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REVIEW

Advancement in the Structures/Characteristics of Potassium and Aluminium Based Polyoxometalates'and Their Applications in Organic Reactions

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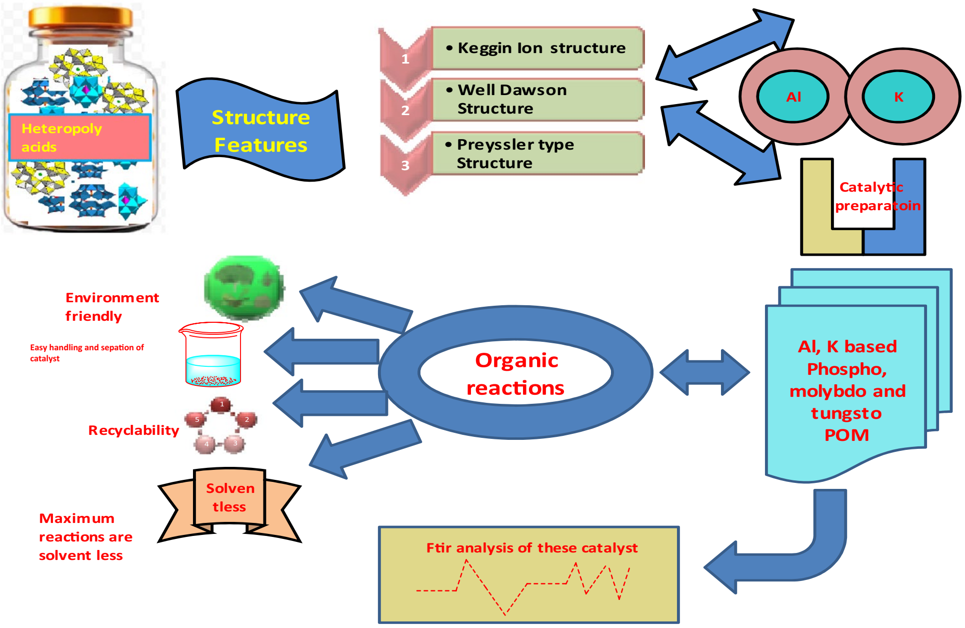
Abstract

Green chemistry and technology involve the development of chemical manufacturing systems that aim to minimize their negative impact on the environment. The primary objective of this field is to reduce the environmental consequences associated with chemical processes and manufacturing, and also improve overall process performance. While it is advantageous to simply decrease the use of organic solvents in chemical processes, green chemistry, and technology take a more comprehensive approach by evaluating the entire process to identify techniques that can minimize hazards while remaining economically viable. Assessing the environmental impacts of manufacturing processes requires a systematic approach and the use of appropriate metrics that enable quantitative evaluation of environmental hazards. This review focuses on the introduction of heteropoly acids, highlighting their unique features and applications in various fields. The structures and preparation of heteropoly acids, specifically Keggin, Wells Dawson, and Preyssler types, salts of potassium and aluminium, as well as their catalytic applications, are discussed in the present review article.

Graphical abstract



Keywords Keggin · Wells Dawson · Preyssler · Aluminium & potassium based heteropolyacid salts

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1 Introduction

In the previous years, the focus has been amplified on using environmentally friendly and recyclable catalysts in industrial processes. This has given rise to the concept of sustainable chemistry, which aims to minimize or completely remove the use of harmful substances in chemical materials [1]. Like healthcare, green chemistry focuses on preventing and taking precautions rather than treating problems after they occur. Recently, there has been a focus on using environmentally friendly catalysts in industrial processes, leading to the development of green chemistry. Green chemistry seeks to minimize [2] the use of harmful substances in chemical processes by taking preventative measures. Using eco-friendly catalysts not only benefits the environment [3, 4] but also allows for their reuse in chemical reactions [5]. Heteropoly compounds have garnered significant attention as catalysts because of their capacity as finely-tuned acidic and redox functions on a molecular scale [6–8]. This versatility makes them useful in various catalytic applications. Heterogeneous acid catalysts, as opposed to homogeneous ones, offer advantages such as increased stability, resistance to corrosion, and the ability to be recovered and regenerated [9]. Hetero polyanions are polymeric oxo anions [10] that exhibit high catalytic activity and can be used in non-polar solvents, as they not only enhance product selectivity but also streamline the separation of catalyst [11]. By replacing homogeneous acid catalysts with heterogeneous alternatives like heteropoly anions, researchers, and industries [5] can improve stability [12], ease of use, and the ability to recover and regenerate catalysts. The Wells–Dawson molecule and the Keggin anion are popular examples of heteropoly anions, which are formed by connecting metal–oxygen polyhedral building [13] blocks through covalent bonding. A generalized diagram showing the characteristics of heteropolyacid salts is represented in Fig. 1.

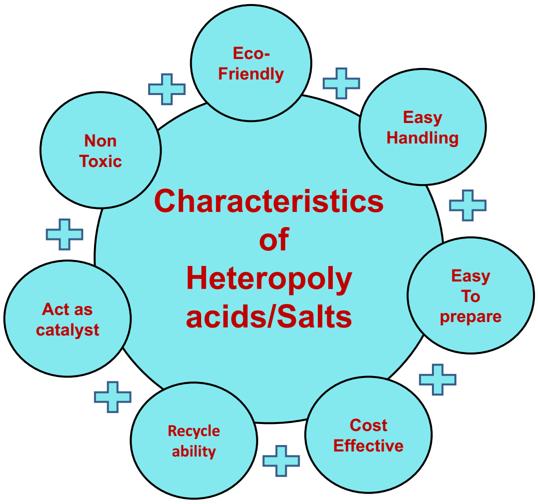


Fig. 1 Characteristics of heteropolyacids/salts

1.1 Special Features of Heteropoly Acids

Researchers are currently dedicated to finding alternative catalysts to replace acid catalysts, as environmental problems have become a major concern for future generations. The new catalysts present numerous applications and advantages across different areas [14, 15]. Heteropolyacid compounds, made up of metal cations and oxygen atoms, have diverse applications due to their unique properties and versatility [16, 17]. They are exceptional catalysts, making them valuable in various industrial processes [18]. In the petrochemical industry, they are widely used to convert crude oil into high-quality fuels and chemicals, improving the efficiency of refining [19, 20], in the synthesis of valuable chemicals and many pharmaceutical entities [21], enabling the production of complex organic compounds with high selectivity and yield. They are effective in environmental remediation, as they can degrade pollutants and contaminants in water and air. Additionally, these acids show promise in energy storage and conversion, contributing to the development of sustainable and clean energy solutions [22].

In conclusion, the application of heteropolyacids spans various industries, including petrochemicals, pharmaceuticals, environmental remediation, and energy storage. Their exceptional catalytic properties and versatile nature make them indispensable in these fields. As research continues to uncover new possibilities, the potential applications of heteropolyacid are expected to expand, further enhancing their significance in the scientific and industrial realms.

In the present study, we have described the structure and characterization features of Heteropoly acid/salts containing Keggin, Wells Dawson, and Preyssler structures. Furthermore, we explore the production of environment-friendly catalysts made from potassium and aluminium based polyoxometalate compounds, which incorporate molybdenum and tungsten. Additionally, we have also highlighted the catalytic uses of these synthesized polyoxometalate compounds in organic transformations. To enhance the clarity and comprehensibility, we have created visually engaging graphical representations of these polyoxometalates.

2 Literature Survey

Polyoxometalates (POMs) are anionic clusters composed of metal-oxo compounds. By substituting transition metals and carefully selecting counter cations these clusters can be manipulated through transition metal substitution and the choice of counter cation to impart distinct chemical properties [23, 24].

Polyoxometalates (POMs) are coordination compounds made up of more than two metal atoms. These are negatively charged d(0) configuration clusters of metal and oxygen atoms and come in two types: Isopoly anions (with only one metal) and heteropoly anions (several metals and are comparatively more studied). The heteropoly anions, which have a tetrahedral structure with a central heteroatom, are essential for creating the metal-oxo framework [25]. Different types of structures are exhibited by these compounds as given below with their application in organic synthesis.

