



The state of the art on Wells–Dawson heteropoly-compounds A review of their properties and applications

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Abstract

The scientific literature concerning the structure, hydrolytic stability in solution, thermal stability in the solid state, redox-acid properties and applications of heteropoly-compounds (HPCs) with Wells–Dawson structure is summarized in the present work.

Wells–Dawson heteropoly-anions possess the formula $[(X^{n+})_2M_{18}O_{62}]^{(16-2n)-}$ where X^{n+} represents a central atom (phosphorous(V), arsenic(V), sulfur(VI), fluorine) surrounded by a cage of M addenda atoms, such as tungsten(VI), molybdenum(VI) or a mixture of elements, each of them composing MO_6 (M-oxygen) octahedral units. The addenda atoms are partially substituted by other elements, such as vanadium, transition metals, lanthanides, halogens and inorganic radicals. The Wells–Dawson heteropoly-anion is associated with inorganic (H^+ , alkaline elements, etc.) or organic counteranions forming hybrid compounds.

Wells–Dawson acids (phospho-tungstic $H_6P_2W_{18}O_{62} \cdot 24H_2O$, phospho-molybdic $H_6P_2Mo_{18}O_{62} \cdot nH_2O$ and arsenic-molybdic $H_6As_2Mo_{18}O_{62} \cdot nH_2O$) possess super-acidity and a remarkably stability both in solution and in the solid state. These properties make them suitable catalytic materials in homogeneous and heterogeneous liquid-phase reactions replacing the conventional liquid acids (HF, HCl, H_2SO_4 , etc.). Although, the application of the acids in heterogeneous gas-phase reactions is less developed, there is a patented method to oxidize alkanes to carboxylic acids on a supported Wells–Dawson catalyst that combines acid and redox properties.

Wells–Dawson anions possess the ability to accept or release electrons through an external potential or upon exposure to visible and UV radiation (electro and photochemical reactions).

Additionally, Wells–Dawson HPCs catalyze the oxidation of organic molecules with molecular oxygen, hydrogen peroxide and iodosylarenes; epoxidation and hydrogenation in homogeneous and heterogeneous liquid-phase conditions.

The ability of transition metal substituted Wells–Dawson HPCs to be reduced and re-oxidized without degradation of the structure is promising in the application of those HPCs replacing metalloporphyrins catalysts in redox and electrochemical reactions.

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1. Introduction

The present work discusses the literature devoted to the properties and applications of Wells–Dawson-type heteropoly-compounds (HPCs) as catalytic materials in heterogeneous and homogeneous liquid and gas-phase reactions, electrochemical and photochemical reactions. The reviewed literature on catalytic applications is focused on the scientific research of the past 12 years (1990–2002) although a few pioneer works published earlier are also mentioned due to their important contribution to the development of Wells–Dawson-type HPCs as catalytic materials.

1.1. A journey from simple to complex Wells–Dawson compounds

Kehrmann described the synthesis of a phospho-tungstic Wells–Dawson-type compound for the first time in 1892 [1]. However, Dawson would publish the first crystallographic study of the structure 60 years later [2]. The general formula of the Wells–Dawson heteropoly-anion is $[(X^{n+})_2M_{18}O_{62}]^{(16-2n)-}$ where X^{n+} represents a central atom such as, phosphorous(V), arsenic(V), sulfur(VI), fluorine; surrounded by a cage of M addenda atoms, such as tungsten(VI), molybdenum(VI) or a mixture of elements, each of them composing MO_6 (M-oxygen) octahedral units. The structure, known as α isomer, possesses two identical “half units” of the central atom surrounded by nine octahedral units XM_9O_{31} linked through oxygen atoms (Fig. 1). The isomeric β structure originates when a half unit rotates $\pi/3$ around the X–X-axis [3]. Similarly to many heteropoly-anions, the Wells–Dawson structure can be chemically manipulate to generate “holes” by removing up to six WO_6 units (from X_2M_{18} to X_2M_{12}). These non-saturated compounds called “lacunary” species are synthesized through the degradation of the $[(X^{n+})_2M_{18}O_{62}]^{(16-2n)-}$ anion in a controlled basic media (no direct synthesis of these species have been reported). The phospho-tungstic anion $P_2W_{18}O_{62}^{6-}$ produces $P_2W_{17}O_{61}^{10-}$ species at pH ~ 8.4 (treated with $KHCO_3$) and $P_2W_{15}O_{56}^{12-}$ at pH = 9.0. These lacunary species and $P_2W_{12}O_{50}^{18-}$ have been isolated from the solution as pure solid salts [3,4]. The lacunary phospho-molybdic anion $P_2Mo_{17}O_{61}^{10-}$ has also been synthesized as potassium and ammonium salts [5].

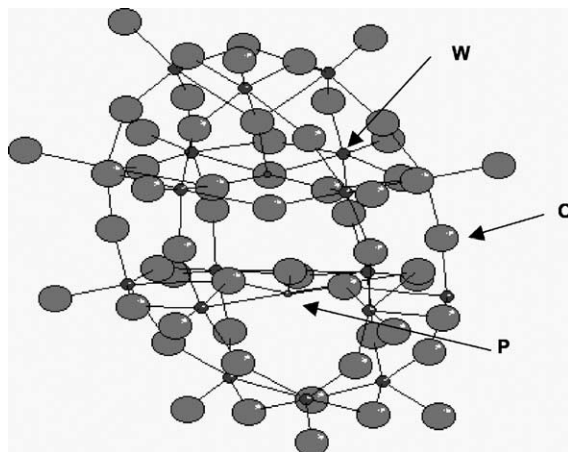


Fig. 1. Structure of the phospho-tungstic Wells–Dawson heteropolyoxo-anion $P_2W_{18}O_{62}^{6-}$ from crystallographic parameters provided in [2]. W: tungsten, P: phosphorous and O: oxygen atoms.

The “holes” of the lacunary species can be filled with a variety of elements, such as molybdenum, vanadium and other metallic elements, lanthanides, etc. These “substituted” HPCs will be further discussed in the following sections.

Most of the heteropoly-compounds with Wells–Dawson structure found in the literature, along with their solubility and thermal stability in the solid state and liquid media (hydrolytic stability), are presented in the Table 1. The table is divided in three sections devoted to heteropoly acids, salts and those compounds with mixed addenda atoms (substituted HPCs). The degree of hydration of the compounds have not been indicated in order to simplify the information. However, is important to notice that HPCs possess from 3 up to 60 molecules of water associated with the unit formula.

More recently, a variety of “sandwich-type” heteropoly-anions have been synthesized. These compounds are formed by two Wells–Dawson anions linked together through one or more transition or noble metals. These materials will not be discussed in the present paper.

