

Review Article

Hybrid Organic-Inorganic Materials Based on Polyoxometalates and Ionic Liquids and Their Application in Catalysis

Svetlana Ivanova

Departamento de Química Inorgánica e Instituto de Ciencia de Materiales de Sevilla, Centro Mixto Universidad de Sevilla-CSIC, Avenida Américo Vespucio 49, 41092 Sevilla, Spain

Correspondence should be addressed to Svetlana Ivanova; svetlana@icmse.csic.es

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An overview of the recent advances in the field of polyoxometalate, ionic liquid hybrids, is proposed with a special attention paid to their application in catalysis, more precisely biphasic and heterogeneous catalysis. Both components of the hybrids are separately outlined pointing to their useful properties and potential for catalysis, followed by the description of the hybrids preparation and synergy between components in a large range of organic transformations. And finally a vision on the future developments is proposed.

1. Polyoxometalates: General Aspects

Polyoxometalates (POMs) are a class of anionic metal-oxygen clusters built by the connection of $[\text{MO}]_x$ polyhedra of the early transition metals in their highest oxidation states [1, 2]. Nevertheless, the strict rules for nomenclature, the polyoxometalate compounds [3], could be referred to also as hetero- or isopolyacids and hetero- or isopolyanions or polyoxoanions. The most studied polyoxo structures formers are molybdenum (VI) and tungsten (VI), structures resulting from accessibility of empty d-orbitals for metal-oxygen π -bonding and favorable combination of ionic radius and charge. Polyoxo structures of the hexavalent Tc, Re, Ru, and Os, the pentavalent Cr, Mo, W, Tc, and Re, and tetravalent Ti, V, Cr, Mo, and W are also known [4]. The formation of the polyoxometalate structures obeys generally on two principles: (i) each atom must occupy only one edge shared $[\text{MO}]_x$ polyhedron in which the metal is displaced toward the edge, as a result of the M–O π -bonding and (ii) the structures with three and more terminal oxo groups are not observed (known as Lipscomb restriction) [4, 5]. Although the first polyoxometalates were reported over almost 200 years ago, continuously new structures are reported together with unusual properties and/or applications. Various reviews resume the main application domains of the polyoxometalates, for example, material science, medicine, or catalysis

[6–9]. There are literally thousands of compounds in the polyoxometalate category which differs on their size, shape, and composition. Recently, Long et al. [10] proposed a very elegant way to classify the POM's compounds in-as-called “*polyoxometalate periodic table*.” They proposed three broad groups taking into account essentially the anionic metal-oxygen cluster type.

- (i) Heteropolyanions: clusters including heteroatoms, such as $[\text{XM}_{12}\text{O}_{40}]^{n-}$ anion, where M is generally Mo or W and X is a tetrahedral template. Inside this group, three main families could be attributed, Anderson $[\text{XM}_6\text{O}_{24}]^{n-}$, Keggin $[\text{XM}_{12}\text{O}_{40}]^{n-}$, and Dawson structure $[\text{X}_2\text{M}_{18}\text{O}_{62}]^{n-}$, with the main difference being the way of coordination of the heteroatom (octahedral for Anderson family and tetrahedral for the other two) [10]. Representative schemes of those three structural families of POMs are presented in Figure 1.
- (ii) Isopolyanions: clusters without heteroatoms in their molecular structure.
- (iii) Molybdenum blue and molybdenum brown reduced POMs: a class of highly reduced POM clusters with potential photochromic and electrochromic applications. Despite the fact that these particular POMs

