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# Polyoxometalates based compounds for green synthesis of aldehydes and ketones

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## ABSTRACT

Molecular oxygen within Polyoxometalates (POMs) based compounds are ideal oxidants with high atom economy and its use results in the production of water as the only byproduct. Significant progress has been made in the development of catalytic methods for aerobic alcohol oxidation to have aldehydes and ketones with POMs based compounds. They are alternative to the use of traditional hypervalent iodine catalyst systems which are with molecular oxygen as a terminal oxidant. Further, POMs based catalysts can be applied to catalytic reactions with different modes of energization such as thermocatalysis, photocatalysis and electrocatalysis. This review summarizes the frontier advances in polyoxometalates for catalytic alcohol selective oxidation in thermocatalytic, electrocatalytic, and photocatalytic applications. The three advantages of POM catalysts in terms of performance, economy, and environmental protection are highlighted. These include the use of sol-gel and electrostatic assembly methods to increase the reaction surface area, reduce the use of precious metals, and improve the stability of POMs catalysts. The field of selective alcohol oxidation is advanced. Finally, the challenges of preparing more efficient and "green" catalysts are presented.

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## 1. Introduction

The selective oxidation of alcohols to carbonyl compounds is one of the most essential organic transformations in the synthesis of fine chemicals and pharmaceutical intermediates [1–5], accounting for about 30% of the total production of the modern chemical industry. As is well known, the selective oxidation of alcohols highly relies on controllable oxidation catalysis process which is most of these conversion processes require the involvement of specific catalysts. According to the conventional approach, these selective oxidation reactions are achieved by means of stoichiometric ratios of metal oxidants, such as permanganates, bromates or chromium [6–8]. In order to catalyze these oxidation reactions, several transition metals like palladium, ruthenium, molybdenum, manganese, rhenium, copper, iron, cobalt, and platinum-based aerobic catalytic systems have been developed up to date [9,10], which undoubtedly allow it to obtain better selectivity and yields. However, there are unavoidable disadvantages: (1) The cat-

alytic system requires precious metals and toxic organic solvents [7]; (2) In most cases, the catalysts used need to be elevated to high temperatures to produce effective catalytic activity; (3) Some oxidation reactions must be carried out at high oxygen pressures [11]; (4) The reaction time is long [9,12–16]. For this reason, there is an urgent need to develop a cost-effective and environmentally friendly catalytic process from an economic and environmental point of view.

Up to now, a number of homogeneous and heterogeneous catalytic systems have been well established for the selective oxidation of alcohols to aldehydes and ketones [17–19]. To date, some useful cases have been reported using homogeneous catalysts with organic ligands combined with metal groups (e.g., ruthenium, palladium, gold, iridium, rhodium) or relying on the use of toxic halide oxidants. Heterogeneous catalysts often use ligands with versatility to modulate the catalytic performance. The advantages of the former catalysts are reported to be their good versatility, but the disadvantages are the use of precious metals and expensive organic ligands [20], the susceptibility of these ligands to oxidative self-degradation, and the required harsh reaction conditions (high temperature or pressure). The latter heterogeneous catalysts have the advantage of being easily separated from the reaction

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mixture for reuse and cost reduction, but these catalysts are not commercially available [7,11,21]. Earlier, Peter's group conducted an exhaustive evaluation comparing heterogeneous and homogeneous catalysts and concluded that heterogeneous catalysts are still the optimal choice, this conclusion has subsequently been proven to be correct due to a large number of facts [1].

Acid catalysis is by now one of the most attractive and predominant ways to catalyze the oxidation of alcohols to produce the corresponding carbonyl compounds in the field of catalysis. In present-day society, a wide variety of chemicals involved in industrial production are associated with it. However, conventional inorganic acids ( $\text{H}_2\text{SO}_4$ , HF, etc.) and Lewis acids ( $\text{AlCl}_3$ ,  $\text{BF}_3$ , etc.) are often dangerous or corrosive, which leads to the industrial production of toxic chemicals or corrosive industrial waste. Therefore, the rapid development of "green" and environmentally friendly acidic catalytic systems (including acidic ionic liquids and solid acids) has attracted a lot of attention from the academic community in the last decades. Among them, polyoxometalates (POMs) have been widely used in catalytic chemistry, energy science,  $\text{CO}_2$  chemistry, materials chemistry, and medicinal chemistry due to their structural, functional, and environmentally friendly properties [22–24].

Polyoxometalates (POMs) are a class of metal oxide clusters based on high-valence transition metal anions with diverse structures and a wide range of modifiable reactivity and structures [25–27]. POMs have been applied to catalyze many organic transformation processes (e.g., energy conversion, electron transfer) [28–30]. This is not only due to their unique physicochemical properties such as thermal stability, hydrolysis, acidity and adjustable oxidation reduction potential, but more importantly because they are environmentally friendly and soluble in water and various non-toxic organic solvents (depending on the POMs counter cation) [8,21]. POMs immobilization has been studied for decades and scholars have started to load them on heterogeneous carriers (including mesoporous silica, covalent organic frameworks (COFs), and metal-organic frameworks (MOFs) to make some "green", environmentally friendly and highly selective heterogeneous catalysts [31–33]. Assembly of POMs molecules into specific shapes and sizes (e.g., nanoparticle size) can improve their catalytic activity. POMs nanoparticles can be synthesized in different ways, such as microemulsion-mediated formation of POMs nanoparticles, formation of self-assembled polymers or cationic micelles for the synthesis of nanostructured POMs matrices (Fig. 1) [26,27].

On the downside, there are two main drawbacks in catalytic systems that involve POMs without any chemical treatment: (1) The low surface area in non-polar solvents ( $<10\text{ m}^2/\text{g}$ ) prevents the reactants from approaching the active site; (2) The high solubility in polar solvents makes it difficult to recycle and causes cost problems [5,34,35]. In order to improve the catalytic activity and stability of POMs based catalysts, different strategies have been adopted. Here, we review the research advances so far in the field of POMs based "green" efficient catalysts in conventional thermal, electrocatalytic and photocatalytic catalysis, furthermore, the future challenges and key points remained in POMs-based compounds design for thermal, electro and photo-catalytic selective oxidation of alcohols are well discussed that could outlook the new progress of cutting-edge research on the development of alternative sustainable technologies on research community of POMs chemistry and related green catalysis.

## 2. Polyoxometalate based compounds for thermocatalytic synthesis of aldehydes and ketones

Thermocatalysis as a traditional and one of the most widely used catalytic methods, plays a significant role in the selective oxidation of alcohols. However, conventional thermocatalytic approaches to achieve high selectivity and conversion usually require

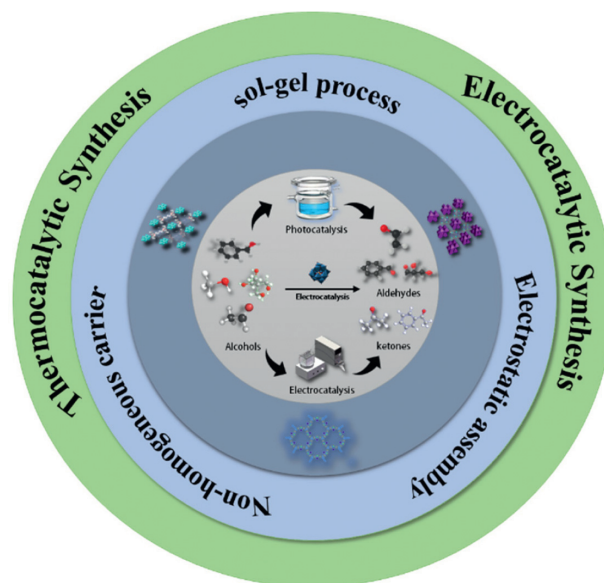


Fig. 1. Schematic diagram of POMs-based nanostructures for thermocatalytic, electrocatalytic, and photocatalytic selective oxidation of alcohols.

high temperature and pressure conditions, and in some cases, the involvement of precious metals [36–38].

POMs and loaded metal ions are efficient catalytic systems for the (aerobic) selective oxidation of many aromatic carbocyclic and heterocyclic benzyl alcohols as well as secondary aliphatic alcohols without active  $\alpha$  protons. In 2001, Peter's group developed a combinatorial approach for the exploration and optimization of catalysts that can selectively oxidize aerobic alcohols. They reported on the selective oxidation of 2-butyl-5-hydroxymethylimidazole and the synthesis of an important pharmaceutical intermediate (the corresponding aldehyde). This reaction utilized two heterogeneous catalyst systems (paraformaldehyde and loaded metals). It verified the versatility of the loaded metal platform and its general applicability through the oxidation of a number of primary and secondary alcohols.

They propose that while homogeneous catalysts generally allow for faster rates of oxidation reactions to occur, heterogeneous catalysts are still the optimal choice because they are easier to separate from the product and are more amenable to recycling, thereby reducing the cost of aging.

It is well established that aqueous hydrogen peroxide is an inexpensive, mild and environmentally friendly reagent with high reactive oxygen content and produces water as a by-product [12,13], which is promising for the selective oxidation of alcohols. In order to further improve the performance of POMs catalytic systems, some "engineering" approaches are needed to help reuse the catalysts in future practical applications. In general, such "engineering" can be divided into two main approaches. The first approach is to immobilize POMs with proven catalytic properties on a solid carrier (e.g., silica) to obtain a catalytic system that can be filtered and reused. Such methods include (1) the simple use of POMs as insoluble bulk materials that dissolve under certain circumstances, and (2) the impregnation of the POMs into a solid (usually inert matrix) [34,39] and its attachment to the carrier by covalent or ionic bonding. The second basic approach is to use a two-phase liquid-liquid system so that at certain separation temperatures (usually ambient) the catalyst and product phases can be separated by phase separation; the catalyst phase is reused. In 2004, Ronny Neumann reported the synthesis of two tripod polyamine cations and their combination with "sandwich" type polyoxometalates  $[\text{ZnWZn}_2(\text{H}_2\text{O})_2(\text{ZnW}_9\text{O}_{34})_2]^{12-}$  to obtain

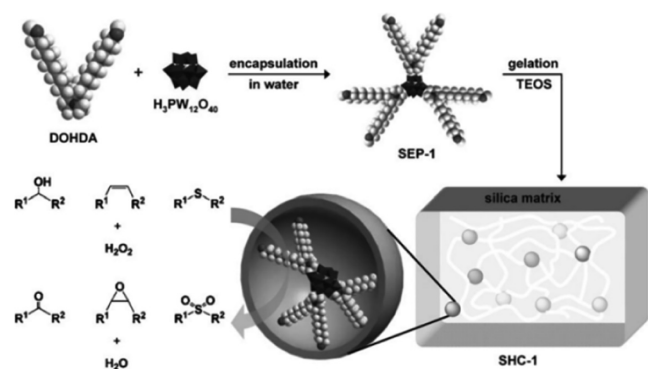


Fig. 2. Schematic representation of the procedure for the fabrication of SHC-1 and the oxidation mechanism of sulfide, alcohol, and olefin substrates under the catalysis of SHC-1. Copied with permission [41]. Copyright 2009, Wiley-VCH.

mesoporous materials with moderate specific surface area. This heterogeneous mesoporous material is characterized by high activity and recoverability. Nitrogen adsorption analysis showed that the specific surface area of the hybrid material was 30–50 m<sup>2</sup>/g with an average pore size of 36 Å, indicating its good selectivity for the epoxidation of allyl alcohol and the oxidation of secondary alcohols to ketones with hydrogen peroxide as the oxidant [40].