1.1.1. Wells–Dawson heteropoly-acids

Table 1 shows that phospho-tungstic $H_6P_2W_{18}O_{62} \cdot 24H_2O$, phospho-molybdic $H_6P_2Mo_{18}O_{62} \cdot nH_2O$ ($n = 33–37$) and arsenic-molybdic $H_6As_2Mo_{18}O_{62} \cdot nH_2O$ ($n = 25–35$) Wells–Dawson acids have been

Table 1

Solubility, pH range of stability in liquid media (hydrolytic stability) and thermal stability in the solid state of compounds with Wells–Dawson structure

Compound	Solubility	Hydrolytic stability	Thermal stability (°C)	Reference
Heteropoly-acids				
H ₆ P ₂ W ₁₈ O ₆₂	H ₂ O, organic solvents	pH ≤ 6	<300 [6d], ≤600 [6b,e]	[6a–f]
H ₆ P ₂ W ₁₈ O ₆₂ supported on SiO ₂ , MCM-41	–	–	<400	[6d,7,8]
H ₆ P ₂ Mo ₁₈ O ₆₂	H ₂ O, organic solvents	–	375	[9]
Heteropoly-salts				
α/β-(NH ₄) ₆ P ₂ W ₁₈ O ₆₂ , K ₆ P ₂ W ₁₈ O ₆₂ , (NH ₄) ₆ As ₂ W ₁₈ O ₆₂ , reduced species (heteropoly-blues) P ₂ W ₁₈ O ₆₂ ⁿ⁻ , As ₂ W ₁₈ O ₆₂ ⁿ⁻ , n = 7–9	H ₂ O, hot H ₂ O for K ⁺ salt	pH = 3–6 for oxidized species pH = 0–13 for reduced species	≤500 for (NH ₄) ₆ P ₂ W ₁₈ O ₆₂ ≤570 for K ₆ P ₂ W ₁₈ O ₆₂	[6a,10a–c]
(NH ₄) ₆ P ₂ W ₁₈ O ₆₂ /TiO ₂	–	–	≤400	[11]
X ₆ P ₂ Mo ₁₈ O ₆₂ , X = Na ⁺ , NH ₄ ⁺ , K ⁺ , Rb ⁺ , Cs ⁺ , Bu ₄ N ⁺ , reduced species (heteropoly-blues)	H ₂ O, alcohols, diethyl ether, acetonitrile	Unstable in aqueous media for extended periods of time	≤270	[3,12a–h]
H ₂ P ₂ Mo ₂ ⁵ Mo ₁₆ O ₆₂ ⁶⁻	Acetonitrile	<50 °C in acetonitrile	≤86 for S ₂ Mo ₁₈ O ₆₂ ⁵⁻	[12h,13a,b]
X _n [S ₂ Mo ₁₈ O ₆₂] ⁿ⁻ , n = 4–6, X = Bu ₄ N ⁺ , Hex ₄ N ⁺	H ₂ O	pH ≤ 8.4	–	[14]
[H ₂ F ₆ W ₁₈ O ₅₆] _z , Z = H ⁺ , K ⁺ , Me ₄ N ⁺	–	–	–	[15a,b]
β-ET ₁₁ P ₂ M ₁₈ O ₆₂ , M = W, Mo	–	–	–	[15a,b]
(NH ₄) ₆ As ₂ Mo ₁₈ O ₆₂	H ₂ O	pH < 5.3	–	[12a]
Lacunary and substituted HPC (mixed addenda atoms)				
P ₂ W ₁₈ M ₄ (H ₂ O) ₂ O ₆₈ ¹⁰⁻ , M = Co ²⁺ , Cu ²⁺ , Zn ²⁺	H ₂ O	–	–	[16a,b]
α ₂ -Z _x P ₂ W ₁₇ O ₆₁ (M ⁿ⁺ ·L), Z = K ⁺ , Bu ₄ N ⁺ ; M ⁿ⁺ = Mn ³⁺ , Fe ³⁺ , Co ²⁺ , Ni ²⁺ , Cu ²⁺ ; L = Br ⁻ , H ₂ O	H ₂ O for Z = K ⁺ , L = H ₂ O Organic solvents for Z = Bu ₄ N ⁺ , L = Br ⁻	6.0 ≤ pH ≤ 7.0 5.5 ≤ pH ≤ 9.0 for M ⁿ⁺ = Co ²⁺	–	[17]
α ₂ -Z _x X ₂ MW ₁₇ O ₆₂ H ₂ , Z = K ⁺ , Li ⁺ , Rb ⁺ , C(NH ₂) ₃ ⁺ , Me ₂ NH ₂ ⁺ , Bu ₄ N ⁺ ; X = P, As, M = Mn ²⁺ , Mn ³⁺ , Ni ²⁺ , Co ²⁺ , Co ³⁺ , Zn ²⁺ , Cr ³⁺ , lanthanides (Sm ³⁺ , Lu ³⁺ , Eu ³⁺), Ce ³⁺	Cold/hot water, organic solvents	1.0 ≤ pH ≤ 9.0	–	[18a–d]
K _x X ₂ M ^{III} (OH) ₂ W ₁₇ O ₆₁ , X = P, As; M = Al, Ga, In, Tl	H ₂ O	pH ≤ 8	–	[19a–c]
K _x X ₂ Fe ^{III} MW ₁₇ O ₆₁ , X = P, As; M = SCN ⁻ , SO ₃ ²⁻ , Fe(CN) ₆ ⁴⁻	–	2.5 ≤ pH ≤ 6.5	–	
α ₂ -Z ₁₀ P ₂ W ₁₇ O ₆₁ , α _i -Z _n P ₂ W _{18-y} V _y O ₆₂ , i = 1, 2; y = 1–3, Z = K ⁺ , Li ⁺ , NH ₄ ⁺ , Na ⁺	Hot water	pH ≤ 7.0	<600 for α ₂ -K ₇ P ₂ W ₁₇ VO ₆₁	[20a,b]
α-[P ₂ W _{18-x} Mo ₂ V _y O ₆₂] ⁿ⁻ , x = y + z, n = 6 + y	H ₂ O	pH < 1	–	[21a,b]

Table 1 (Continued)

Compound	Solubility	Hydrolytic stability	Thermal stability (°C)	Reference
$\alpha_2\text{-Z}_a\text{H}_b\text{P}_2\text{W}_{18-x}\text{Ti}_x\text{O}_{62}$ and $\alpha\text{-}1,2,3\text{-Z}_a\text{H}_b\text{P}_2\text{W}_{18-x}(\text{TiO}_2)_x\text{O}_{62-x}$, $Z = \text{K}^+, \text{Bu}_4\text{N}^+, \text{Et}_4\text{N}^+$; $x = 1, a + b = 8; n = 3, a + b = 12$	H ₂ O	Stable at pH = 2.0	–	[22]
(NH ₄) ₈ FeW ₁₇ O ₅₆ F ₆ NaH ₄ , (NH ₄) ₉ CoW ₁₇ O ₅₆ F ₆ NaH ₄ Z ₈ VW ₁₇ O ₅₆ F ₆ NaH ₂ , Z = K ⁺ , Bu ₄ N ⁺	Cold/hot H ₂ O	–	–	[23a,b]
K ₆ [Ti(H ₂ O)P ₂ W ₁₆ MoO ₆₁]	H ₂ O	4.0 ≤ pH ≤ 5.6	≤590	[24]
K _x P ₂ M _n W _{17-n} O ₆₂ , x = 6–9; M = Mo, V, n = 1–3	Cold/hot H ₂ O, pH 1.5	Stable at pH = 1	–	[25a,b]
Z _{9-x} H _x P ₂ W ₁₅ V ₃ O ₆₂ , Z = K ⁺ (x = 8), Me ₄ N ⁺ (x = 3), Bu ₄ N ⁺ (x = 0–4)	Organic solvents	Stable upon deprotonation in basic media	–	–
Na ₁₆ [M ₄ (H ₂ O) ₂ (P ₂ W ₁₅ O ₅₆) ₂], M = Mn ²⁺ , Ni ²⁺ , Co ²⁺ , Cu ²⁺ , Zn ²⁺	H ₂ O	–	–	[26a–d]
[(n-C ₄ H ₉) ₆ N] ₆ [C ₅ H ₅ TiP ₂ W ₁₅ V ₃ O ₆₂]	Organic solvents	–	–	[27]
$\alpha\text{-P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}\text{X}_9$, X = K ⁺ , Li ⁺ , Cs ⁺ , Na ⁺ and Bu ₄ N ⁺	H ₂ O (K ⁺ , Li ⁺ , Cs ⁺ and Na ⁺ salts)	–	473, 492, 529, 534 for Li ⁺ , Na ⁺ , K ⁺ and Cs ⁺ , respectively	[28]
[(η ⁵ -C ₅ Me ₅)M](P ₂ W ₁₅ Nb ₃ O ₆₂)]X ₇ , X = Bu ₄ N ⁺ , (Bu ₄ N ⁺) _{7-x} Na _x ; M = Rh, Ir	Organic solvents [TBA, (η ⁵ -C ₅ Me ₅) and 1,5-COD salts]	–	–	–
[(n-C ₄ H ₉) ₄ N] ₅ Na ₃ [(1,5-COD)MP ₂ W ₁₅ Nb ₃ O ₆₂] M = Ir, Rh, 1,5-COD	–	–	–	–