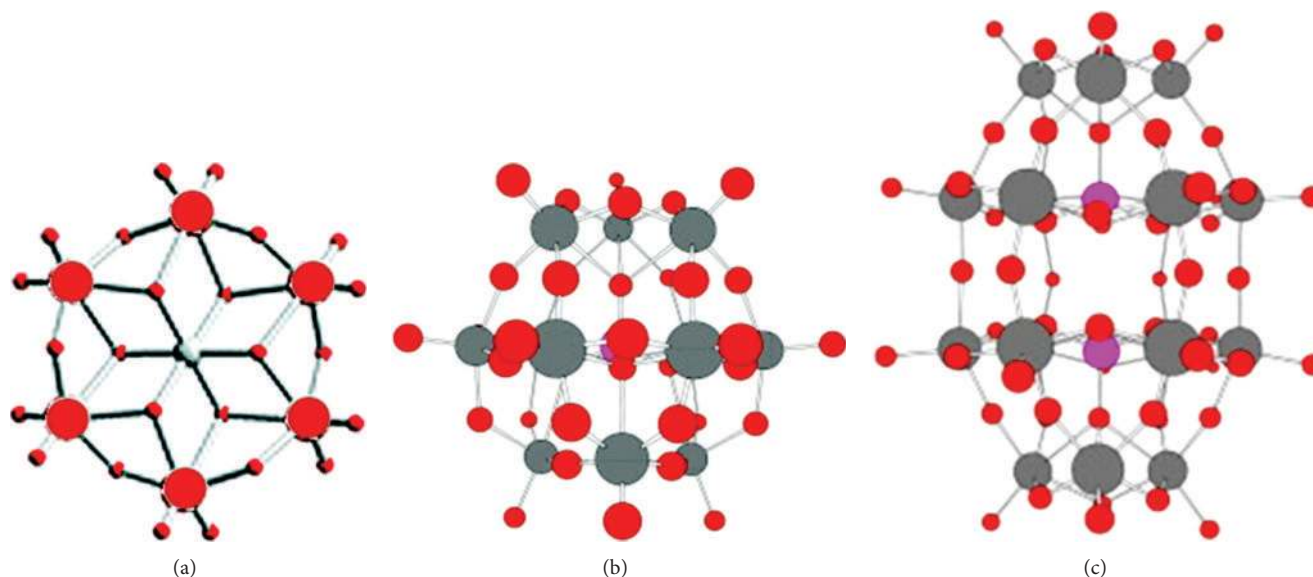


FIGURE 1: The three main families of polyoxometalates: (a) Anderson ($\text{XM}_6\text{O}_{24}^{n-}$), (b) Keggin ($\text{XM}_{12}\text{O}_{40}^{n-}$), and (c) Dawson structure ($\text{X}_2\text{M}_{18}\text{O}_{62}^{n-}$).

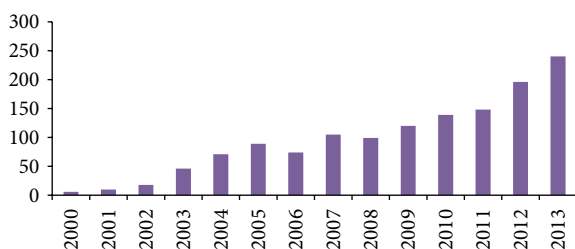


FIGURE 2: Number of published articles containing both polyoxometalates and hybrids according to Science Direct survey in September, 2013.

properties will not be a subject of this paper, this is the place to highlight the attractive and promising character of these materials for that kind of applications. At the first place, the photo- or electrochromic properties of the POMs depend on their composition, for example, on the components of the material and on the synergy between them. Since the charge transfer plays a key role in both phenomena, it is very important to increase the charge (electrons, holes, and protons) interactions between the components either by introduction of heteroatoms or by the cross-breeding of the organic and inorganic ions in hybrid materials. The progress in this field was summarized in various works [11–17].

Going back to the classification stated above, it should be pointed that it is based only on the polyoxoanion, which is generally compensated by the presence of different type of cations, inorganic (H^+ , Na^+ , Cs^+ , etc.) or organic. The organic cations compensation mechanism results in a new class of hybrid organic/inorganic molecular structures. This ability to combine inorganic and organic components at

molecular level provides one of the newest directions in the material science pointing the possibility of developing multifunctional materials on the base of properties tuning. The hybrid materials are constructed then in order to take advantage of both inorganic (strength, thermal stability, and chemical resistance) and organic parts (lightness, flexibility, and versatility), but with properties independent of the chemical nature of each component but dependent on the synergism between them [17].

The POMs hybrids field experiences a continuous development in the last years. A simple search in the Science Direct database using keywords as “polyoxometalates” and “hybrids” shows an almost exponential increase in the last ten years (Figure 2).

The hybrid organic polyoxometalates can be separated in two types [1, 18]: type I hybrids referring to compounds in which a weak nonbonding interaction between both (inorganic and organic) parts exists (e.g., electrostatic, hydrogen bonds, and van der Waals interactions) and type II where a stronger bonding interaction takes place (covalent or ionocovalent). The type II hybrids group includes all the organic ligands allowing a direct substitution of oxo group of the POMs, such as alkoxides, carboxylates, organosilyl derivatives, and organoamides. Extensive reviews on the advances in the field of type II POMs were reported by Dolbecq et al. [1] and Gouzerh and Proust [2] and will not be a subject of this paper. On the contrary, this review will focus on POM derivatives involving nonbonding interactions such as molecular complexes between polyoxometalates and organic substrates and more precisely ionic liquids derived cations forming ionic salts and their application in the field of biphasic and heterogeneous catalysis.

