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Polyoxometalates as Catalysts for Biomass Conversion: Properties, Applications, and Regenerability

Haryo P. Winoto[1,*], Rezky O. Anggaswara[1], Dian H. Wahyudi[2,3], Rino R. Mukti[2,4,5], Veinardi Suendo[2], & Ismunandar[2]

[1]Chemical Engineering Department, Institut Teknologi Bandung, Jalan Ganesa No. 10, Bandung 40132, Indonesia
[2]Division of Inorganic and Physical Chemistry, Faculty of Mathematics and Natural Sciences, Institut Teknologi Bandung, Jalan Ganesa No. 10, Bandung 40132, Indonesia
[3]Doctoral Program of Chemistry, Faculty of Mathematics and Natural Sciences, Institut Teknologi Bandung, Jalan Ganesa No. 10, Bandung 40132, Indonesia
[4]Research Center for Nanosciences and Nanotechnology, Institut Teknologi Bandung, Jalan Ganesa No. 10, Bandung 40132, Indonesia
[5]Center for Catalysis and Reaction Engineering, Institut Teknologi Bandung, Jalan Ganesa No. 10, Bandung 40132, Indonesia

*Corresponding author: haryowinoto@itb.ac.id

Abstract

Polyoxometalates (POMs) have emerged as exceptionally versatile catalysts for green chemical reactions, demonstrating significant potential in the sustainable valorization of biomass. Their tunable Brønsted/Lewis acidity and redox properties enable a broad range of chemical transformations, offering remarkable flexibility in process design. This mini review provides a summary of recent advances in the thermocatalytic conversion of biomass using POMs, addressing their utilization as both homogeneous and heterogeneous catalysts. Key reaction pathways, including solvolysis, oxidation, esterification, and condensation, are highlighted as fundamental processes in biomass valorization. A central focus is placed on the crucial challenge of catalyst regenerability and stability, examining strategies to ensure the long-term viability and economic feasibility of these systems while facing the apparent low-temperature stability challenge of POMs. Finally, this review synthesizes current regeneration methods and presents a forward-looking perspective on the future challenges and opportunities in the field of biomass conversion catalyzed by polyoxometalates.

Keywords: *acid catalysis; biomass; catalytic process; polyoxometalates; redox catalysis.*

Introduction

In recent decades, polyoxometalates have attained significant attention due to their wide structural and chemical versatility. Polyoxometalates (POMs), formerly known as heteropolyanions, are large clusters of inorganic molecular anions consisting of high oxidation state metals coordinated by oxo ligands. These complexes consist of pseudo-octahedral metal-oxo building blocks linked by their corner- and edge-sharing oxygens (Breibeck et al., 2022). In general, polyoxometalates can be determined as either isopolyoxometalates [MmOy]n- or heteropolyoxometalates [XxMmOy]n- (A. Gao et al., 2025). POMs can be formed by the expansion of the tetrahedral monomeric metal oxide [MO4]n- to pseudo-octahedral oxoanion {MO6} in conjunction with the formation of a double-bonded pπ-dπ interaction between the transition metal and terminal oxo-ligand due to the existence of vacant transition metal d-orbitals (Kai Walters, 2022).

POMs have been known to have several dominant and common POM structural classes (POM platforms), i.e., Anderson-Evans, Lindqvist, and Dawson. Figure 1 shows the vast structural diversity of POMs that have been developed from foundational types such as the Anderson type to highly intricate assemblies such as the nona-cobalt architecture. This type of evolutionary developed structure resulted from the existence of a highly modifiable metal-oxo cluster surrounding central atoms, typically phosphate or silicate. Nowadays, the majority of widely used hetero-POMs have

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the Keggin structure as their primary structure, due to their thermal stability (Mir et al., 2020). Interestingly, other POM types, such as Wells-Dawsons $[X_2M_{18}O_{62}]^{n-}$ or the X_2M_{18} structure, originate from two lacunary Keggin units $[XM_9O_{31}]^{n-}$, each of them lacking an $\{M_3O_{13}\}$ triad and connected by corner-sharing oxygens (Long et al., 2010). Thus, the Keggin structure is frequently considered as a POM building block. Especially for the catalysis aspect, by modifying the structure of POMs, one can tune their acid-base, redox, and even electron mobility (Iftikhar et al., 2024). The importance of structure modification of POMs has been addressed in many previous reviews. This structure modification, when harnessed carefully, will lead to variation of the physical and chemical properties of the POMs and eventually optimized catalytic properties (T. Wang et al., 2025). Therefore, the discussion of POM usage, structure modification, and their comparison with other more conventional catalysts for bio-product valorization is the goal of this mini review.

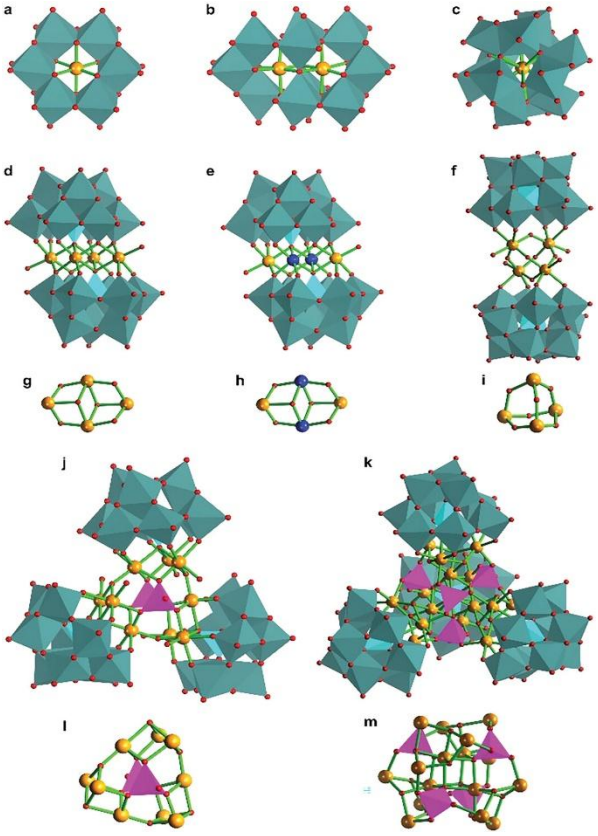

Figure 1

There are various known electron-rich polyoxometalate (POM) structures (Ahmad et al., 2024), such as: a) the Anderson POM structure; b) the Co_2Mo_{10} structure; c) the Dexter-Silverton structure; d) the sandwich-POM structure; e) the sandwich-type POM with a 'cubane' of four different atoms; f) the sandwich-type polyoxotungstate cluster with a central core of tetra-ruthenium oxide $[Ru_4O_4]$, $[Ru_4(\mu\text{-}O)4(\mu\text{-}OH)_2(H_2O)_4](\gamma\text{-}SiW_{10}O_{36})_2]_{10}^{-}$; g) the electroactive tetra-cobalt core Co_4O_4 'cubane', which is usually sandwiched between two oxidatively resistant tri-lacunary units, such as the $[PW_9O_{34}]_9^{-}$, wheel-shaped $[Mo_{154}]$ cluster; h) the same but with another electroactive core and different atoms; i) an electroactive $[Ru_4O_4]$ core stabilized by two units of $(\gamma\text{-}SiW_{10}O_{36})_2]_{10}^{-}$ to make a complete sandwich structure, as shown in (f); j) the nona-cobalt architecture $Co_9(H_2O)_6(OH)_3(HPO_4)_2(PW_9O_{34})_{316}^{-}$ (= Co_9-POM or Co_9); k) a $[CoxFe_4–x(OH)_3\ Fe_4\text{-}x(OH)_3\ (PO_4)]_4$ core surrounded by four $(SiW_9O_{34})_4]n-$ units; l) a central core of Co_9, where orange balls represent cobalt atoms, while pink tetrahedrons show phosphorus atoms; m) an active cobalt-iron core of $[(Co_3Fe(OH)_3PO_4)_4(SiW_9O_{34})_4]_{28}^{-}$.