ET, bis(ethylenedithio)tetra-thiafulvalene; Me₄N⁺, tetra-methylammonium (CH₃)₄N⁺; Et₄N⁺, tetra-ethylammonium (C₂H₅)₄N⁺; Bu₄N⁺, tetra-*n*-butylammonium (n-C₄H₉)₄N⁺; Hex₄N⁺, tetra-*n*-hexylammonium; 1,5-COD: 1,5-cyclooctadiene.

synthesized [6–9]. The heteropoly-acids are obtained through the “etherate method”, by ion exchange and by precipitation with sulfuric acid [5]. The “etherate method” requires a strongly acidified aqueous solution of the heteropolyanion (from an aqueous soluble heteropoly-salt) that is shaken with diethyl ether in order to separate three phases: an upper ether layer, an aqueous layer and a heavy oily layer. The oily layer contains an etherate of the heteropoly-acid which nature is unknown. The etherate is decomposed with water and the solution is evaporated until the acid crystallizes. According to early studies by Wu and our own experience, this method does not yield pure H₆P₂Mo₁₈O₆₂·*n*H₂O but a mixture with phosphomolybdic Keggin-type acid H₃PMo₁₂O₄₀ [29].

The phospho-tungstic acid is soluble and stable (up to pH 6) in aqueous media and also some organic solvents, such as methanol, acetonitrile and methyl-*tert*-butyl ether (MTBE) [30,31]. Studies on the catalytic activity in homogeneous reaction con-

ditions demonstrated that the acid is stable upon heating at 128 °C in organic media [7,31]. A detailed thermogravimetric and spectroscopic analysis of the phospho-tungstic acid H₆P₂W₁₈O₆₂·24H₂O showed that 17, 5 and 2 water molecules per Wells–Dawson unit evolved upon heating at 66–72, 97–114 and 308–318 °C, respectively [6e,f]. The nature of the acid sites is greatly modified upon dehydration although the Wells–Dawson structure remains unaltered up to 600 °C. The fully hydrated acid possesses large protonated water clusters H⁺(H₂O)_{*n*} which degrade to H₅O₂⁺ at 200 °C and finally to isolated protonic sites when the acid is completely dehydrated. The isolated acid sites trapped between Wells–Dawson units are inaccessible to the reagents causing the drop of the catalytic activity of the acid. The deactivation of the acid upon full dehydration was observed during methanol reaction and the synthesis of MTBE in the gas-phase at temperatures above 200 °C [6e].

Wells–Dawson heteropoly-acids (HPAs) are considered super-acids since they possess an acid strength higher than 100% H_2SO_4 [32]. The comparison of the acid strength of different compounds through ammonia adsorption (basic probe to measure acidity in the solid state) and Hammett indicators in acetonitrile (determination of acidity in the liquid media) show the following decreasing trend: $\text{H}_3\text{PW}_{12}\text{O}_{40} > \text{H}_4\text{SiW}_{12}\text{O}_{40} > \text{H}_6\text{P}_2\text{W}_{21}\text{O}_{71}(\text{H}_2\text{O})_3 > \text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$. The observation that the Wells–Dawson HPA possesses lower acid strength than Keggin-type heteropoly-acids could be attributed to the fact that the experiments were performed after the dehydration of the acid at about 400°C .

Misono and coworkers demonstrated that Wells–Dawson HPAs are suitable to adsorb polar molecules, such as alcohols, into the solid bulk. This unique behavior called “pseudoliquid-phase behavior” allows the reactions (both in the liquid-phase and gas-phase conditions) to take place at the surface and solid bulk of the heteropoly-anion.

Few studies about the effect of oxide supports on the catalytic activity of Wells–Dawson phospho-tungstic acid are available in the literature due to the reaction of the acid with most of the metal oxides, such as TiO_2 , ZrO_2 , Nb_2O_5 , and Al_2O_3 that are used as supports [33]. The dispersion of the acid on a support improves the surface area (the specific surface area of fully hydrated $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ is ~ 5 and $\sim 2.5 \text{ m}^2/\text{g}$ after calcination at 400°C) but diminishes the pseudoliquid-phase ability of the heteropoly-anion. Only silica oxide and MCM-41 are inert towards aqueous solutions of the acid (see Table 1). The dispersion of the acid on SiO_2 greatly affects the thermal stability causing the decomposition of the Wells–Dawson structure to Keggin-type species upon calcination at 400°C .

The phospho-molybdic acid $\text{H}_6\text{P}_2\text{Mo}_{18}\text{O}_{62}$ has been less studied than the parent phospho-tungstic heteropoly-acid. Wijesekera et al. patented a method to synthesize the acid by passing a cold aqueous solution of the ammonium salt $(\text{NH}_4)_6\text{P}_2\text{Mo}_{18}\text{O}_{62}$ through a strongly acidic ion exchange resin [9]. This method yields a compound free of the Keggin-phase at difference with Wu’s method described above. The authors demonstrated that the acid supported on a cesium Keggin-type salt $\text{Cs}_3\text{PMo}_{12}\text{O}_{40}$ is stable during

propane oxidation at 375°C in the gas-phase (higher temperatures are not reported).

No reports on the hydrolytic stability of the acid in liquid media have been found in the literature, however many studies on the stability of the $\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$ anion have been performed. Those studies will be discussed in the following sections.

1.1.2. Wells–Dawson heteropoly-salts

Table 1 shows the variety of inorganic and organic counteranions that have been used to synthesize Wells–Dawson-type salts (substituted and non-substituted compounds). In general, it is observed that the nature of the counteranion influences the solubility of the salt: all inorganic salts are water-soluble and those with organic counteranions are soluble in organic media. In general, phospho-tungstic salts are stable in the $3 \leq \text{pH} \leq 6.5$ range, although reduced species (heteropoly-blues) are stable up to $\text{pH} = 13$ and molybdenum and vanadium substituted compounds exist at $\text{pH} = 1$ in solution (Table 1).

