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Preparation of Phosphotungstic Acid Materials and Their Application in Acidic Redox Catalysts

Xiang Fan

College of Materials Science and Engineering, Zhejiang University of Technology, Hangzhou, China
11581399@qq.com

Abstract. Phosphotungstic acid ($H_3PW_{12}O_{40}$) is a typical representative of Keggin-type heteropoly acids. Its superstrong Brønsted acidity with $H_0 \leq -13.16$ and reversible multi-electron transfer ability of W^{6+}/W^{5+} endow it with a unique position in the field of acidic redox catalysis. This paper reviews the research progress of phosphotungstic acid-based catalysts over the past 15 years from five dimensions: structural characteristics, preparation methods, immobilization strategies, catalytic applications and device configurations. In oxidative desulfurization, ultra-deep desulfurization (<10 ppm) and multiple cycles have been achieved in multiple systems. In energy devices, heteropoly acid-based flow batteries deliver an output of 282.4 $mW \cdot cm^{-2}$ at -20 °C, and cobalt-tungstic acid fuel cells reach an energy density of 27.2 $Wh \cdot L^{-1}$. In photocatalysis, the H_2O_2 yield of the phosphotungstic acid (HPW)@COF system reaches 897.94 $\mu mol \cdot L^{-1} \cdot h^{-1}$. Host-guest confinement immobilization is the core pathway to solve the problem of homogeneous recovery.

Keywords: Phosphotungstic acid, Acidic redox catalyst, Heteropoly acid, Keggin structure, Catalytic oxidation

1. Introduction

Acidic redox catalysis is one of the core research directions in the fields of green chemistry and clean energy, and its key lies in the efficient coupling of two elementary steps, proton transfer and electron transfer, in the same catalytic system [1]. With the dual catalytic features of superstrong Brønsted acidity ($H_0 \leq -13.16$) and reversible multi-electron transfer ability of W^{6+}/W^{5+}, phosphotungstic acid exhibits outstanding application potential in oxidative desulfurization, low-temperature redox flow batteries [2], direct liquid fuel cells [3] and photocatalytic H_2O_2 production [4]. Ai et al. constructed a low-temperature aqueous flow battery with Dawson-type heteropoly acid, which delivers a power density of 282.4 $mW \cdot cm^{-2}$ at -20 °C. Liu et al. designed HPW-based renewable fuels through redox potential engineering, achieving an energy density of 27.2 $Wh \cdot L^{-1}$ for DLFC. Rong et al. realized an H_2O_2 yield of 897.94 $\mu mol \cdot L^{-1} \cdot h^{-1}$ with the HPW@COF photocatalytic system. This paper systematically reviews the structural characteristics, preparation methods, immobilization strategies and catalytic applications of phosphotungstic acid, and discusses the design points of five typical catalytic devices, so as to provide references for the rational design and practical application of phosphotungstic acid-based acidic redox catalysts.

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2. Introduction to acidic redox catalysts and their devices

2.1. Introduction to acidic redox catalysis

Acidic redox catalysis describes a type of catalytic process in which the catalyst simultaneously utilizes its acidic centers and redox centers to drive chemical transformation in an acidic environment. Compared with acid catalysis or oxidation catalysis that only relies on a single function, the advantage of this bifunctionality lies in the synergy of the two pathways: acidic sites are responsible for activating substrates, guiding proton transfer and stabilizing reaction intermediates, while redox sites complete electron transfer in a relay manner.

This paper will focus on systems where two types of active centers coexist in the same catalyst. Supported noble metal catalysts belong to supported two-component systems, in which the acid function (support) and redox function (metal) are distributed in different phases or sites, and the synergy mechanism usually involves interfacial mass transfer steps. They are essentially different from the single-component bifunctional Keggin anion system focused on in this paper, and thus are not included in the core discussion.

In organic synthesis, acidic redox catalysts have been applied to reactions such as selective oxidation of alcohols, epoxidation of olefins and oxidative desulfurization of sulfides [1, 5]. In the energy field, related materials represented by heteropoly acids have entered the research scope of redox flow batteries and direct liquid fuel cells. In the environmental field, such catalysts can photocatalytically produce H_2O_2 or oxidize and transform heavy metal ions [5]. The above applications jointly point to a core issue: how to obtain catalysts with both sufficient acid strength and redox activity.

2.2. Classification of acidic redox catalysts

According to the chemical composition and structural characteristics of active components, acidic redox catalysts can be mainly divided into the following four categories (as shown in Table 1): heteropoly acid catalysts, transition metal oxide catalysts, supported noble metal catalysts and metal-organic framework (MOF)-based catalysts [6-9].

According to the strict definition given in Section 2.1, that is, two types of active centers must coexist in the same catalyst and operate synergistically: among the above four categories, only HPAs (typically phosphotungstic acid) and some MOF-based catalysts (HPAs-encapsulated type) fully meet this criterion. Although transition metal oxides have both surface acidic sites and redox metal centers, they are prone to structural degradation under strong acid conditions. The acidic support and metal active components of supported noble metals are physically combined, which does not conform to the strict definition of "the same catalyst". Therefore, the following part of this paper focuses on the heteropoly acid system represented by phosphotungstic acid.