Properties and Applications of POMs

Polyoxometalates Properties

POMs are renowned for their remarkable catalytic activities with numerous different properties, such as being capable of conducting protons, having a number of anchored oxygen atoms, and possessing metal-redox centers (Yao Zhang *et al.*, 2024). Their excellent catalytic activities for redox reactions results from their electron-transfer properties, so that these materials can also be utilized as good electron storages (Du et al., 2020). POMs themselves sometimes function as very weak bases, since they can connect Lewis acid centers or donate electrons from their surface oxo ligands to electron acceptors groups. POMs are also capable of acting as Lewis acid due to the existence of metal ions with empty orbitals, so that electrons can be accepted onto their surface. Due to previously mentioned properties, alteration of

POM molecules can be done extensively and by carefully modifying their molecules different catalytic properties can be achieved. Thus, as has been reported by several previous studies, POMs' acid-base and redox properties can easily be altered based on the environmental conditions and this trait makes POMs a flexible materials class when it comes to acid-base and redox reactions (Zhong et al., 2021).

Apart from their modifiability, POMs have also been reported to have stable properties, to be capable of transferring protons, while they are also very active in the UV-near visible spectrum. These traits make them versatile for both electrochemical and photochemical redox reactions (Qian Wang *et al.*, 2025). However, it is imperative to bear in mind that acid-base, redox, and chiral properties are greatly affected by external factors such as solvents used, POM-cation interactions, and covalently bonded organic moieties of POM anions. For example, POMs' acidity can be maintained by the existence of a polar protic solvent. Meanwhile, Lewis acidity and redox activity may change due to electron movement between POM cations and anions or an organic moiety attached to them, or for other reasons (Iftikhar et al., 2024). The nature of cations in POMs has been reported to have a significant impact on the properties and solubility of POM molecules. Cations in POMs are usually inorganic ones, for example H^+, Na^+, K^+, Cs^+, NH_4^+, and Ag^+. On the other hand, several currently recognized POMs have organic cations, which can be altered to suit different needs (Soria-Carrera et al., 2023).

Generally, thermal stability of POMs is crucial for supporting catalytic reactions, since various catalytic reactions occur in extreme conditions, and some reactions can produce coke, which leads to catalyst deactivation and loss of active sites. In contrast, POM regeneration or decoking is needed to recover catalytic activity. This process usually requires a high temperature, at which some POM catalysts may lose their active protons. Therefore, POM catalysts require excellent thermal stability to ensure high recyclability. Under high temperatures, POM deactivation typically starts with dehydration, oxygen removal from the supramolecular structure, partial decomposition, and primary structure degradation to form its oxides (Yanmei Zhang et al., 2011). The same work found that the Keggin cubic structure can be preserved at higher temperatures by introducing Cs atoms as its counter-ions. A more recent study had a similar finding for the effect of counter-ion variability towards thermal stability (Misra et al., 2020).

Chemical stability is also found to be an important aspect of utilizing POMs as catalysts. Normally, conventional POMs tend to suffer from leaching in corrosive media (D. Gao *et al.*, 2019; Mialane et al., 2021). Other work has reported that coke formation rapidly deteriorates POM-based catalysts (L. Liu et al., 2023) and, therefore, making catalysts that are less susceptible to coke formation has become an important research focus. In 2001, Kozhevnikov found that Pd-doped POM catalysts can inhibit the formation of polyaromatic coke so that the regeneration temperature decreases (Siddiqui et al., 2000). The chemical stability of POMs, including hydrolytic and oxidative stability, is also crucial for catalytic systems, since water is the commonly used reactant or generated product, and oxidative catalytic requires oxygen-rich systems. In most cases, POMs exhibit remarkable chemical stability due to the non-existence of organic ligands. However, it should be clear that the importance of thermal and chemical stability of POMs relatively depends on the type of catalysis and transformation (Hu et al., 2024; Changzhen Wang et al., 2015).

Table 1 Comparison of known properties that affect catalytic activities of POM-based catalysts and zeolites.

Properties	Factors affecting POM catalysts	Factors affecting zeolite catalysts
BrØnsted acidity	Proton atoms bonded with oxygen in their primary structure (Marcio Jose da Silva *et al.*, 2023)	Bridging hydroxyl groups adjacent to Al atoms (Schroeder *et al.*, 2020)
Lewis acidity	Transition metal sites in their primary structure (Dang *et al.*, 2024)	Intra-framework embedded metals (Al, Sn, Zr, Ti for example) (Ravi *et al.*, 2020)
Redox center	A central atom within the primary structure (R. Wang *et al.*, 2022)	Metal-exchanged atoms within the zeolite framework (Pietrzyk *et al.*, 2020)

Different active site centers have been investigated thoroughly and used accordingly based on the required reaction (Table 1). Once the metal center has been pinpointed and studied, the catalyst's controllability can be enhanced and optimized as well. Due to the controllability of POMs at the elemental and molecular levels, they have been widely utilized for their appealing applications, particularly in catalysis (Y. Liu et al., 2025; Márcio José da Silva et al., 2025; Vizcaíno-Anaya et al., 2025), medicine and biotechnology (Mbage et al., 2023; Salazar Marcano et al., 2024), electrochemistry (Gusmão et al., 2022), molecular magnetism (Clemente-Juan et al., 2012), as well as photoluminescent (Zheng et al., 2024), photochromic (L. Li et al., 2024), sensing (Veríssimo et al., 2022), energy storage applications (Chen Wang et al., 2023) , etc. This mini review presents the latest development on POMs' usage as catalysts, particularly for biomass conversion.

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Polyoxometalates as Catalyst

For over two decades, catalytic materials based on polyoxometalates have garnered considerable attention due to their many advantages in catalysis. Due to the versatility of POM properties, POMs can be used for multiple catalysis reactions, including acid-catalyzed reactions, base-catalyzed reactions, and redox-catalytic reactions (S.-S. Wang et al., 2015). POMs with protons as the only counter-cation, also called heteropolyacids (HPAs), are usually used for acid-catalyzed reactions, such as esterification, transesterification, and solvolysis (Kozhevnikov, 2007). Protons present in POMs or HPAs act as Brønsted acids that can be used as promotors of acid-catalyzed reactions (Timofeeva, 2003). In addition, the oxo ligands on the surface of POMs can transfer electrons to electron acceptors, rendering them appropriate for base-catalyzed reactions. Furthermore, metals in POMs can participate in redox catalytic activities and form Lewis acids, which are active sites for acid-catalyzed reactions (Z. Li et al., 2023). Thus, there are at least four reaction groups that are well catalyzed by POMs (Figure 1): C-O bond scission (solvolysis); C-C bond formation (condensation); R-OR bond formation (esterification); and even oxidation of targeted substances. These catalytic schemes are also known to be well catalyzed by zeolite (Table 2).

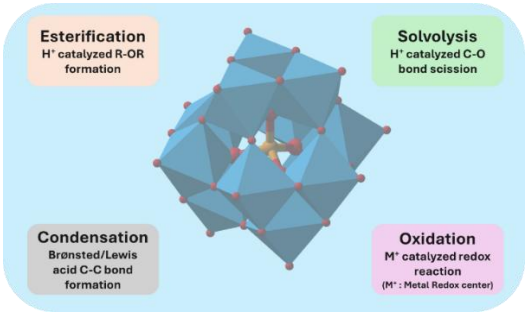

Figure 2 Schematic of recognized biomass valorization reactions that are well catalyzed by POMs.

Interestingly, as can be seen in Table 2, there are a number of studies that discuss and compare the use of zeolites with POMs. Briefly, when these two material classes are used separately, each of them suffers from each's inherent limitations. It can be noted that by embedding POMs into zeolite, one can harness both of those materials' properties, such as the high Brønsted acidity strength of POMs and the thermal stability of zeolites. Thus, these hybrid materials are noteworthy to be studied.