A detailed study on the hydrolytic stability of phospho-molybdic ammonium salt $(\text{NH}_4)_6\text{P}_2\text{Mo}_{18}\text{O}_{62} \cdot 12\text{H}_2\text{O}$ demonstrated that the heteropoly-anion $\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$ is not stable in aqueous media for extended periods of time [12g]. The phospho-molybdic Dawson-type anion decomposes to the Keggin-type anion $\text{H}_x\text{PMo}_{12}\text{O}_{40}^{(3-x)-}$, pentamolybdodiphosphate $\text{H}_x\text{P}_2\text{Mo}_5\text{O}_{23}^{(6-x)-}$ and heptamolybdate $\text{Mo}_7\text{O}_{24}^{6-}$ or molybdate MoO_4^{2-} species regardless of the concentration or pH conditions. Moreover, the Keggin-type anion decomposes to the lacunar anion $\text{H}_x\text{PMo}_{11}\text{O}_{39}^{(7-x)-}$ and molybdate species in the aqueous medium or precipitates as the ammonium phospho-molybdic salt $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40} \cdot 4\text{H}_2\text{O}$ at high acidity values ($\text{pH} \leq 2$). An indirect confirmation of the above mentioned results are the studies published by Combs-Walker and Hill [12d]. The authors demonstrated that aqueous solutions of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ degrade to the lacunary Keggin heteropoly-anion $\text{P}_2\text{Mo}_{11}\text{O}_{39}^{7-}$, $\text{P}_2\text{Mo}_5\text{O}_{23}^{6-}$ and the Dawson heteropoly-anion $\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$. However, the phospho-molybdic $\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$ anion is stable in a variety of organic solvents such as, methanol, ethanol, 2-propanol, acetone and acetonitrile [12h,34].

Many studies demonstrated that the tertiary structure of the Keggin-type salts is influenced by the size of the counteranion. The salts with small metal

cations such as sodium and copper (group A salts) possess low surface area and are soluble in water, while those with large ions (group B salts), such as cesium or ammonium, possess much higher specific surface areas. Moreover, the nature of the counteranion influences the thermal stability of the Keggin compounds [5]. An extensive work on that subject has not been performed in the particular case of Wells–Dawson anions. However, in general is observed that the nature of the addenda (tungsten/molybdenum) and the central (phosphorous/sulfur) atoms, and the size of the counteranions (particularly in tungsten-based compounds) influence the thermal stability of the heteropoly-anions in the solid state rather than the specific surface area of the Wells–Dawson compounds (both potassium and ammonium phospho-tungstic salts $K_6P_2W_{18}O_{62} \cdot nH_2O$ and $(NH_4)_6P_2W_{18}O_{62} \cdot nH_2O$ possess $\sim 1 \text{ m}^2/\text{g}$) [10b,11].

Nomiya et al. studied the thermal stability of the niobium substituted compound $\alpha\text{-P}_2W_{15}Nb_3O_{62}X_9$ with $X = K^+$ (ionic radii: 1.33 \AA), Li^+ (0.68 \AA), Cs^+ (1.67 \AA), Na^+ (0.97 \AA) and Bu_4N^+ [28]. The authors found the following order of thermal stability in the solid state: Cs salt > K salt \gg Na salt > Li salt. However, similar studies performed by Guerbais and coworkers on the thermal stability of the phospho-molybdic anion $P_2Mo_{18}O_{62}^{6-}$ with varying counteranions [K^+ , Rb^+ (1.47 \AA), Cs^+ , NH_4^+ (1.43 \AA), $(CH_3)_4N^+$] demonstrated that the anion decomposes at 260°C regardless of the nature of the counteranion [12f]. Both phospho-tungstic and molybdic Wells–Dawson salts degrade to the Keggin salt, P_2O_5 , and WO_3 or MoO_3 upon calcination.

In general, is observed that Wells–Dawson compounds with molybdenum as addenda and sulfur as central atoms, are less thermally stable than those containing tungsten and phosphorous (see Table 1 for $S_2Mo_{18}O_{62}^{n-}$).

Although, there are no studies addressing the effect of mixed addenda atoms on the thermal stability, the information gathered in Table 1 allows to conclude that the nature of the “substitution element” do not influence the thermal stability of phospho-tungstic potassium salts. In fact, the non-substituted phospho-tungstic potassium salt $K_6P_2W_{18}O_{62}$, vanadium substituted salt $K_7P_2W_{17}VO_{61}$, niobium substituted salt $K_9P_2W_{15}Nb_3O_{62}$ and molybdenum

substituted salt $K_6[Ti(H_2O)P_2W_{16}MoO_{61}]$ decompose at about 600°C .

Few studies on the influence of a metal oxide support on the specific surface area and thermal stability in the solid state of Wells–Dawson heteropoly-salt have been performed. Briand et al. demonstrated that the dispersion of $(NH_4)_6P_2W_{18}O_{62}$ on TiO_2 improves the specific surface area of the heteropoly-anion (from 1 up to $50 \text{ m}^2/\text{g}$) however, the surface species decomposes at a lower temperature than the non-supported heteropoly-salt [11].

Wells–Dawson heteropolyanions form hybrid materials (organic counteranion–inorganic cluster) with organic radicals counteranions such as bis(ethylendithio)tetra-thiafulvalene (ET), tetra-methylammonium [$(CH_3)_4N^+$], tetra-ethylammonium [$(C_2H_5)_4N^+$], tetra-*n*-butylammonium [$(n\text{-}C_4H_9)_4N^+$], tetra-*n*-hexylammonium (Hex_4N^+) and 1,5-cyclooctadiene (1,5-COD) (see Table 1). The organic counteranion makes these materials soluble in organic media. In the particular case of $\beta\text{-ET}_{11}P_2M_{18}O_{62}$ (with $M = W, Mo$), the counteranion is an organic π -donor radical that confers unique electrical properties to the compound [15]. Conductivity measurements performed on the crystal demonstrated for the first time, that the compound possesses a metallic-like behavior.

1.2. Redox properties and applications of Wells–Dawson HPCs

The applications of Wells–Dawson compounds as redox or acid catalytic materials in homogeneous (electrochemical and photochemical reactions) and heterogeneous liquid-phase processes and heterogeneous gas–solid reactions are presented in Tables 2 and 3, respectively. The Tables summarize the reactants, products (with selectivity when reported) and the reaction conditions.

