₁₈ (<i>p</i> -MeOC ₆ H ₄ N)] ²⁻	[24]
[H _x Cp [*] TiMo ₅ O ₁₈] ^{(3-x)-} (x = 0, 1, 2)	[25]
α-[RP(O)] ₂ SiW ₁₁ O ₃₉ ⁴⁻ (R = C ₆ H ₁₁ , PhCH ₂ , PhCH ₂ CH ₂)	[26]
[Mo ₄ O ₈ (C ₄ O ₄) ₄] ⁴⁻	[27]
One or two types of organic multi-dentate ligand bonded into inorganic substructures	
[Mo ₃ O ₈ (2, 2'-bipy) ₂] (bipy = bipyridine)	[28]
[Cu(2, 2'-bipy)] ₂ {Cu(IN) ₂ }{Mo ₄ O ₁₂ (OH) ₂ } (IN ⁻ = isonicotinate ion)	[29]
[V ₄ O ₁₀ (phen) ₂] (phen = 1, 10-phenanthroline)	[30]
[VO ₂ (phen) ₂] · 6H ₂ O, [2, 2'-(bipy) ₂ VO ₂] (H ₂ BO ₃) · 3H ₂ O	[31]
[{Cd(phen) ₂ }] ₂ V ₄ O ₁₂ · 5H ₂ O	[32]
M(phen)V ₂ TeO ₈ (M = Cu, Ni)	[33]
[{VO ₂ (2, 2'-bipy)} ₂ (tp)] _∞ (tp = terephthalate)	[34]
Organic ligands acting as charge-compensation groups	
[C221H] ₂ [H ₅ V ₁₄ O ₃₈ (PO ₄) ₈ · 8H ₂ O] (C221 is cryptand)	[35]
(Me-NC ₅ H ₅) ₄ n[Mo ₈ O ₂₆] _n	[36]
(enH) ₃ .5[As ₈ V ₁₄ O ₄₂ (PO ₄) ₈ · 2H ₂ O] (en = ethylenediamine)	[37]
[HPDA][H ₂ PDA] ₂ [As ₃ Mo ₈ V ₄ O ₄₀] · 3H ₂ O (PDA = propane diamine)	[38]

If one or two types of organic bi- or multi-dentate ligands are introduced into the inorganic substructures, one-dimensional (1D), two-dimensional (2D) or three-dimensional (3D) assembly can be attained, such as [Mo₃O₈(2, 2'-bipy)₂] (bipy = bipyridine), [Cu(2, 2'-bipy)]₂{Cu(IN)₂}{Mo₄O₁₂(OH)₂} (IN⁻ = isonicotinate ion), and so on (Figs. 4, 5)^[28, 29].

Organic ligands can be used as charge-compensation groups which is a well-known design strategy to build up inorganic-organic hybrid compounds (Table 2). Co-crystallization of [N, N, N-tris[2-(dimethylamino)ethyl]-1, 3, 5-benzenetricarboxamide]³⁺ with [PW₁₂O₄₀]³⁻ yields an insoluble channeled or microporous structure with the aid of C-H...O hydrogen bonding^[39]. The [Ln(NMP)₄(H₂O)₄]^{3+/4+} cation and [H_xGeMo₁₂O₄₀]⁴⁻ (Ln = Ce, Pr, x = 0; Ln = Nd, x = 1; NMP = N-methyl-2-pyrrolidone) anion can construct a porous structure by hydrogen-bonding interactions (Fig. 6)^[40].

Fig. 4. A polyhedron representation of the 1D chain of [Mo₃O₈(2, 2'-bipy)₂].Fig. 5. Network of [Cu(2, 2'-bipy)]₂{Cu(IN)₂}{Mo₄O₁₂(OH)₂} (2, 2'-bipy omitted for clarity).Fig. 6. Porous structure of [Ce(NMP)₄(H₂O)₄][GeMo₁₂O₄₀] · 2NMP · 3H₂O.