It is well known that the proton compensated (H^+ , H_3O^+ , H_5O_2^+ , etc.) polyoxometalate anions have several advantages as heterogeneous catalysts, such as very strong Brønsted

acidity, approaching the superacid region, and fast reversible multielectron redox transformations converting them to efficient oxidants. These acid-base and redox properties can be varied by changing the chemical composition [9]. The acidity of the POMs materials originates from the fact that the negative charge of the anion is shared over numerous external oxygen atoms (36 in Keggin and 56 in Wells-Dawson structure), thus producing weaker attraction for protons than, for example, in the case of sulphuric acid. It has been demonstrated that MO_6 octahedra with one terminal oxygen are strongly distorted and its partial negative charge residing on the outermost M–O double bond is generally lower than those on the bridging oxide anions embedded within the clusters. The counterion (cation) is then shifted towards the exterior of the anion, which results in the formation of a strongly polarized (due to $d\pi$ - $p\pi$ interactions) layer of oxygen atoms, inside the polyanion. Such polarized oxygen atoms are weakly basic and weakly attract protons [19]. In addition, the acidity of the POMs is strongly affected by their structural composition and geometry in a way that closer the geometry to the spherical one, stronger the intrinsic acid character [20].

Although the $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ in the solid state are reported to be stronger Brønsted type acids than the conventional HX, HY, and H-ZSM₅ zeolites, the question with the acidity of the salts seems to be more complex. For the metal salts, five mechanisms are proposed for the generation of acidity based on (i) the dissociation of occluded water molecules, (ii) on the Lewis acidity of the proper metal ions, (iii) on the protons formed by the reduction of the metal ions, (iv) on the existing protons in the partially acidic sites, or (v) on the partial hydrolysis during the preparation process [8]. While the mechanism of acidity formation in these cases is well elucidated, the acidity of the hybrid materials is still under investigation but should depend on the acidity of the POM building block and on the acidity of the organic constituent, and not, at the last place, on those produced by the interaction between them.

The POMs materials are also known to possess very flexible redox behaviors which could be finely tuned on purpose, by changing smoothly their composition as, for example adding a heteroatom or by varying their structure [21]. As a matter of fact, one of the most important electronic properties of POMs is that of acting as electron reservoirs. The POMs oxidized forms may only accept electrons; on the contrary, their reduced forms may behave as donors or acceptors of several electrons while maintaining their structure [22]. In fact, the POMs owing to their electron and proton transfer and/or storage abilities could be reversibly reduced by addition of various specific numbers of electrons (heteroatoms), which yield in deeply colored mixed valence species (“heteropoly blues”) [23].

All the applications of the POMs (hybrids or not), since their discovery, are mainly based on their peculiarities, such as size, mass, electron and proton transfer/storage abilities, lability of the “lattice oxygen,” and high acidity [4]. However, the unabated interest to this kind of materials in almost two centuries is based on their versatility, centered basically on the possibility of the fine tuning of their properties, and

on the high degree of liberty in the moment to choose the structure pointing directly to the desired application. Still *incognitas* exist in the elucidation of the hybrids structure and properties. Literally, every day a new combination of polyoxometalate anion and organic cation could be originated for which an application should be founded, thus opening a large spectrum of possibilities and research challenges. In this context this paper pretends to give an insight in a small but rapidly developing recent area dedicated to the production, structure elucidation, properties and application of a hybrids based on polyoxometalates and ionic liquids. After a small introduction of the ionic liquids a detailed description of the current state of art on the preparation and application in catalysis, more precisely in biphasic and heterogeneous catalysis, will be given.

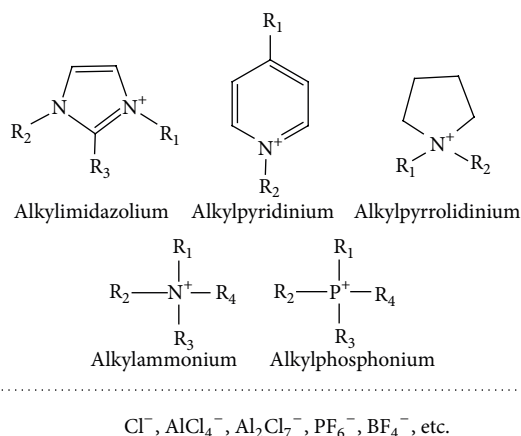
2. Ionic Liquids: General Aspects

Ionic liquids (ILs) are generally defined as compounds with melting points below 100°C consisting entirely of ions, most typically organic cation (quaternary ammonium salts or based on cyclic amines) and an inorganic anion. Although developed as the organic solvents alternative, the ionic liquids differ from the latter by their ionic character and their structure and organization. Coulombic interactions are the dominant interactions between the ions; however, intermolecular interactions like H bonding, π - π stacking, van der Waals interaction, and so forth help the supramolecular organization of the ILs [24, 25]. The Coulomb interactions are responsible for the ion pairs formation and for the higher order ion clusters, but the presence of a cooperative network of hydrogen bonds between them induces the structural directionality [26, 27]. This directionality presents one of the most interesting features of the ionic liquids, especially useful in the materials synthesis [28–31].