1.2.1. Applications in homogeneous redox reactions in liquid-phase

1.2.1.1. Electrochemical activity. Many research efforts have been devoted to study the redox properties of Wells–Dawson heteropoly-compounds in the liquid media. Similarly to Keggin-type compounds, the ability of the Wells–Dawson compounds to accept and release electrons can be controlled by

Table 2

Catalytic applications of Wells–Dawson-type heteropoly-compounds in liquid-phase acid and redox reactions

Catalyst	Reaction	Products (selectivity (%))	Reaction conditions	Reference
$K_6P_2W_{18}O_{62}$, $K_{10}P_2W_{17}O_{61}$, $K_8P_2W_{17}O_{61}M$ ($M = Cu^{2+}$, Ni^{2+} , Co^{2+} , Mn^{2+} , Mn^{3+} , Fe^{3+})	Electrocatalytic reduction of nitrite	Ammonia	pH = 2.0, 4.5	[36a,b]
$P_2Mo_2W_{15}O_{61}^{10-}$, V^{4+} , Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Zn^{2+} and Cu^{2+} derivatives	Electrocatalytic oxidation of NADH	NAD ⁺	pH = 8	[37]
$K_6P_2W_{18}O_{62}$, $Na_{12}(P_2W_{15}O_{56})$, $Na_{12}[Fe^{III}_4(H_2O)_2(P_2W_{15}O_{56})_2]$	Electrocatalytic reduction of H_2O_2 and NO_2^-	H_2O	pH = 4.5–5.0	[38]
$(NH_4)_6P_2W_{18}O_{62}$	Photochemical degradation of thioethers [tetra-hydrothiophene, $(CH_3)_2S$]	$C_8H_{14}S_2$, sulfoxides, sulfones	Acetonitrile as solvent, aerobic/anaerobic, 25 °C, $h\nu = 550-10^3$ W	[39]
α -(NH_4) ₆ $P_2W_{18}O_{62}$	Selective photocatalytic transformation of C–H bonds of <i>cis</i> -1-decalone	Monounsaturated ketones (octalones)	Acetonitrile as solvent, 25 °C, $\lambda = 250-380$ nm	[40]
β -(NH_4) ₆ $P_2W_{18}O_{62}$	Photodehydrogenation of branched acyclic alkanes and cycloalkanes	Alkenes	Acetonitrile as solvent, argon atmosphere, 25 °C, $\lambda > 280$ nm	[41]
$P_2W_{18}O_{62}^{6-}$	Photocatalytic dehydrogenation of alcohols	H_2	2-Propanol 1.1 M and $HClO_4$ 0.1 M, Xe lamp	[35]
α_2 -(Bu_4N) _{<i>n</i>-1} $P_2W_{17}O_{61}(M^{n+} \cdot Br)$, $M^{n+} = Mn^{3+}$, Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+}	Cyclo-octene/-hexene, <i>cis</i> -stilbene epoxidation, cyclohexane, adamantane, heptane oxidation, hydroxilation of naphthalene	Epoxides (68–88%), alcohols and ketones (5–40%), 1- and 2-naphthol (3–43%)	Aerobic conditions, 20 °C, 2–24 h, PhIO as oxidant	[42]
$Cs_6H_2P_2W_{17}O_{61}CoOH_2/SiO_2$	Aerobic oxidation of aldehydes	Carboxylic acids (63–96%)	Dichloromethane as solvent, flowing O_2 , refluxing for 30 h	[43]
$K_8H_2F_6NaVW_{17}O_{56}$	Aerobic oxidation of alkyl aromatic compounds	Alcohols, ketones	Biphasic reaction media pH = 5, 5 atm of O_2 , 120 °C, 16 h	[23b]
Polyfluorooxometals (PFOM), $[M(L)H_2F_6NaW_{17}O_{55}]$, $M = Zn^{2+}$, Co^{2+} , Mn^{2+} , Fe^{2+} , Ru^{2+} , $Ni^{2+}V^{5+}$; $L = H_2O$, O^{2-}	Selective epoxidation of alkenes and alkenols with H_2O_2	Epoxides	Biphasic reaction media	[44]
$[(CH_3)_4N]_6P_2Mo_{18}O_{62}$, $[(CH_3)_4N]_4S_2Mo_{18}O_{62}$	<i>iso</i> -Butylaldehyde oxidation with H_2O_2	<i>iso</i> -Butyric acid	Acetonitrile as solvent, 50 °C	[12i]
$K_8P_2W_{16}V_2O_{62}$, $K_7P_2W_{17}VO_{62}$, $K_8HP_2W_{15}V_3O_{62}^{8-}$, $K_7P_2W_{15}Mo_2VO_{62}$	Benzene hydroxylation with H_2O_2	Phenol	Acetonitrile as solvent, 25 °C	[45]
$K_7P_2W_{15}Mo_2VO_{62}$	Toluene and nitrobenzene oxidation with H_2O_2	<i>o</i> -, <i>m</i> -, <i>p</i> -Cresol (72%), benzaldehyde (20%), benzyl alcohol (8%); <i>o</i> -, <i>m</i> -, <i>p</i> -Nitrophenol (43, 42, 15%)	Acetonitrile as solvent, 25 °C	[46]
$[(n-C_4H_9)_4N]_5Na_3[(1,5-COD)IrP_2W_{15}Nb_3O_{62}]$	Cyclohexene hydrogenation	Cyclohexane (100%)	Acetone as solvent, 40 psig H_2 , 22 °C	[47]
$H_6P_2W_{18}O_{62}$, $H_6P_2W_{18}O_{62}/SiO_2$	Deprotection of phenol, methoxymethyl ethers	<i>o</i> -Hydroxyacetophenone, phenol (70–100%)	Various organic solvents, 65–80 °C	[31]
$H_6P_2W_{18}O_{62}$, $H_6P_2W_{18}O_{62}/SiO_2$	Tetrahydropyrylation/depyrylation of phenol and alcohols	2-Tetrahydropyryl acetals (100%)	Organic solvent, r.t.	[48]

Table 2 (Continued)

Catalyst	Reaction	Products (selectivity (%))	Reaction conditions	Reference
H ₆ P ₂ W ₁₈ O ₆₂	Michael addition of alcohols (<i>iso</i> -Pr, Me, Et, <i>t</i> -Bu, Bn) to cyclohexenone	β - <i>iso</i> -Propoxycyclohexenone (100%)	Argon atmosphere, r.t., cyclohexane as solvent	[49]
H ₆ P ₂ W ₁₈ O ₆₂ , H ₆ P ₂ Mo ₁₈ O ₆₂	Acylation and alquilation of <i>iso</i> -butylene with methanol	MTBE (CH ₃) ₃ COCH ₃ (~100%), traces of <i>cis</i> -2-butene	42 °C, 100 kPa	[30]
H ₆ P ₂ W ₁₈ O ₆₂ , H ₆ P ₂ W ₁₈ O ₆₂ /SiO ₂	Alkylation of <i>iso</i> -butane with C4 olefins	Dimethylhexanes (~80%), dimethylhexenes (~10%), trimethylpentanes (~10%)	25–80 °C, 30 kg/cm ² , regeneration with ozone at 125 °C	[7]
H ₆ P ₂ W ₁₈ O ₆₂	Decomposition of <i>iso</i> -butyl propionate, ester exchange with methanol and acetic acid, esterification of propionic acid with <i>iso</i> -butyl alcohol	Olefins, acids, alcohols, esters	70–128 °C, homogeneous	[50]

NADH: nicotinamide adenine dinucleotide; PhIO: iodosylbenzene; 1,5-COD: 1,5-cyclooctadiene; *o*-, *m*-, *p*-: *ortho*, *meta*, *para*; r.t.: room temperature; *iso*-Pr: *iso*-propyl alcohol; Me: methanol; Et: ethanol; *t*-Bu: *tert*-butanol; Bn: benzyl alcohol.