In 2010, Qi's group used a sol-gel process of tetraethyl orthosilicate to covalently and uniformly bind hydroxyl-terminated surfactant-encapsulated polyoxometalate complexes to a silica substrate. The resulting hybrid catalysts have a defined hydrophobic nanoenvironment surrounding the inorganic cluster, which facilitates the compatibility between the polyoxometalate catalytic center and the organic substrate. It was found that the supramolecular synergy between substrate adsorption, reaction and product desorption during the oxidation process has a significant effect on the reaction kinetics and the catalyst activity is greatly enhanced.

Meanwhile, they proposed a new strategy for efficient and selective oxidation reactions using supramolecular hybrid catalysts (SHCs) based on surfactant-encapsulated POM (SEP) complexes (Fig. 2). This catalytic system uses hydrogen peroxide as the oxidant, which effectively promotes the oxidation of alcohols and can be easily recycled and reused. Through electrostatic interaction, quaternary ammonium cations such as dimethylammonium (DOHDA) can replace the counter ions in POMs to obtain a series of SEP supramolecular complexes. The structure of SEPs is similar to that of the anti-micellar catalytic system, which can improve the compatibility between the organic substrate and the catalytic center of POM [41].

SEPs with hydroxyl groups at the periphery can be covalently immobilized in silica substrates by sol-gel condensation reaction with ethyl or tetraethylorthosilicate (TEOs). Immobilized supramolecular hybrid catalysts have unique properties for the catalytic oxidation of organic substances. Thus, they have a well-defined hydrophobic nanoenvironment to trap organic substrates, thus maximizing the catalytic efficiency. They are solvent-independent and can be adapted to different POMs and thus can meet different requirements. In 2010, Ronny's group reported an active catalyst for the rapid aerobic oxidation of alcohols, Pd-POM, using a "sandwich" type of cetyltrimethylammonium salt of a polyoxometalate as the ligand to the Pd(II) center. The reaction mechanism is shown in Fig. 3.

The Pd-POM catalyst shows some unique and significant features, which are evident in the oxidation of saturated fatty alcohols. There are several main points: (1) A significant preference for the oxidation of aliphatic primary and secondary alcohols. This may be the result of spatial factors that attenuate the inherently higher probability of primary alcohol oxidation (more C-H bonds).

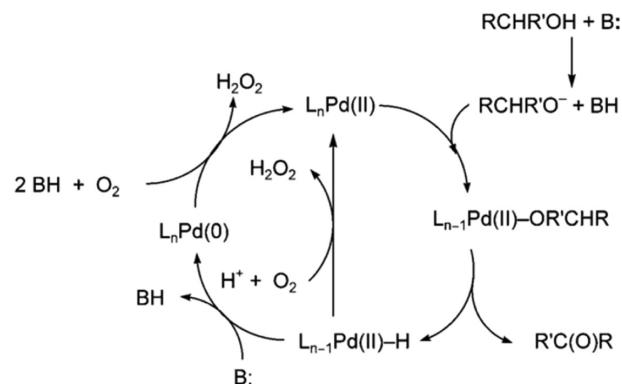


Fig. 3. Mechanistic scenarios in the literature for the aerobic oxidation of alcohols by Pd(II) complexes. Copied with permission [2]. Copyright 2010, Wiley-VCH.

(2) The reaction is highly selective for aldehydes and produces fewer carboxylic acids; autoxidation is inhibited. (3) Activation of alcohols does not require alkali. (4) Fast reaction seems to be related to the electron acceptor nature of the polyoxometalate ligand, which may contribute to alcohol dehydrogenation and may also be the catalyst reoxidation pathway leading to atypical (for Pd(II)-catalyzed alcohol oxidation) [2].

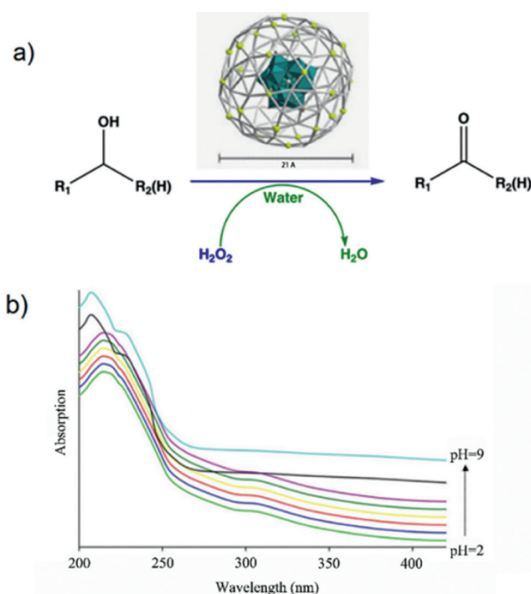
Among the various transition metals, vanadium is one of the most abundant ones on the earth's surface and vanadium-based oxidizers can be used effectively in a variety of oxidation reactions. In 2011, Dewan's group first reported a method for the oxidation of primary aliphatic alcohols to carbonyl compounds by vanadium polyoxometalates without organic solvents at room temperature. They used a new vanadium polyoxometalate catalyst  $[(C_6H_5CH_2)(CH_3)_3N]_3[H_3V_{10}O_{28}]_3 \cdot H_2O$ , which was obtained by treating  $V_2O_5$  with hydrogen peroxide in the presence of trimethylammonium chloride. The synthesis of this catalyst is very simple, the starting materials used for its synthesis are commercially available and inexpensive, moreover, there is no need for precious metals.

To demonstrate the feasibility of this new vanadium polyoxometalate as a catalyst for alcohol oxidation, they performed a series of experiments. In addition, they were surprised to find that the oxidant and ethanol were milled at room temperature in a special environment without solvent at the same time with the addition of *p*-toluenesulfonic acid (PTSA). The ethanol was converted to its carbonyl derivative in a very high yield within 1 min [42].

In 2014, Kasprzyk *et al.* [43] used the easily synthesized  $[WZn_3(H_2O)_2][ZnW_9O_{34}]_2]^{12-}$  polyoxometalate as catalysts under microwave pressurized conditions and the accessible 30% aqueous hydrogen peroxide solution as oxidant to rapidly react in a relatively short reaction time (~15 min) to oxidize primary and secondary alcohols, respectively, to carboxylic acids and ketones. Their reported method has the advantages of low cost, simple reaction setup and easy availability of catalyst.

The oxidation reaction they studied was carried out under single-phase conditions, which used POM/Zn as the catalyst for alcohol oxidation and a commercially available 30% aqueous hydrogen peroxide solution as the oxidant. The experiment was carried out in a sealed Teflon vessel by simply mixing ethanol, POM/Zn, 30% aqueous hydrogen peroxide and acetonitrile in a molar ratio of 1:0.004:3:11 (total volume of reactants about 100%, 15 mL) and heating the reaction for 15 min at 135 °C and 3 bar pressure.

In 2015, Nikbakht *et al.* [44] investigated a water-soluble polyoxometalate oxygenate nanocapsule  $H_xPMo_{12}O_{40} \cdot CH_4Mo_{72}Fe_{30}(CH_3COO)_{15}O_{254}$ . The nanocapsules are highly stable and are used for the selective oxidation of alcohols to aldehydes and ketones. This catalyst, which has both good environmental

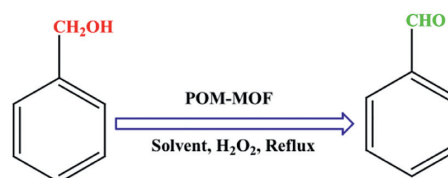


**Fig. 4.** (a) Selective oxidation of various alcohols with  $H_xPMo_{12}O_{40} \subset H_4Mo_{72}Fe_{30}(CH_3COO)_{15}O_{254}$  in water. Copied with permission [44]. Copyright 2015, Elsevier. (b) Screening the stability of  $H_xPMo_{12}O_{40} \subset H_4Mo_{72}Fe_{30}(CH_3COO)_{15}O_{254}$  nano capsule in the oxidation of benzyl alcohol at different pH's by UV-vis. Reproduced with permission [44]. Copyright 2015, Elsevier.

and economic value, can be used with water as the solvent. Good selectivity and extremely high conversions can be obtained even at very low catalyst usage. The catalytic experiments were initiated by oxidation of benzyl alcohol (1 mmol) with  $H_2O_2$  (4.5 mmol) in the presence of 1  $\mu$ mol POM nanocapsules in double distilled water at 45 °C. After only 45 min, complete conversion of benzyl alcohol was possible, using a small amount of catalyst (1  $\mu$ mol), and was able to produce benzaldehyde in 100% yield by a simple separation using ethyl acetate as a safe solvent. However, due to the pH-dependent structure of the POMs, the exact same conversion and selectivity can be obtained only when the pH is adjusted to less than or equal to 6.6 (Fig. 4).

It is worth mentioning that after the completion of the reaction, in which ethyl acetate was added as a safe solvent, the hydrophobic organic products were isolated without further purification, subsequently the aqueous solution of the catalyst could be directly reapplied to the next round of reaction. Surprisingly, due to the intrinsic stability of  $H_xPMo_{12}O_{40} \subset H_4Mo_{72}Fe_{30}(CH_3COO)_{15}O_{254}$ , the catalyst could be effectively recovered more than 10-fold in the oxidation reaction of benzyl alcohol, and only after the ninth use was a decrease in catalyst performance observed to a very small extent (<2%).