Organic amine is usually used as template or structure-directing agent in the construction of POMs-organic hybrid compounds. In the final structure, it is incorporated with metal cation and acts as bridging block or charge-compensation groups. For example, in Ni(en)₃{V₁₁V₅O₃₈Cl}[Ni(en)₂]₃ · 8.5 H₂O, [Ni(en)₂]²⁺ covalently bonds [V₁₆O₃₈Cl]⁸⁻

clusters to form a three-dimensional network, whereas $[\text{Ni}(\text{en})_3]^{2+}$ groups are not bonded to POMs and only act as charge-compensation groups^[41].

Metal cation can also be bonded to the oxygen atom from POMs, for example, in $[\text{Cu}(2, 2'\text{-bipy})(\text{H}_2\text{O})_2\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]_n^{n-}$, Cu^{2+} covalently bridges two trans terminal oxygen atoms from two different Anderson anions $[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$ and forms a spiral chain. The spiral-shape chain is due to the intra- and inter-chain O-H...O hydrogen-bonding interactions^[42]. Recently, there is a novel building block approach to constructing inorganic-organic com-

pound, which exploits decorated POM clusters with some symmetrical directional bonding sites to determine the ultimate connectivity and dimensionality (Fig. 7)^[43]. Based on this principle, a series of compounds are synthesized, for example, $[\{\text{Co}(\text{phen})_2(\text{H}_2\text{O})_2\}\{\text{Co}(\text{phen})_2(\text{H}_2\text{O})\}\{\text{Mo}_5\text{O}_{15}\}[\text{O}_3\text{P}(\text{CH}_2)_4\text{PO}_3]\} \cdot 6\text{H}_2\text{O}]$ is a new linear polymer and in its $\{\text{Mo}_5\text{O}_{15}\}[\text{O}_3\text{P}(\text{CH}_2)_4\text{PO}_3]\}_n^{4n-}$ anionic chain, the 1, 4-butylenediphosphonate groups bridge the adjacent common $\{\text{Mo}_5\text{O}_{21}\}$ cyclic cluster^[43]. $[\{\text{Cu}_2(\text{tpyprz})\}\{\text{Mo}_6\text{O}_{18}(\text{O}_3\text{AsC}_6\text{H}_5)_2\}] \cdot 2\text{H}_2\text{O}$ (tpyprz = tetra-2-pyridinyl pyrazine) is a 2D material^[44].

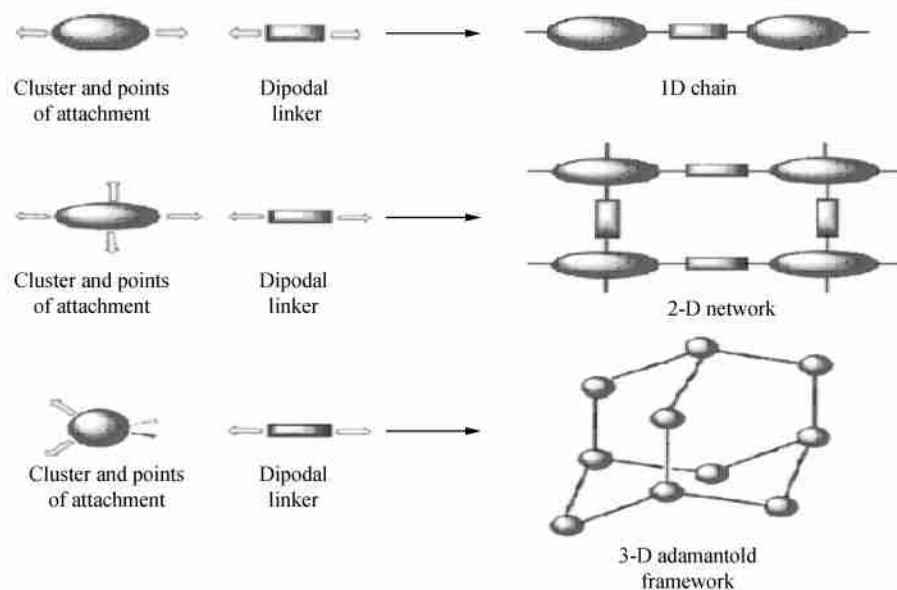


Fig. 7. Decorated POM clusters with symmetrical directional bonding sites.