Table 2 Current exemplary comparative POM performances compared with conventional catalysts.

Class of Reactions	Conventional Catalysts	POM-based Catalysts	Key finding	Reference
Hydroisomerization of hexane	Pt/Hβ zeolite	Pt-PW_{12}/Hβ zeolite	Increased yield of hydroisomerized compounds due to the introduction of POM	(Lefebvre, 2016)
Esterification	H-Y zeolite	PW_{12}/HY zeolite	Increased yield of ester compounds due to the introduction of POM	(Patel *et al.*, 2024)
Cascade transformation furfural into GVL	Zr-MOF	POM encapsulated within organic framework	Significant increase of GVL yield from 0 to 58%	(M. Ma *et al.*, 2024)
Alcohol dehydration	H-mordenite	PW_{12}/SiO_2	Significant coke reduction found for POM-based catalyst compared to zeolite-based catalyst	(Alasmari *et al.*, 2024)

POMs/HPAs can be utilized as both homogeneous and heterogeneous catalysts. Their high solubility in most polar and organic solvents (depending on the POM counter-cation) makes them appropriate for effective homogeneous catalytic reactions. In some cases, as demonstrated by Ishii's work, POMs/HPAs can act as catalyst precursors (Mizuno et al., 2006). These compounds can undergo decomposition, resulting in the formation of soluble small active species during the reaction. While excellent reaction rates can be achieved with a homogeneous catalytic system, its drawbacks in terms of product separation and catalyst discovery should not be overlooked. Therefore, it is essential to develop POM-based catalysts that are easy to recover and reuse for practical application in industry. Several approaches have been devised to improve the recoverability and recyclability of POM catalysts, including the heterogenization of originally homogenous POM/HPA catalysts. Heterogeneous catalysis is favored due to the benefit of effortless separation between catalyst and product (Aghajani et al., 2023). While the high solubility of Polyoxometalates (POMs) enables their effective use as homogeneous catalysts or active precursors, the industrial requirement for efficient product separation

and catalyst recovery has required the development of heterogeneous POM systems that combine high reactivity with the practical benefits of easy recyclability. In Table 3, diverse utilization of POM has been tabulated, and from the work of Ghasemi compared with Malmir, slight change in the cationic POM structure might shift its usage thus making it as a versatile class catalyst "building block" that can be modified easily through cation modification.

Table 3 Types of POM-catalyzed reactions.

Reaction Type	Reaction	Used POMs	Reference
Acid Catalysis	Alkene Polymerization: Propene oligomerization Styrene polymerization	Ni-POM/SBA-15 $H_3PW_{12}O_{40}$	(Magazova *et al.*, 2022) (Aouissi *et al.*, 2010)
	Dehydration: Fructose to HMF	Silica-PEI-POM	(Pulido-Díaz *et al.*, 2025)
	Etherification: Cyclization of (+)-citronellal	Homogenous POMs	(Qiwen Wang *et al.*, 2023)
	Cyanosilylation: Aldehydes/ketones compounds to cyanohydrin	TBA-$ZrPW_{11}$	(Yekke-Ghasemi *et al.*, 2022)
	Aminolysis: Aromatic amines to β-amino alcohols	$H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$	(T. Li *et al.*, 2018)
	Condensation: 1,3-dicarbonyl compound condensation with aldehydes and urea	MOF/POM hybrid	(Maru *et al.*, 2022)
	Esterification: Acetic acid esterification with selected alcohol and acid	$H_3PMo_{12}O_{40}/TiO_2.ZrO_2$	(Viswanadham, 2023)
	Transesterification: Long/branched chain triglycerides conversion into biodiesel	$H_3PMo_{12}O_{40}$/SOM-ZIF-8	(Xie *et al.*, 2024)
	Hydrolysis: Hydrolysis of cellulose	$H_5PMo_{10}V_2O_{40}$/Silica	(Qi *et al.*, 2025)
Base Catalysis	Cyanosilylation: Cyanosilylation of carbonyl compounds	TBA-PW_{11}	(Malmir *et al.*, 2022)
	Condensation: Knoevenagel condensation	Cu-containing heteropolyoxoniobate	(Zuo *et al.*, 2024)
Oxidation	Epoxidation: Oxidation of alkenes to epoxides	Na-subtituted $H_3PW_{12}O_{40}$	(Fernández *et al.*, 2023)
	Carbonylation: Oxidation of styrene to benzaldehyde	Fe-Mo Modified $H_3PW_{12}O_{40}$	(Yulin Zhang *et al.*, 2022)
	Dehydrogenation: Dehydrogenation of alkanes to alkenes	$K_5[\alpha\text{-}1,2\text{-}PV_2W_{10}O_{40}]$ (PV_2W_{10})	(Orozco *et al.*, 2020)
	Arenes oxidation: Selective oxidation of anthracene to anthraquinone	Supported-POM	(Maksimchuk *et al.*, 2023)
	Organosilane oxidation: Oxidation of organosilanes to silanols	[CuI3(pz)3{PMo12O40}]·H2O	(X. Ma *et al.*, 2022)
	Phenols oxidation: Oxidation of phenols to produce quinone and its derivatives	2D POM-based coordination polymers	(Chang *et al.*, 2021)
	Alcohols oxidation: Benzyl alcohol to corresponding aldehydes	Ag-Cu/POM	(Lukato *et al.*, 2021)
	Oxidative cleavage of C-C bonds: Lignin depolymerization Glucose, cellulose, and other biogenic feedstocks to formic acid	Pd-doped POM $H_8[PV_5Mo_7O_{40}]$	(L. Zhao *et al.*, 2025) (Maerten *et al.*, 2020)
	Oxidative cleavage of M-C bonds: n-Bu4Sn to 1-butanol	$H_5V_2PMo_{10}O_{40}$	(Khenkin *et al.*, 2013)
Reduction	Reduction of Organic Compounds Hydrogenation of carbonyl compounds	Ru-POM	(Peng *et al.*, 2022)
	Photoreduction of CO_2 Photoreduction of CO_2 to CO	POM-COF	(M. Lu *et al.*, 2022)
	Photoreduction of Metal Cations Photocatalytic metal recovery	$[PW_{11}Si_2O_{40}C_{26}H_{16}N_2]TBA_3$	(Huo *et al.*, 2025)

Generally, there are two strategies to obtain more heterogeneous POMs catalyst, including solidification and immobilization of catalytically active POMs. Insoluble solids can be obtained by complexing POMs with cations that have a suitable molecule size, anion/cation composition, molecular charge, shape, and apparent polarity. These factors result in a strong ionic interaction between the ionic components. For instance, rather than using pure HPAs, POMs with large inorganic counter-cations (e.g., NH_4^+, Cs^+, Na^+, K^+, Ag^+, etc.) or dendritic organic cations are used to achieve lower solubility in polar and organic solvents (Misra et al., 2020). Furthermore, it is possible to solidify POMs through their

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immobilization within MOFs (metal-organic frameworks) (Jia *et al.*, 2024), covalent organic frameworks (COFs) (Xue et al., 2023), mesoporous silica (Ortiz-Bustos *et al.*, 2021), porous polymers (Y. Lu et al., 2021), transition metal oxide (Vilà et al., 2024), porous carbon (S. Ma et al., 2022), and so on. The porous supports, aside from providing a large surface for the distribution of highly active sites, also have the potential to affect the catalytic activity via strong support-HPA interactions that alter the active center atoms.