• (1) Heteropoly acid catalysts. Heteropoly Acids (HPAs) are metal-oxygen clusters assembled from heteroatoms (such as P, Si) and addenda atoms (such as W, Mo) via oxygen bridges, among which the most classic is phosphotungstic acid ($H_3PW_{12}O_{40}$) with Keggin structure. The Hammett acidity function H_0 of HPAs can reach -13.16, much lower than that of concentrated sulfuric acid (-11.93), and they can reversibly accept and release multiple electrons without destroying the Keggin skeleton. Colombo Migliorero et al. [6] summarized the dual roles of HPAs as acid catalysts and oxidation catalysts in organic synthesis in a review, and discussed the synergistic effect of these two functions in the same reaction.

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• (2) Transition metal oxide catalysts. Transition metal oxides such as MnO_x, V_2O_5, CeO_2 and WO_3 constitute another important branch of acidic redox catalysis. Lewis acid sites and variable-valence metal cations are simultaneously distributed on their surfaces, so they perform well in selective oxidation reactions. Liu et al.'s research points to WO_3 and its derivatives, suggesting that such materials have potential in photocatalysis and electrocatalytic water oxidation by virtue of their high redox activity and acidic surface sites. A problem that has not been fully solved is the structural degradation of transition metal oxides under strong acid conditions.

• (3) Supported noble metal catalysts. Loading Pt, Pd, Ru, Au nanoparticles on acidic supports (acidic molecular sieves, sulfonated carbon, WO_3-ZrO_2, etc.) is a classic approach to achieve acid-redox bifunctional catalysis under heterogeneous conditions. The acidic centers of the support and the redox activity of noble metals act synergistically, which has been verified in hydroformylation and selective oxidation of alcohols. The high cost and resource constraints of noble metals limit the large-scale promotion of such catalysts.

• (4) MOF-based catalysts. The tunable channels and abundant unsaturated metal sites of metal-organic frameworks open up space for the rational construction of acidic redox catalysts. Encapsulating HPAs into the nanocages of MIL-101(Cr) or ZIF-67 not only retains the strong acidity of phosphotungstic acid, but also inhibits the loss of active components through the confinement effect. Jiang et al. co-encapsulated HPW and ionic liquid BMImBr in MIL-101(Cr), and the obtained BMImPW@MIL-101(Cr) has both high activity and stable cycling performance in oxidative desulfurization. Mohamed et al. [7] loaded HPW into ZIF-67, and demonstrated the enhancement effect of encapsulation on the stability and antibacterial activity of HPW through a combination of DFT and experiments. These studies collectively show that phosphotungstic acid in MOF encapsulation systems not only maintains superstrong Brønsted acidity ($H_0 \leq -13.16$) and reversible multi-electron transfer ability of W^{6+}/W^{5+}, but also obtains additional dispersibility and anti-leaching property due to the confinement effect. From the perspective of practical application, the dissolution loss of encapsulated phosphotungstic acid catalysts in solvents is greatly reduced, and they can be recycled for many times with limited activity decay. The specific surface area and accessibility of active sites are also significantly improved due to the confinement of nanochannels. These engineering properties lay a foundation for subsequent continuous flow operation and industrial scale-up [7]. The classification and typical representatives of acidic redox catalysts are shown in Table 1.

Table 1. Classification and typical representatives of acidic redox catalysts

Catalyst Category	Active Components	Acid Source	Redox Mechanism
Heteropoly acids	$H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$	Brønsted acid protons, Keggin structure	Reversible valence change of W^{6+}/W^{5+}, multi-electron transfer
Transition metal oxides	MnO_x, V_2O_5, CeO_2, WO_3	Lewis acid sites, surface hydroxyl groups	$M^{n+}/M^{(n-1)+}$ redox couple
Supported noble metals	Pt, Pd, Ru, Au / acidic support	Acidic sites of support (molecular sieves, etc.)	Electron transfer via noble metal d-orbitals
MOF-based composites	HPW@MIL-101, HPW@ZIF-67	HPAs protons + MOF unsaturated sites	Confinement effect + HPAs valence change

2.3. Acidic redox catalyst devices

Catalytic devices are the bridge that promotes catalytic materials from laboratory to practical application. Different types of reactions (gas-solid, liquid-solid, gas-liquid-solid three-phase) require

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matching device configurations, and operation modes (batch/continuous) and energy inputs (heat, electricity, light) also have their own requirements. The following summarizes five mainstream devices from these three perspectives.