Method of inserting POMs into MOFs has opened new research paths in various fields, especially in catalysis. POM/MOF composites have a highly acidic, oxygen-rich surface and redox ability due to the typical characteristics of POMs and a highly ordered structure due to the presence of MOFs, POM/MOF composites have a highly ordered structure, large surface area, tunable pore size and shape due to the presence of MOF [23]. Because of their amazing structural features, these hybrid materials have been attracting much attention. What is more, those features have potential applications in the fields of organocatalysis, proton conduction, adsorption and separation, magnetism, lithium-ion batteries, supercapacitors, medicine, electrochemistry, biofuels, etc. The special chemical and physical properties of POM-MOFs lead to their high capacity and selectivity as catalysts in simple organic transformations [31,45,46]. In 2016, Babahydari *et al.* [47] synthesized  $[Cu_3(4,4'-bpy)_3][HSiW_{12}O_{40}](C_3H_4N_2)$  (abbreviation: HSiW-MOF),  $[Cu_3(4,4'$



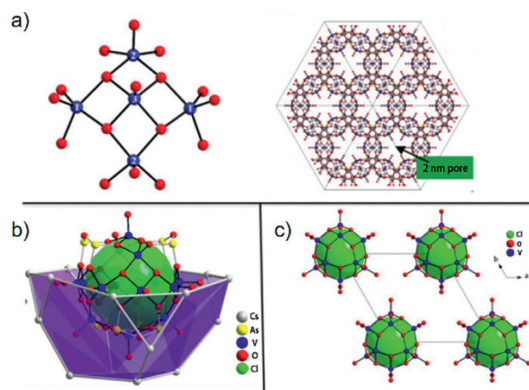
**Fig. 5.** Oxidation of alcohols with  $H_2O_2$  catalyzed by POM-MOF. Copied with permission [47]. Copyright 2016, Iranian Chemical Society.

$bpy)_3][PMo_{12}O_{40}](C_5H_6N_2) \cdot 0.5H_2O$  (abbreviation: PMO-MOF),  $[Cu_2(4,4'-bpy)_2][HPMo_{12}O_{40}](C_5H_6N_2)$  (abbreviation: HPMO-MOF) and  $[Cu(Phen)(4,4'-bpy)(H_2O)]_2[PW_{12}O_{40}](4,4'-bpy)$  (abbreviation: PW-MOF). All four compounds are organic-inorganic polyoxometalate oxidate based skeletons, which can be used in acetonitrile with 30% hydrogen peroxide as oxidant and the above four POMs-MOF as catalysts for the targeted oxidation of alcohols to the corresponding aldehydes and ketones (Fig. 5). Their study led to the conclusion that PW-MOF has higher catalytic activity than all the other three organic-inorganic polyoxometalate catalysts and can be successfully used for the selective oxidation of benzyl alcohols, straight-chain alcohols and secondary alcohols to their corresponding aldehydes and ketones. In addition to this, the conversion of allyl alcohols to their corresponding aldehydes was outstandingly selective (97%–99%) with very high conversions in the catalytic system of PW-MOF.

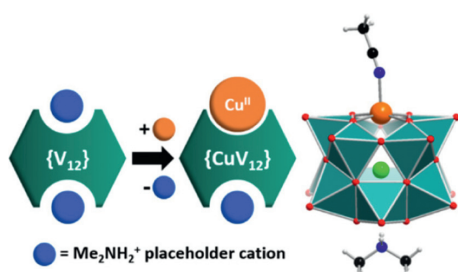
It is worth pointing out that the PW-MOF catalyst is easily recoverable by filtration and can be reused four times while maintaining a high catalytic performance, with a slight decrease in catalytic activity observed only after more than four repeated uses.

In 2017, Yang *et al.* [48] developed a method to synthesize substituted *o*-aryl ethyl ketones (or amides) *via* the carbon hydroxylation reaction of terminal alkynes (or nitrile) with secondary aromatic alcohols in yields up to 95% by using inexpensive  $H_3PMo_{12}O_{40}$  as a catalyst and non-volatile propylene carbonate (PC) as a green solvent to form a catalytic system, which is not only simple to operate, but also has the remarkable advantages of inexpensive, non-toxic catalyst and solvent systems. What is more, the reacting conditions are mild.

POMs with vanadium substituted anionic skeletons are widely known catalysts for selective oxidation reactions, but POMs with vanadium as the only transition metal cation in the polyoxo-core structure have not been reported. In 2017, Campbell *et al.* [49] reported for the first time the synthesis of POMs with vanadium as the only transition metal cation in the polyoxo-core structure (*i.e.*, polyoxovanadates (POVs)) by salt inclusion chemistry (SIC) and their use in the field of organic oxidation catalysts. The usage of SIC has led to a unique combination of vanadium atoms as the only transition metal within the anionic POMs framework. They investigated respectively in depth the catalytic performance of three reduced POV catalysts (Fig. 6):  $Cs_{2.5}(V_5O_9)(AsO_4)_2$  (**1**),  $Cs_5(V_{14}As_8O_{42}Cl)$  (**2**) and  $Cs_{11}Na_3Cl_5(V_{15}O_{36}Cl)$  (**3**) for alcohol oxidation reactions. They found that catalyst **2** and **3** showed the highest product conversions. They both successfully achieved feedstock (1.0 mmol of starting alcohol). Further experimental studies showed that catalyst **2** had a more pronounced catalytic effect than catalyst **3**, the quantitative conversion of product was higher for catalyst **2** than catalyst **3** (due to the fact that catalyst **3** could only catalyze the quantitative conversion of some aryl-activated alcohols), and the reaction time was shorter for catalyst **2**. Their approach successfully solves some of the problems associated with POM-mediated oxidation strategies, including: high catalyst loading (*e.g.*, 40 mol%), high reaction temperatures (90–135 °C), etc., as their reported method can facilitate the oxidation of a range of



**Fig. 6.** Polyoxovanadate structures for catalysts (a) (salt)- $\text{Cs}_{2.5}(\text{V}_5\text{O}_9)(\text{AsO}_4)_2$  (**1**), (b)  $\text{Cs}_5(\text{V}_{14}\text{As}_8\text{O}_{42}\text{Cl})$  (**2**), (c)  $\text{Cs}_{11}\text{Na}_3(\text{V}_{15}\text{O}_{36}\text{Cl})_5$  (**3**). In **3**, only  $[\text{V}_{15}\text{O}_{30}\text{Cl}]^9-$  clusters are shown for clarity. Reproduced with permission [49]. Copyright 2017, Wiley-VCH.



**Fig. 7.** Left: Controlled self-assembly of the oxidation catalyst  $\{\text{CuV}_{12}\}$  by reaction of  $\{\text{V}_{12}\}$  with  $\text{Cu}^{\text{II}}$ . Right: Polyhedral representation of  $\{\text{CuV}_{12}\}$ ,  $(\text{Me}_2\text{NH}_2)[\text{Cu}(\text{MeCN})\text{V}_{12}\text{O}_{32}\text{Cl}]^{2-}$ . Colour scheme: V, teal; Cu, orange; O, red; Cl, lightgreen; N, blue; C, black; H, grey. Copied with permission [50]. Copyright 2017, Wiley-VCH.

secondary alcohols using only 2 mol% of catalyst and can be performed under relatively mild conditions (room temperature).

It is noteworthy that the group also found that catalyst **3** could only be used to catalyze the oxidation of alkyl secondary alcohols and did not activate the oxidation of C-H or primary alcohols, as was the case with catalyst **2**. Furthermore, it was confirmed that catalyst **1** is not actually a catalyst for alcohol oxidation reactions.

In 2017, several studies conducted by Katharina Kastner *et al.* [50] provided great assistance to the problem of catalyst deactivation. They discovered a new class of metal-functionalized polyoxovanadates (POVs): programmed reactivity tuning was successfully achieved by centering the catalytic transition metal and selectively fitting it into the framework of the dodecanoate cluster (Fig. 7).

The use of this programmed binding mechanism they reported made possible the reactivation of the polyoxometalate catalyst:  $\{\text{V}_{12}\}$  was first reacted with  $\text{Cu}^{\text{II}}$  to give the homogeneous oxidation catalyst  $\{\text{CuV}_{12}\}$  ( $= (\text{Me}_2\text{NH}_2)[\text{Cu}(\text{MeCN})\text{V}_{12}\text{O}_{32}\text{Cl}]^{2-}$ ), which their experiments measured to have a yield of about 50%. They investigated the oxidation activity of the catalyst and found that the catalyst was self-assembled by  $\text{Cu}^{\text{II}}$  and  $[(\text{Me}_2\text{NH}_2)_2\text{V}_{12}\text{O}_{32}\text{Cl}]^{3-}$  in solution and selectively catalyzed the oxidation of the secondary alcohol (here: 1-phenylethanol) to the corresponding ketone in near-quantitative yields. Temporary deactivation of the catalyst in solution can be achieved by removing the  $\text{Cu}^{\text{II}}$  site from the catalyst (achieved by the addition of a complexing agent). The catalyst can then be reassembled by the addition of  $\text{Cu}^{\text{II}}$  to achieve reactivation of the catalytic activity. This system can be used as a basic template to help scholars understand more about the POM catalyst deactivation-repair procedure.

The oxidation of benzyl alcohol to the corresponding aldehyde is one of the most important transformations in the field of alcohol oxidation [51]. In 2018, Farhadi *et al.* [52] chemically anchored

aminosilylated magnetic graphene oxide on the surface of 12-molybdenum phosphate ( $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ , HPMo) ( $\text{Fe}_3\text{O}_4/\text{GrOSi}(\text{CH}_2)_3\text{-NH}_2$ ) to prepare  $\text{Fe}_3\text{O}_4/\text{GrOSi}(\text{CH}_2)_3\text{-NH}_2/\text{HPMo}$  nanocomposite, which is a catalyst for oxidation reactions that can be separated without solvent. They studied the selective oxidation of benzyl alcohol to benzaldehyde and used this reaction as a basis for the evaluation of their prepared nanocomposite catalysts. Under the optimized conditions they set, multiple alcohols were converted to the corresponding carbonyl compounds by the oxidation of hydrogen peroxide with high yields, and the catalytic oxidation reaction was highly selective for benzyl alcohol, reaching 99%. Furthermore, they found in this study that the strongly electron-absorbing substituents exhibited lower yields compared to other substituents during the oxidation reaction of benzyl alcohols. This shows that the carbon-positive ionic intermediate is involved in the catalytic oxidation reaction due to the elimination of hydride from the  $\beta$ -proton of the substrate.