Table 3

Catalytic applications of Wells–Dawson-type heteropoly-compounds in gas-phase acid and redox reactions

Catalyst	Reaction	Products (selectivity (%))	Reaction conditions	Reference
K ₆ P ₂ W ₁₈ O ₆₂	Oxidative dehydrogenation of <i>iso</i> -butane	<i>iso</i> -Butylene (60–80%)	327–427 °C, 1 atm	[10a]
K ₆ P ₂ W ₁₈ O ₆₂ , K ₁₀ P ₂ W ₁₇ O ₆₁ , K _x P ₂ W ₁₇ MO _{62-x} · <i>n</i> H ₂ O, M = Fe, Mn, Co, Cu	Oxidative dehydrogenation of <i>iso</i> -butane	<i>iso</i> -Butylene (55–79%), propylene (3–8%), CO + CO ₂ (14–29%)	380–450 °C, 1 atm, <i>iso</i> -butane/O ₂ /H ₂ O (26/13/12 mol%)	[53]
K ₆ P ₂ W ₁₈ O ₆₂ , K ₇ P ₂ W ₁₇ VO ₆₁	Methanol selective oxidation	Formaldehyde (100%)	350–450 °C, 1 atm	[20b]
X ₆ P ₂ Mo ₁₈ O ₆₂ , X = NH ₄ ⁺ , K ⁺ , Rb ⁺ , Cs ⁺ , (CH ₃) ₄ N ⁺	Oxidative dehydrogenation of <i>iso</i> -butyraldehyde	Methacrolein, methacrylic acid, acetone and CO _x	225–300 °C, 1 atm	[12f]
H ₆ P ₂ Mo ₁₈ O ₆₂ , H ₂ (VO) ₂ P ₂ Mo ₁₈ O ₆₂ , H ₄ (VO) ₂ P ₂ Mo ₁₈ O ₆₂ , H ₂ (VO) ₂ P ₂ W ₁₅ Mo ₃ O ₆₂ , H ₂ (VO) ₂ P ₂ W ₁₅ Mo ₂ VO ₄₀ supported on Cs ₃ PMo ₁₂ O ₄₀ , Cs ₆ P ₂ Mo ₁₈ O ₆₂ or (Cs ₃ PMo ₁₂ O ₄₀ + K ₆ P ₂ W ₁₈ O ₆₂)	Oxidation of propane and <i>iso</i> -butane to unsaturated carboxylic acids and nitrites	Acrylic acid (28%) or acrylonitrile from propane, methacrylic acid or methacrylonitrile from <i>iso</i> -butane	225–450 °C, 1 atm	[9]
H ₆ P ₂ W ₁₈ O ₆₂ , H ₆ P ₂ W ₁₈ O ₆₂ /SiO ₂	Acylation and alquilation of <i>iso</i> -butylene with methanol	MTBE (~100%)	100 °C, 1 atm	[6c–e]
H ₆ P ₂ W ₁₈ O ₆₂	Methanol dehydration	Dimethyl ether (100%)	100–400 °C, 1 atm	[6e]

applying an external potential making them suitable for polarographic/voltametric measurements. Moreover, Wells–Dawson compounds are reduced upon exposure to visible and UV radiation.

Electrochemical studies demonstrated that Wells–Dawson anions are reduced through multi-steps of two-electrons (in neutral solutions) without degradation of the heteropoly structure. The process generates a mixture of reduced species known as heteropoly-blues due to its characteristic blue color. The process is influenced by the pH of the solution since the anion is protonated during reduction therefore; an acidic solution shifts the redox waves to more negative potentials and splits the two-electron polarographic waves to two one-electron waves (the splitting is not observed in $P_2Mo_{18}O_{62}^{6-}$) [35].

Studies of Pope demonstrated that α/β - $P_2W_{18}O_{62}^{6-}$, $As_2W_{18}O_{62}^{6-}$, $P_2Mo_{18}O_{62}^{6-}$ and $As_2Mo_{18}O_{62}^{6-}$ are able to receive up to six electrons per anion both in neutral or acidic media (pH < 3) [5]. In general, molybdenum based heteropoly-anions are more easily reduced (half-wave potentials = +0.4 to –0.2 volts at pH = 0–6) than tungsten-based ones (half-wave potentials = +0.1 to –1.0 volts at pH = 0–6). Reduced Wells–Dawson species such as, $P_2W_{18}O_{62}^{n-}$, $As_2W_{18}O_{62}^{n-}$ ($n = 7–9$) and $[H_2P_2Mo_2^{5+}Mo_{16}O_{62}]^{6-}$ are more stable in basic solutions than non-reduced species. In fact reduced species are stable up to pH = 13 and fully oxidized species decompose at pH = 6 as was discussed in Section 1.1.1 (see Table 1).

According to spectroscopic studies the reduction of the above-mentioned compounds begins in one of the twelve equatorial tungsten or molybdenum atoms [5]. In the particular case of mixed addenda atoms the electron is localized on the more electronegative metal in an equatorial site [35]. The α_1 - $[P_2W_{17}MO_62]^{n-}$ ($M = Mo^{6+}$, V^{5+} in equatorial position) is reduced at a more positive potential than the corresponding polar substituted isomer α_2 - $[P_2W_{17}MO_62]^{n-}$, and non-substituted anion phospho-molybdc anion $P_2Mo_{18}O_{62}^{6-}$.

McCormac et al. performed a comparative electrochemical study of transition metal substituted Wells–Dawson lacunary heteropoly-anion $K_xP_2W_{17}(M^{n+}.OH_2).yH_2O$ with $M^{n+} = Fe^{3+}$, Cu^{2+} , Co^{2+} , Ni^{2+} , Mn^{3+} and Mn^{2+} [36]. Similarly to non-substituted compounds, all the mixed addenda complexes pos-

sess three, two-electron reduction waves of the oxo-tungsten sites and are protonated during the process. Cyclic voltametric measurements showed that transition metal cations are suitable to be reduced and re-oxidized within the heteropoly-structure and that Mn^{3+} and Mn^{2+} can be oxidized to Mn^{4+} , without degradation of the structure. This property of the transition-metal substituted heteropolyoxo-metallates is attractive due to the possibility of replacing porphyrins as catalysts in electrochemical reactions. In fact, the electrochemical properties of Wells–Dawson heteropoly-anions found important application as catalysts in the electroreduction of nitrite, hydrogen peroxide and the oxidation of the co-enzyme NADH [36–38]. Table 2 summarizes the reaction conditions and the literature references concerning those applications.

The dispersion of the heteropoly-anion on an electrode through adsorption or electrodeposition extended the electrochemical activity of Wells–Dawson compounds. Baoxing and Shaojun demonstrated that the phospho-molybdc anion $P_2Mo_{18}O_{62}^{6-}$ can receive ten electrons without decomposition when is adsorbed on a carbon fiber microelectrode [51]. Keita et al. discovered that the surface of an electrode is activated through the electrodeposition of Keggin and Dawson-type heteropolyoxo-anions [52]. The authors demonstrated that a thin film of $P_2Mo_{18}O_{62}^{6-}$, $P_2W_{18}O_{62}^{6-}$, α_2 - $P_2W_{17}MoO_62^{6-}$, $P_2W_{15}Mo_3O_62^{6-}$, $P_2W_{14}Mo_4O_62^{6-}$, $P_2W_{12}Mo_6O_62^{6-}$, $As_2Mo_{18}O_{62}^{6-}$ along with Keggin-type compounds are suitable to be electrodeposited on an electrode surface at mild pH and potential conditions.