Some of the commonly used families of cations and anions forming the ILs are presented in Scheme 1.

Analogically to the polyoxometalates, some specific ILs physicochemical properties could be easily tuned by variations of cation and anion, which requires good knowledge of the field as more than 10^6 possible combinations are already known [32] and it is estimated that 10^{18} different ILs are theoretically possible [33]. The melting point, viscosity, density, solubility, polarity, and acidity/coordination properties are some examples of the properties subjected to modification [34]. These properties are also greatly influenced by the molecular asymmetry built into at least one of the ions for example, the higher the asymmetry of the cation the lower the melting point [35]. However, in some cases the tunability of the properties could also be a disadvantage; for example, the change in the structure might result in more than one altered property. The ILs are sometimes referred to as “designer”-solvents [31, 36] and some of their principle advantages can be summarized as follows:

- (i) ILs have an extremely low vapor pressure; they are practically not volatile;
- (ii) ILs can dissolve a large range of various organic and inorganic and polar and nonpolar species;



SCHEME 1: Most commonly used cations and anions forming the ILs.

- (iii) ILs can form biphasic systems with classical solvents; their low interface tension permits them to adapt to the second solvent and facilitates the separation of the products;
- (iv) ILs present a wide temperature window of the liquid state (from 80 to 350°C);
- (v) ILs can have acidic and superacidic properties;
- (vi) ILs often have large electrochemical windows; they can be used as solvents and electrolytes.

However, the role of the ILs in the chemical reactions is far away of being simple; it can act either as a solvent, as a catalyst or presenting a dual character—solvent and catalyst or cocatalyst, solvent and support, or solvent and ligand [37].

Although the first catalytic process with an IL as a catalyst was carried out in the mid-90s (Friedel-Crafts acylation of benzene in [ethyl methyl imidazolium][Cl]–AlCl₃ ionic liquid) [38] the real “boom” of the use of ILs in catalysis starts with the beginning of the 21 century (Figure 3).

Numerous reviews dedicated to the use of ILs in either homogeneous, organometallic or heterogeneous catalysis [33, 37, 39–41] are published. ILs resulted to be very useful in the field of homogeneous catalysis. They could be used as solvents in the “biphasic catalysis” in which the products and the catalyst separate one from another by its different miscibility in ILs and the reuse of the catalyst is possible. Another emerging field in the ionic liquid catalysis is the immobilization concept, claiming as principal advantages the minimizations of the required amount of often expensive ILs, the diminution of the transport and mass transfer limitations between the existing phases, and of course approaching the IL materials to the heterogeneous catalysts and their advantages—fast separation and long-term use. Two types of materials are possible, materials consisting of IL catalyst supported on inert solid or thin homogeneous IL layer covering the catalytic material.

To some extent the ILs could be considered as the “POMs” of the organic chemistry. Although they could not be considered fully organic their versatility and possibility for properties design allow the metaphor relating their exceptional structural and morphological flexibility to those of

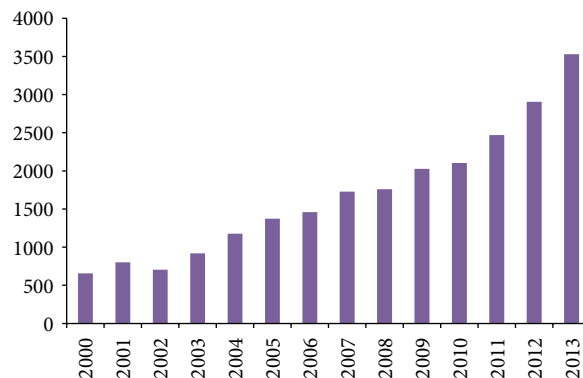


FIGURE 3: The number of published articles containing both “ionic liquid” and “catalysis” according to Science Direct survey on September, 2013.

the polyoxometalates. Both types of materials separately presents a great potential for use in the heterogeneous catalysis and so one could expect that their union will potentiate or combine in a beneficial manner their peculiarities in a new and interesting class of materials.