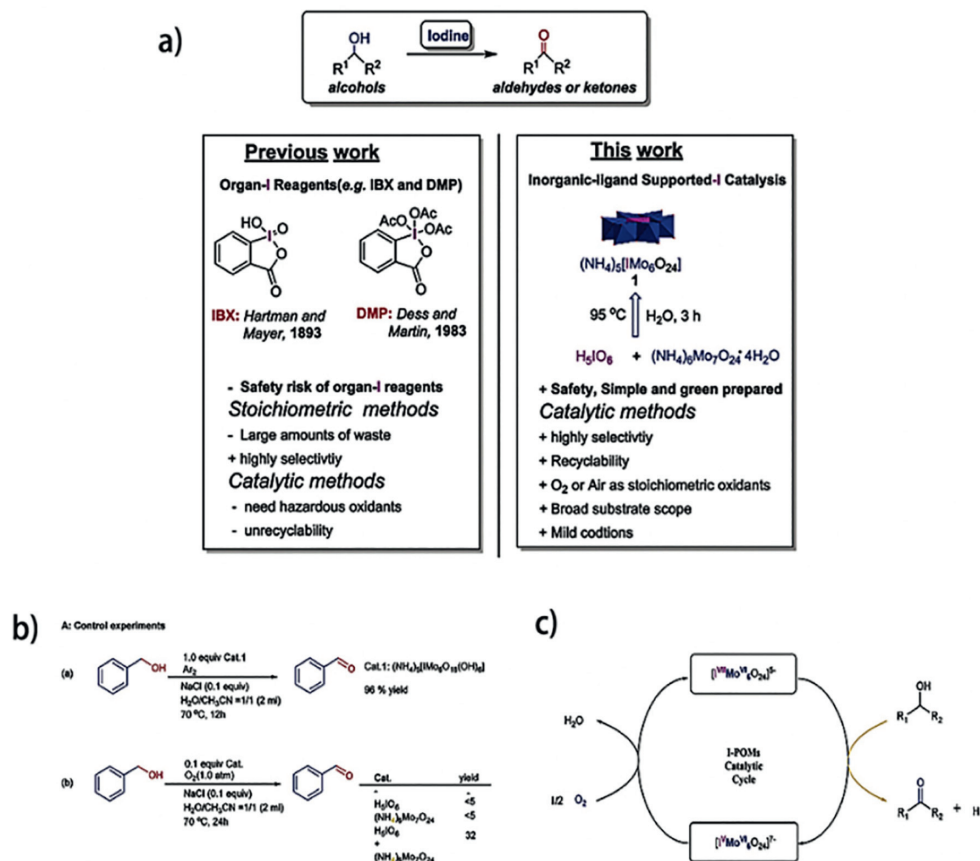
In 2018, Zhang *et al.* developed an inorganic-ligand iodine POM ( $(\text{NH}_4)_5[\text{IMO}_6\text{O}_{24}]$ ) catalytic oxidation system (this is a remarkable improvement over the conventional iodine-catalyzed system as shown in Fig. 8a), which is not only catalytically active but also has the advantages of mild reaction conditions and thus is suitable for catalyzing the oxidation reactions of various alcohols [53]. The catalyst system is tolerant of a wide range of substrates and has excellent selectivity and good recoverability. In addition, the catalytic system has good safety properties, which can effectively enhance its application in the field of pharmaceuticals, fragrances and food additives without the use of organic ligands or toxic substances.

The group performed catalytic experiments as well as catalytic tests to determine the usefulness of the catalytic system (the reaction mechanism is shown in Figs. 8b and c). They used pure  $\text{O}_2$  for the reaction of 60 mmol of benzyl alcohol and obtained 5.724 g of benzaldehyde in 16 h with a guaranteed 90% conversion and 99% selectivity. These results indicate that the experiment retains high activity and selectivity at low catalytic amounts of iodine-POM catalyst, allowing scalable aerobic oxidation of alcohols. Subsequently, they also evaluated the ability to recycle the catalyst. The solid catalyst was separated by filtration (catalyst precipitation after addition of ether to the reaction system) and could be used directly for subsequent benzyl alcohol oxidation without further purification. The data showed that the catalyst could be used repeatedly at least six times with no deactivation of performance.

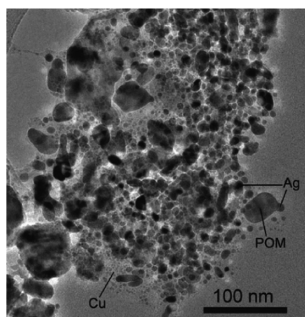
In 2020, Aghay *et al.* [12] investigated the loading of  $[(\text{nC}_4\text{H}_9)_4\text{N}]_5[\text{PW}_{11}\text{ZnO}_{39}] \cdot 3\text{H}_2\text{O}$  and  $[\text{PW}_{11}\text{ZnO}_{39}]_5$  on Dowex 22 as catalysts to catalyze the homogeneous or heterogeneous oxidation of alcohols with hydrogen peroxide as oxidant in this work. This study used water as a medium to convert different alcohols to the corresponding aldehydes and ketones with high yields. Dowex 22 loaded polyoxometalate  $\text{PW}_{11}\text{Zn@Dowex}$  can also oxidize unsaturated alcohols to the corresponding carbonyl compounds with very high stability as well as good selectivity.

Their extensive and reliable experiments with this loaded catalyst have led to the following results: the loaded POMs catalyst still has good catalytic performance after multiple leaching and recovery, which proves the high stability and reusability of the loaded POMs catalyst.

Also in 2020, Wang *et al.* [9] reported a study that a single-atom cobalt compound  $(\text{NH}_4)_3[\text{CoMo}_6\text{O}_{18}(\text{OH})_6]$  (abbreviated as  $\text{CoMo}_6$ ) loaded by a pure inorganic ligand could be used as a heterogeneous catalyst, and the study was able to effectively promote this type of reaction in the presence of 30%  $\text{H}_2\text{O}_2$  using KCl as an additive. In general, the oxidative cross-esterification of various alcohols (aromatic and aliphatic) can be achieved under mild conditions, capable of providing the corresponding esters, including several drug molecules and natural products, and ensuring high



**Fig. 8.** (a) Representative organic-iodine catalyst systems and inorganic-ligand supported iodine-catalyst for aerobic oxidation of alcohols. (b) Experimental studies providing insight into the mechanism of the iodine-catalyzed oxidation of alcohols. (c) Proposed mechanism for the iodine-POM-catalyzed oxidation of alcohols. Reproduced with permission [53]. Copyright 2018, RSC.



**Fig. 9.** TEM image of Ag-Cu particles after deposition on the POM support. Area with intimate mixtures of small Ag metal particles (usually darker from diffraction contrast), flake-like POM crystals and Cu-oxide nanoparticles. Copied with permission [7]. Copyright 2021, Elsevier.

yields. They found through a more in-depth study that chloride ions are able to combine with  $\text{CoMo}_6$  to form supramolecular dimer  $2(\text{CoMo}_6\text{-Cl})$ . Through the synergistic effect of chloride ion and  $\text{CoMo}_6$ , this supramolecular dimer  $2(\text{CoMo}_6\text{-Cl})$  was able to catalyze the reaction effectively. Both the mechanistic study and the controlled reaction indicated that the esterification was carried out through a key oxidation process of aldehyde.

In 2021, Lukato *et al.* [7] reported an effective method for the catalytic oxidation of benzyl alcohol using a silver-copper catalyst (Ag-Cu/POM catalyst) with polyoxometalate as an effective carrier and using molecular oxygen as an oxidant (Fig. 9). Among them,

the Ag-Cu/POM catalyst was prepared by electrical substitution in the presence of polyvinylpyrrolidone and polyethylene glycol.

The Ag-Cu/POM catalysts achieved nearly 100% conversion of benzyl alcohol and higher than 99% selectivity for benzaldehyde at  $85^\circ\text{C}$  and 5 h reaction conditions. The Ag-Cu/POM catalyst was also tested for the catalytic oxidation of various benzyl alcohol derivatives, and the Ag-Cu/POM catalyst showed excellent conversion and >99% selectivity for the corresponding aldehydes. In addition, the Ag-Cu catalyst loaded on POM is highly stable and therefore does not leach or deactivate. At the same time, the catalyst is heterogeneous, easily recoverable after the reaction and can be reused at least five times, and no significant decrease in activity and selectivity was observed.

Faced with such excellent catalytic performance of Ag-Cu/POM, Lukato's group attributed it to the stabilization of Ag-Cu NPs by POM. Although the monometallic Ag catalyst loaded with POMs showed good conversion in catalyzing the oxidation of benzyl alcohol, the selectivity for benzaldehyde was poor, which was largely solved by the group by adding Cu to the system. There is one kind of polyoxometalate so called Anderson-Evans polyoxoanions, for which the corresponding physico-chemical properties are basically depended on heteroatoms, however, few studies of such POMs applied in current catalysis have been reported so far. Otherwise, Anderson POMs is easy to graft with organic groups, which is due to its six hydroxyl groups on both sides, giving rise to unique catalytic properties.

In 2021, Wang *et al.* [11] reported a highly stable Anderson-type POM  $[\text{N}(\text{C}_2\text{H}_9)_4]_3[\text{CrMo}_6\text{O}_{18}(\text{OH})_3\text{C}(\text{OCH}_2)_3\text{CH}_2\text{OH}]$  modified by a single pentaerythritol, which is a novel chromium-based catalyst that can catalyze the oxidation of alcohols by hydrogen peroxide to

produce the corresponding reaction of alcohols to esters with high conversion and high selectivity without the need for additional organic ligands. The system allows the use of a wide range of alcohols with different functionalities, including some natural products and pharmaceutical intermediates. The low loading required for this catalyst eliminates the need for expensive organic ligands, which greatly reduces the cost.

It should be noted that Wei and his team [54] previously demonstrated that the catalytic activity of the polyoxometalate catalyst can be tuned by binding to halide ion supramolecules.