2.1 Keggin Structure

The primary structure is known as the Keggin structure (Fig. 2), which has a roughly spherical shape [26]. It is represented by the formula XM_{12}, wherein X represents the heteroatom and M represents the metal having a d(0) configuration. The heteroatom tetrahedron in this structure is connected to four M_3O_{13} units at each corner. For example; By acidifying a mixture of metasilicate and tungstate with a 1:12 molar ratio, a negatively charged anion called $[SiW_{12}O_{40}]^{3-}$ can be obtained containing Si as a hetero atom, which is incorporated in the cavity generated by W, addenda atoms [24]. These addenda atoms, which are coordinated with oxygen atoms in an octahedral arrangement, can be replaced by other metal atoms. The triplet M_3O_{13} is made up of three WO_6 octahedra that share octahedral edges and four triplets then come together tetrahedrally around the heteroatom Si. The oxygen atoms that are shared by the triplet M_3O_{13} are coordinated to the Si atom, resulting in a T_d symmetric polyoxometalate [25, 26].

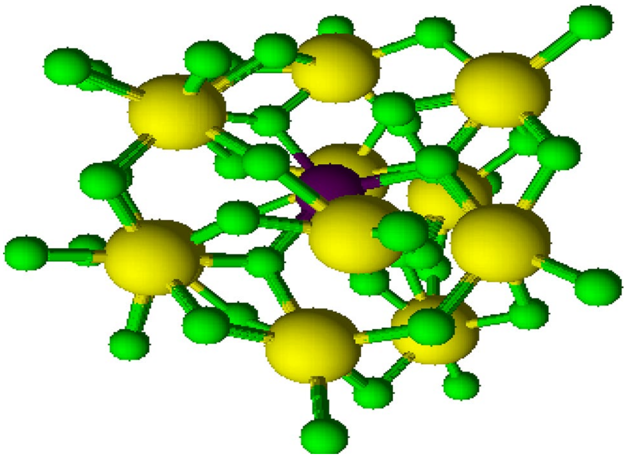


Fig. 2 Keggin type structure of heteropolyacid/salts

2.1.1 Preparation of Keggin Type Structure

Keggin HPA can be modified by either removing or filling a specific unit to create lacunar HPA or introduce transition metal ions. Additionally, the metal ions in these POM salts can be substituted with other metal ions. The mentioned changes empower Keggin HPA to go beyond its initial use restricted to acid-catalysed reactions, granting it the capability to function as a catalyst in oxidation reactions, too. The most common method to produce Keggin HPA potassium salt involves reacting commercially available HPA with a solution containing the required amount of KCl or K_2CO_3 in water.

2.1.1.1 Preparation of $K_4SiW_{12}O_{40}$ The synthesis of various types of HPA salts was performed using various methods detailed in literature sources [27–32]. Sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$) was dissolved in distilled water, and concentrated hydrochloric acid (40 mL) was slowly added. Twenty millilitres were added before heating and another 20 mL were added after heating the mixture. A solution of sodium silicate (7.5 g) and concentrated hydrochloric acid (60 mL) was then, added to the mixture and boiled for half an hour. A precipitates formed, which were subsequently filtered. The remaining liquid was mixed with hydrochloric acid (40 mL) and ether (50 mL). The lower oily layer was separated, and the complex was vacuum-dried overnight to obtain a white solid product, $H_4SiW_{12}O_{40} \cdot xH_2O$. Potassium chloride (13.4 mmol) was added to an aqueous solution containing $H_4SiW_{12}O_{40} \cdot nH_2O$ (100 mL containing 6.29 mmol), which was then reacted with K_2CO_3 to produce potassium-based HPA salts [32]. A schematic representation of this methodology is given in Fig. 3. By following this method (Fig. 3), Shenzhen Chane et al. were able to produce high-quality HPA salts suitable for use in various applications.

2.1.1.2 Synthesis of $K_{2.5}H_{0.5}PW_{12}O_{40}$ The synthesis of MCM-41-supported $K_{2.5}H_{0.5}PW_{12}O_{40}$ salts was achieved through the utilization of the incipient wetness impregnation method (Fig. 4) [33, 34].

To synthesize the potassium salt of phosphotungstic acid ($K_{2.5}H_{0.5}PW_{12}O_{40}$), a precise quantity of an aqueous solution containing the corresponding carbonates was gradually introduced into the phosphotungstic acid (PTA) solution, accompanied by continuous stirring [33–35]. Subsequently, the resulting precipitate underwent a thorough drying process at 110 °C under vacuum conditions for 24 h, followed

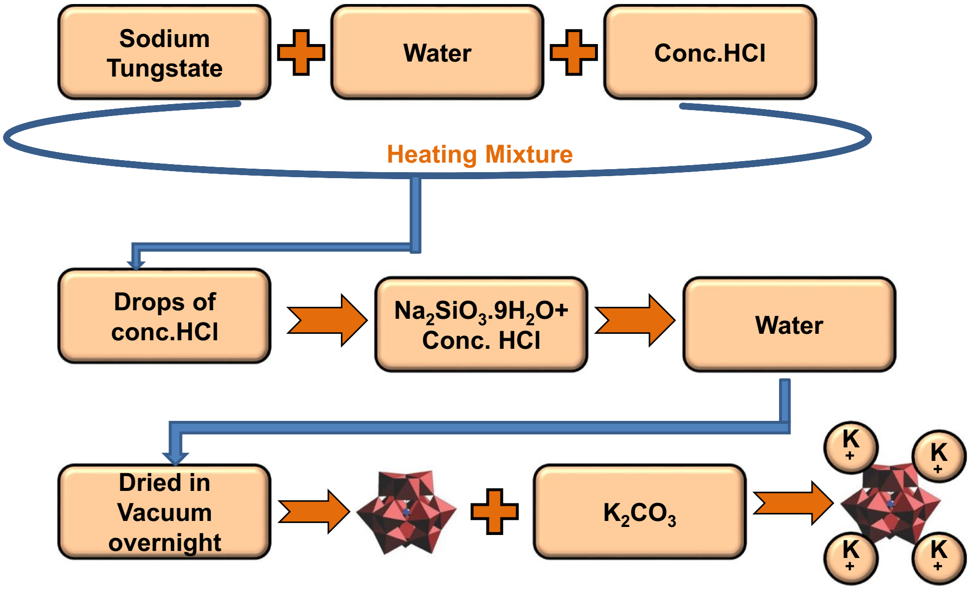


Fig. 3 Layout depicting the preparation of $K_4SiW_{12}O_{40}$

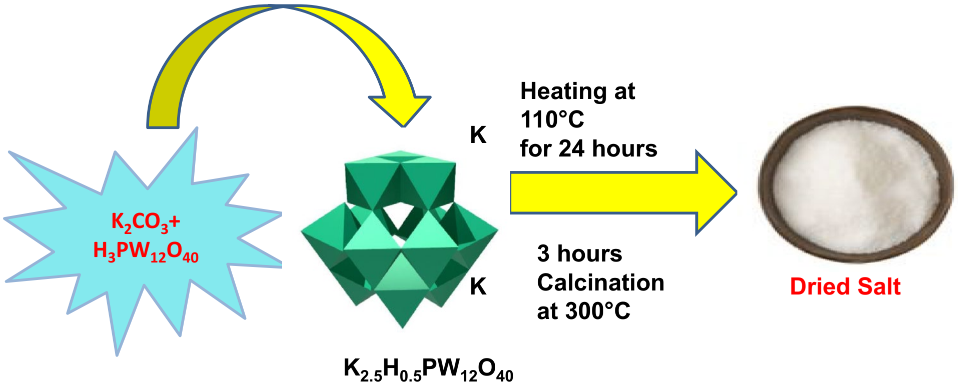
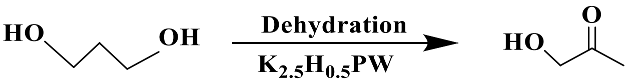