1.3 Host-guest complexes based on POMs

Nowadays, host-guest chemistry plays an important role in molecular or ionic recognition, transportation and isolation. As a result, much effort has been made on the encapsulation of guest into host. Recently, effective routes have been reported to construct host-guest complex. Robust cluster skeleton $\{\text{Mo}\}\{\text{Mo}_5\}_{12}\{\text{linker}\}_{30}$ can build up a series of cages and encapsulate some cations such as Na^+ , NH_4^+ (Fig. 8)^[45]. The size of the cage can be controlled by the species of the linkers^[46]. Keggin ion can be encapsulated into the $\{\text{Mo}\}\{\text{Mo}_5\}_{12}\{\text{linker}\}_{30}$ giant cluster cage if the linkers are $\{\text{Fe}(\text{H}_2\text{O})_2\}^{3+}$ and the Keggin ion fits exactly into the cavity (Fig. 9)^[46]. The interactions between the cage (host) and Keggin ion (guest) are noncovalent.

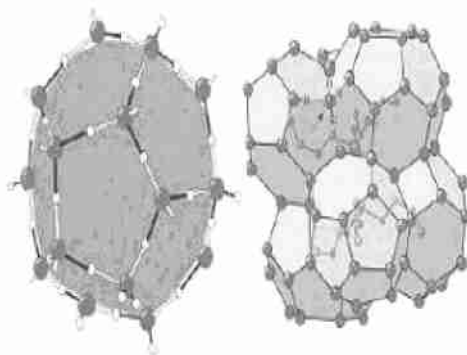


Fig. 8. Cluster skeleton of $\{\text{Mo}\}\{\text{Mo}_5\}_{12}\{\text{H}_2\text{O}\}_{30}$.

Keggin POMs $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ and macro cations $[\text{Cr}_3\text{O}(\text{OOCH})_6(\text{H}_2\text{O})_3]^+$ can line up to construct a straight channel by electrostatic attraction. This channel can selectively bind alcohols and nitriles^[47].

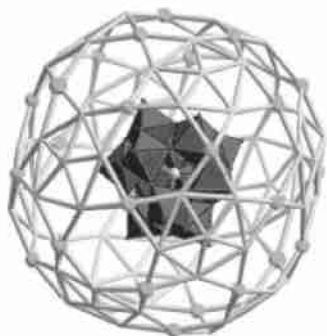


Fig. 9. Keggin ion encapsulated in $\{(\text{Mo})\text{Mo}_5\}_{12}\{\text{Fe}(\text{H}_2\text{O})_2\}_{30}$ cluster.

Host-guest complex can be always built up by self-assembly. A novel compound, $[\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3](\text{H}_3\text{O})_2\{[\text{Mn}(\text{phen})_2]_4[\text{MnMo}_{12}^{\text{V}}\text{O}_{30}(\text{HPO}_4)_6(\text{H}_2\text{PO}_4)_2]\} \cdot 4\text{H}_2\text{O}$, has been hydrothermally synthesized, in which $\text{Mn}(\text{phen})_2$ fragments are covalently bonded to the $\text{Mn}(\text{Mo}_6\text{P}_4)_2$ dimers to form a 1D chain with rectangular cavities. Tetramethylene-diamine cations occupy the cavities by electrostatic attraction (Fig. 10)^[48]. Similarly, novel 3D solid material $\text{H}_3[\text{V}^{\text{V}}\text{Mo}_8^{\text{VI}}\text{V}_6^{\text{IV}}\text{O}_{42}[\text{Cu}(\text{en})_2]_4[\text{MoO}_4]_2 \cdot 14\text{H}_2\text{O}$ was assembled by hydrothermal technique, in which porous structure is formed by $[\text{Cu}(\text{en})_2]^{2+}$ covalently bridging bicapped Keggin structure clusters $\text{V}^{\text{V}}\text{Mo}_8^{\text{VI}}\text{V}_6^{\text{IV}}\text{O}_{42}$. The MoO_4^{2-} anions reside in the cavities of the 3D network^[49].