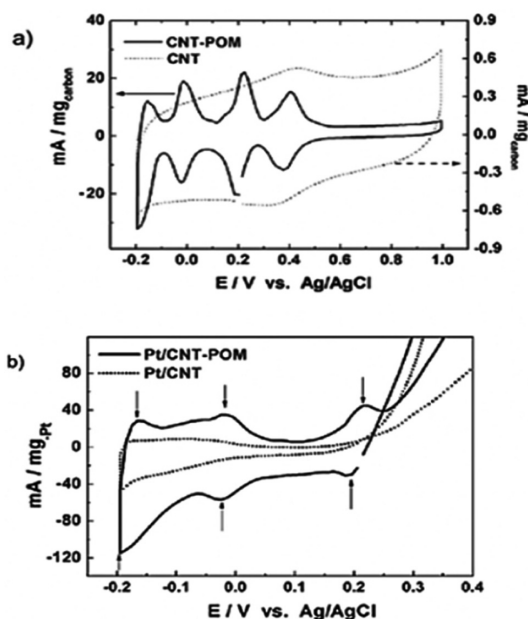
### 3. Polyoxometalate based compounds for electrocatalytic synthesis of aldehydes and ketones

In comparison to conventional oxidation processes, electro-oxidation is a viable alternative to traditional thermocatalytic methods due to its efficiency and sustainability [16]. Driven by electricity, alcohols can be oxidized at room temperature and atmospheric pressure at the anode electrode while releasing hydrogen from the cathode electrode [32,55]. Although a number of electrocatalysts have been developed for the anodic oxidation of alcohols, the selective oxidation of alcohols to the corresponding aldehydes remains a challenge, and the reactivity in many of the currently reported catalytic systems is significantly dependent on the addition of basic additives. The preparation of electrocatalysts usually requires tedious experimental steps and the introduction of reducing agents. In addition, the experimental equipment is complex and expensive. Therefore, there is an urgent need for a simple synthetic method to prepare efficient electrocatalysts for alcohol oxidation. As a nanoscale polyoxometalate cluster with high electronegativity, oxygen-rich surface, exceptional redox potential and electron transfer capability, POMs can be used as reducing agents to reduce noble metal nanoparticles and can be coated on the nanoparticle surface to form an encapsulated structure. Meanwhile, POMs can be used as a linker to connect carbon-based carriers and noble metal nanoparticles through hydrogen bonding. Generally, the preparation of electrodes by drop coating requires the use of an adhesive to fix the catalyst on the surface, but only the surface is involved in the reaction.

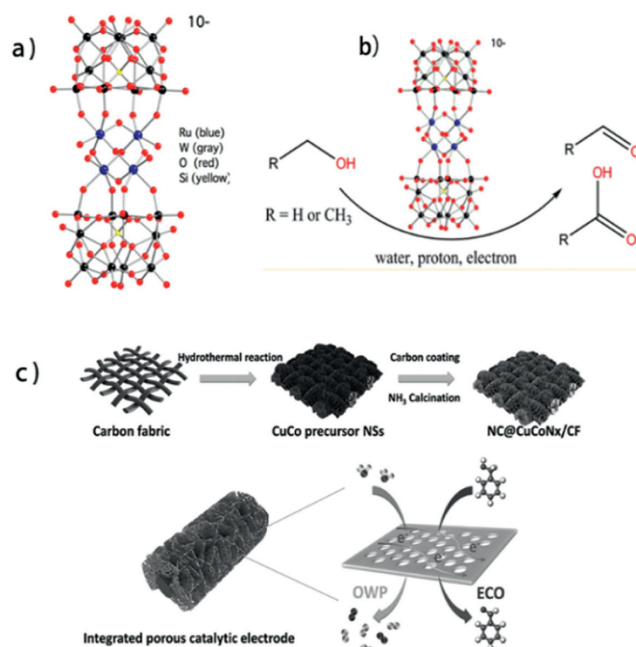
In recent years, carbon nanotubes (CNTs) have received much attention as electrocatalysts due to their good electrical properties, chemical stability under acidic electrolyte conditions and high specific surface area [56,57]. In 2008, Nyman *et al.* [57] chemically impregnated the polyoxometalate anion  $\text{PMo}_{12}\text{O}_{40}^{3-}$  into Pt-loaded carbon nanotubes (Pt/CNTs) catalysts prepared by colloidal methods. They compared this catalyst with Pt/CNTs or POM-impregnated Pt/C (Pt/C-POM) in terms of activity and stability, and the POM-impregnated Pt/CNTs catalyst system (Pt/CNTs-POM) showed a catalyst system with at least 50% catalytic mass activity and improved stability of methanol electrooxidation (Fig. 10).

Through their experiments and studies, they determined that the improved activity of Pt/CNTs-POM could be attributed to a combination of (1) the improved electrical conductivity of carbon nanotubes, (2) the high dispersion of Pt nanoparticles on CNT using a polyol process, and (3) the improved oxidation of methanol due to the presence of polyoxometalate, which induced the oxidative removal of some toxic substances on Pt. However, the use of expensive metal electrodes (Pt or Pt alloys) or metal complex-based catalysts like this one can lead to a high cost of the whole process and become a major obstacle to the development of this route.

In 2016, Liu *et al.* [58] achieved efficient electrocatalytic oxidation of ethanol and methanol using a molecular oxygen catalyst  $[\{\text{Ru}_4\text{O}_4(\text{OH})_2(\text{H}_2\text{O})_4\}(\gamma\text{-SiW}_{10}\text{O}_{36})_2]^{10-}$  (Fig. 11a) containing ruthenium polyoxometalate (the reaction mechanism is shown in Fig. 11b). They conducted voltammetric studies on the soluble form



**Fig. 10.** (a) Cyclic voltammograms of CNTs with or without POM in 0.5 mol/L  $\text{H}_2\text{SO}_4$  electrolyte at a scan rate of 50 mV/s at room temperature. (b) CVs for first cycle for Pt/CNTs-POM (solid line) and Pt/CNTs (dotted line) over enlarged potential range of  $-0.2\sim 0.4$  V (vs. Ag/AgCl) in 0.5 mol/L  $\text{H}_2\text{SO}_4$  containing 2 mol/L  $\text{CH}_3\text{OH}$  solution at 50 mV/s at room temperature. Reproduced with permission [57]. Copyright 2008, Elsevier.



**Fig. 11.** (a) Structure of  $[\{\text{Ru}_4\text{O}_4(\text{OH})_2(\text{H}_2\text{O})_4\}(\gamma\text{-SiW}_{10}\text{O}_{36})_2]^{10-}$ . (b) Schematic diagram of  $[\{\text{Ru}_4\text{O}_4(\text{OH})_2(\text{H}_2\text{O})_4\}(\gamma\text{-SiW}_{10}\text{O}_{36})_2]^{10-}$  catalyzed selective oxidation of alcohols. Reproduced with permission [58]. Copyright 2016, ACS. (c) Schematic of  $\text{NC@CuCo}_2\text{N}_x/\text{CF}$  synthesis and  $\text{NC@CuCo}_2\text{N}_x/\text{CF}$  utilization as integrated porous catalytic electrode for OWP and selective ECO of benzyl alcohol. Copied with permission [59]. Copyright 2017, Wiley-VCH.

of  $[\{\text{Ru}_4\text{O}_4(\text{OH})_2(\text{H}_2\text{O})_4\}(\gamma\text{-SiW}_{10}\text{O}_{36})_2]^{10-}$  as well as the surface-limited form, and the experimental results showed that the oxidized form of  $[\{\text{Ru}_4\text{O}_4(\text{OH})_2(\text{H}_2\text{O})_4\}(\gamma\text{-SiW}_{10}\text{O}_{36})_2]^{10-}$  can act as an active catalyst for alcohol oxidation in both aqueous (acidic, neutral and basic in a wide pH range) and ethanol media.

Under these conditions mentioned above, the initial form of  $[\{\text{Ru}_4\text{O}_4(\text{OH})_2(\text{H}_2\text{O})_4\}(\gamma\text{-SiW}_{10}\text{O}_{36})_2]^{10-}$  also exhibited considerable reactivity, especially in neutral solutions containing 1.0 mol/L  $\text{NaNO}_3$ . In order to identify the products of the oxidation reaction, preparative-scale monolithic electrolysis experiments were performed: the ethanol oxidation products were measured as 1,1-diethoxyethane and ethyl acetate formed by the condensation of acetaldehyde or acetic acid with excess ethanol by NMR, gas chromatography (GC) and GC mass spectrometry detection. Oxidation of methanol produces formaldehyde or formic acid, which then condenses with excess methanol to form dimethoxymethane and methyl formate, respectively. These results suggest that the electrocatalytic oxidation of ethanol and methanol produces aldehydes and acids *via* two- and four-electron oxidation processes. The total Faraday efficiencies of the electrocatalytic oxidation of the two alcohols exceeded 94%. They were compared with other values reported in the literature. The results indicate that  $[\{\text{Ru}_4\text{O}_4(\text{OH})_2(\text{H}_2\text{O})_4\}(\gamma\text{-SiW}_{10}\text{O}_{36})_2]^{10-}$  is one of the most active molecular electrocatalysts for the oxidation of methanol and ethanol.

All these lead up to one conclusion: the molecular water oxidation catalyst  $[\{\text{Ru}_4\text{O}_4(\text{OH})_2(\text{H}_2\text{O})_4\}(\gamma\text{-SiW}_{10}\text{O}_{36})_2]^{10-}$  exhibited high catalytic activity for the electrooxidation of methanol and ethanol at the carbon electrode when dissolved in the solution phase or confined to the electrode surface, and after long-term electrolysis data showed that after a charge of 100 C charge ( $> 1000$  electrons per catalyst), they did not observe a significant catalytic current. This confirms the high stability of  $[\{\text{Ru}_4\text{O}_4(\text{OH})_2(\text{H}_2\text{O})_4\}(\gamma\text{-SiW}_{10}\text{O}_{36})_2]^{10-}$ .

In 2017, Zheng *et al.* [59] developed a self-supporting 3D integrated structure consisting of an array of  $\text{CuCoN}_x$ -based porous nanosheets grown on carbon fibers (CF) with a conductive nitrogen-doped carbon shell ( $\text{NC@CuCo}_2\text{N}_x/\text{CF}$ ) in the outer layer, resulting in good electrooxidation activity under alkaline conditions (Fig. 11c). At a constant current of 15 mA, the conversion of benzyl alcohol was up to 96% and the selectivity for benzaldehyde was over 95%. In addition, the structure exhibits good electrocatalytic hydrogen precipitation activity in alkaline media: a current density of  $10 \text{ mA/cm}^2$  can be achieved at voltages below 1.62 V. When  $15 \times 10^{-3} \text{ mol}$  benzyl alcohol was used, the cell voltage showed a significant reduction (1.55 V), demonstrating a more pronounced electrocatalytic activity than most of the well-studied overall water splitting (OWP) catalysts reported so far. This excellent electrocatalytic activity is attributed to the synergistic effect between  $\text{CuCoN}_x$  and N-doped carbon shells. The porous nanosheet array structure also provides a large active surface area for ion and molecular diffusion, facilitating rapid electron transport. In addition, the key substances can be tuned to their appropriate adsorption energies based on density flooding theory (DFT) calculations. Thus, these results demonstrate the potential of  $\text{NC@CuCoN}_x/\text{CF}$  not only to be an attractive non-precious metal bifunctional electrocatalyst for OWP, but also to generate high-value products through selective electrochemical oxidation (ECO).