Fig. 4 Preparation of $K_{2.5}H_{0.5}PW_{12}O_{40}$



Scheme 1 Dehydration of glycerol to acrolein catalysed by $K_{2.5}HPW$

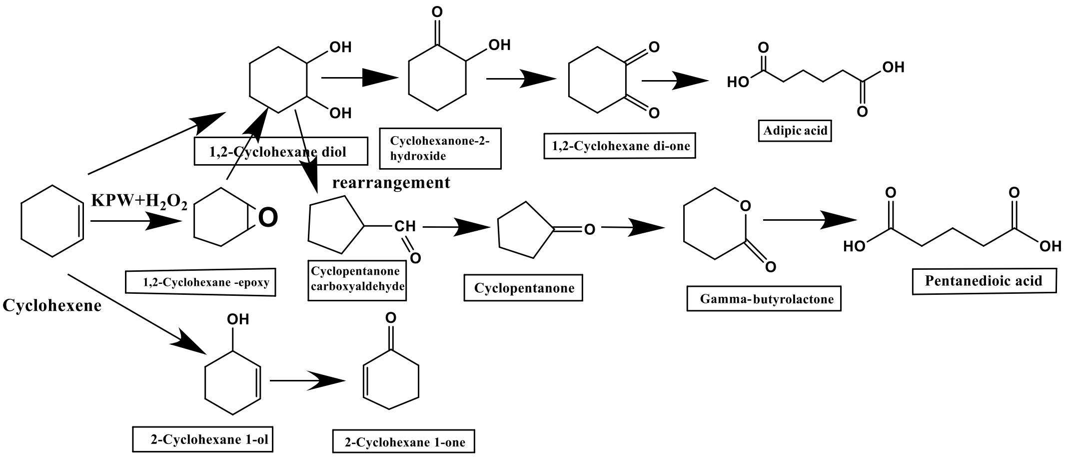
by 3 h calcination at 300 °C. The product obtained in the above process was utilized by S.B. Hamid et al. who conducted an analysis on the dehydration process of glycerol to acrolein in the presence of $\mathbf{K_{2.5}HPW}$ as a catalyst (Scheme 1) [37]. The study yielded a remarkable conversion rate of 91.3% and a selectivity of 95.6% [36, 37].

Joao Carlos Soares et al. conducted an experimental study on the oxidation reaction of cyclohexene (Scheme 2) to adipic acid using $K_3PW_{12}O_{40}$ as a catalyst. The study also investigated the thermal effect treatment on catalyst for the reaction [38].

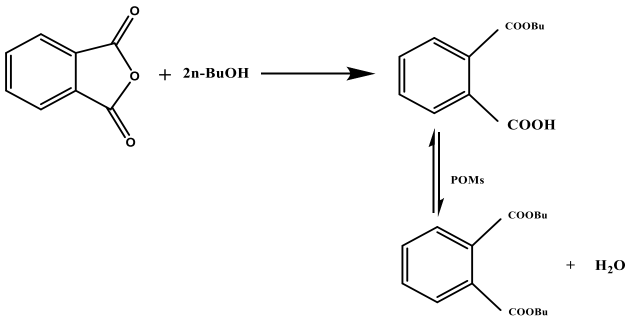
Himmat Singh et al. conducted an experimental study on the esterification and trans-esterification of waste oil. They utilized potassium-imbued tungstophosphoric acid supported by graphene oxide as a heterogeneous catalyst. The reaction was carried out at 65℃ for 1.5 h with a molar ratio of 9:1 and 10% catalyst by weight [39].

2.1.1.3 Preparation of K_3 $[PMo_6W_6O_{40}]$ To prepare $K_3[PMo_6W_6O_{40}]$, an equimolar solution of sodium tungstate and sodium molybdate dissolved and sodium dihydrogen phosphate in a 2/5 molar ratio in 60 ml of deionized water. Next, the solution was heated to 80 °C and left to stir for 3 h. Afterward, the solution was concentrated to nearly 30 ml to change the solution's colour from yellow to its desired state, and 30 ml of 24% hydrochloric acid was added. Finally, the crystal was obtained by extracting the solution with diethyl ether at room temperature [40].

The esterification process of phthalic anhydride with alcohol occurs in two distinct stages as the experimental proof is given by S. Sheshmani et al. [40]. The initial stage is remarkably swift, allowing it to be conducted without the



Scheme 2 Oxidation reaction of cyclohexene to adipic acid by KPW



Scheme 3 Reaction catalysed by $K_3[PMo_6W_6O_{40}]$

need for a catalyst. On the other hand, the esterification of the next takes place at a very miserable rate and necessitates the assistance of an acid catalyst $\mathbf{K_3[PMo_6W_6O_{40}]}$ showing the highest conversion i.e. 97% (Scheme 3) [40].

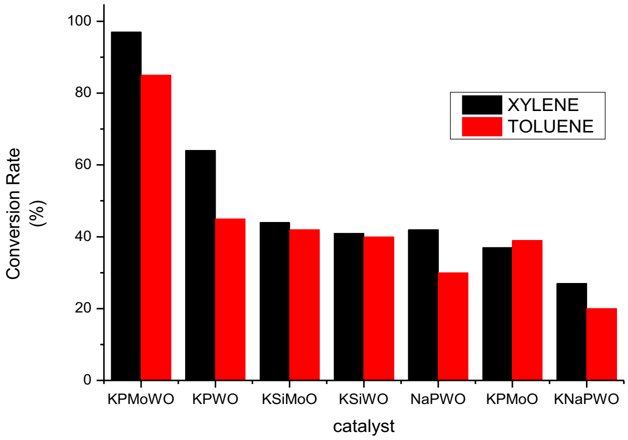


Fig. 5 Activity of different POM catalysts at variable Ph in xylene and toluene

2.1.1.4 Preparation of K_3 $[PMo_{12}O_{40}]$ This salt was synthesized through the reaction between 0.01 mol of disodium hydrogen phosphate and a solution of 0.04 mol of sodium molybdate in 30 ml of water. The solution was vigorously stirred and heated to its boiling point. Subsequently, 8 ml of 37% hydrochloric acid was added. The purification process was done by diethyl ether. The esterification process of phthalic anhydride reagent catalysed by $K_3[PMo_{12}O_{40}]$ provided 37% yield in xylene solvent [40].

A comparison of the activity of different POM catalysts at variable Ph in xylene and toluene is explained in Fig. 5. [40].

2.1.2 Metal substituted Lacunary Keggin ion Structure

The $K_{8-x}SiW_{11}M^{x+}O_{39}$ catalysts, where M^{x+} represents Cu^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, and Al^{3+}, were prepared using a modified method described in the literature [41–46]. To prepare lacunary HPA salts, a solution containing $H_4SiW_{12}O_{40}{\cdot}nH_2O$ (6.29 mmol; 100 mL) and KCl (13.4 mmol) is vigorously stirred. pH 5.5 was adjusted using $KHCO_3$, and the solution was filtered and concentrated to obtain a white precipitate. A flow diagram for the preparation of $K_{8-x}SiW_{11}M^{x+}O_{39}$ is represented in Fig. 6 [47].

The precipitates, $K_8SiW_{11}O_{39}{\cdot}nH_2O$, were separated and dried [47]. A metal cation was incorporated into the lacunar heteropoly anion, $K_8SiW_{11}O_{39}$ (5 g in 30 ml) by dissolving in water and then a metal precursor solution was added slowly as stated by M. J. da Silva et al. In the study, M. J. da Silva et al. carried out a study on the reaction catalyzed by lacunary ion for conversion of benzaldehyde to benzoic acid (Scheme 4) with a conversion rate of 91% and selectivity of 100% [30].