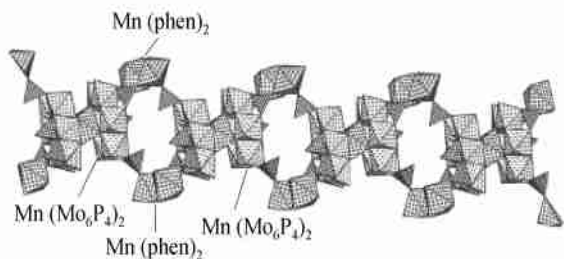


Fig. 10. Polyhedral view of the cavity of $[\text{Mn}(\text{phen})_2]_4[\text{MnMo}_{12}^{\text{V}}\text{O}_{30}(\text{HPO}_4)_6(\text{H}_2\text{PO}_4)_2]$.

$[\text{Ln}_2(\text{DNBA})_4(\text{DMF})_8][\text{Mo}_6\text{O}_{19}]$ ($\text{Ln} = \text{La}$, Ce or Eu , $\text{DNBA} = 3, 5$ -dinitrobenzoate, $\text{DMF} =$ dimethylformamide) has been synthesized, in which $[\text{Ln}_2(\text{DNBA})_4(\text{DMF})_8]^{2+}$ groups are joined together to form a 3D “host” network by supramolecular forces such as π - π stacking, etc. Noncoordinating “guest” $[\text{Mo}_6\text{O}_{19}]^{6-}$ is encapsulated in it^[50].

$[\text{Ge}_7\text{O}_{13}(\text{OH})_2\text{F}_3]^{3-} \cdot \text{Cl}^- \cdot 2[\text{Ni}(\text{dien})_2]^{2+}$ (dien = diethylenetriamine) has been solvothermally synthesized recently. The $[\text{Ge}_7\text{O}_{13}(\text{OH})_2\text{F}_3]^{3-}$ clusters

can form a chain by sharing the bridging oxygen atoms. $[\text{Ni}(\text{dien})_2]^{2+}$ cations, as guests, occupy the cavities between chains. Owing to the $\text{N-H} \cdots \text{O}$ (F , Cl) hydrogen bonding interaction between host ($[\text{Ge}_7\text{O}_{13}(\text{OH})_2\text{F}_3]^{3-}$) and guest ($[\text{Ni}(\text{dien})_2]^{2+}$), each $[\text{Ge}_7\text{O}_{13}(\text{OH})_2\text{F}_3]^{3-}$ chain is chiral (Fig. 11)^[51].

Crown ethers were introduced into the POM-based supramolecule due to their multiple functions such as ion selection and molecular recognition. Alkali metal-crown ether complexes $[\{\text{Na}(\text{DB18C6})(\text{H}_2\text{O})_2\}_3(\text{H}_2\text{O})_2]\text{XM}_{12}\text{O}_{40} \cdot 6\text{DMF} \cdot \text{MeCN}$ ($\text{X} = \text{P}$ or As), ($\text{DB18C6} =$ dibenzo-18-crown-6) were synthesized, in which Na^+ is encapsulated in the crown ether. They contain a novel trimer cation $[\{\text{Na}(\text{DB18C6})(\text{H}_2\text{O})_2\}_3(\text{H}_2\text{O})_2]^{3+}$ and in their π - π packing arrangement, a 2D “honeycomblike” “host” network is formed and the $[\text{XM}_{12}\text{O}_{40}]^{3-}$ “guest” resides in it (Fig. 12)^[52].

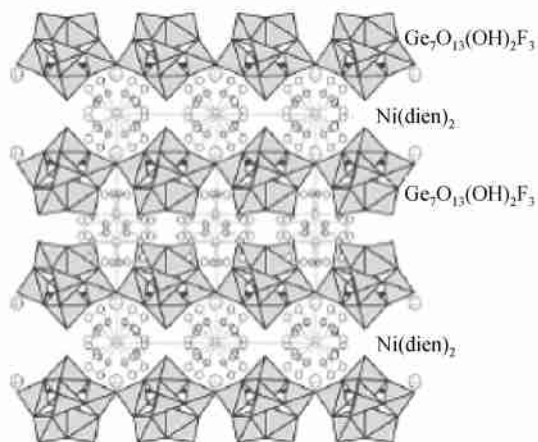


Fig. 11. $[\text{Ni}(\text{dien})_2]^{2+}$ in the cavity between $[\text{Ge}_7\text{O}_{13}(\text{OH})_2\text{F}_3]^{3-}$ chains