In 2019, Adarsh and Chandrasekaran [60] reported transition metal ion-assisted trimerization of polyisocyanurates and their pyrolytic derivatives as synergistic electrocatalysts for the selective oxidation of alcohols. They studied the trimerization reaction of aromatic isocyanates with polyisocyanurate nanofoams under the conditions catalyzed by transition metal salts ( $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ) and found that the presence of metal ions accelerated the gelation of the polyisocyanurate network. The nickel-cobalt-polyisocyanurate (Ni-Co-PIR-RT) hybrid monolithic material was pyrolyzed at different temperatures (from 600 °C to 1000 °C) under inert atmosphere conditions to produce oxides and metallic forms of Ni and Co with significant carbon content. Ni-Co-PIR-

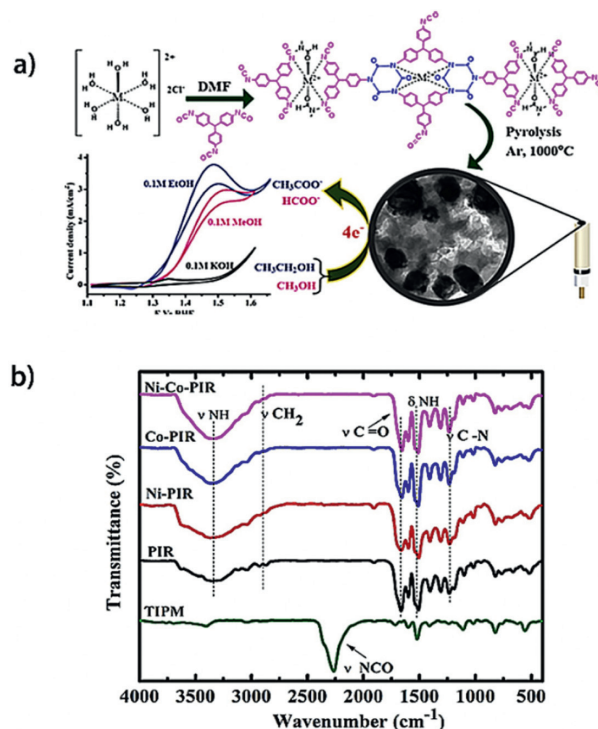


Fig. 12. (a) Schematic diagram of catalyst synthesis and comparative plots of current density. (b) FT-IR spectra of TIPM, PIR Ni-PIR, Co-PIR and Ni-Co-PIR before pyrolysis. Reproduced with permission [60]. Copyright 2019, ACS.

RT pyrolysis at 600 °C (Ni-Co-PIR-600) resulted in the Ni ions and Co ions are completely reduced to the metals Ni and Co, while the sample at 800 °C (Ni-Co-PIR-800) results in the partial conversion of the metals Ni and Co to their respective oxides. At a temperature of 1000 °C (Ni-Co-PIR-1000), the metal Co is completely converted to CoO, which contains significant amounts of metallic Ni and NiO. The Ni-PIR-1000 sample shows minimal activity towards the methanol oxidation reaction (MOR) with an onset potential and maximum current density of 1.44 V (compared to the reversible hydrogen electrode) and  $0.6 \text{ mA/cm}^2$ . The Co-PIR-1000 sample, on one hand, showed no significant activity for the oxygen evolution reaction (OER) at a starting potential of 1.33 V for MOR in 0.1 mol/L KOH and 0.2 mol/L  $\text{CH}_3\text{OH}$ . On the other hand, under the same conditions, Ni-Co-PIR-1000 showed a 5-fold increase in current density relative to MOR (onset potential of 1.34 V and current density of  $4 \text{ mA/cm}^2$ ) with a 100 mV decrease in onset potential to Ni-PIR-1000. The presence of Ni, NiO and CoO combination makes Ni-Co-PIR-1000 synergistic and superior activity (Fig. 12).

The polyoxometalate mentioned above, whether ruthenium-containing or Pt-containing, are still limited for their direct use as electrode materials because of their poor adhesion and conductivity on the electrode surface. In 2020, in order to address the limitations of precious metal catalysts for electrocatalytic oxidation in this research, Li and his team [16] firstly proposed a strategy for the electrostatic assembly of polyoxometalate through the polyoxometalate catalyst  $\text{PMo}_{10}\text{V}_2$  with a strategy of electrostatic assembly of porous cationic covalent triazine framework (CTF) was finally successfully prepared as a polyoxometalate electrode material  $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}@\text{CTF}$  (denoted as  $\text{PMo}_{10}\text{V}_2@\text{CTF}$ ), which has many remarkable advantages, especially showing excellent catalytic activity for the catalytic oxidation of alcohols to the corresponding aldehydes. Through extensive experiments, they found a 99% conversion of benzyl alcohol and a selectivity of more than 99% for benzaldehyde, along with the generation of hydrogen. This cat-

alytic system possesses good atomic economy, high energy conversion (96% Faraday efficiency), significant catalytic activity, and stability for at least 8 cycles. They also mentioned in their report through various experimental and spectroscopic analyses that because of the versatile redox ability of  $\text{PMo}_{10}\text{V}_2$  and the good porosity and adsorption properties of CTF in the  $\text{PMo}_{10}\text{V}_2\text{@CTF}$  composite after electrostatic assembly,  $\text{PMo}_{10}\text{V}_2\text{@CTF}$  has a relatively good catalytic performance.

Han *et al.* [14] selected carbon dots (CDs) and Co-substituted intercalated polyoxometalate  $\text{K}_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]\cdot 20\text{H}_2\text{O}$  (Co-POM) as the building blocks to construct a novel ternary composite electrocatalyst CDs/Co-POM/ Pt, which was used to catalyze the oxidation reaction of methanol. It was characterized by FTIR, field emission scanning electron microscopy (FESEM), high-resolution electron microscopy (HRTEM), energy dispersive X-ray spectroscopy (EDX), elemental analysis, X-ray diffractometer (XRD) and X-ray photoelectron spectroscopy (XPS). The characterization results show that the CDs/Co-POM/Pt catalyst is a Pt nanoflower-like structure with high dispersion as well as good homogeneity. They also found that the electrocatalytic ability of Pt was significantly enhanced by the presence of CDs and Co-POM, and the highest peak value of current density reached  $7.98\text{ mA/cm}^2$ , which was 3.6 times that of the CDs/Pt catalyst, 6.5 times that of the Co-POM/Pt catalyst, and 10.8 times that of the pure Pt catalyst by electrochemical experiments. CDs/Co-POM/Pt have good stability in electrocatalytic process. This work makes an important contribution to the development of polyoxometalate-based electrocatalysts and opens up a brand new path.

As a unique branch of POMs, polyoxo-niobates (PONbs) have received attention in various fields due to their diverse structures and diverse applications in re-catalysis, nuclear waste treatment and virology [57,61]. However, the lack of soluble Nb precursors, as well as their low reactivity and narrow working pH range, have led to the relatively slow development of PONbs compared to other POM members such as polyoxotungstates, polyoxomolybdates and polyoxovanadates [62]. Recently, great progress has been made in studies concerning polyoxo-niobates, and some large clusters, such as  $\{\text{Nb}_{27}\text{O}_{76}\}$ ,  $\{\text{Nb}_{32}\text{O}_{96}\}$ ,  $\{\text{Nb}_{52}\text{O}_{150}\}$ ,  $\{\text{Nb}_{81}\text{O}_{225}\}$ ,  $\{\text{Nb}_{114}\text{O}_{316}\}$ , and the highest nuclei  $\{\text{Nb}_{288}\text{O}_{768}(\text{OH})_{48}(\text{CO}_3)_{12}\}$  have been reported one after another [3,63,64]. Previously, the covalent triazine framework immobilized  $\{\text{PMo}_{10}\text{V}_2\text{O}_{40}\}$  showed excellent activity in the electrocatalytic oxidation of benzyl alcohol and ethylbenzene, while the catalytic performance of vanadium-containing PONbs has not yet been fully and comprehensively investigated. In this context, in 2022, Li *et al.* [65] obtained  $[\text{Ni}(\text{En})_2]_5[\text{PNb}_{12}\text{O}_{40}(\text{VO})_5](\text{OH})_5\cdot 18\text{H}_2\text{O}$  (**4**) and  $[\text{Ni}(\text{En})_3]$  in the controlled synthesis of two vanadium-containing Keggin-type PONbs by varying the source of vanadium and hydrothermal temperature.  $5[\text{PNb}_{12}\text{O}_{40}(\text{VO})_2]\cdot 17\text{H}_2\text{O}$  (**5**, En = ethylenediamine), two novel POM catalysts (Fig. 13). Compound **4** contains a five-capped Keggin-type polyvanadium oxide  $\{\text{PNb}_{12}\text{O}_{40}(\text{VO})_5\}$ , which is linked by adjacent  $[\text{Ni}(\text{En})_2]^{2+}$  units into a three-dimensional (3D) organic-inorganic framework, representing the first nickel complex-linked 3D vanadium oxide based material. Compound **5** is a discrete double-capped Keggin-type polyhydroxybenzoate  $\{\text{PNb}_{12}\text{O}_{40}(\text{VO})_2\}$  with  $[\text{Ni}(\text{En})_3]^{2+}$  units as anti-balance cations. Compounds **4** and **5** have poor solubility in common solvents and will remain stable in the pH range of 4–14. Notably, as electrode materials, compounds **4** and **5** are active for the selective oxidation of benzyl alcohol to benzaldehyde. Under ambient conditions without the addition of alkaline additives, compound **4** as a noble metal-free electrocatalyst achieves 92% conversion of benzyl alcohol, giving a Faraday efficiency of 93%; in contrast, compound **5** converts 79% of the substrate, giving a Faraday efficiency of 84%, and a small amount of *N*-benzylacetamide is detected as its only by-product. The results of the control experiments suggest that

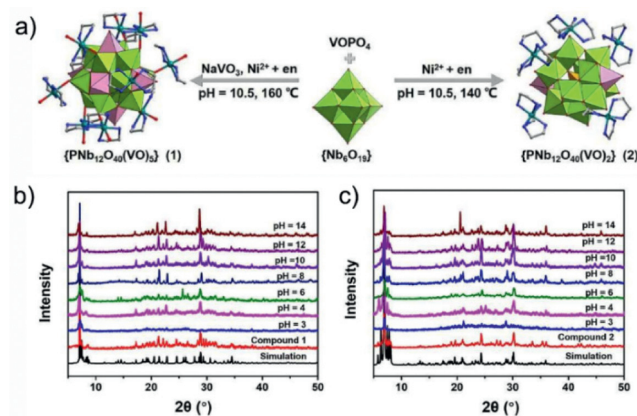


Fig. 13. (a) Controllable synthesis of **4** and **5**. PXRD patterns of (b) **4** and (c) **5** after being soaked in aqueous solutions with different pH values for 24 h. Reproduced with permission [65]. Copyright 2022, MDPI.

both the basic poly (silica oxide) cluster and the capped vanadium atom play an important role in the electrocatalytic oxidation process (Fig. 13).