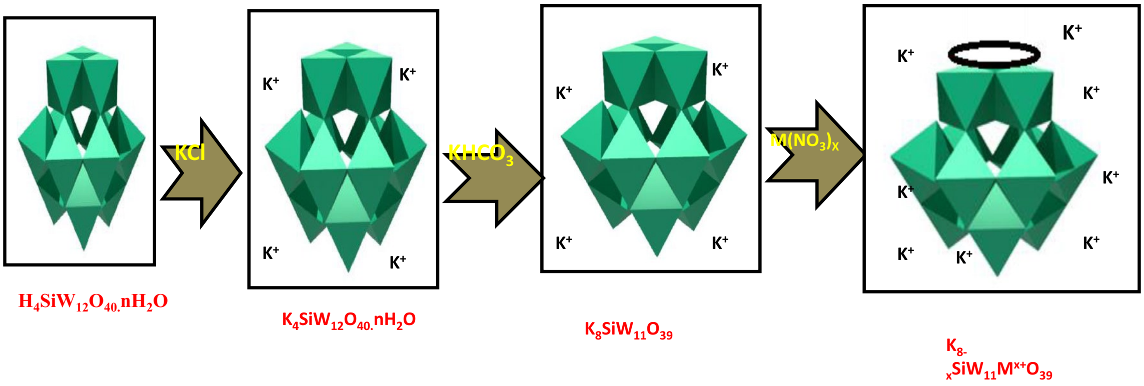
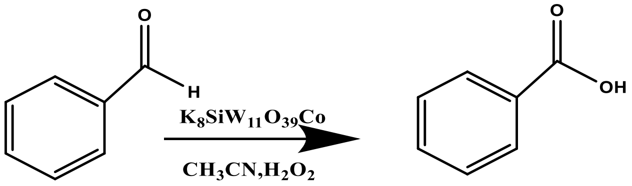


Fig. 6 Preparation of lacunary Keggin ion



Scheme 4 Reaction Catalysed by Lacunary $K_8SiW_{11}O_{39}$ Keggin ion

Fig. 7 Wells Dawson structure

2.2 Polyoxometalate with Wells Dawson structure:

The Well-Dawson structure is a type of structure that has an ellipsoidal shape and is represented by the formula X_2M_{18} [48, 49]. The Dawson structure [50] is based on the truncated Keggin unit (XM_9) and the $[X_2M_{18}O_{62}]$ cluster can be created by symmetrically assembling two of these fragments, as shown in Fig. 7 [24, 25]. The phosphotungstate and phosphomolybdate anions, $[P_2M_{18}O_{62}]^{6-}$ (abbreviated as P_2M_{18} where M is either W or Mo), are responsible for the majority of the compositions connected to the Dawson structure. This structure consists of two heteroatoms stacked on the top of each other, with each end composed of an M_3O_{13} cap. Additionally, there are two six-metal belts encircling the molecule. The eighteen metal atoms in P_2M_{18}, and other Dawson structure derivatives, are arranged in four parallel rings, consisting of 3, 6, 6, and 3 unit metal ions each, forming a local pseudo-octahedral environment. The Dawson structure is different from the Keggin anion because it has two distinct specific positions. The M_3 rings, acting as caps, are strategically located in the polar regions, while the two M_6 rings form a belt in the equatorial region [24].

These structural differences lead to different chemical behaviour. In terms of electronic structure, the Dawson anion has the first unoccupied molecular orbital (LUMO) across the equatorial region. Moreover, the first virtual orbital in the cap region is calculated to be 0.85 eV higher in energy [51–53]. The original structure also allows for multiple metal substitutions.

2.2.1 Preparation of $K_6[P_2W_{18}O_{62}]$

30 ml of water was mixed with 0.01 ml of sodium tungstate, and then 2 ml of phosphoric acid was added. For a continuous 8 h, the solution underwent reflux. Potassium chloride (1 g) was added to precipitate the salt, which was then purified by re-crystallization and allowed to cool to 5℃ overnight. After filtering and washing, the product was vacuum-dried for 8 h [54]. M Moudjahed et al. investigated the relationship between catalyst mass, the nature of the substrate and the POM composition during the reaction and their reaction parameters are detailed in Fig. 8 [54].

Hugo. C. Novais et al. demonstrated the oxygen reduction experiment using a $K_7[P_2W_{17}(FeOH_2)O_{61}]$ catalyst immobilized onto graphene flakes and multi-walled carbon nanotubes doped with nitrogen. This setup exhibited excellent activity and selectivity toward the oxygen reduction reaction [55].

Fig. 8 Reaction catalysed by $K_6[P_2W_{18}O_{62}]$

2.2.2 Preparation of $K_6[P_2Mo_{18}O_{62}]$

Molybdenum-based Well-Dawson compounds, such as $X_6P_2Mo_{18}O_{62}$ with different cations, can be used as catalysts in the gas-phase oxidative dehydrogenation process of iso-butyraldehyde to produce methacrolein and acetone [56]. These compounds have relatively (~ 30% conversion) low activity when heated to 260 °C, but supported molybdenum-based Well-Dawson compounds patented by Lyons and co-workers for use in heterogeneous gas-phase oxidation reactions [57]. These substances have the ability to catalyze the conversion of alkanes, such as propane to acrylic acid and iso-butane to methacrylic acid, into unsaturated carboxylic acids or nitrites. It has been discovered that, in comparison to Keggin-type compounds, partially protonated Well-Dawson compounds exhibit greater activity in these oxidation processes [58–61]. Reza Tayebeeet al. carried out a study to explore the interaction between 2, 3 butadione and urea while using different heteropoly acids/salts as presented in Fig. 9. The objective was to ascertain the rate of conversion and produce a high yield of glycoluril derivative as an outcome and the eactions catalysed by K_6 $[P_2Mo_{18}O_{62}]$ provided 95% conversion rate [62].

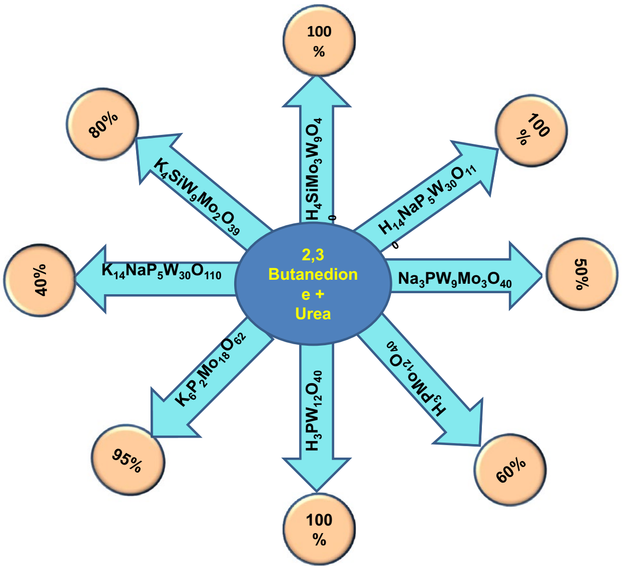


Fig. 9 Reaction of 2, 3 butanedione and urea in the presence of different catalyst

2.2.3 Lacunary Wells Dawson Preparation Methods

The following procedure was used to synthesize the metal-doped α_2-WD POMs [63, 64]. A generalised layout for the

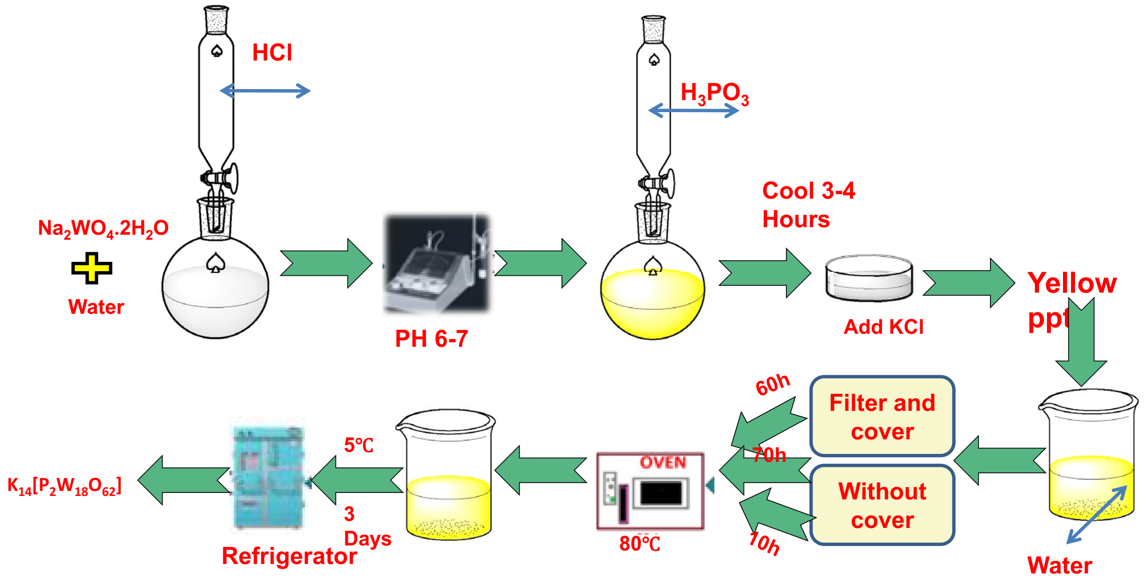


Fig. 10 Diagrammatic representation of preparation of Lacunary Wells Dawson Heteropolyacid salt

synthesis of metal doped Wells Dawson type's heteropoly acid salts (Fig. 10).