Heterogeneous POM catalysts certainly have good recoverability and recyclability. However, the modified heterogeneous POM catalyst must also maintain good activity and selectivity for the catalytic reaction, such as an adequate pore structure to facilitate substrate diffusion, including distribution of pore opening, total pore volume, and apparent surface area. In addition, POM catalysts must have notable surface properties, such as hydrophilic/hydrophobic properties designed for specific catalytic reaction systems. Furthermore, it is essential to protect active sites from leaching, thermal decomposition, coke formation, and catalyst poisoning to maintain their catalytic activity (Argyle et al., 2015; R. Liu et al., 2021).

Polyoxometalates for Biomass Conversion

Solvolyis Reaction

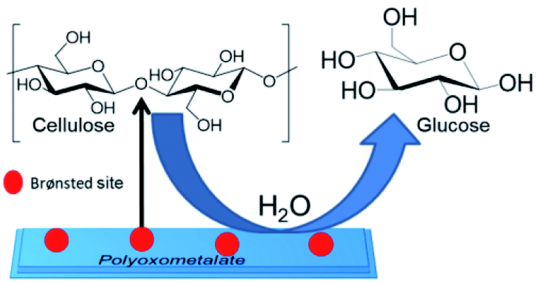
Solvolysis reactions are among the most well-known polyoxometalate (POM) catalyzed processes, owing to the Brønsted acidic nature of POMs. Particularly, this class of material is also known as heteropolyacid (HPA). The heteropolyacid (HPA) structure's intricate network of solvent-facilitated tunnels enables reactants to access more active sites throughout the framework, enhancing catalytic efficiency compared to surface-based catalysis (Mateos et al., 2023). Often, covalent bond cleavage reactions are well catalyzed by the presence of proton atoms (Costentin et al., 2013). The inherent ability of HPAs to act as solid acid catalysts themselves, providing protons to facilitate bond cleavage, has led to their widespread use in solvolysis reactions for biomass conversion and other applications. The tunable acidity and structural versatility of POMs allow for optimized catalytic performance in various solvolysis processes.

Table 4 Solvolysis catalyzed by homogeneous POMs.

State of POM	Solvent	Reaction Feed/Temperature	Ref
$H_3PW_{12}O_{40}$	Water	Cellobiose/120-160 °C	(Q. Liu et al., 2022)
$H_3PW_{12}O_{40}$	Water	Cellulose/180 °C	(Tian et al., 2010)
$H_5BW_{12}O_{40}$	Water	Cellulose/60 °C	(Ogasawara et al., 2011)
HPV_1W	Ethanol/water	Cellulose/180 °C	(Jagannivasan et al., 2025)
HSiW	Ethanol	Celluose/200 °C	(Y. Wang et al., 2022)

Typically, a certain polysaccharide solvolysis reaction is started with an acidic proton and oxygen that bind two monosaccharide units. This phenomenon is followed by conjugated acid formation and eventually ends with C-O bond cleavage. Continuing from the previous step, the formed cyclic carbocation is then rapidly added with water molecules to form sugar molecules.

Figure 3



Schematic of representative selected cellulose solvolysis catalyzed by POM (Nakamura et al., 2021).

Oxidative Reaction

Oxidation reactions are crucial in modern chemistry and the chemical industry, accounting for approximately 30% of total production processes. Traditionally, oxidation was defined as a reaction involving the interaction of a substance with oxygen. Today, oxidation reactions are performed for various purposes, including environmental catalysis, chemical synthesis, and combustion. These reactions play a key role in producing valuable intermediates, such as

alcohols, epoxides, aldehydes, ketones, and organic acids through catalytic oxidation (Niatouri et al., 2023; Qin et al., 2023; T. Zhang et al., 2021).

Oxidation reactions are fundamental to both natural chemical processes and key transformations in organic chemistry. Catalysts play a crucial role in facilitating these reactions and a wide range of catalysts is utilized for oxidative processes. Common catalysts include metal ions, metal complexes, zero-valent metals, metal oxides, and metal-metal oxide composites. Recently, HPA-based catalysts have demonstrated excellent performance in oxidation reactions, as summarized in Table 5. For example, Leng *et al.* reported the successful oxidation of benzyl alcohol to benzaldehyde using hydrogen peroxide (H_2O_2) and HPA catalysts (AVIM-DPB-PW and PDIM-DPB-PW). The aforementioned catalysts displayed high activity and selectivity, and can easily be reused after simple separation (Leng et al., 2012). Additionally, cobalt-containing heteropolyanion-based heterogeneous catalysts have been developed for selective aldehyde oxidation in an aerobic condition. Kholdeeva *et al.* have reported that $TBA_4[HPW_{11}CoO_{39}]$ and $TBA_5[PW_{11}CoO_{39}]$ supported on silica demonstrated high activity and selectivity, achieving 90 to 93% conversion and 98% selectivity to isobutyl acetate (IBAc) after 6 hours at room temperature (kholdeeva, 2004).

Table 5 Oxidative reaction catalyzed by POMs.

Reactant	Catalyst	Temp. (°C)	Time (h)	Product	Conv. (%)	Sel. (%)	Yield (%)		Ref.
2-decanol with H_2O_2	Poly(ethylene oxide-pyridinium) with $H_3PW_{12}O_{40}$	80	24	2-decanone	N/A	N/A	96%		(Yamada *et al.*, 2010)
2-hexanol with H_2O_2	Poly(ethylene oxide-pyridinium) with $H_3PW_{12}O_{40}$	80	24	2-hexanone	N/A	N/A	99%		(Yamada *et al.*, 2010)
Benzyl alcohol with H_2O_2	AVIM-DPB-PW	90	2	Benzaldehyde	92	100	N/A		(Leng *et al.*, 2012)
Benzyl alcohol with H_2O_2	PDIM-DPB-PW	90	2	Benzaldehyde	90	100	N/A		(Leng *et al.*, 2012)
Benzyl alcohol with H_2O_2 Solvent: CH_3CN	[Cu(Phen)(4,4-bpy) $(H_2O)]_2[PW_{12}O_{40}]$. (4,4-bpy)	85	5	Benzaldehyde	85	98	N/A		(Babahydari *et al.*, 2016)
Benzyl alcohol with H_2O_2 Solvent: CH_3CN	[Cu3(4,4-bpy)$_3$] $[HSiW_{12}O_{40}]$・(C3H4N2)	85	5	Benzaldehyde	59	97	N/A		(Babahydari *et al.*, 2016)
Isobutyraldehyde (IBA) with O_2 Solvent: CH_3CN	$TBA_4HPW_{11}CoO_{39}$	20	6	Isobutylacetate	94	N/A	54		(Kholdeeva, 2004)
Formaldehyde with O_2 Solvent: H_2O	$TBA_4HPW_{11}CoO_{39}$	40	5	Acetic acid	20	N/A	5		(Kholdeeva, 2004)
Benzyl alcohol with H_2O_2	$H_6P_2W_{18}O_{62}$@SBA-16	Reflux temp.	6	Benzaldehyde	83	>99	N/A		(Masteri-Farahani *et al.*, 2016)
Cyclooctane with H_2O_2	$H_6P_2W_{18}O_{62}$	Reflux temp.	24	Epoxycyclooctane	>99	>99	N/A		(Masteri-Farahani *et al.*, 2016)
Cellulose in H_2O	$H_8[PV_5Mo_7O_{40}]$	90	24	Formic acid	76	37	N/A		(Albert *et al.*, 2014)
Cellulose in H_2O	$H_5[PV_2Mo_{10}O_{40}]$	90	24	Formic acid	39	48	N/A		(Albert *et al.*, 2014)
Lignin in H_2O	$H_8[PV_5Mo_7O_{40}]$	90	24	Formic acid	100	32	N/A		(Albert *et al.*, 2014)
Lignin in H_2O	$H_5[PV_2Mo_{10}O_{40}]$	90	24	Formic acid	95	33	N/A		(Albert *et al.*, 2014)
Xylan in H_2O	$H_8[PV_5Mo_7O_{40}]$	90	24	Formic acid	100	58	N/A		(Albert *et al.*, 2014)
Xylan in H_2O	$H_5[PV_2Mo_{10}O_{40}]$	90	24	Formic acid	97	55	N/A		(Albert *et al.*, 2014)
Glucose in H_2O	$H_5[PV_2Mo_{10}O_{40}]$	90	26	Formic acid	>98	47	N/A		(Wölfel *et al.*, 2011)
Sorbitol in H_2O	$H_5[PV_2Mo_{10}O_{40}]$	90	26	Formic acid	>98	56	N/A		(Wölfel *et al.*, 2011)
Cellobiose in H_2O	$H_5[PV_2Mo_{10}O_{40}]$	90	26	Formic acid	>98	47	N/A		(Wölfel *et al.*, 2011)
Xylose in H_2O	$H_5[PV_2Mo_{10}O_{40}]$	90	26	Formic acid	>98	54	N/A		(Wölfel *et al.*, 2011)