#### 4. Polyoxometalate based compounds for photocatalytic synthesis of aldehydes and ketones

The main limiting factor which is affecting the efficiency of photocatalytic organic synthesis is the lack of high selectivity. For this reason, people have spent a lot of time and effort to solve this problem.

In marked contrast to conventional thermocatalysis, photocatalysts can initiate spontaneous reactions ( $G_0 < 0$ ) and at the same time non-spontaneous reactions ( $G_0 > 0$ ). In the spontaneous reaction, the light energy, as the energy source of the photocatalyst, can help the photocatalyst to break the energy barrier, thus allowing the reaction to proceed at a faster rate or under milder conditions. While in non-spontaneous reactions, part of the light energy is converted into reaction products and stored as chemical energy. The mechanism of polyoxometalates as photocatalysts is well known, in other words, POM solutions have a high oxidation capacity due to the charge transfer excited state from O to M ( $M = \text{W}$  and  $\text{Mo}$ ) resulting from UV-vis light irradiation, thus enabling the oxidation of organic substrates [66,67]. The photoexcited POM is reduced by transferring one or two electrons from the organic substrate. The reoxidation of photo-reduced POMs back to its original oxidation state is easily affected by oxygen, and this reaction is the basis of its photocatalytic activity [68].

In addition to this, POM photocatalysts have several advantages besides easy photoexcitation using UV or near-visible light [36], including strong light absorption with high molecular absorption coefficients ( $\epsilon > 1 \times 10^4$ ), high redox activity, high structural stability, as well as multi-electron redox properties and easy reoxidation of the reduced material [15,66,67]. However, an important issue is that the light absorption of POM anions usually occurs only in the region of 200–500 nm. Therefore, photosensitization becomes an effective strategy to utilize visible light [66,67]. From the application point of view, heterogeneous polyoxometalate/heteropolyacid (POM/HPA) photocatalysts are the focus of research in the field of POM/HPA photocatalysis. The parent POM/HPA is usually loaded on other materials to form composite heterogeneous photocatalysts [69], of which the most commonly used carriers are  $\text{TiO}_2$ ,  $\text{SiO}_2$ ,  $\text{ZrO}_2$ , etc. In addition to the curing of POM/HPA, the combination of POM/HPA and carriers provides POM/HPA with a larger specific surface area, allowing it to enhance its catalytic activity by provid-

ing a large contact area between catalyst and substrate for surface-mediated electron transfer reactions. In addition, another series of heterogeneous POM photocatalysts are acidic Cs salts  $\text{Cs}_x\text{H}_{3x}\text{PW}_{12}$  ( $x \leq 3$ ) with porous structures, which have relatively high surface area and strong acid sites.  $\text{Cs}_3\text{PW}_{12}$  is the first heterogeneous POM photocatalyst for the photooxidation of propan-2-ol to acetone in aqueous solution. The POM anion in the ground state can be excited in the ultraviolet or near-visible light range. The essence of excitation is the charge transfer from the oxygen atom to the d0 TM in the presence of light of sufficient energy. For example, the excitation of  $\text{PW}_{12}$  is the charge transfer from  $\text{O}^{2-}$  to  $\text{W}^{6+}$ , leading to the formation of a hole center ( $\text{O}^-$ ) and a captured electron center ( $\text{W}^{5+}$ ). As electron donors and electron acceptors, excited POM anions usually exhibit better properties than their ground state. As a consequence, some POMs that are not catalytically active under dark conditions may become capable of oxidizing or reducing various substrates under UV or near-visible light irradiation even when high reaction temperatures are used. In addition to this, the well-defined HOMO-LUMO band gap of the POM anion produces an inhibition of the complexation of electrons and holes generated by light energy irradiation above or equal to its band gap energy [70–73]. Thus, the ability of photogenerated electrons and holes to initiate chemical reactions is due to the strong photooxidation ability of holes and the photoreduction ability of electrons. Under mild conditions, many photocatalytic reactions are readily carried out in the presence of POM, including alcohol oxidation, oxidative bromination of aromatics and olefins, and reduction of  $\text{CO}_2$ . More importantly, its photo-oxidation property is useful for the degradation of various aqueous organic pollutants, which is of environmental importance, and its photoreduction property can be used to remove inorganic TM ions from water [15].

POMs are readily soluble in organic solvents, which makes them difficult to be recycled, and the use of semiconductor metal oxides as carriers is a combination that facilitates the photo reactivity of the catalysts due to the synergistic effect between the two components, while improving the stability of the catalytic system. In 2005, Farhadi *et al.* [66] used acetonitrile as the sole solvent and encapsulated  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  with silica was prepared as an efficient, green, and highly selective heterogeneous photocatalyst using acetonitrile as the sole solvent. A highly efficient and highly selective green process for the photocatalytic oxidation of primary and secondary benzyl alcohols to the corresponding aldehydes and ketones was successfully achieved. The reaction oxidizes only the sec-benzyl alcohol to the benzene ring with high selectivity for vicinal-diol.

The photocatalytic efficiency of polyoxotungstates (POTs) is known to rival that of the semiconductor  $\text{TiO}_2$ , thanks to the presence of the  $\text{O}^- \rightarrow \text{W}^-$  LMCT band in their UV-vis absorption spectrum. Therefore, irradiation of POTs in this band generates a strong oxidation excited state, which can accept a certain number of electrons from the organic substrate material without decomposing. After oxidizing the organic substrate, the photo reduced form of POT is usually reoxidized to its original oxidation state by an electron acceptor (*e.g.*, oxygen) [74]. This reaction is the basis for the photocatalysis of POTs. In 2007, Saeid [74] also used the sol-gel method to introduce  $\text{Na}_4\text{W}_{10}\text{O}_{32}$  clusters into zirconia base to prepare green, recyclable heterogeneous photocatalyst  $\text{Na}_4\text{W}_{10}\text{O}_{32}/\text{ZrO}_2$  compounded by zirconia-loaded sodium decatungstate, which can react with  $\text{O}_2$  in  $\text{CH}_3\text{CN}$  and selectively generate the corresponding aldehydes and ketones.

In 2009, Farhadi and Zaidi [6] prepared a phosphotungstic acid-zirconium oxide (POM/ $\text{ZrO}_2$ ) nanocomposite by encapsulating  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  POMs a matrix of zirconium oxide by sol-gel technique and used it under mild conditions (*e.g.*, room temperature, oxygen, atmospheric pressure) as an efficient heterogeneous photocatalyst

for the aerobic oxidation of alcohols to the corresponding carbonyl compounds.

In the presence of photoexcited POM/ $\text{ZrO}_2$  nanocomposites, various primary and secondary benzyl alcohols were oxidized to the corresponding aldehydes and ketones with very high conversion rates in an  $\text{O}^{2-}$  rich environment. Moreover, the unactivated aliphatic alcohols were oxidized in good yields despite the longer reaction times compared to the benzyl alcohols. Consequently, the selective oxidation of benzyl OH groups can be achieved by choosing a suitable reaction time in the presence of non-benzy OH groups.

They have also reported an explanation for the reason why the catalytic activity of the photocatalyst is greatly enhanced by using this nanocomposite: this is due to the fact that the specific surface area of the POM/ $\text{ZrO}_2$  nanocomposite is  $292\text{ m}^2/\text{g}$ , which is much larger than that of the original POM ( $<10\text{ m}^2/\text{g}$ ). The higher surface area not only increases the contactable area between the oxidant and the catalyst, thus achieving a higher electron transfer efficiency, but also exposes the photocatalyst to a larger surface area under UV-vis light irradiation, thus greatly improving the oxidation efficiency.

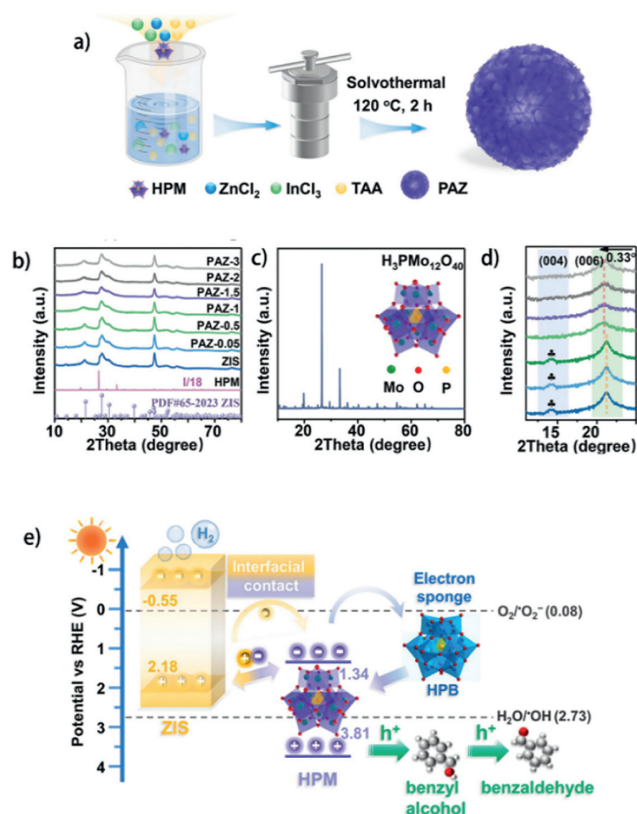
In 2020, Dong *et al.* [75] prepared an  $\text{Ag}_2\text{S}$ -CDs p-n nanojunction (NJ). As a noble metal-free photocatalyst, it oxidized ethanol to the corresponding aldehyde with high quantum efficiency (59.6% and 36.9% at 380 and 420 nm, respectively) in an air atmosphere at room temperature. The photoluminescence results show that the excellent performance is mainly due to the enhanced generation and separation of charge-carrying electrons by the p-n junction, which activates  $\text{O}_2$  (in air) and ethanol.