2.3.1. Batch reactor

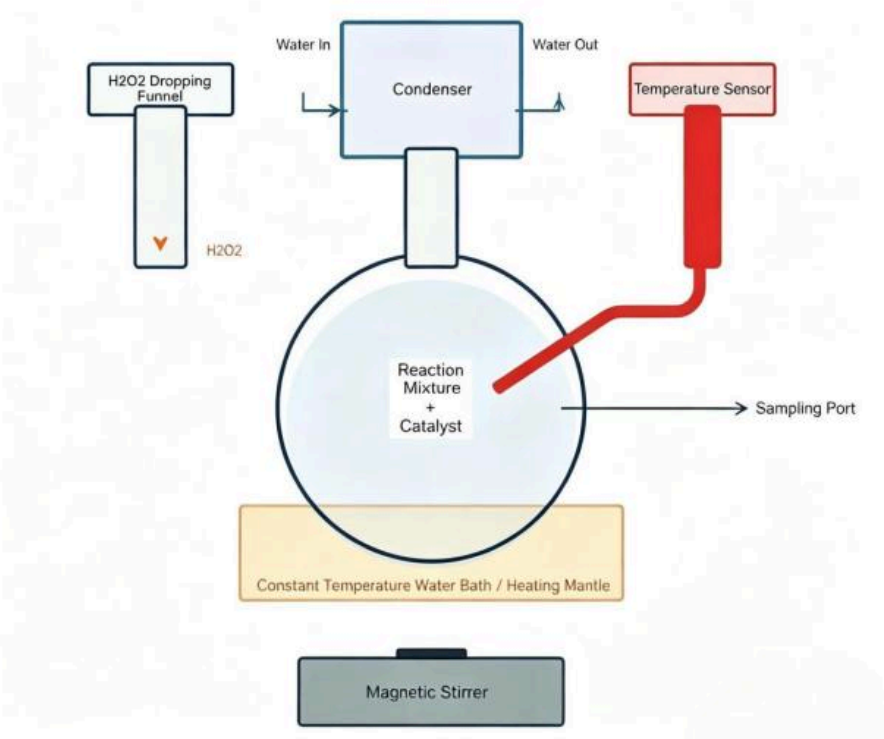


Figure 1. Schematic diagram of batch reactor

Zhong et al. [8] used a three-necked flask system in the oxidative desulfurization work: the flask was immersed in a 50 °C water bath, and magnetic stirring maintained the dispersion of $ZrPTA_x$-BTC in the oil phase. A constant-pressure dropping funnel controlled the addition rate of H_2O_2, and a condenser prevented volatilization loss. Under the condition of O/S=4, dibenzothiophene was completely removed within 30 minutes. Xiong et al. [9] adopted a similar configuration in the CQDs/C_{18}PWIL system, and also achieved quantitative desulfurization within 30 minutes at room temperature. The device schematic is shown in Figure 1.

The advantages of batch reactors are simple setup and adjustable parameters, which are suitable for preliminary screening of catalysts and condition exploration. Maghami et al. [10] completed various epoxide ring-opening tests catalyzed by Fe_3O_4/SiO_2-Ampy-HPW in a batch device, and the catalyst can be recovered by magnetic attraction after the reaction. However, batch operation has small single-batch processing capacity and batch-to-batch fluctuations, making it difficult to directly transfer to continuous production lines, and is generally positioned as a pre-research platform for scale-up.

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2.3.2. Fixed-bed flow reactor

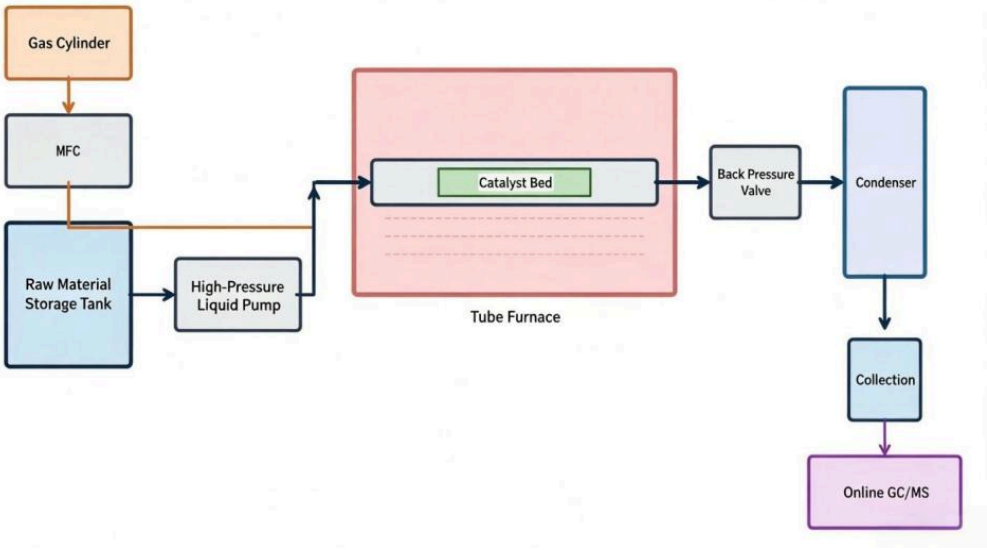


Figure 2. Schematic diagram of fixed-bed flow reactor

Cutright et al. [11] granulated HPW-SiO_2 co-condensed solid acid with Al_2O_3 and packed it into a fixed bed for olefin isomerization. No HPW leaching was detected during continuous operation. The quartz tube reactor was equipped with a mass flow meter to precisely control the vapor feed. However, carbonaceous deposition requires regular burning off. The device schematic is shown in Figure 2.

Jiang et al. [5] also conducted a long-term evaluation of BMImPW@MIL-101(Cr) for oxidative desulfurization using a fixed bed: with continuous feed of simulated oil, the catalyst maintained its structure and activity after multiple cycles. The main advantages of fixed beds are continuous operation, easy scale-up and high degree of automatic control; the cost is that higher requirements are placed on the mechanical strength, thermal stability and carbon deposition resistance of the catalyst [1, 6].