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Sucrose in H_2O	$H_5[PV_2Mo_{10}O_{40}]$	90	26	Formic acid	>98	48	N/A	(Wölfel *et al.*, 2011)

Albert et al. have explored various Keggin-type heteropolyanions for the selective oxidation of biomass into formic acid. Among these, the heteropolyanion catalyst $H_8[PV_5Mo_7O_{40}]$ (HPA-5) has demonstrated outstanding catalytic efficiency in converting the primary components of lignocellulosic biomass (Albert et al., 2014). Similarly, Wolfel et al. have reported HPA-5 utilization as a homogeneous catalyst for the direct oxidation of multiple biogenic carbohydrate substrates. This reaction exhibits remarkable selectivity, particularly in the production of formic acid (FA) in the liquid phase (Wölfel et al., 2011).

Typically, oxidation of biomass substance follows the Mars–van Krevelen mechanism. In this case, the metal center that acts as oxygen-rich center binds with hydroxyl bonds from biomass-derived compounds. Following the previous step, the water molecule is released and the metal center becomes oxygen-deficient. Reactivation of this center is done through reoxidation by oxygen or oxidant, so that the metal center becomes reactivated.

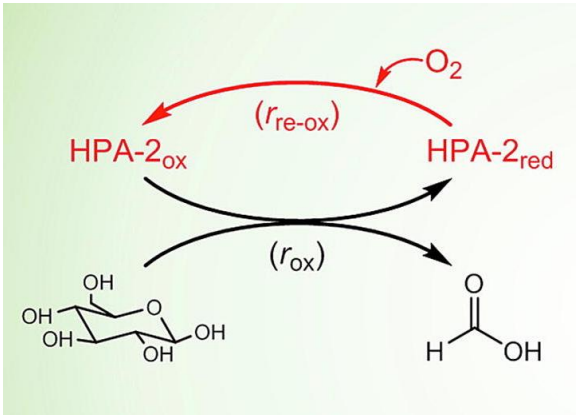

Figure 4

Schematic of representative oxidation of glucose to formic acid (Z. He *et al.*, 2023).

Esterification Reaction

The class of reactions between alcohol and organic acid to produce esters is well-known and has been widely studied in organic chemistry. Esterification is a basic reaction in organic synthesis that results in compounds that can be found in both natural and man-made form. Esters are very important for industry and are a major area of study for many industrial chemists. Common ester-based products include biofuels such as biodiesel (Nisar et al., 2021); solvents such as ethyl acetate, methyl acetate (Yansong Zhou et al., 2022), and butyl acetate; and plasticizers like triacetin and dibutyl phthalate (Huang et al., 2021; Johar et al., 2023). Other examples are ester gums, glyptals, and cellulose-based materials such as cellulose nitrate for paints and cellulose acetate for textiles (El Nemr et al., 2021; W. Liu et al., 2022). Esters are also widely used as flavorings (Jaiswal *et al.*, 2022), food preservatives (Novais et al., 2022), perfumes, fragrances (Alemdar et al., 2023), and ingredients in personal care products (Ortega-Requena et al., 2024).

In order to ramp up the production rate of certain esters, the right organic and/or inorganic catalyst needs to be selected appropriately. Because of this, different ester compounds can be obtained from different types of catalysts. Polyoxometalates (POMs), which are molecular metal oxides formed through early transition metal-oxygen anions condensation, have been utilized as catalysts in esterification reactions. In these POMs, metals like W, Mo, and V are often in their highest oxidation states. For instance, Cardoso et al. in 2008 utilized $H_3PW_{12}O_{40}$ as a homogeneous catalyst to accelerate the reaction rate of the esterification of fatty acids. Studies have shown that this HPW catalyst can be used to produce many things, even when the conditions are not very harsh. This is a substantial advantage compared to traditional homogenous acid catalysts like H_2SO_4 and PTSA. This means that HPW may be an affordable means to make biodiesel, especially if one utilizes oils that have a lot of free fatty acids (Cardoso et al., 2008).

Figure 5 briefly explains a typical esterification of fatty acid with alcohol catalyzed by POM. As the initial step, POM molecules donate their proton atoms to the hydroxyl moiety group to form protonated carboxylic moieties. Subsequently, this step is followed by the formation of a resonance structure. From this step, alcohol molecules and electron-poor carbocation go through an additional reaction, followed by dehydration of the corresponding ester.

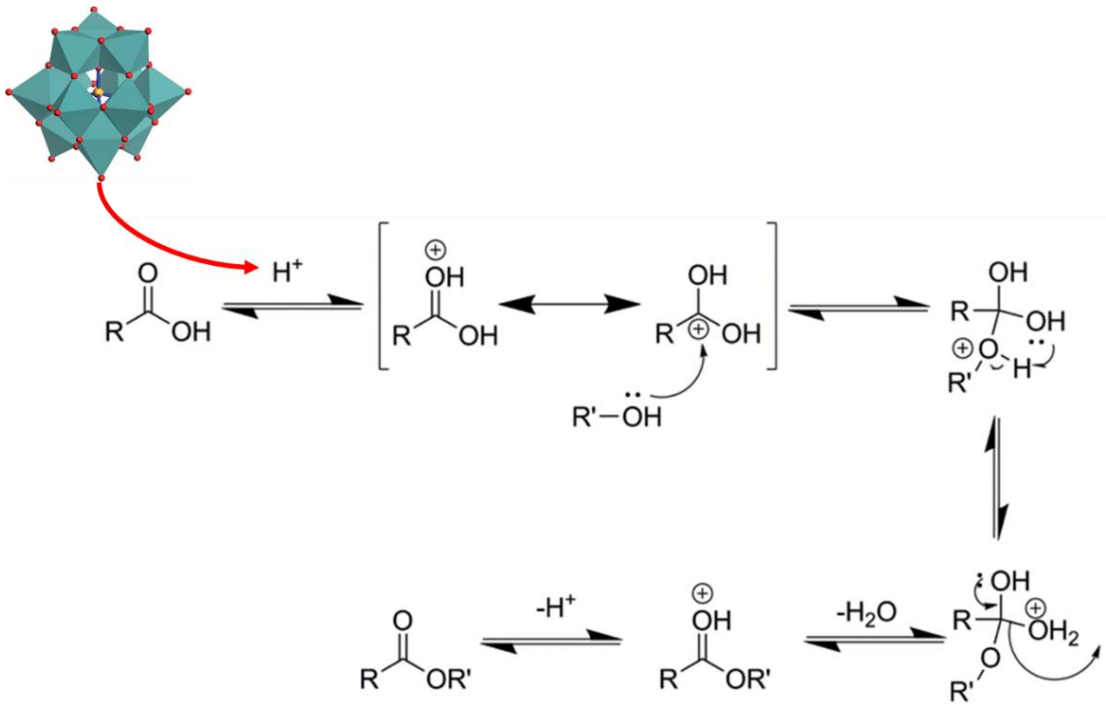

Figure 5

Schematic representation of esterification catalyzed by Keggin polyoxometalate (Abu Hassan, 2017; Vilanculo et al., 2020).