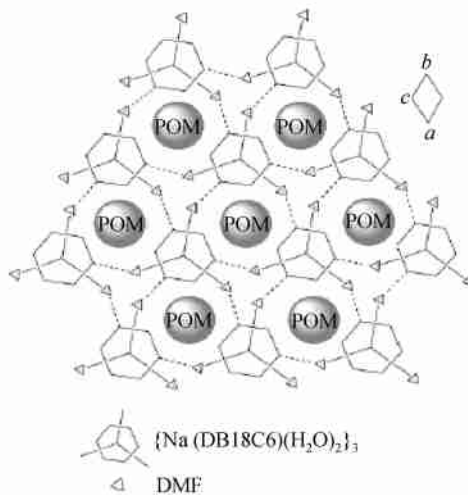


Fig. 12. POMs reside in the network interwoven by crown ethers and DMF.

2 Research progress of POMs in catalysis

POM compounds can be used as catalysts owing to their unique physicochemical properties. POMs are strong Brønsted acid and most of them are stronger in acidity than the usual inorganic acids (HCl, H₂SO₄, HNO₃, HBr), even stronger than HClO₄ and CF₃SO₃H. This is of fundamental importance for POM application in acid catalysis. The differences in the acid strength between heteropolyacids and typical

inorganic acids can be attributed to the fact that heteropoly anions are larger than inorganic acids, so the strength of bonding between the proton and heteropoly anions should be lower, which implies that the dissociation constants should be higher compared to the usual acids. POMs show acidity as well as oxidizing ability. POMs can be profitably used in homogeneous, biphasic, or heterogeneous systems. Several industrial processes based on POM catalysis have been developed and commercialized (Table 3)^[53].

Table 3. Commercialized project catalyzed by POMs

No.	Production	Scale(k t/a)	System	Year	Catalyst	Place
1	2-propanol	50	L	1972	H ₄ SiW ₁₂ O ₄₀	Tokuyama Soda
2	Methacrylic acid	220	G-L	1982	Mo-V-POM	Mitsubishi
3	Tert-butyl alcohol	5.6	L	1984	H ₃ PMo ₁₂ O ₄₀	Asahi Kasei
4	Butyl ketone-2	40	L	1985	H ₃ PMo ₁₂ O ₄₀	Dehigary
5	PTMC	2-3	L	1987	H ₃ PW ₁₂ O ₄₀	Asahi Kasei
6	Acetic acid	10	L	1997	Pd(Te)-SiW ₁₂ O ₄₀	Showa Denko (Oita)
7	Ethyl acetate		L	1997	ibid	
8	2,6-di-tert-butyl-p-methyl phenol	1-2	L	1996	H ₃ PMo ₁₂ O ₄₀	Jilin, Liaoning, Hebei

The primary, secondary and tertiary structures of solid heteropoly acid are important for the understanding of the heterogeneous POM catalysis process. The primary structure is the structure of heteropolyanion itself, i.e. the metal oxide cluster. The secondary structure is the three-dimensional arrangement consisting of polyanions, counter cations and additional molecules. The tertiary structure represents the manner in which the secondary structure assembles into solid particles and relates to properties such as particle size, surface area, and pore structure. Based on this hierarchical structure, it can be demonstrated that there are three completely different modes of catalysis for solid POMs: surface-type catalysis, pseudo-liquid bulk-type catalysis and bulk-type catalysis in the presence of electrons or protons (Fig. 13)^[53]. Surface-type catalysis (Fig. 13(a)) is ordinary heterogeneous catalysis which takes place on the solid surface (two-dimensional reaction field on outer surface). Figure 13(b) and (c) represent bulk-type catalysis where the reaction fields are three-dimensional in contrast to the surface-type catalysis. When the diffusion of reactant molecules in the solid (diffusion in the lattice rather than pores) is faster than the reaction, the solid bulk forms a pseudo-liquid phase in which catalytic reaction can proceed (Fig. 13(b)). In the pseudo-liquid phase such catalysts appear as solids but behave like liquids (solvent). As the active sites in the solid bulk, e.g. protons, take part in catalysis very high catalytic activities are often ob-

served in the bulk phase^[53].