2.3.3. Redox flow battery (RFB)

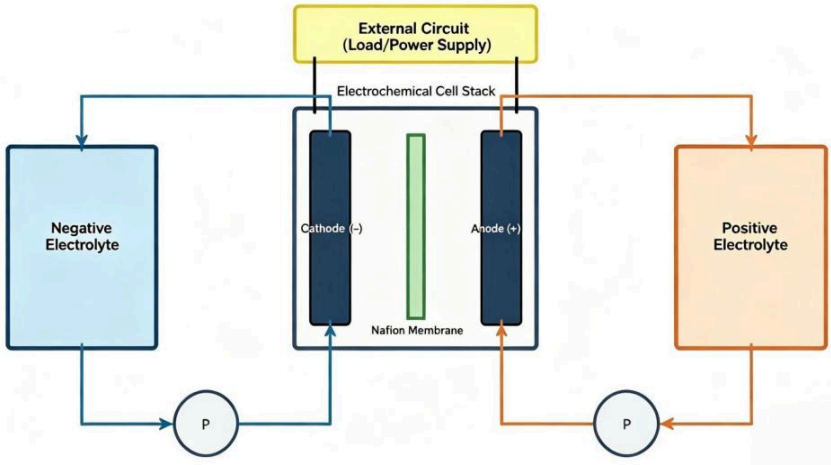


Figure 3. Schematic diagram of redox flow battery

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Ai et al. [2] constructed a low-temperature aqueous RFB using Dawson-type heteropoly acid ($H_6P_2W_{18}O_{62}$) as the anolyte, with carbon felt electrodes and Nafion membrane. The membrane permeability of HPW is 6.17×10^{-10} $cm^2\cdot min^{-1}$, and it delivers a specific capacity of 12.8 $Ah\cdot L^{-1}$ at 100 $mA\cdot cm^{-2}$, with the capacity basically maintained after more than 700 cycles. The device schematic is shown in Figure 3.

2.3.4. Direct liquid fuel cell (DLFC)

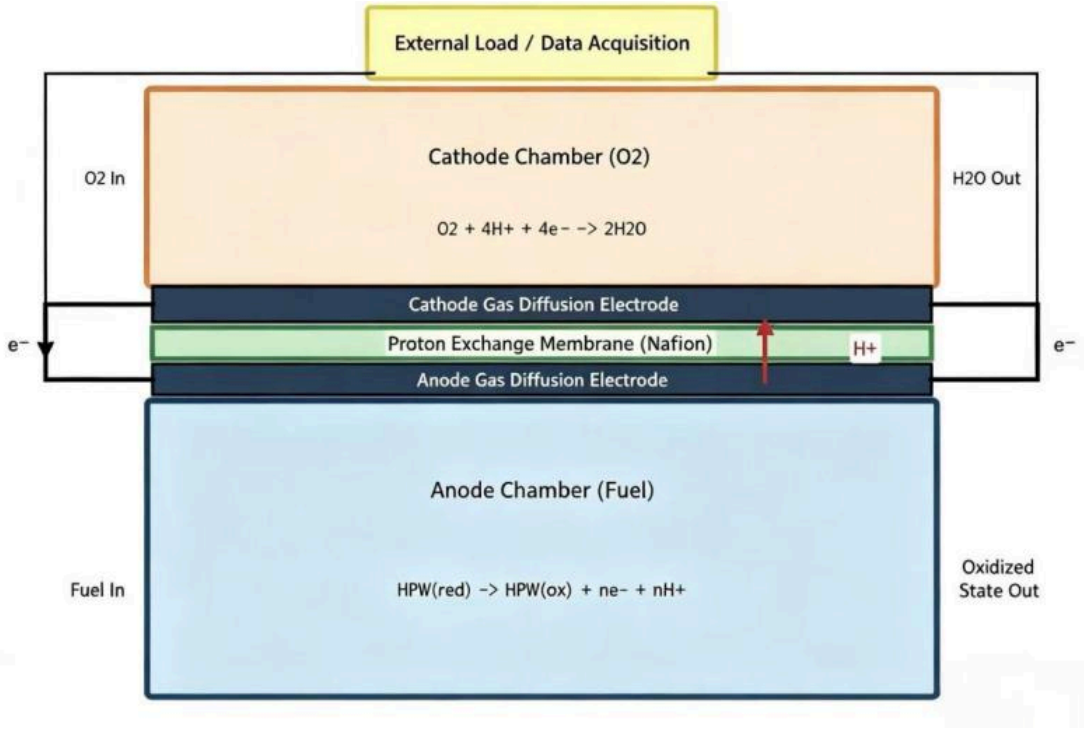


Figure 4. Schematic diagram of direct liquid fuel cell

Direct liquid fuel cells (DLFC) directly convert the chemical energy of heteropoly acids into electrical energy. Liu et al. [3] proposed the idea of using Keggin-type heteropoly acid itself as a recyclable fuel to replace traditional organic fuels. A DLFC single cell is composed of an anode compartment (containing HPA solution), a cathode compartment (O_2/air), a proton exchange membrane and gas diffusion electrodes. The anode undergoes the oxidation half-reaction of HPAs, and the cathode undergoes oxygen reduction. The device schematic is shown in Figure 4.

Liu et al. [3] compared three Keggin-type HPAs (see Section 4 for detailed DFT analysis) and found that $\{CoW_{12}\}$ narrows the four-electron reduction potential to a concentrated window through the PCET effect of Co(II), inhibiting hydrogen evolution. The single cell delivers an energy density of 27.2 $Wh\cdot L^{-1}$ and a peak power of 0.529 $W\cdot cm^{-2}$ at 0.58 V, which are 2.18 times and 1.46 times those of the control $\{PW_{12}\}$, respectively. No obvious voltage decay was observed after 30 hours of constant current discharge. The whole process operates at room temperature without noble metals and humidification.