Table 6 Esterification reactions catalyzed by POMs.

Reactant	Catalyst	Temp. (°C)	Time (h)	Product	Conv. (%)	Sel. (%)	Yield (%)	Ref.
Palmitic acid and ethanol	$H_3PW_{12}O_{40}$	Reflux temperature	10	Ethyl palmitate	86	95	N/A	(Cardoso et al., 2008)
Palmitic acid and methanol	$Cs_xH_{4-x}SiW_{12}O_{40}$	60	6	Methyl palmitate	94	98	N/A	(Pesaresi et al., 2009)
Palmitic acid and methanol	$Zn_{1.2}H_{0.6}PW_{12}O_{40}$	65	10	Methyl palmitate	96.1	N/A	97.2	(J. Li et al., 2009)
Palmitic acid and ethanol	$[MIM\text{-}PSH]_xH_{3-x}PW_{12}O_{40}$	80	4	Ethyl Palmitate	90.8	N/A	91.8	(Han et al., 2013)
Oleic acid and ethanol	$H_3PW_{12}O_{40}$	Reflux temp.	10	Ethyl Oleate	90	95	N/A	(Cardoso et al., 2008)
Oleic acid and PEG	$Cs_xH_{4-x}SiW_{12}O_{40}$	130	24	PEG-Monooleate	100	100	N/A	(Abdullah et al., 2017)
Oleic acid and n-butanol	BiPW	100	4	Butyl Oleate	90.1	N/A	N/A	(J. Wang et al., 2014)
Oleic acid and methanol	SWIL/SiO_2	100	4	Methyl Oleate	98.5	N/A	N/A	(Zhen et al., 2012)
Stearic acid and ethanol	$H_3PW_{12}O_{40}$	Reflux temp.	10	Ethyl Stearate	87	97	N/A	(Cardoso et al., 2008)
Stearic acid and n-butanol	BiPW	100	4	Butyl Stearate	88.3	N/A	N/A	(J. Wang et al., 2014)
Linoleic acid and ethanol	$H_3PW_{12}O_{40}$	Reflux temp.	10	Ethyl Linoleate	92	93	N/A	(Cardoso et al., 2008)
Lauric acid and n-butanol	BiPW	100	4	Butyl Laurate	87.7	N/A	N/A	(J. Wang et al., 2014)
Myristic acid and ethanol	$H_3PW_{12}O_{40}$	Reflux temp.	10	Ethyl Myristate	90	97	N/A	(Cardoso et al., 2008)
Myristic acid and n-butanol	BiPW	100	4	Butyl Myristate	88.1	N/A	N/A	(J. Wang et al., 2014)
2-keto-L-gulonic acid and methanol	$K_{2.2}H_{0.8}PW_{12}O_{40}$	65	5	Methyl 2-keto-L-gulonate	N/A	N/A	96	(Vu et al., 2013)
Glycerol and acetic acid	PDVC- $H_3PW_{12}O_{40}$	100	3	TAG	>99	73	N/A	(Betiha et al., 2016)

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From Table 6, it can be seen that most reaction conditions of the esterification reaction do not exceed the reflux temperature. This can be attributed to the substantially low activation energy of POM protonation (Ling *et al.*, 2024). Wang *et al.* used polyoxometalates (POMs) as heterogeneous catalysts to produce fatty acid esters. The BiPW catalyst was also designed to esterify different alcohols with different fatty acids, which is a large improvement compared to traditional homogeneous catalysts. In addition, these different types of catalysts can be easily recovered and used again (J. Wang *et al.*, 2014). The Cs HPA (Cesium heteropolyacid) is another example, which is a strong Brønsted acid catalyst that works very well in making PEG-monooleate ester. When oleic acid and PEG-600 were used at a 1:4 molar ratio, the catalyst achieved 100% selectivity for PEG-monooleate without producing any byproducts (Abdullah *et al.*, 2017). Table 4 shows a summary of other POM-based catalysts that are used in esterification reactions to make different ester products.

Condensation Reaction

Condensation reactions provide a facile route to synthesize larger products with desirable properties and functionalities that can be utilized for selected biofuels and specialty chemicals production. These reactions can be conducted in more benign conditions with the use of homogeneous or heterogeneous acid, base, or amphoteric catalysts. Heteropolyacid catalysts have been recognized as suitable catalysts for condensation reactions. Based on Julian's work (Sánchez-Velandia *et al.*, 2022), HPA, especially phosphotungstic acid, can catalyze the condensation reaction of monoterpenes and aldehydes, resulting in heterocyclic products of various types, such as 3-oxabicyclo [3,3,1] nonane, that can be used as biological precursors. Furthermore, Ferreira (Ferreira *et al.*, 2010) has demonstrated that heteropolyacid can be used for the utilization of glycerol, which is the byproduct of biodiesel production by transesterification of triglyceride with methanol or ethanol. Glycerol can be converted to solketal through a condensation reaction with acetone (conversion >99% and selectivity 97%). Solketal is known as an additive in fatty acid methyl ester fuel production, improving its cold flow properties.

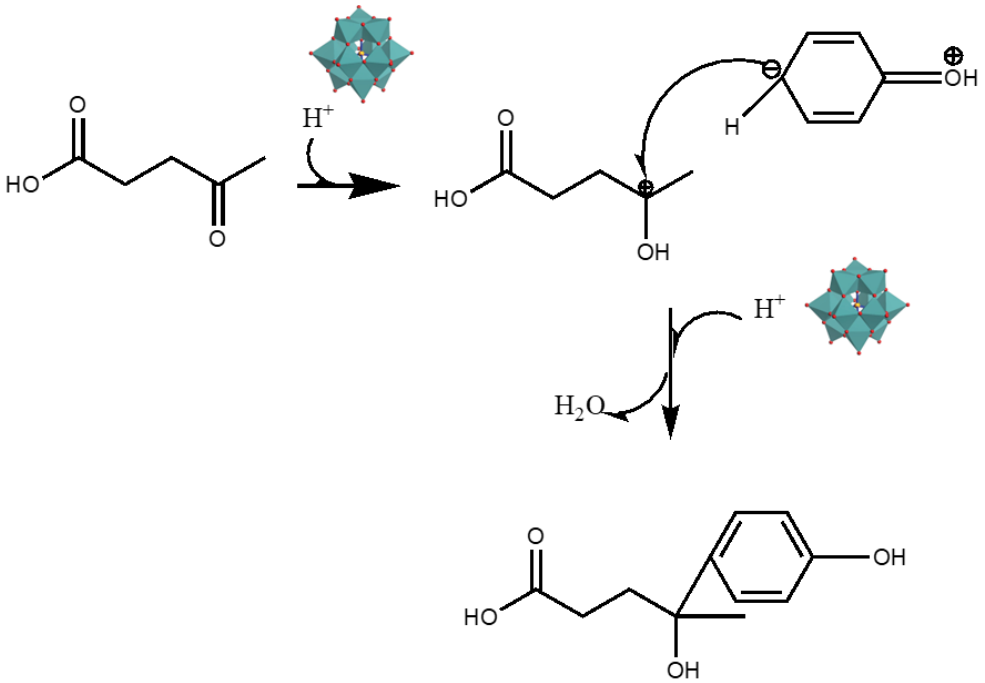

Figure 6

Schematic of representative aldol condensation catalyzed by Keggin polyoxometalate (Guo et al., 2008).