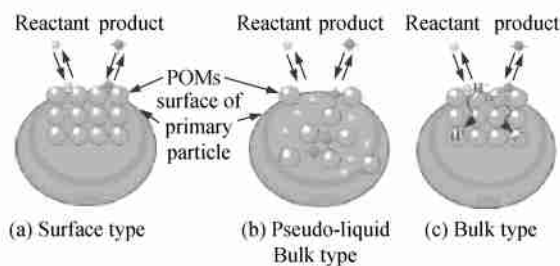


Fig. 13. Three types of catalysis for solid heteropoly compounds: (a) surface type; (b) pseudo-liquid bulk type; (c) bulk type.

On the other hand, POMs are efficient photocatalysts and their photochemical activities originate from their unique structures. They have a number of features in common with semiconductor metal oxide clusters and can be considered to be the analogs of the latter. Both classes of materials are composed of d⁰ transition-metals and oxide ions and exhibit similar electronic attributes including well-defined HOMO-LUMO gaps (semiconductor “band gaps”). The “gaps” inhibit the recombination of electrons and holes that are generated by the irradiation of the surface of the photocatalysts with the light energy higher than the band gaps. The electrons and holes thus formed are capable of initiating chemical reactions because of the formation of OH° radicals resulting from the subsequent reaction of holes and OH⁻ groups coming from water. Their acid-base, redox, as well as photocatalytic or photochemical properties can be

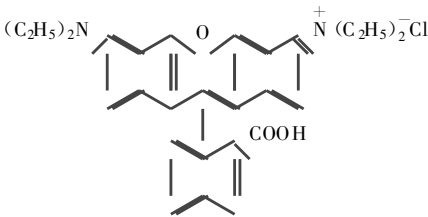
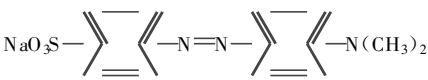
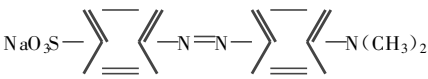
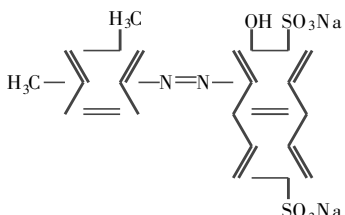
varied over a wide range by changing the chemical compositions.

Soluble POM catalysts can catalyze a large variety of reaction types but suffer from their inability to be recycled. Moreover, the specific surface areas of solid POMs are low ($1-5 \text{ m}^2/\text{g}$), so there are very few active sites on their surfaces. Thus, immobilization of POMs onto solids to create hybrid catalysts is necessary to recovery and possible recyclability. At the same time, their catalytic activities are expected to be improved. In general, the supports used for supporting POMs include silica or titania, mesoporous pure-silica molecular sieve MCM-41 or MCM-48, and activated carbons. Other supported POMs include layered double hydroxide (LDH) pillared by polyanions. The POMs supported or intercalated on the supports are Keggin or Dawson units, or some isopoly compounds e. g. $\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_{3+n}\text{PMO}_{12-n}\text{V}_n\text{O}_{40}$, $\text{PW}_9\text{V}_3\text{O}_{40}^{6-}$, $\text{H}_2\text{W}_{12}\text{O}_{40}^{6-}$, $\text{SiW}_9\text{V}_3\text{O}_{40}^{7-}$, $\text{Mo}_7\text{O}_{24}^{6-}$, $\text{W}_7\text{O}_{24}^{6-}$, and $\text{W}_{10}\text{O}_{32}^{4-}$. Other important solid POMs are acidic Cs salts, $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$, which have

porous structures and exhibit relatively high surface areas ($100-200 \text{ m}^2/\text{g}$) and strong acid sites.