2.2.3.1 Synthesis of M-WD (α_2-$KXP_2MW_{17}O_{61}$) The researchers synthesized lacunary POM doped with different metals (Ru, Pd, Fe, and Pt) by modifying existing protocols [65–68]. They started the process by dissolving α_2-$K_{10}P_2W_{17}0_{61}$ (α_2-WD) {0.42 mmol} in water (8 ml) at 90 °C. Next, a metal precursor (α- WD) solution (0.45 mmol) was gradually added drop wise while stirring the α_2-WD solution. The solution obtained was agitated at 90 °C. The reaction solution was allowed to cool to room temperature, after that KCl was dissolved in it. The precipitates were collected, washed, and recrystallized to obtain the desired product [69, 70].

2.3 Preyssler Structure

$[(NH_4)_{14}NaP_5W_{30}0_{110}]$ is a Preyssler-type catalyst in which the ammonium salt unit cell comprises two $[P_5W_{30}0_{110}]^{15-}$ anions that the centre of symmetry connects. The anions have an internal fivefold symmetry and resemble ellipsoids (prolate spheroids). Each is built of five PW_6 units arranged in a crown so that the whole anion has an internal fivefold symmetry axis (Fig. 2). Perpendicular to this axis is a mirror plane containing five phosphorus atoms. The tungsten atoms are distributed in four parallel planes perpendicular to the axis: each of the outer planes contains five tungsten atoms; each of the inner ones contains ten tungsten atoms. A PW_6 unit consists of two groups of three corner-shared WO_6 octahedra [71–73]. Two pairs of octahedra of each group are joined together by sharing one edge located in the mirror plane. Each octahedron contains only one $W=O$ double bond which is directed toward the exterior of the polyanion.

2.3.1 Preparation of Potassium Based Preyssler Type Catalyst

The polyoxometalate with Preyssler structure, K_{14} $[NaP_5W_{30}O_{110}]$, was made by following a series of steps [74] showing in Fig. 11. This method ensures the desired polyoxometalate is obtained in its purest form.

In the majority of Preyssler-type phosphotungstate, the enclosed cation occupies one of the two side cavities, forming co-ordination with five Oa oxygen, five Ob oxygen, and one water molecule for coordination [75–77].

2.3.1.1 Preparation of $K_{14}[P_5W_{30}O_{110}K]{\cdot}17H_2O$ A solution containing $K_{13}[P_5W_{30}O_{110}Ca(H_2O)]0.25H_2O$ (2.39 g) and KCl (0.45 g) was mixed with a potassium acetate buffer (5 ml) at pH 4.7. The mixture was stirred at room temperature for 5 min before being transferred to an oven set at 170 °C for 24 h. After cooling, the solution produced colourless crystals which were isolated and underwent two rounds of recrystallization. The resulting product was then suitable for analysis using X-ray diffraction. The crystals were carefully collected, dried, and ultimately provided a 2% yield based on the initial materials used. Further analysis showed that the elemental composition of the final product was K_{14} $[P_5W_{30}O_{110}K]0.17H_2O$ [74].

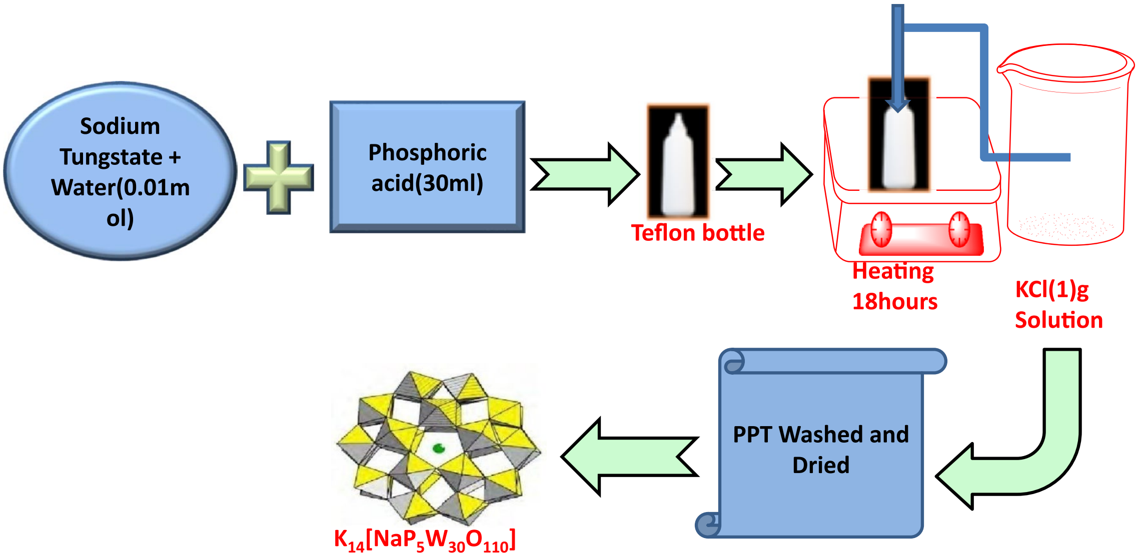


Fig. 11 Schematic diagram of potassium Preyssler type catalyst [74]

2.3.1.2 Preparation of $H_{14}[P_5W_{30}O_{110}K]0.40H_2O$ $K_{14}[P_5W_{30}O_{110}K]0.17H_2O$ (0.20 g) compound was dissolved in water and passed through a special substance 2.5 g of Dowex 50 WX8 to make it neutral. The liquid was then evaporated at 60 °C and water was added. The resulting solution was dried and yielded a high percentage of the desired compound. The elemental composition of the compound was measured and compared to the expected values, showing close agreement [78–80].

A new type of phosphotungstate compound called $[P_5W_{30}O_{110}K]^{14-}$ was created and studied. It contains one potassium ion inside the central cavity. When heated, one