Figure 6 briefly describes the aldol condensation mechanism. The reaction is always started with the protonation of aldehyde substance to form electron-poor carbocation moiety groups. This step is followed by C-C bond formation from electron rich moiety groups such as hydroxyl and aromatic ones. Subsequently, by another addition of proton atoms from the POM followed by the release of H_2O molecules, an aldol product (adduct) is formed. Formaldehyde and methyl formate, which are produced in significant quantities from coal and natural gas derivatization, can also be utilized as more valuable chemical intermediates through condensation reactions. He *et al.* demonstrated formaldehyde condensation with methyl formate to obtain methyl glycolate and methyl methoxy acetate, which are important for chemical intermediate medicine production. Furthermore, Rahaman *et al.* conducted the synthesis of diphenolic acid (DPA) via a condensation reaction of levulinic acid and phenols using an $H_3PW_{12}O_{40}$ catalyst. Diphenolic acid is already

known as a potential renewable alternative for toxic bisphenol A (BPA) in water bottles, containers, and dental sealants. Other uses of heteropolyacid catalysts for condensation reactions are summarized in Table 5.

Table 7 **T**Condensation reactions catalyzed by POMs.

Reactant	Catalyst	Temp. (°C)	Time (h)	Product	Conv. (%)	Sel. (%)	Yield (%)	Reference
Limonene and benzaldehydes	$H_3PW_{12}O_{40}$	50	5	3-oxabicyclo [3,3,1] nonane	>99	80	N/A	(Sánchez-Velandia et al., 2022)
Glycerol and acetone	$H_3PW_{12}O_{40}$	70	6	(2,2 dimethyl-[1,3]di oxan-4-yl)-methanol (solketal)	>99	97	N/A	(Ferreira et al., 2010)
Formaldehyde and methyl formate	$H_3PW_{12}O_{40}$	160	5	Methyl glycolate and methyl methoxy acetate	N/A	N/A	16 mmol/g-cat	(D. He et al., 1999)
Benzene and formaldehyde	$H_3PW_{12}O_{40}$	160	2	Diphenylmethane	93.2	37.9	35.3	(Hou et al., 2003)
Benzaldehyde and ethyl cyanoacetate	$Na_8H[PW_9O_{34}]$	25	6	Ethyl 2-cyano-3-phenylacrylate	N/A	N/A	83	(Yu Zhou et al., 2014)
Levulinic acid and phenols	$H_3PW_{12}O_{40}$	100	6	Diphenolic acid	87	98	N/A	(Rahaman et al., 2021)
O-methoxy benzaldehyde and phenols	$H_3PW_{12}O_{40}$/Si-MCM-41	100	3	4-[(4-hydroxyphenyl) (phenyl)methyl]phenol	N/A	N/A	73.8	(Udayakumar et al., 2006)

POM Catalyst Regenerability

Typically, POM catalysts cost more than conventional mineral/organic acids, thus making them reusable is important for their practical utilization. Since POMs can be utilized as either homogeneous or heterogeneous catalysts, regeneration methods and strategies for POM catalysts may vary depending on the reaction system, catalyst stability, and other issues to be considered, such as the potential for structural degradation, leaching, aggregation, and catalyst poisoning (Schwiedrzik et al., 2023). For example, in homogeneous catalysis systems, the primary challenge lies in the difficulty of separating the product from the catalyst. In contrast, in heterogeneous catalysis systems, the main issue is the loss of active sites (Darekar et al., 2025). As tabulated in Table 8, conventional regeneration methods employ standard physical unit operations, such as precipitation, solvent extraction, and membrane filtration, to isolate catalysts based on distinct physicochemical differences. More comprehensive design strategies focus on modifying the catalyst architecture with ionic liquids or responsive surfactants to engineer intrinsic, tunable phase-separation behaviors, and the second approach has been attracting numbers of researchers lately.

Table 8 Regeneration methods/strategies for homogeneous POM catalysis systems.

Strategies/Methods	Descriptions	Ref
	Regeneration Methods	
Precipitation	HPA can be recovered from polar organic solutions without neutralization by precipitating with a hydrocarbon solvent	(Nlate *et al.*, 2007; Schmid *et al.*, 2022)
Decantation	Removing the liquid layer at the top from the layer of solid or liquid below	(Zhu *et al.*, 2013)
Solvent extraction	HPA can be extracted from an acidified aqueous solution of its salt with a polar organic solvent	(Yunfei Zhang *et al.*, 2024)
Solvent evaporation	HPA in ethanol or water can be recovered by evaporation of the solvent	(Heravi *et al.*, 2018)
Membrane filtration	Separation through nanofiltration	(Esser *et al.*, 2022)
Biphasic system	Certain system that separates catalyst and reaction mixture into two phases	(Schmid *et al.*, 2022)
	Regeneration Strategies	
Ionic liquid-POM	Incorporation of room temperature ionic liquid to tune POM solubility	(H. Wang *et al.*, 2024)
Surfactant type catalyst	Catalysts that have surfactant properties and mostly have automatic behavior, sensitive to temperature, chemical, or light	(J. Zhao *et al.*, 2023)

Only a limited number of homogeneous reactions facilitate straightforward POM catalyst recycling, such as olefin hydration (Y. Ma et al., 2022). Moreover, in some cases, POM catalysts can also decompose to small active species during the reaction, which could make it more challenging to recover and recycle the catalyst, requiring additional

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purification steps. Homogeneous POM catalysts can be separated and reused through various methods, such as precipitation (Nlate et al., 2007), decantation (Zhu et al., 2013), solvent extraction (H. Zhang et al., 2024), solvent evaporation (Heravi et al., 2018), and membrane filtration (Esser *et al.*, 2022). One more viable strategy to overcome the separation problem is the utilization of a biphasic catalytic system (Schmid et al., 2022; Wan et al., 2023) and surfactant-type modified catalyst (J. Zhao et al., 2023). A certain homogeneous catalytic reaction with a biphasic system allows easier separation, since the reaction system can be separated into two liquid phases during the reaction. The biphasic system consists of two immiscible liquid phases: the catalyst phase and the product phase. The catalyst phase is usually in the heavier first layer, insisting on a solution of POM with a polar solvent. The higher phase, on the other hand, allows for the transfer of the organic product with its less polar solvent (Schmid *et al.*, 2022). Furthermore, some POM catalysts can be modified with cationic surfactants, which can be applied for the homogenization of catalysts with non-polar organic solvents (Leng et al., 2009). For easier separation, a cationic surfactant with a dendritic type is preferable, since it can make the catalyst easily recover precipitation from organic solvents of low polarity (Nlate et al., 2007).

The regeneration methods and strategies of heterogeneous POM catalysts are quite different from those of homogeneous ones. In heterogeneous catalysis, the main regeneration problem is the deactivation of active sites through decomposition, leaching, poisoning, aggregation, dehydration, and especially coke formation in organic catalytic reactions (Ni et al., 2025). To understand optimum coke removal, one needs to consider the nature of coke formation. Soft coke, which can be considered as an oligomer of hydrocarbon, tends to form at lower temperatures (Al-Shathr et al., 2023). Along with catalytic reaction progression, highly polymerized hydrocarbon is steadily formed to produce hard coke (Verdeş et al., 2022). Conventional heterogeneous catalyst regeneration through a decoking process or aerobic oxidation in 450 to 550 °C is not suitable for POM catalysts, because their thermal stability is insufficient. For instance, the temperature at which Keggin HPAs lose all their acidic protons decreases in the following order: $H_3PW_{12}O_{40}$ (465 °C) > $H_4SiW_{12}O_{40}$ (445 °C) > $H_3PMo_{12}O_{40}$ (375 °C) > $H_4SiMo_{12}O_{40}$ (350 °C) (Kozhevnikov et al., 2001). At higher temperatures, the Keggin structure may undergo decomposition to form the constituent oxides but follow the same order: 610, 540, 495 and 375 °C, respectively (Pandey, 1994). Thus, it is important to select viable regeneration methods, enhance the catalyst's thermal stability, and inhibit coke formation during the reaction.