1.2.1.2. Photochemical activity. The photosensitivity upon exposure to visible light and UV radiation in organic liquid media is another important property of Wells–Dawson compounds [35]. Under these conditions, the heteropoly-anion is reduced to heteropoly-blue species and the organic molecules are oxidized. Papaconstantinou showed that $P_2Mo_{18}O_{62}^{6-}$ selectively oxidizes primary alcohols to aldehydes and secondary alcohols to ketones when exposed to a 254 nm radiation. Similarly to the electrochemical experiments, the photoreduction generates 2, 4 and 6 electron-blues and the HPC is suitable to be re-oxidized with molecular oxygen [34]. Additionally, Hill et al. demonstrated that tungsten-based

anion $\text{P}_2\text{W}_{18}\text{O}_{62}^{6-}$ is catalytically active in the photochemical degradation of thioethers in anaerobic and aerobic conditions, photo-dehydrogenation of alkanes and the selective oxidation of C–H centers remote from carbonyl groups of complex ketones (Table 2).

The re-oxidation of the HPCs is carried out in the presence of molecular oxygen as was discussed above. However, in anaerobic conditions the re-oxidation of HPCs lead to the reduction of protons to molecular hydrogen [35]. The evolution of hydrogen through the dehydrogenation of 2-propanol (with and without a platinum catalyst) was observed in the presence of $\text{P}_2\text{W}_{18}\text{O}_{62}^{6-}$.

The photochemical activity of Wells–Dawson compounds is also applied in photogalvanic cells [35]. These devices involve two cells containing the HPC, typically $\text{P}_2\text{W}_{18}\text{O}_{62}^{6-}$ and $\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$ anions, and an organic reagent. The photolysis of the electrolyte and the photoreduction of the HPCs are produced through the irradiation of one half-cell. Therefore, the potential difference between the photoreduced and oxidized species of the irradiated and non-irradiated half-cells respectively, produces an electric current (typically 150 μA).

1.2.1.3. Other applications of Wells–Dawson compounds in catalyzed redox reactions in liquid media.

The redox properties of Wells–Dawson compounds found application in homogeneous/heterogeneous non-electro/photochemical reactions, such as oxidation with molecular oxygen, hydrogen peroxide and iodosylarenes; epoxidation and hydrogenation (see Table 2).

Transition metal substituted polyoxo-tungstate complexes $[\text{P}_2\text{W}_{17}(\text{M}^{n+}\cdot\text{Br})]^{11-n}$ with $\text{M}^{n+} = \text{Mn}^{3+}$, Fe^{3+} and Co^{2+} catalyze the epoxidation of cyclic olefins, oxidation of aliphatic and cyclic alkanes to alcohols and ketones and the hydroxylation of naphthalene in the presence of iodosylbenzene [42]. According to studies of Finke et al., the mixed addenda anion containing manganese(III) possesses similar catalytic properties and stability as metalloporphyrin catalysts that are regularly applied to transfer oxygen from iodosylarenes to organic molecules in liquid media processes.

More recently, Khenkin and coworkers demonstrated that the mixed addenda vanadium-substituted polyfluorooxo-anion $[\text{H}_2\text{F}_6\text{NaVW}_{17}\text{O}_{56}]^{8-}$ is active

in the catalytic oxidation of alkyl aromatic compounds in biphasic media (water-catalyst and substrate) with molecular oxygen at high pressure [23b,44].

Molybdenum based heteropoly-anions and vanadium/molybdenum mixed addenda phospho-tungstic compounds, such as $\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$, $\text{S}_2\text{Mo}_{18}\text{O}_{62}^{4-}$, $[\alpha_2\text{-1,2-P}_2\text{W}_{16}\text{V}_2\text{O}_{62}]^{8-}$ and $[\alpha_2\text{-P}_2\text{W}_{15}\text{VMo}_2\text{O}_{62}]^{7-}$ catalyze the oxidation of organic molecules with hydrogen peroxide [12i,45,46]. In situ spectroscopic studies performed by Burns and coworkers during the oxidation of *iso*-butyraldehyde with H_2O_2 indicated that the heteropolyoxo-molybdate anions $\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$ and $\text{S}_2\text{Mo}_{18}\text{O}_{62}^{4-}$ undergo a minor degradation to peroxy-species. Nevertheless, those catalysts activate the reactant through an *iso*-butyraldehyde–heteropolyoxo-metallate complex before the oxygenation.

In the particular case of vanadium and molybdenum mixed addenda compounds the reaction proceeds on the vanadium species within the framework ($\alpha_2\text{-K}_7\text{P}_2\text{W}_{15}\text{VMo}_2\text{O}_{62}$) or on the vanadium species generated from the heteropoly-compound $[\alpha_2\text{-1,2-K}_8\text{P}_2\text{W}_{16}\text{V}_2\text{O}_{62}]^{8-}$ [45]. In fact, Nomiya et al. observed that benzene hydroxylation in the presence of $[\alpha_2\text{-P}_2\text{W}_{15}\text{VMo}_2\text{O}_{62}]^{7-}$ can be run for many days without the leaching of the active vanadium species. The oxidation of substituted benzene (toluene and nitrobenzene) catalyzed with the same anion yields ring-oxidation rather than side-chain oxidation products [46].

1.2.2. Applications of Wells–Dawson compounds in heterogeneous gas-phase redox reactions

Wells–Dawson heteropoly salts have been applied in heterogeneous gas-phase redox reactions such as, oxidative dehydrogenation and selective oxidation (Table 3). Finke and coworkers studied the activity of the phospho-tungstic potassium salt $\text{K}_6\text{P}_2\text{W}_{18}\text{O}_{62}\cdot 10\text{H}_2\text{O}$ and mono-substituted with metals (Fe, Cu, Co, Mn) in the oxidative dehydrogenation of *iso*-butane to *iso*-butylene [10a,53]. The authors demonstrated for the first time in the literature that the Dawson salt $\text{K}_6\text{P}_2\text{W}_{18}\text{O}_{62}\cdot 10\text{H}_2\text{O}$ decomposes to the Keggin-type salt $\text{K}_3\text{PW}_{12}\text{O}_{40}$ and an amorphous compound upon calcination above 577 °C. The mixture was more active and selective than the Dawson and pure Keggin salts towards oxidative dehydrogenation of *iso*-butane. The substitution of one tungsten atom

by a metal does not influence the catalytic activity of the phospho-tungstic Wells–Dawson salt.

Baronetti and coworkers gave more evidences on the thermal decomposition of Dawson-type structures [20b]. The authors reported that the monosubstituted vanadium compound α_1 -1-K₇P₂VW₁₇O₆₁·18H₂O also re-crystallizes in a potassium/tungsten Keggin salt and the vanadium is expelled out of the tungsten framework covering the surface of the new phases.

Both vanadium mono-substituted and non-substituted potassium salts catalyze the selective oxidation of methanol to formaldehyde however, the activity is low due to the almost null specific surface area of those materials (<1 m²/g).

Recent studies of the authors demonstrated that the dispersion of the phospho-tungstic anion P₂W₁₈O₆₂⁶⁻ on TiO₂ enhances the specific surface area (~50 m²/g) but diminishes the thermal stability [11]. In situ stability studies through in situ Raman spectroscopy demonstrated that bulk (NH₄)₆P₂W₁₈O₆₂ does not decomposes upon calcination at 500 °C however, the TiO₂ supported heteropoly-compound decomposes to WO₃ at 400 °C regardless of the loading.