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2.3.5. Photocatalytic reaction device

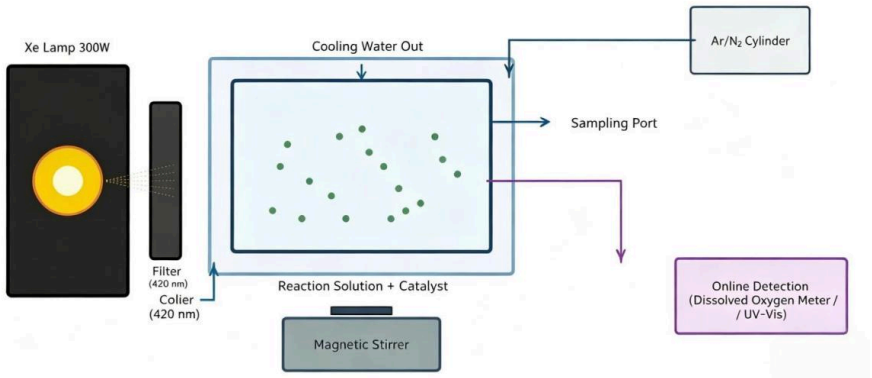


Figure 5. Schematic diagram of photocatalytic reactor

Rong et al. [4] used a 300 W xenon lamp with a 420 nm cut-off filter as the visible light source in the photocatalytic H_2O_2 production work with PTA@TTB-EB. A Pyrex top-illuminated reactor was equipped with 25 °C circulating water cooling, and no sacrificial agent was added in pure water, with an H_2O_2 yield of 897.94 $\mu mol \cdot L^{-1} \cdot h^{-1}$. The device schematic is shown in Figure 5.

Li et al. summarized several factors that need attention in POMs photocatalytic devices in a review: matching between the light source spectrum and catalyst absorption, light transmittance of reactor window materials, mass transfer efficiency at the gas-liquid-solid three-phase interface, and the combination of sacrificial agents/hole scavengers. The multi-electron storage-release mechanism of POMs is sensitive to both the separation efficiency of photogenerated charges and interfacial transfer kinetics, which is currently the focus of device optimization.

2.3.6. Device comparison and prospect

The five types of devices each have their own application logic. Batch reactors are suitable for preliminary screening and condition optimization. Fixed beds target continuous production, but have higher requirements for catalyst molding and lifetime. RFB and DLFC have their own focuses in electrochemical energy storage and power generation scenarios. Photocatalytic devices follow a solar-driven route. In practical selection, comprehensive matching of reaction type, catalyst form, processing scale and energy consumption needs to be considered. The comparison of the five devices is summarized in Table 2.

Table 2. Comparison of acidic redox catalytic devices

Device Type	Operation Mode	Applicable Reactions	Advantages	Limitations
Batch reactor	Batch operation	Liquid-phase oxidation, catalyst screening	Simple operation, flexible and controllable parameters	Limited processing capacity, batch-to-batch variation
Fixed-bed flow reactor	Continuous operation	Gas/liquid-solid continuous catalysis	Continuous operation, easy scale-up	Catalyst requires granulation, carbon deposition requires regeneration

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Table 2. (continued)

Redox flow battery	Electrochemical cycling	Electrical energy storage and conversion	High capacity, long cycle life	Complex system, high membrane cost
Direct liquid fuel cell	Electrochemical discharge	Chemical energy → electrical energy conversion	Noble metal-free, room temperature operation	Power density needs to be improved
Photocatalytic reaction device	Light-driven batch/continuous	Green synthesis, pollutant degradation	Solar-driven, mild conditions	Limited light utilization, difficult scale-up

Noteworthy directions at the device level include: developing modular continuous flow microreactors for HPW-based catalysts to improve mass and heat transfer and reduce scale-up risks; integrating online detection and automatic control into catalytic devices to realize real-time monitoring and feedback regulation of reaction processes; exploring reactor designs with synergistic multiple external fields such as light, electricity and microwave to serve HPW tandem catalysis scenarios [12, 13].

3. Preparation methods of phosphotungstic acid

The synthesis route of HPW has evolved from solvent extraction to green processes, and various methods differ significantly in yield, purity, safety and scale-up potential.

As shown in Table 3, the acidification-ether extraction method is the earliest route established by Drechsel in 1887. Using Na_2WO_4 and H_3PO_4 as starting materials, the mixture is heated to reflux in the presence of concentrated hydrochloric acid. After cooling, ether is added to form an oily adduct with HPW. The organic layer is separated and the ether is evaporated to obtain the solid product, with a yield of about 80%. This route has mature technology and high product purity. The problem is that ether has a boiling point of only 34.6 °C, is flammable, explosive and toxic, and imposes a heavy burden on waste liquid treatment.

The ion exchange method avoids ether: HPW ammonium salt is first prepared, then NH_4^+ is replaced with H^+ using H-type cation exchange resin, and HPW is obtained after evaporation to dryness. This method eliminates the safety hazards of organic solvents, but it has a long process, requires frequent resin regeneration, and consumes high energy for evaporating a large amount of solvent, making it difficult to adapt to industrial-scale production.