Other regeneration methods have also been attempted to make up for the drawbacks of the conventional methods, such as solvent extraction and ozone treatment. Soluble coke can be removed from the recovered catalyst through solvent extraction using suitable solvents such as CCl_4 and CH_2Cl_2 due to similar coke-solvent polarity. Moreover, the coke removal process can also be conducted using SO_2 or CO_2 through supercritical extraction (Steven A. Bradley et al., 1989). However, this method cannot be used to remove insoluble coke (mostly hard coke), resulting in lower catalytic activity of the recycled catalyst. It can have the potential to dismember the catalyst network through leaching (Dashtian et al., 2024). Furthermore, ozone treatment can also be used to regenerate heavily coked HPA catalysts by oxidizing them at a temperature as low as 150 °C. Thus, this method can prevent the destruction and loss of active sites of HPA catalysts in contrast to conventional oxygen regeneration (Srour et al., 2019). However, these two methods are not practical on a large scale due to their inefficiency and high costs.

Based on the aforementioned regenerability issues, some researchers have focused on modifying and developing solid HPA catalysts with high thermal stability to enhance their regenerability. It is known that anchoring HPA to metal oxide surfaces renders the catalyst more thermally stable. Previous studies have reported that by modifying the structure of POMs, their recyclability can also be improved (Devassy et al., 2006; Okumura et al., 2007). However, lower acidity results from this recycling activity, which means their activity as acid catalyst are impaired compared to fresh catalyst. Researchers have also made HPA bonded with ferromagnetic nanoparticles such as Fe_3O_4 to make it separable by magnetic field (Ayati et al., 2016).

Other methods to regenerate catalysts include doping addition and coke inhibitors utilization. The addition of platinum group metals (PGM) such as Pd and Pt to HPA catalysts has been reported as a good strategy for coke inhibition (Alhanash et al., 2010). These metal additives assist the bifunctional metal-acid mechanism of alkane conversion and make the catalyst more stable against coking (Kozhevnikov et al., 2001). This metal doping can prevent polyaromatic as the precursor of hard coke from forming, which lowers the temperature needed for regeneration (Alhanash et al., 2010). However, it is important to take into account that PGM doping may also lead to the occurrence of side reactions, which could make the process less selective. In aqueous solvent cases, for acid-catalyzed processes that can handle water, adding nucleophilic molecules like water, methanol, and acetic acid can help in preventing coke from forming. These nucleophilic molecules can react with the carbenium ion intermediate, which is the coke precursor, to make oxygenates. This can automatically lower the amount of coke that forms (Alhanash et al., 2010).

Putting it into a more simplified explanation, Figure 7 shows typical POM catalyst recycling and regeneration strategies, which commonly involve either a modified or unmodified structure. For any strategy that includes structure modification, certain POM molecules can be separated from the reaction mixture easily, either utilizing different polarity or ferromagnetism properties. More practical approaches such as physical separation, solvent extraction, and usage of ozone usually do not require tedious structure modification, but the risk of activity loss during regeneration still has to be mitigated carefully.

Table 9 Regeneration methods/strategies for heterogeneous POM catalysis systems.

Strategies/Methods	Definition	Ref
	Regeneration Methods	
Ozone treatment	Coke removal with ozone acts as the oxidant and provides a lower regeneration temperature	(Kozhevnikov et al., 2001; Srour et al., 2019)
Solvent extraction	Coke removal using a solvent	(Yunfei Zhang et al., 2024)
Aerobic oxidation	Conventional coke removal using oxygen at high temperatures has the potential to cause HPA catalyst decomposition	(Kozhevnikov et al., 2001)
	Regeneration Strategies	
Immobilization	Trapping or coating HPA in metal oxide composites to enhance catalyst thermal stability	(Alhanash et al., 2010; Devassy et al., 2006)
Doping	Use of metal additives to improve catalyst stability against coking	(Ji et al., 2025)
Coke inhibitor	Addition of nucleophilic molecules to reduce coke formation	(Alhanash et al., 2010)

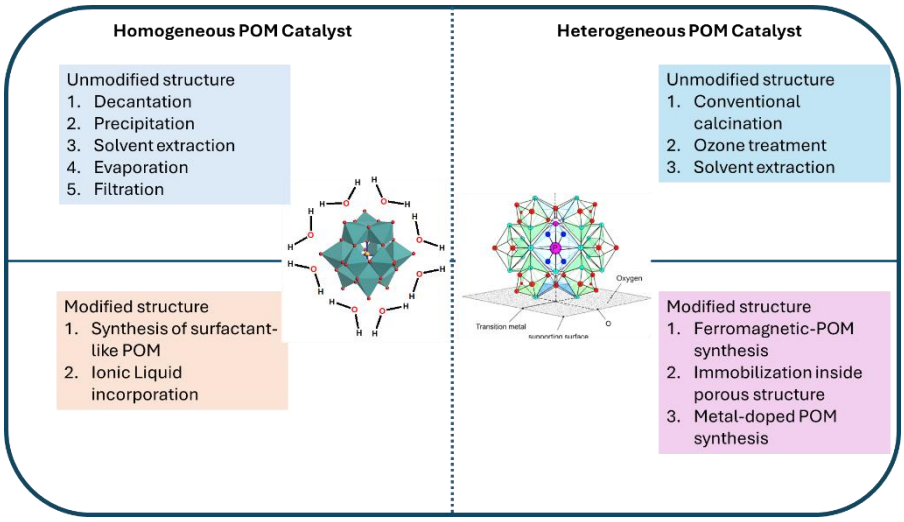

Figure 7

Schematic drawing of known strategies for POM catalyst recycling and regeneration.

Industrial Utilization of POM Catalysts

In the end, industrial applications of POM catalysts are the aspect that is required for sustainable utilization of POMs in biomass valorization. In the field of biomass valorization through conventional thermal catalytic schemes, the use of POMs is still hindered by their deactivation through rapid coke formation and catalyst leaching (Jiang *et al.*, 2025; Xiao *et al.*, 2023). Thus, the use of POMs in biomass valorization through photo/electrocatalysis needs to be developed (Shah *et al.*, 2024). Remarkable inherent proton conductivity, tunable redox properties, and modifiability of POMs are versatile options for multiple catalytic reactions, thus making them viable for any chemical industry as a more sustainable approach in the future (Yu Zhang *et al.*, 2019). Remaining challenges in improving the structural stability of POMs during catalyst regeneration is pivotal for their application in future industrial-scale application.

Conclusion

Polyoxometalates (POMs) have emerged as versatile and effective catalysts for biomass conversion due to their tunable acidic and redox properties. This review comprehensively discussed the properties, preparation methods, and applications of POMs in catalytic processes, with a focus on their use in biomass valorization. POMs demonstrate

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excellent performance in various reactions, including oxidation, esterification, and condensation. Their ability to function as both homogeneous and heterogeneous catalysts offers flexibility in their application. However, the challenge of catalyst recovery and recycling, particularly for homogeneous systems, has led to the development of heterogeneous POM catalysts through solidification and immobilization techniques.

The reusability aspect of POM catalysts is crucial for their practical application. Different regeneration strategies have been explored for both homogeneous and heterogeneous systems, addressing issues such as product separation, catalyst deactivation, and thermal stability. These activities include the usage of biphasic solvent systems, surfactant modifications, doping addition, and the development of more thermally stable solid POM catalysts.

Future research in this field should be directed to further enhance the thermal and chemical stability of POM catalysts, improving their regenerability and developing a more benign heterogeneous catalytic system that allows lower-temperature usage. Thus, by developing more benign conditions and also more thermally stable POM catalysts, their usage in biomass valorization for producing biofuels and chemicals can contribute to the development of sustainable green chemistry and chemical engineering. In conclusion, POMs have been shown to have great potential as catalysts for biomass conversion, offering a combination of high activity, selectivity, and potential for regeneration. Continued research and development in this area may significantly contribute to the advancement of sustainable chemical processes and the utilization of renewable resources.

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Compliance with ethics guidelines

The authors declare they have no conflict of interest or financial conflicts to disclose.

This article contains no studies with human or animal subjects performed by the authors.

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