Molybdenum based Wells–Dawson compounds such as, X₆P₂Mo₁₈O₆₂ with X = NH₄⁺, K⁺, Rb⁺, Cs⁺ and (CH₃)₄N⁺ catalyze the gas-phase oxidative dehydrogenation of *iso*-butyraldehyde to methacrolein and acetone [12f]. Similarly to the tungsten-based structures, those catalysts decompose to the phospho-molybdic Keggin anion PMo₁₂O₄₀³⁻ upon calcination at 260 °C and possess low activity (≤30% conversion).

The only application of supported molybdenum based Wells–Dawson compounds on an oxidation process was patented by Lyons and coworkers [9]. The inventors demonstrated that the acid H₆P₂Mo₁₈O₆₂, mixed addenda (molybdenum and tungsten) atoms and counteranions (protons and vanadyl) compounds supported on wide pore cesium polyoxo-metallate salt catalyze the heterogeneous gas-phase oxidation of alkanes to unsaturate carboxylic acids or nitrites. Specifically, the inventors presented the one-step oxidation of propane to acrylic acid (or acrylonitrile) and *iso*-butane to methacrylic acid (or methacrylonitrile). The experiments demonstrated that partially protonated Wells–Dawson compounds are more active than Keggin-type compounds on that processes.

1.3. Acid properties and applications of Wells–Dawson HPC

1.3.1. Applications of Wells–Dawson compounds in catalyzed acid reactions in liquid media

The application of Wells–Dawson compounds as solid acid catalysts replacing the conventional inorganic liquid acids (HF, HCl, H₂SO₄, etc.) is the leading edge in organic synthesis. The use of solid (bulk or supported on an oxide) HPAs in heterogeneous reaction conditions allows recovering and re-using the catalyst diminishing undesirable liquid wastes.

Thomas and coworkers demonstrated that bulk and silica-supported phospho-tungstic acid H₆P₂W₁₈O₆₂ is more active and selective than sulfuric and hydrochloric acids in the deprotection of methoxymethyl ethers of phenols [31,48]. The removal of protecting groups proceeds at room temperature yielding up to 100% acetals depending on the organic solvent.

An early application of the same acid was reported by Maksimov and Kozhevnikov on the acylation/alkylation of *iso*-butylene with methanol to produce methyl-*tert*-butyl ether [30]. The phospho-tungstic and molybdic Wells–Dawson acids showed the highest activity among a variety of Keggin-type and Dexter–Silverton-type acids, HZSM-5, sulphuric acid and an industrial catalyst.

Misono and coworkers demonstrated for the first time in the literature that the alkylation of cyclohexanone with alcohols (Michael addition) proceeds in the pseudoliquid-phase of the Wells–Dawson H₆P₂W₁₈O₆₂ and Keggin-type acids [49]. The authors observed that the reactants absorb into the catalysts' bulk turning the solid to a viscous liquid lump. In fact, the reaction rate was influenced by the quantity of reactants absorbed in the catalysts.

More recently, Baronetti and coworkers studied the alkylation of *iso*-butane with C₄ olefins catalyzed with bulk Wells–Dawson acid H₆P₂W₁₈O₆₂ and supported on silica at different loadings (9, 20 and 28 wt.%). The supported heteropolyoxo-anion presents high activity for *iso*-butane alkylation but lower selectivity towards trimethylpentanes production than a lanthanum-exchanged Y-zeolite catalyst [7]. The inactivity of the bulk acid indicates that *iso*-butane alkylation is a surface-type reaction that depends on

the number of surface acid sites to proceed. The authors observed the deactivation of supported catalysts due to the coverage of the surface active sites with coke. However, the catalysts are suitable to be regenerated with ozone at 125 °C without degradation of the structure.

Wells–Dawson phospho-tungstic acid $H_6P_2W_{18}O_{62}$ is also active in *iso*-butyl propionate decomposition, ester exchange with acetic acid and *n*-propyl alcohol and esterification of propionic acid with *iso*-butyl alcohol in homogeneous liquid-phase conditions. Misono and coworkers demonstrated that Keggin and Wells–Dawson HPAs possess similar activity than H_2SO_4 and *p*-toluenesulfonic acids in ester exchange with *n*-propyl alcohol and the esterification reactions. Additionally, the HPAs are 60–100 times more active in ester decomposition and exchange with acetic acid than liquid acids [50].

1.3.2. Application of Wells–Dawson compounds in heterogeneous gas-phase acid catalyzed reactions

Wells–Dawson phospho-tungstic acid $H_6P_2W_{18}O_{62}$ catalyzes the liquid-phase acylation and alkylation of *iso*-butylene as was discussed above. Additionally, Misono and coworkers and Thomas and coworkers demonstrated that the acid (bulk and silica-supported) is also active in heterogeneous gas-phase conditions ([6c,d]; Table 3). Again, Misono and coworkers demonstrated that the alkylation/acylation of *iso*-butylene with methanol produces MTBE through a pseudoliquid-phase mechanism. The rate of reaction is influenced by methanol pressure due to the absorption of methanol in the bulk of the acid. The ability of the Wells–Dawson acid to absorb a larger amount of methanol than Keggin-type acids explained the higher activity of that HPAs, even though the Wells–Dawson acid possesses a lower acid strength than Keggin-type acids.

More recently, Thomas and coworkers gave more evidences in the influence of the pseudoliquid behavior and the degree of hydration in the catalytic activity of the acid in MTBE production and methanol dehydration [6e,f]. The authors demonstrated that the anhydrous acid deactivates due to the decrease of the distance between the $P_2W_{18}O_{62}^{6-}$ primary units diminishing the ability of absorb methanol into the bulk (see Section 1.1.1).

1.4. Conclusions and future investigations

The application of Wells–Dawson heteropoly-compounds as catalytic materials is growing continuously in the catalytic field. These compounds possess unique properties such as: well-defined structure, Brønsted acidity, possibility to modify their acid-base and redox properties by changing their chemical composition (substituted HPCs), ability to accept and release electrons, high proton mobility, “pseudoliquid behavior”, etc. The wide variety of properties of Wells–Dawson compounds make them multipurpose catalysts since they can be applied as redox or acid catalytic materials in homogeneous (electrochemical and photochemical reactions) and heterogeneous liquid processes under mild conditions. The substitution of harmful liquid acids by solid reusable HPAs as catalysts in organic synthesis is the most promising application of Wells–Dawson HPCs.

The application of those compounds in heterogeneous gas–solid reactions is less developed due to the low surface area and/or thermal stability in the solid state. In fact, many studies on the stability of Wells–Dawson HPCs have been performed in the liquid media but few address the stability of the structure upon calcination (see the lack of information about “thermal stability” in Table 1). Future investigations should be focus in fundamental studies concerning the influence of counter-cations and oxide supports in the specific surface area and thermal stability of Wells–Dawson compounds in order to extend the application of those HPCs in heterogeneous gas-phase processes. Moreover, the development of useful catalysts requires more fundamental knowledge on the mechanisms and surface sites involved in the adsorption-reaction of molecules with the heteropolyoxo-anion structure.

Other future trend in the application of Wells–Dawson anions is in the field of molecule-based materials. The heteropolyoxo-anions possess the ability of forming hybrid compounds composed by the inorganic heteropolyoxo-anion and a variety of organic radicals (counter-cations). These materials possess unique conducting properties (metallic behavior and electron delocalization) with promising applications.

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