Chen et al. reported a two-step method: sodium tungstate is first acidified to prepare active tungstic acid intermediate, then reacted with phosphoric acid under mild hydrothermal conditions, and HPW crystals are precipitated by salting-out method, with a yield of about 78%, and no ether is involved in the whole process. In the electrodialysis method, tungstate and phosphoric acid solutions are placed in a DC electric field, and HPW is directly generated in the anode chamber, with a yield close to 100% and zero waste.

The sol-gel method is suitable for preparing HPW-based nanostructures. Greijer et al. [14] used HPW as a precursor, added polyvalent cations at low pH to induce oriented self-assembly, and obtained microspheres composed of ~20 nm secondary spheres. This material maintains structural integrity in neutral and alkaline aqueous solutions and delivers usable activity in OER. Cutright et al. [11] covalently incorporated HPW into the SiO_2 network via sol-gel co-condensation. The obtained solid acid catalyzes olefin isomerization in a fixed bed reactor, and no HPW leaching is detected during operation, but carbon deposition requires regular burning off for regeneration.

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The comparison of main preparation methods of phosphotungstic acid is shown in Table 3.

Table 3. Comparison of main preparation methods of phosphotungstic acid

Preparation Method	Raw Materials	Key Conditions	Yield / %	Characteristics
Ether extraction method	Na_2WO_4, H_3PO_4, HCl	Heating reflux + ether extraction	~80	Mature process, high purity; ether is flammable and toxic
Ion exchange method	HPW ammonium salt, cation resin	Ion exchange + evaporation to dryness	~75	No organic solvent; long process, high energy consumption
Hydrothermal/salting-out method	Na_2WO_4, H_3PO_4	Acidification → hydrothermal → salting-out	~78	Ether-free, mild conditions; moderate yield
Electrodialysis method	Tungstate, H_3PO_4	DC electric field	~100	Zero waste; high equipment requirements
Sol-gel method	PTA precursor, polyvalent cations	Self-assembly at low pH	—	Suitable for nanostructure construction; not suitable for batch production

4. Structural characteristics and acidic redox mechanism of phosphotungstic acid

HPW samples obtained by different preparation methods have different purity and structures, and these differences ultimately boil down to the atomic arrangement of their Keggin anions. The Keggin anion $[PW_{12}O_{40}]^{3-}$ of phosphotungstic acid ($H_3PW_{12}O_{40}$, HPW) is assembled from a central PO_4 tetrahedron and 12 peripheral WO_6 octahedra, with overall Td symmetry and a diameter of about 1.2 nm. It is one of the smallest known metal oxide clusters [1, 10]. In this structure, oxygen atoms are divided into four categories according to their chemical environment: tetrahedral oxygen coordinated with P (Oa), bridging oxygen across trimetallic clusters (Ob), intra-cluster bridging oxygen (Oc) and terminal oxygen (Od) [1, 8]. This precise atomic arrangement provides HPW with two core capabilities in acidic redox catalysis.

First, Brønsted acidity. The three protons of HPW are highly dispersed on the surface of the Keggin anion. The measurement by Okuhara et al. gives $H_0 \leq -13.16$ for solid HPW, and the acid strength order is $H_3PW_{12}O_{40} > H_4SiW_{12}O_{40} > H_3PMo_{12}O_{40} > H_4SiMo_{12}O_{40}$. The physical origin of this superacidity lies in charge delocalization: the net negative charge of the Keggin anion is spread over the 36 outer oxygen atoms of the 12 WO_6 octahedra, and the negative charge shared by each oxygen atom is very small. Therefore, the electrostatic binding of protons is extremely weak, and their mobility and reactivity are both high.

Second, redox reversibility. All W in HPW is in the +6 oxidation state. Without destroying the Keggin skeleton, W^{6+} can accept electrons and transform into W^{5+}, forming dark blue "heteropoly blue" [13]. This multi-electron process is highly reversible. HPW can be reoxidized back to the initial state by H_2O_2 or O_2 under mild conditions to complete the catalytic cycle. Liu et al. [3] tracked the proton-coupled electron transfer pathway of phosphotungstic acid using DFT calculations, confirming that the central P^{5+} has a modulating effect on the redox potential of the Keggin anion. Ai et al. [2] verified the multi-electron transfer kinetics of phosphotungstic acid anolyte in low-temperature aqueous flow batteries, with a membrane permeability of only 6.17×10^{-10} $cm^2\cdot min^{-1}$.

The acidity and redox properties of HPW are not simply superimposed. In the catalytic cycle, in addition to creating an acidic environment to activate substrates, protons are directly embedded in the redox step through the proton-coupled electron transfer (PCET) pathway. Liquid-phase oxidation using H_2O_2 as oxidant is a typical example: the acidic sites of HPW first promote the protonation dissociation of H_2O_2 to form peroxotungsten species $W(O_2)_n$, which then act as the real oxidation

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centers [1, 2]. In the $ZrPTA_x$-BTC catalyst prepared by Zhong et al. [8], the open sites of Zr(IV) decompose H_2O_2 into $O_2^{-}\cdot$, and PTA molecules capture $O_2^{-}\cdot$ to form peroxotungstate. Dibenzothiophene is completely removed within 30 minutes at 50 °C. Xiong et al. [9] introduced carbon quantum dots (CQDs) as co-catalysts into the HPW-ionic liquid system, and CQDs/C_{18}PWIL also achieved quantitative desulfurization within 30 minutes at room temperature.