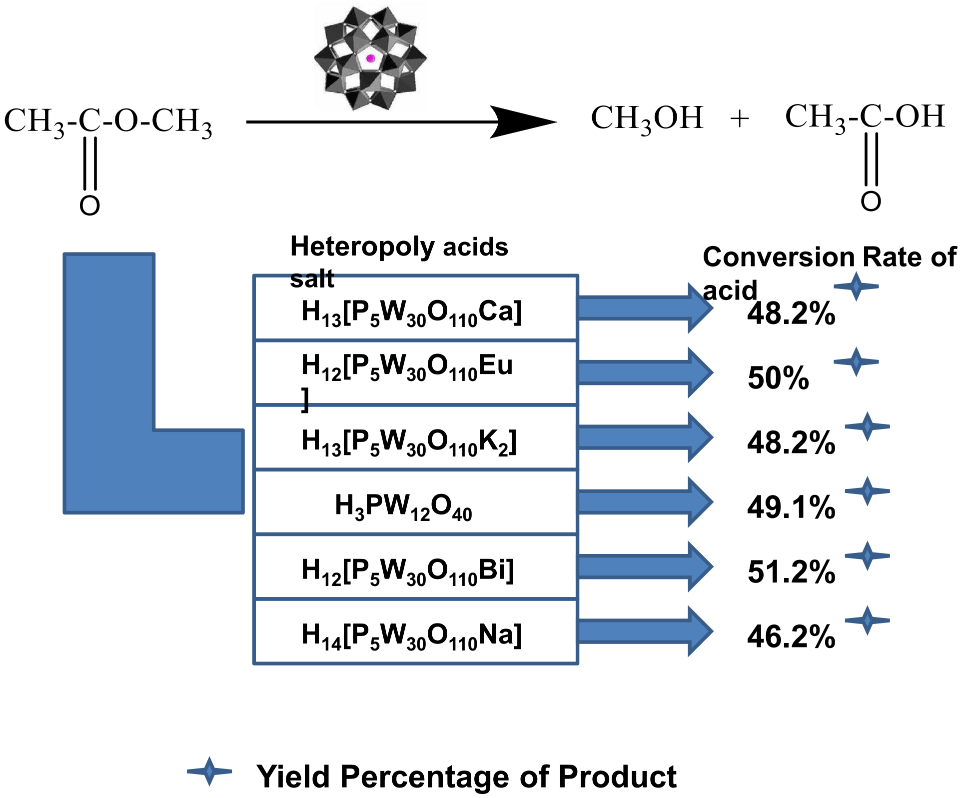


Fig. 12 Diagram represents the hydrolysis of ethyl acetate

of the potassium ions moved from the central cavity to a side cavity, making room for another potassium ion to be trapped inside, resulting in a compound with two trapped potassium ions [76].

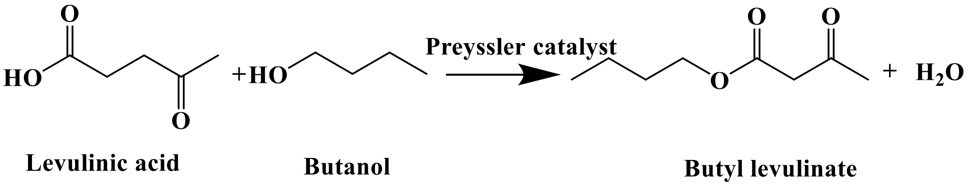
Hayashi Akio et al. conducted research on the catalytic aspects of Preyssler type catalyst for hydrolysis of ethyl acetate. The following diagram (Fig. 12) shows the conversion rate of different metal-substituted Preyssler catalysts [75].

Luis A. Gallego-Villada et al. investigated the reaction of levulinic acid (Scheme 5) with butanol using a Preyssler catalyst ($K_{14}NaP_5W_{30}O_{110}$) at a concentration of 40 mg. The ratio of butanol to levulinic acid was 5:1, and the reaction was conducted at 160℃ for 3 h. The results showed a 77% conversion rate with 100% selectivity [81].

2.3.2 Aluminium Based Catalyst

2.3.2.1 Preparation of AlPW To prepare the catalyst, a solution was formed by dissolving 2 g of aluminium phosphotungstate in 25 mL of 50% aqueous methanol at room temperature. While stirring, an inorganic support weighing 1 g was gradually introduced into the solution. The solution was continuously stirred for duration of 4 h. Subsequently, the slurry underwent filtration using a G4-grade crucible. The resulting catalyst was then dried in an air oven at a temperature of 70 °C for 6 h. Finally, the dried catalyst was carefully stored in an airtight bottle within desiccators, ensuring its preservation and quality. Tipnis et al. performed the experiment on the conversion of benzylation of benzyl chloride and benzyl alcohol in the presence of AlPW (Scheme 6),

Scheme 5 Reaction of Levulinic acid with Butanol



Scheme 6 Represent the Benzylation of benzyl chloride and benzyl alcohol

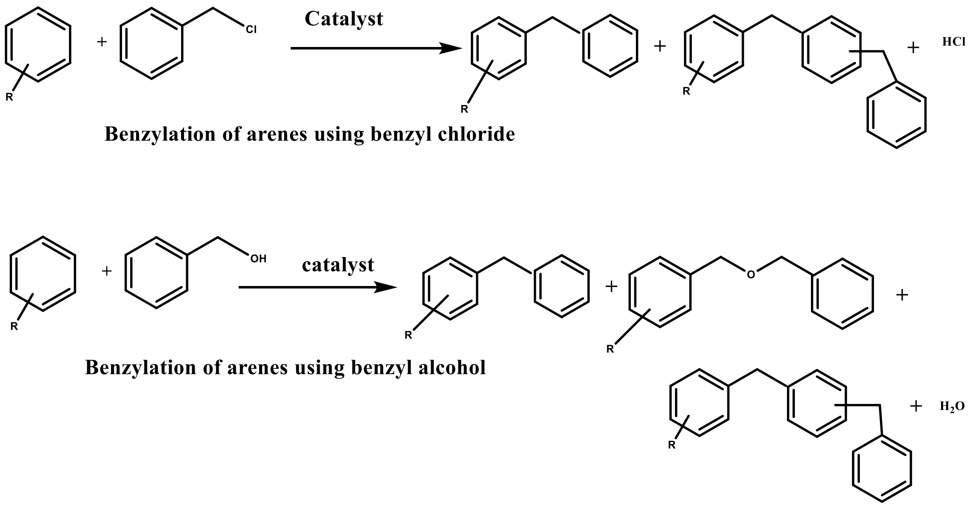


Table 1 Selectivity and conversion rate with different catalyst at 80 °C temperature

Catalyst	Benzyl alcohol (conversion) %	Benzyl chloride (conversion) %	Selectivity (benzyl alcohol) %			Selectivity (benzyl chloride) %			Benzylation %
			DBE	DPM	Dibenzylation	DBE	DPM	Dibenzylation	
HPW	48.6	4.7	75.6	24.6	0	–	–	–	100
AlPW	55.0	24.6	77.2	22.8	0	–	–	–	100
AlPW/K-10	10.5	56.0	76.2	23.8	0	–	100	0	–
AlPW/Silica	5.9	-	85.7	14.6	0	–	–	–	–
AlPW/H-ZSM-5	11.4	100	92.3	6.7	0	–	93.4	6.6	–

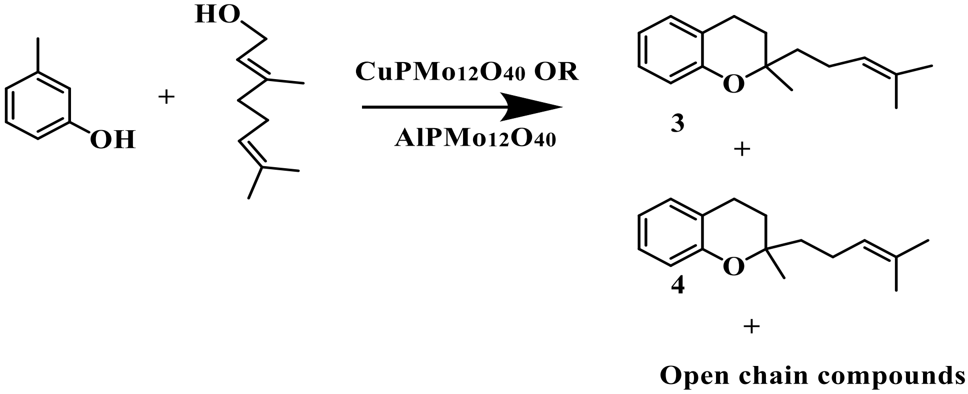
DBE Dibenzyl ether, *DPM* Dipropylene glycol monomethyl ether which showed conversion and selectivity as represented in Table 1 [82].

2.3.2.2 Preparation of $AlPMo_{12}O_{40}$ $H_3PMo_{12}O_{40}$ (MPA) was typically dissolved in 12 ml of distilled water. To obtain the desired salt, the previous solution was supplemented with the required milligrams of $Al_2(SO_4)_3.18H_2O$, $Al_2O(CH_3COO)_4$, or $CuSO_4.H_2O$. Once the solution reached between 50 and 60 ℃, it was constantly stirred. After that, $BaCO_3$ was gradually added, and the reaction was carried out until all CO_2 had been eliminated. The mixture was stirred for 2 h while it cooled. After that, the $BaSO_4$ or Ba $(CH_3COO)_2$ solid was eliminated through filtration and it underwent three rounds of distilled water washings. After a week, the leftover water was evaporated to produce Al or Cu salts [83, 84].