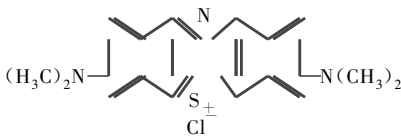
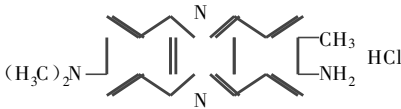
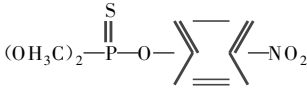
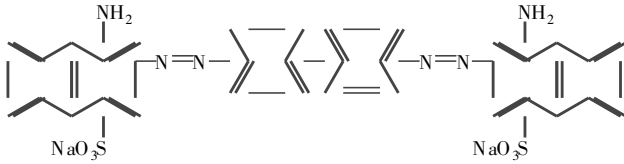
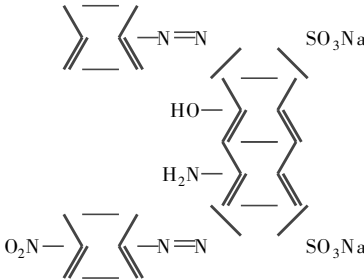
Most recently, we have prepared a series of new and water-tolerant porous POM-containing hybrid catalysts with different pore sizes. These materials were prepared by soft chemical synthesis techniques including sol-gel chemistry, intercalation chemistry, colloidal crystal templating, cluster chemistry, and hydrothermal process, and the interaction between the POM cluster and the porous support was acid-basic, covalent or coordination bond. The inorganic precursors selected were free acids of saturated Keggin units, Paratungstate A, decatungstate, mono- and divacant Keggin-type units, and transition metal substituted polyoxometalate clusters. We also reported the heterogeneous photocatalytic behaviors of these as-prepared materials, including activity, kinetics, and reaction mechanism. The model reactions selected are photodegradation of aqueous pollutants such as pesticides, organic acid, and dyes, which are resistant to biodegradation and direct photolysis (Table 4).

Table 4. Photocatalysis based on the water-tolerant porous POM-containing hybrid catalysts

Photocatalyst	Model molecule	Light source	Time ^{a)} (min)
Microporous $\text{Na}_4\text{W}_{10}\text{O}_{32}/\text{SiO}_2$	$\text{HOOC}-\text{CH}_2-\text{CHOH}-\text{COOH}$	HPM L ^{b)}	60 ^{54c)}
Mesoporous $\text{K}_4\text{Ni}(\text{H}_2\text{O})\text{SiW}_{11}\text{O}_{39}/\text{APS}-\text{SiO}_2$		HPML	180 ⁵⁵
Macroporous $[\text{X}^{n+}\text{W}_{11}\text{O}_{39}]^{(12-n)-}/\text{SiO}_2(\text{TiO}_2)$ or $\gamma\text{-SiW}_{10}\text{O}_{36}^{8-}/\text{SiO}_2(\text{TiO}_2)$	$\text{HOOC}-\text{CH}_2-\text{CHOH}-\text{COOH}$ 	HPML	240
Micro- and mesoporous		Xe lamp	300
$\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$		Xe lamp	180

To be continued

Continued

Photocatalyst	Model molecule	Light source	Time ^{a)} (min)
		Xe lamp	60
		Xe lamp	60
Micro- and mesoporous H ₆ P ₂ W ₁₈ O ₆₂ /TiO ₂		Xe lamp	30 ⁵⁷
PW ₁₁ O ₃₉ ⁷⁻ /TiO ₂ film		HPML	240 ⁵⁸
PW ₁₁ O ₃₉ ⁷⁻ /SiO ₂ film	HCOOH	HPML	260 ⁵⁹
Li ₃ PW ₁₁ TiO ₄₀ /ZrO ₂ K ₇ PW ₁₀ Ti ₂ O ₄₀ /ZrO ₂		HPML	60 ⁶⁰

a) irradiation time for the conversion of model molecule reaching 100%;

b) high pressure mercury lamp;

c) reference.

3 Perspectives

The synthetic chemistry of POMs has seen great progress in the past few years, and each year there are a lot of published papers reporting new POMs. But so far, the formation mechanism of new POMs is not fully understood and usually is described as self-assembly. So rational synthesis of novel POMs and investigation on the mechanism of their formation is still a challenge. It is expected that more and more POMs with novel structures will be produced. Progress has been achieved recently in heterogeneous catalytic reactions of POMs. If the structure, composition and stability of polyanions are properly controlled on supports, solid POMS catalysts will find much wider practical applications. Green chemistry

will play an important role in the future society, and the development of environmentally friendly process catalyzed by POMs has practical significance. It is also expected that there will be more great achievements in POMs' catalytic chemistry.

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