The Keggin structure of HPW endows it with superstrong acidity and reversible multi-electron redox ability, and the two operate synergistically through the proton-coupled electron transfer pathway. However, in homogeneous systems, HPW has low specific surface area, is prone to agglomeration, and is highly soluble in polar solvents, making recovery and reuse difficult [1, 4]. To this end, researchers have developed various immobilization strategies to achieve the convenience of heterogeneous operation while retaining its intrinsic bifunctionality.

5. Immobilization strategies of phosphotungstic acid

Homogeneous HPW has a specific surface area of only 1-10 m^2/g, is prone to agglomeration, and is highly soluble in polar solvents, making recovery and reuse difficult [1, 4]. To this end, researchers have developed several immobilization routes, attempting to anchor or confine HPW on porous supports, so that homogeneous catalysts can gain the convenience of heterogeneous operation [1, 9].

Mesoporous SiO_2 is an early support used for HPW immobilization. Impregnation or sol-gel methods can disperse HPW in the channels of SBA-15 or MCM-41, effectively expanding its accessible surface. Zheng et al. [13] grafted 2-methylimidazole on the surface of activated carbon, and then achieved chemical anchoring of HPW through the ion pair interaction between imidazolium cations and $[PW_{12}O_{40}]^{3-}$. The catalyst (AC-COIMI-HPW) gives 90.2% conversion and 91.8% benzaldehyde selectivity when used for benzyl alcohol oxidation, and the activity remains basically unchanged after five recycles.

Magnetic supports facilitate the magnetic separation and recovery of catalysts. Maghami et al. [10] modified 3-aminopyridine (Ampy) on the surface of Fe_3O_4/SiO_2, and completed immobilization through the electrostatic interaction between protonated amino groups and HPW. TEM shows a particle size range of 10-30 nm. The catalyst achieves 93% conversion and nearly quantitative selectivity in the methanolysis of styrene oxide, and can be separated by an external magnetic field.

MOF encapsulation is an active direction in recent years. MIL-101(Cr) has mesoporous cages of 2.9-3.4 nm with windows of 1.2-1.6 nm, which can just trap Keggin anions with a diameter of ~1.2 nm. Jiang et al. [5] combined the "bottle around ship" and "ship in bottle" strategies to co-lock HPW and BMImBr into MIL-101(Cr) cages, with HPW loading reaching 23.1-50.7 wt%. The bulky $BMIm^+$ cations effectively block the escape channel of PW^{3-}, and no deterioration of the catalyst structure and activity is observed after multiple cycles.

Covalent organic frameworks (COFs) provide another encapsulation option. Rong et al. [4] implanted HPW into the channels of cationic COF (TTB-EB). HPW acts as an electron relay station, building a fast electron transport path between the COF conduction band and O_2, and simultaneously changing the pathway of oxygen reduction reaction. $HPW_{0.5}$@TTB-EB achieves a visible-light-driven H_2O_2 yield of 897.94 $\mu mol\cdot L^{-1}\cdot h^{-1}$ in pure water without sacrificial agents, which is 2.2 times that of pristine TTB-EB.

Al_2O_3 loading is more practical in industrial catalysis. The review by Colombo Migliorero et al. [6] covers the whole chain of preparation-loading-application of HPAs-Al_2O_3. The surface hydroxyl groups of γ-Al_2O_3 anchor Keggin anions through hydrogen bonding or electrostatic interaction, achieving high dispersion of HPW.

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Immobilization strategies improve the dispersibility and recyclability of HPW, laying a foundation for expanding its applications from traditional organic synthesis to emerging fields such as oxidative desulfurization, energy conversion and photocatalysis. The following summarizes recent research progress from these three directions.

6. Research on phosphotungstic acid for acidic redox catalysts

In the past three to five years, research on HPW-based catalysts has been active in three directions.

First, ionic liquid (IL) hybridization. HPW itself has poor dispersion in the oil phase and limited activation ability for H_2O_2 [1, 2]. Pairing organic cations with PW anions to form large-sized ion pairs not only suppresses the loss of active components, but also pulls the catalyst into the oil phase through the long alkyl chains on the cations. Meanwhile, the distance between sulfides and active sites is shortened. Xiong et al. [9] further improved the room-temperature catalytic efficiency of the HPW-IL system through CQDs doping. Ai et al. [2] used phosphotungstic acid as a redox medium in RFB work, and verified its cycling stability with no decay for 1200 hours at 160 $mA \cdot cm^{-2}$, with a power density of 282.4 $mW \cdot cm^{-2}$.

Second, defect and metal doping. Partial substitution of W in the Keggin skeleton with transition metal ions (Cu, Ni, Mn, V, Fe, etc.) yields transition metal-substituted heteropolyoxometalates. In addition, lacunary heteropolyoxometalates can be obtained by controlled removal of framework W atoms. Both are important means of structural regulation. The substituted metals provide additional redox sites, and their Lewis acidity can complement the Brønsted acidity of the parent HPW [1, 5]. The DFT analysis by Liu et al. [3] further points out that the valence state of the central heteroatom directly shapes the redox potential distribution of the Keggin anion. The low-valent Co(II) center compresses the four-electron reduction potential into a narrow window of -0.035 to -0.151 V through PCET, inhibiting the hydrogen evolution competition.