In 2022, Mosleh *et al.* [8] designed two novel nanocomposites based on  $\text{Co}_3\text{O}_4$ -QDs and  $\text{PMo}_{12}\text{O}_{40}^{3-}$  species for the selective oxidation of benzyl alcohol (BA) using photocatalysis and photocatalysis with glycine (gly) and 4-aminobenzoic acid (ABA) as linker groups. The nanocomposite structure exhibited high efficiency in the photocatalytic oxidation of BA by molecular oxygen. Their experimental approach was to disperse 20 mg of  $\text{Co}/(\text{gly})_3\text{PMA}$ ,  $\text{Co}/(\text{ABA})_3\text{PMA}$  nanocomposite and  $\text{Co}_3\text{O}_4$ -QD in 10 mL of acetonitrile and maintain a rate of 10 mL/min at room temperature to add 1 mmol of BA to the mixture and expose the mixture to visible light irradiation for a defined period of time (9 W. Nama Noor Co., Iran) for a defined period of time, which resulted in a highly efficient and selective conversion of benzyl alcohol.

Using the method of calculating the energy levels of the nanocomposites, they proposed a mechanism for BA oxidation: the presence of  $\text{Co}_3\text{O}_4$ -QDs increased the light absorption efficiency.  $\text{Co}_3\text{O}_4$ -QDs and phosphomolybdic acid ( $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ ) (denoted as PMA) can effectively separate  $\text{e-h}^+$  pairs through good contact of amino acids. Their reports make a great contribution to the design of new products that are more environmentally friendly and cost effective.

In 2022, Xing *et al.* [76] has designed a bifunctional Z-type photocatalyst by doping polyoxometalate clusters into  $\text{ZnIn}_2\text{S}_4$  (ZIS) nanoflakes using a secondary component doping method. The method achieves selective oxidation of aromatic alcohols in aqueous phase conditions to a great extent and is accompanied by hydrogen generation during the oxidation process.

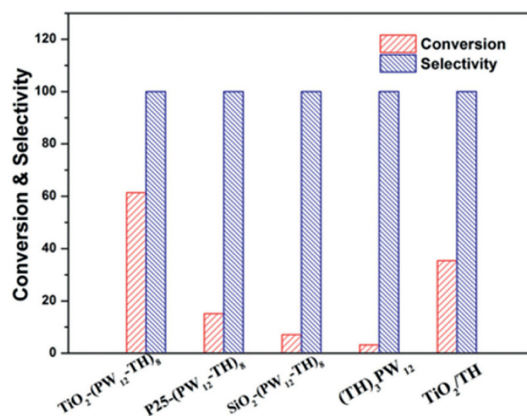
The driving forces from the built-in potential and the close contact interface contribute to the efficient interfacial charge transfer-separation. With the synergistic effect between POMs and ZIS, the synergistic photo-redox coupling of the targeted oxidation of benzyl alcohol and hydrogen precipitation can be achieved under anaerobic conditions using only water as the medium without any organic solvent or oxidant-1, showing significant photo-redox advantages in both oxidative hydrogen production and ethanol conversion compared to those reported recently (Fig. 14).



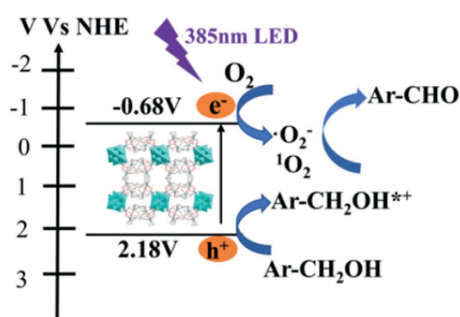
**Fig. 14.** (a) Schematic synthesis process of HPM-incorporated ZIS nano hybrids (PAZ). (b) XRD patterns of HPM, ZIS and PAZ-*x* samples (*x* represents the mass ratio of HPM to ZIS). (c) Enlarged part from (b). (d) XRD pattern and Keggin structure of HPM. Schematic illustration of the Z-scheme transfer path of photogenerated carriers between HPM and ZIS heterojunctions. (e) HPB refers to the reduction state of an HPM derived from the formation of a built-in electric field. Reproduced with permission [76]. Copyright 2022, Elsevier.

The present study is the first application of POM-based photocatalytic materials for the synergistic coupling of anaerobically selective organic synthesis and hydrogen production, which opens a new path for the design of multifunctional POM-based photocatalytic systems.

As a semiconductor material, titanium dioxide is widely used in green photocatalysis for the following reasons: (1) TiO<sub>2</sub> is abundant, stable in state and easy to prepare; (2) The conduction band (CB) and valence band (VB) of TiO<sub>2</sub> have proper redox potentials, which can ensure the simultaneous reduction of O<sub>2</sub> and oxidation of H<sub>2</sub>O or organic compounds. However, the large band gap of TiO<sub>2</sub> ( $E_g > 3.0$  eV) greatly hinders its application in visible light photocatalysis, and the fast electron-hole complexation usually leads to poor selectivity of the products. There have been many solutions to this problem, including compounding TiO<sub>2</sub> with other materials to increase the photoresponsive region, doping TiO<sub>2</sub> with metal or non-metal ions, doping carbon nanotubes into TiO<sub>2</sub>, supporting photocatalysts on graphene with large surface area, combining TiO<sub>2</sub> with other narrow bandgap semiconductors to form heterojunctions or sensitizing with dyes. Unfortunately, these doping processes may reduce the redox potential of photo-hole or photoelectrons and lead to a consequent decrease in photocatalytic activity. In 2017, Yang *et al.* [37] reported a dye-sensitized TiO<sub>2</sub>-polyoxometalate system (denoted as TiO<sub>2</sub>-(PW<sub>12</sub>-TH)<sub>8</sub>, where PW<sub>12</sub> = PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> and TH = thionine) for the selective oxidation of alcohols in selective oxidation of alcohols under visible light. Their study demonstrated that the TiO<sub>2</sub>-(PW<sub>12</sub>-TH)<sub>8</sub> catalyst has an extended spectral response for the selective photo-oxidation of alco-



**Fig. 15.** The oxidation of benzyl alcohol over different photocatalysts. Copied with permission [37]. Copyright 2017, Elsevier.



**Fig. 16.** The possible photocatalytic oxidation mechanism of aromatic alcohols with CPIS **6** as photocatalyst. Copied with permission [78]. Copyright 2022, Elsevier.

hols under mild conditions. Thus, the polyoxometalates and TiO<sub>2</sub> co-catalyst system obtained an effective electron transfer, while greatly improving the photoactivity and selectivity of alcohol oxidation (Fig. 15). TH enables the photoresponse of TiO<sub>2</sub> and PW<sub>12</sub> to respond effectively to the visible region.

Crystalline porous ionic salts (CPISs) are novel porous materials that are synthesized by electrostatic assembly and have received much attention in the field of photocatalysis [77,78]. In 2022, Gu *et al.* [78] constructed CPIS **6-8** by a facile synthesis of a series of photocatalytically active polyoxometalates with cationic Zr-based capsules. In the presence of the catalytic unit of POM, the intrinsically porous Zr-capsules and polar channels accessible to the substrate, CPIS **6-8** exhibited permanent porosity, and not only that, it was able to drive the process of selective conversion of aromatic alcohols to the corresponding carbonyl compounds by photocatalytic oxidation. It was experimentally confirmed that CPIS **6** exhibited the best performance with moderate to excellent conversions (36% to 99%) (the reaction mechanism is shown in Fig. 16), notably with more than 99% selectivity for aldehydes, due to the synergistic effect of {W<sub>10</sub>}, Zrcapsule and polar open channels, resulting in a higher photocatalytic performance.

## 5. Conclusion and perspectives

This review summarizes the research progress of polyoxometalates as catalysts for the catalytic oxidation of alcohols to their corresponding aldehydes or ketones in the traditional thermocatalytic, electrocatalytic and photocatalytic fields. In-depth discussion on the preparation of new "green" catalytic systems by loading non-homogeneous carriers (e.g., titanium dioxide, silica), sol-gel method and electrostatic assembly, which can improve the

selectivity of alcohol oxidation, avoid the use of precious metals, and achieve effective recycling.

Although a certain degree of progress has been made in the research of new POMs catalysts in recent years, the design of more promising POMs catalytic systems for the efficient selective oxidation of alcohols is worth further study in many aspects in the future, but not limited to the following aspects:

- (1) There is a lack of studies on the branch of the polyoxometalate family, such as PONBs and POTs [30]. The already reported study by Chi's group using vanadium-containing polyoxoniobates for the preparation of noble metal-free electrocatalysts can achieve 92% conversion of benzyl alcohol with a Faraday efficiency of 93%. There are few similar studies available [59].
- (2) Along with the rational application of their intrinsic properties, more efficient POMs assembly or synthesis processes should be explored to improve the structural stability (which helps their recycling) and electronic conductivity of POM-based nanomaterials. This is the basic condition to judge and explain the mechanism of photo/electrocatalytic reaction based on the structure of POMs compounds.
- (3) Due to the tunable redox properties of POMs, the assembly (or encapsulation) of POMs guests in the reduced state may be an effective strategy to obtain high selectivity and stability in the catalytic oxidation of alcohols. Furthermore, it is of great importance to construct efficient POM-based catalysts with precise catalytic activity centers that are capable of durable oxidation of alcohols to the corresponding aldehydes and ketones.
- (4) For photo/electric POMs catalysts, *in situ* photo/electrochemical characterization or devices should be developed to monitor the dynamic structural changes of POM-based compounds during photo/electrocatalytic reactions and then reveal the real catalytic reaction mechanism.
- (5) In order to improve the prospects of POMs for photocatalytic applications, POMs molecules can be introduced into organic/inorganic supramolecular bodies as guests, in addition to solid loading of POMs [22,23].

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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