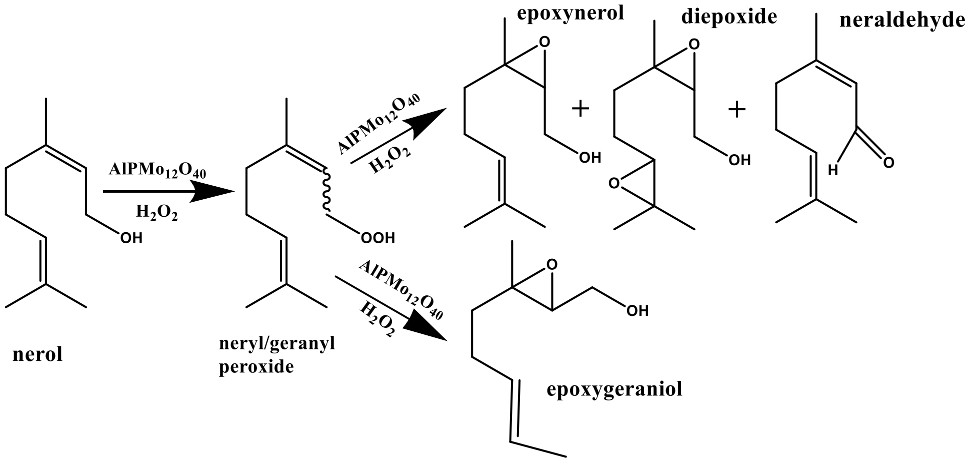
S. Mansilla et al. conducted research on synthesizing chromanes to demonstrate the catalytic action of MPA salts in this process (Scheme 7). They particularly decided to examine the interaction between m-cresol (1) and geraniol (2) in order to conduct additional research [83].

A.A. Rodrigues et al. analyzed the conversion and reaction selectivity of nerol oxidation reactions (Scheme 8) with H_2O_2 in the absence or presence of $AlPMo_{12}O_{40}$. The Reaction conditions include nerol (1.0 mmol), H_2O_2 (2.0 mmol), catalyst (0.5 mol %), temperature (363 K) in the presence of CH_3CN solvent (10.0 mL) [85].

2.3.2.3 Preparation of $Al_{2/3}H_2SiW_{12}O_{40}$ To synthesize $Al_2/_3H_2SiW_{12}O_{40}$ (AlHSiW), 0.7 mmol of $H_4SiW_{12}O_{40}$ was dissolved in 100 mL of water using ultrasonic dispersion. Subsequently, 0.47 mmol of $AlCl_3$ was added and the mixture was continuously stirred at a temperature of 93 °C for the duration of 12 h. Excess water was then removed through vacuum distillation. AlHSiW was obtained by washing the resulting solid with diethyl ether and drying it at 105 °C for 12 h. The synthesis of the Al-modified catalyst was carefully controlled by combining $AlCl_3$ and HSiW in a stoichiometric molar ratio of 2:3:1 during the feeding process. This process was repeated to prepare various metal-modified HPAs using different metal salts and HPAs [86, 87]. C. Tao et al. conducted research on an aluminium-based catalyst to determine the production of alkyl levulinate derived from cellulose and lignocellulosic materials (Scheme 9), resulting in a yield of 50–72% [86].

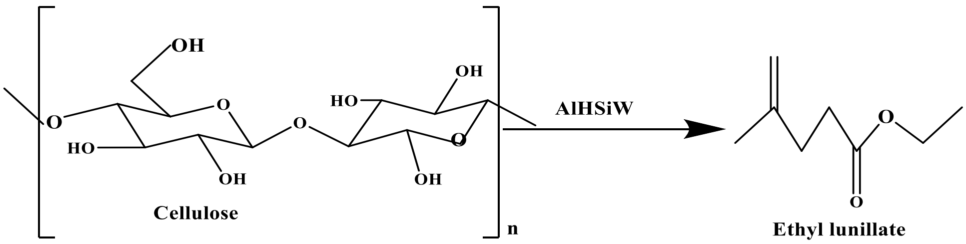


Scheme 7 Represent the formation of chromanes in the presence of $AlPMo_{12}O_{40}$

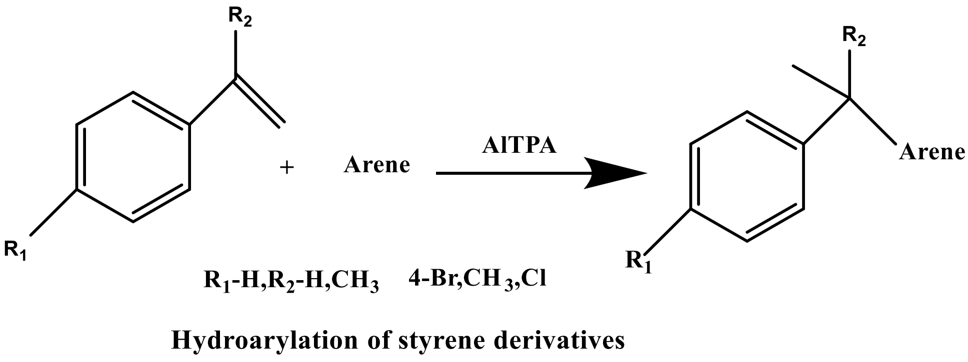


Scheme 8 Oxidation of nerol in the presence of $AlPMo_{12}O_{40}$

Scheme 9 Formation of Ethyl levulinate using $Al_{2/3}H_2SiW_{12}O_{40}$ as catalyst



Scheme 10 Hydro arylation of a styrene by AlTPA



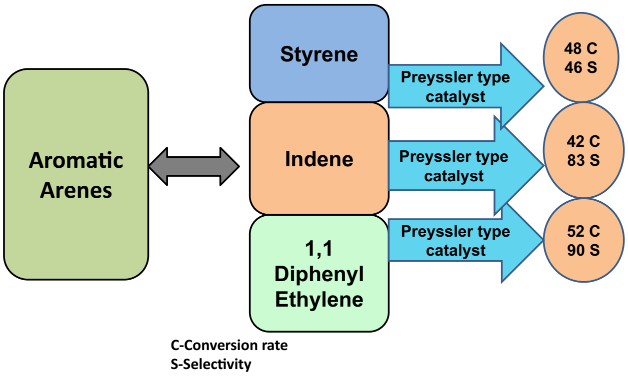


Fig. 13 Diagram represents the epoxidation of aromatic alkanes

2.3.2.4 Preparation of AlWP Catalyst The aluminum and copper salts of tungstophosphoric acid (TPA) were synthesized through a carefully controlled process. These salts will be referred to as AlTPA and CuTPA, respectively. To create these compounds, aqueous solutions of $Al_2[SO_4]_3$ or $Cu[NO_3]_2$ were slowly added to an aqueous solution of $H_3PW_{12}O_{40}$, with the appropriate stoichiometric amounts [87–90]. This addition was done under vigorous stirring to ensure thorough mixing.

Once the solutions were combined, they were stirred at room temperature for 1 h. After this time, the solvent was evaporated in air at a temperature of 70 ℃. The resulting salts were then washed with ethanol and dried again at 100˚C to remove any remaining impurities. This process was repeated to obtain the salts of tungstosilicic acid [91].

Hydro arylation of a styrene derivative (Scheme 10) was investigated by K. Mohan Reddy et al. under solvent-free conditions [92]. The researchers found that adding AlTPA noticeably enhanced the product formation efficiency [92].