Third, light/electric external field driving. Coupling the acid-redox function of HPW with photocatalysis or electrocatalysis is a route to expand its application boundaries [14]. The "electron sponge" behavior of POMs under illumination (rapid accumulation and gradual release of multiple electrons) originates from their multi-electron redox ability, which requires device design to take into account both the separation efficiency of photogenerated charges and the interfacial electron transfer rate. Wang et al. [15] reviewed the latest progress of POM-based materials in electrochemical energy storage, pointing out that the multi-electron redox properties of Keggin and Dawson type POMs have intrinsic advantages in flow batteries and supercapacitors, and structural regulation (heteroatom substitution, vacancy introduction) is the core strategy to optimize their energy storage performance.

The above applications show that the catalytic function of HPW can naturally extend to electrochemical energy storage scenarios, as shown in Table 4.

Table 4. Summary of performance data of phosphotungstic acid-based catalysts in acidic redox catalysis

No.	Catalyst Material	Reaction/Application Type	Temperature (°C)	Conversion/Yield (%)	Selectivity (%)	Cycling Stability	Reference
1	PTA/imidazolized activated carbon	Alcohol oxidation (H_2O_2)	80	95 (conversion)	>99	No significant decrease after 5 cycles	[13]

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Table 4. (continued)

2	$ZrPTA_x$-BTC	Oxidative desulfurization (DBT)	60	99.9 (desulfurization rate)	—	Remain >95% after 6 cycles	[8]
3	PTA-IL@MIL-101(Cr)	Oxidative desulfurization (solvent-free)	70	100 (desulfurization rate)	—	Maintain activity after 8 cycles	[5]
4	CQD/PTA ionic liquid	Oxidative desulfurization	50	99.5 (desulfurization rate)	—	>98% after 5 cycles	[9]
5	$H_6P_2W_{18}O_{62}$ (HPOM)	Redox flow battery	-20~25	79.6 Ah L^{-1}	—	No decay for 1200 h	[2]
6	CoW_{12} (cobaltotungstic acid)	Direct liquid fuel cell	25	27.2 Wh L^{-1} (energy density)	—	Stable discharge for 30 h	[3]
8	PTA/SiO_2 (covalently embedded)	Esterification/acylation reactions	60-120	85-98 (yield)	—	Multiple cycles	[11]
9	Fe_3O_4@SiO_2-PTA	Epoxide alcoholysis	25-60	92 (yield)	>99	6 times by magnetic separation/o:p>	[10]
10	PTA@COF (cationic framework)	Photocatalytic H_2O_2 production	25 (visible light)	1080 μmol g^{-1} h^{-1}	—	4 light cycles	[4]
11	$Ag_3PW_{12}O_{40}$ (silver salt)	Oxidation reactions (review)	Review	Review	Review	Review	[6]
12	PTA sol-gel precursor	Nanostructure construction	Review	Review	Review	Review	[12]

Note: The performance data of review literature are summaries of representative catalytic systems.

7. Conclusion

Phosphotungstic acid is a representative member of Keggin-type heteropoly acids. With its superstrong Brønsted acidity, reversible multi-electron redox ability and structural designability, it occupies a unique position in the field of acidic redox catalysis. This paper systematically reviews it from five dimensions: structural characteristics, preparation methods, immobilization strategies, catalytic applications and device configurations. At the structural level, the spherical cluster configuration of the Keggin-type $[PW_{12}O_{40}]^{3-}$ anion is the structural cornerstone of all catalytic functions of phosphotungstic acid. Its superacidity originates from the extremely low charge density on the surface of discrete anions, while the redox property originates from the reversible electron transfer of W^{6+}/W^{5+}. At the preparation level, the ether extraction method is still the first choice for laboratory preparation of high-purity HPW. Hydrothermal method and sol-gel method show greater potential in structural regulation and scale-up [1, 10]. At the immobilization level, the host-guest confinement strategy (MIL-101, COF encapsulation) is currently the most effective means to solve the solubility problem of HPW. Covalent anchoring strategies (SiO_2 covalent embedding, magnetic nanoparticle grafting) perform outstandingly in catalyst recovery and reuse. At the catalytic application level, oxidative desulfurization is the most mature field of HPW catalytic application. Ultra-deep desulfurization and multiple recycling have been achieved in multiple systems. In the field of energy devices, heteropoly acid-based flow batteries and direct liquid fuel cells have broken

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through the two major technical bottlenecks of low-temperature operation and noble metal-free anodes, respectively. Looking forward, the development of phosphotungstic acid-based acidic redox catalysts should focus on directions such as in-situ characterization techniques to reveal reaction mechanisms, DFT calculation and machine learning-assisted screening, engineering transition of continuous flow reactors, and photo-electro-thermal multi-field synergistic catalysis. It should be pointed out that the stability problem of the HPW Keggin skeleton under hydrothermal and strong alkaline conditions is still the key bottleneck restricting its industrial promotion. The formation of lacunary species $[PW_{11}O_{39}]^{7-}$ will weaken the acid strength and change the redox potential. Future research should strengthen in-situ tracking of the failure mechanism and quantitative description of structural degradation pathways. In addition, the gap from laboratory to factory is also reflected in engineering aspects such as the supply chain cost of WO_3 raw materials, equipment material selection caused by acid corrosion, and catalyst deactivation and regeneration schemes in long-term continuous operation. Solving these problems requires the cross-collaboration of catalytic chemistry, materials science and chemical engineering.

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