2.4 Preyssler Aluminium Based Catalyst

The highly complex isopolycation Al_{13}^{7+} was synthesized by carefully adjusting the ratio of OH^- to Al^{3+} to 2.4 in an aqueous solution [93]. In order to achieve this, a solution of 1.25 M sodium carbonate was meticulously added drop by drop to a vigorously stirring 1.67 M boiling solution of $AlCl_3$. The resulting solution was then utilized to precipitate the heteropoly anion from the aqueous solution. This process yielded a visually striking white emulsion, from which a solid was precisely separated using a centrifuge operating at 2000 rpm. The solid was subsequently dried at 80 °C under 5 Torr for a duration of 24 h. Prior to conducting any catalytic tests, the catalyst underwent a crucial calcination process at 300ºC for 2 h. The molecular weight of the compound $[Al_{13}O_4\,(OH)_{24}(H_2O)_{12}]_2[NaP_5W_{30}O_{110}]$ is determined to be 9530 g/mol [94]. Nemati Kharat et al. conducted a study on the epoxidation of aromatic alkanes using acetonitrile as the solvent (Fig. 13) Remarkably, the catalysts exhibited consistent activity throughout three consecutive cycles, without any noticeable decrease. This finding highlights the stability of the catalysts employed in the process [94].

2.5 Preparation of Aluminium Based Catalyst Wells Dawson Catalyst

Two potassium salts, $K_{10}[\{Al_4(\mu\text{-}OH)_6\}(\alpha,\alpha Si_2W_{18}O_{66})].28.5H_2O$ and $K_{10}[\{Ga_4(\mu\text{-}OH)_6\}(\alpha,\alpha Si_2W_{18}O_{66})]\cdot 25H_2O$-open POM, were synthesized and characterized. Al-containing open Wells Dawson was obtained with a yield of 13.7% and Gallium (Ga) containing with a yield of 26.2%. Al based-open Wells Dawson was prepared by reacting $Na_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}]0.18H_2O$ with $Al(NO_3)_3.9H_2O$, while Ga based Wells Dawson was prepared by reacting $K_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}]0.10H_2O$ with $Ga(NO_3)_3.nH_2O$. The samples were characterized using various analytical techniques. The formation of polyoxoanions was described by crystallization of A_{14}-open resulted in the formation of minor products, including Al_{16}-tetramer. By removing the crude crystals and adding saturated KCl aqueous solution, pure aluminium based POM was obtained from the mother liquor [95, 96].

3 Characterization Techniques HPA Salts

Keggin HPAs are characterized using a variety of methods in both the liquid and solid phases. But in this discussion, we will specifically focus on the most widely utilized techniques. Fourier Transform Infrared Spectroscopy (FTIR). The characterization data and accompanying graphs presented in this study have been sourced from previously published papers."

3.1 Infrared Spectroscopy

Infrared spectroscopy serves as an invaluable tool in unravelling the primary structure of Keggin HPAs. By analysing the characteristic chemical bonds found within Keggin anions, we can pinpoint their primary vibration bands, which are predominantly situated within the fingerprint region. The FTIR analysis allows us to examine the vibrational modes and functional groups found in the silicotungstate salt, molybdotungstate, and phosphomolybdate structures. By studying the characteristic absorption peaks in the infrared spectra, we can identify the specific bonds and interactions within these compounds. This technique allows us to gain profound insights into the intricate composition of Keggin HPAs.

The Keggin-type molybdophosphate and molybdotungstate compounds display distinct spectral bands at specific wave numbers. Specifically, these bands are observed at 973 cm^{-1} for the M=O bond, 878 cm^{-1} for the M-O_b-M bond, and 789 cm^{-1} for the M-O_C-M bond. Moreover, the vibration absorption peak positions of the P-O, W=O, and W–O–W bonds are expected to occur at 1085 cm^{-1}, 962 cm^{-1}, and 893 cm^{-1}, respectively [97–99]. IR frequency of one of the Keggin structures is shown in Fig. 14 [99].

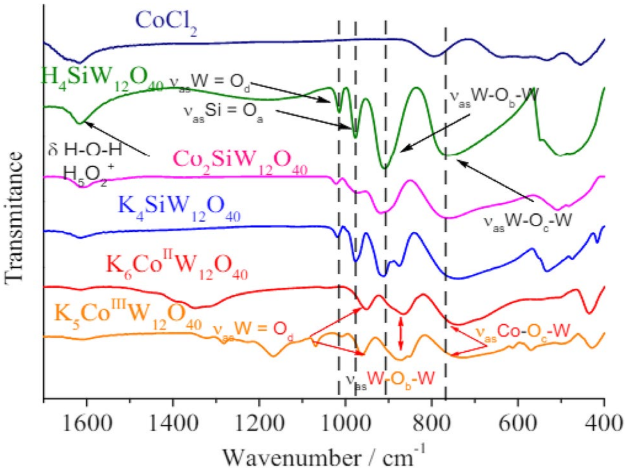


Fig. 14 IR spectra of substituted tungtophosphate heteropolyacid salts

The parent P_2Mo_{18} Dawson unit has characteristic bands at various wavelengths, including 3567–3287 cm^{-1} for water, 1609 cm^{-1} for OH bending, 1058–1035 cm^{-1} for P-O stretching, 946 cm^{-1} for terminal Mo–O stretching, 880 cm^{-1} for edge sharing Mo-Oe-Mo stretching, and 737 cm^{-1} for corner sharing Mo-Oe-Mo stretching. This means that different types of chemical bonds are present in the parent P_2Mo_{18} Dawson unit at these specific wavelengths.

On the other hand, the α-WD (α-phospho-tungstic-WD metal substituted Wells Dawson) has stretching bands at 1087 cm^{-1}, 1021 cm^{-1}, and 996 cm^{-1} in the P-O (phosphorus-oxygen) region, as well as other stretching bands at 953 cm^{-1}, 901 cm^{-1}, and 733 cm^{-1} in the W–O-W (tungsten-oxygen-tungsten) region, and bending vibrations in the 600–500 cm^{-1} region. These bands correspond to different types of stretching and bending motions present in the α-WD structure [70, 99–101]. When tungsten is removed from the α-WD to form α_2-WD (α_2 -phospho-tungstic Wells Dawson), the band at 1087 cm^{-1} splits into three distinct bands at 1079, 1047, and 1013 cm^{-1}. This splitting occurs because the bonding interactions with the removed tungsten octahedra are no longer present in α_2-WD [70, 101, 102].

The Preyssler structure exhibits four distinct types of oxygen, which contribute to the characteristic bands of the Preyssler anion between 1200 and 600 cm^{-1}. Notably, the Preyssler structure, $H_{14}[NaP_5W_{30}O_{110}]0.25H_2O$, is responsible for several key bands. These include the P–O stretching band at 1163 cm^{-1}, the W–O-W bands at 948 cm^{-1} and 917 cm^{-1}, and a band at 760 cm^{-1} corresponding to W=O stretching [103].

This figure is taken from potassium tungstocobaltate(III)-catalysed borneol oxidation 2 with hydrogen peroxide manuscript by author permission.

This review paper also focuses on the Fourier Transform Infrared (FTIR) analysis of potassium-based Keggin, Wells Dawson, and Preyssler-type structures of silicotungstate salt, molybdotungstate, and phosphomolybdate.

4 Conclusion

Based on recent research articles, it has been observed that heteropolyacids have numerous applications across various fields, including pharmaceuticals and organic reactions. These catalysts, known as heteropolyacid catalysts, possess distinctive properties for the exchange of metal ions. These catalysts possess commendable environmental and are considered environmentally friendly. An important property of these catalysts is that they can be used without solvents in many reactions. Their activity remains unaffected as they can be effortlessly regenerated, separated, and reused numerous times.

This review provides an overview of the structure features of heteropolyacids mainly Keggin, Wells Dawson, and Preyssler types of polyoxometalate. Furthermore, we have provided insights into the preparation methods for molybdo, phospho, and tungstate compounds of potassium and aluminium based on these polyoxometalate structures. The article also highlights the application of these catalysts in various organic reactions. Moreover, we have also included FTIR data of Keggin, Preyssler and Wells Dawson structure from the previous studies to enhance the understanding and clarification of these catalysts.

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Data availability The authors confirm that the data supporting the findings of this study are available within the article [10.1007/s42250-024-01038-6].

Declarations

Conflict of Interest Not applicable.

Ethical Approval Not applicable.

Informed Consent Not Applicable.

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