3. Ionic Liquid: Polyoxometalates Hybrids

In various studies, Ranga Rao and coworkers [42–44] used 1-butyl 3 methyl imidazolium (Bmim) bromide ionic liquid and several heteropolyacids (silicotungstic, phosphomolybdic or phosphotungstic) to produce molecular salts with the formula [Bmim]₃[XM₁₂O₄₀]. The single crystal structural analysis of the phosphomolybdic hybrid suggests a compound crystallizing orthorhombic structure in Pca2₁ space group with one formula unit in the asymmetric unit excluding water molecules, shown in Figure 4.

The method of preparation includes a simple precipitation of the salts from aqueous solution of the initial acid and ionic liquid components. The hybrids were characterized and the interaction between cation and anion confirmed by UV-vis DRS and solid state NMR. When the hybrid is formed normally a blue shift of the electronic transitions and splits of the C–H stretching modes of the imidazolium ring are observed. Ionothermal method of preparation was proposed by Chen et al. [45] for the synthesis of transition metal containing polyoxotungstate ionic liquid hybrids. The three synthesized hybrids; [Dmim]₂Na₃[SiW₁₁O₃₉Fe(H₂O)]·H₂O (Dmim = 1,3-dimethylimidazole), [Eemim]₉Na₈[(SiW₉O₃₄{Fe₃(μ₂-OH)₂(μ₃-O)₃(WO)₄}]·0.5H₂O (Emim = 1-ethyl,3-methylimidazole) and [Dmim]₂[HMim]Na₆[(AsW₉O₃₃)₂{(Mn^{III}(H₂O))₃}·3H₂O (Dmim = 1,3-dimethylimidazole; Mim = 1-Methylimidazole). The first compound presents a monoclinic crystal structure attributed to the space group C2/c, in which each Dmim cation is connected with three polyoxoanions via hydrogen bonds (Figure 5(a)) resulting in the formation of 1D square channels [45].

It is impossible not to realize the analogy of this structure organization with the ionic liquid 3D arrangements proposed by Dupont [25]. As already explained above, some ionic

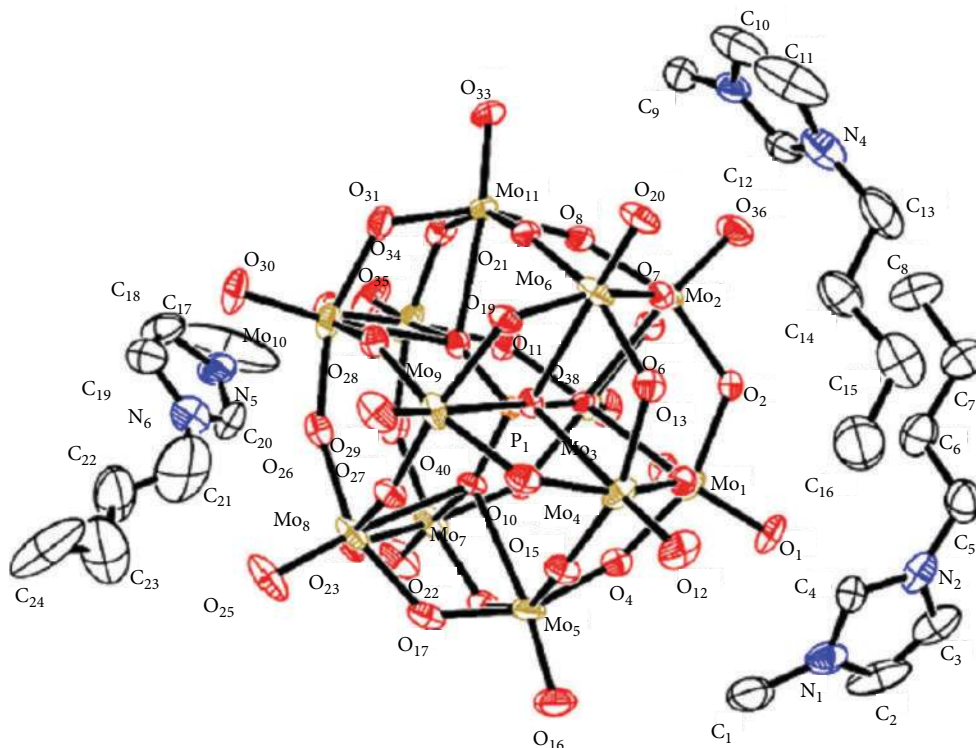


FIGURE 4: ORTEP representation of the $[Bmim]_3[XM_{12}O_{40}]$ molecular salt, reprinted from [42].

liquids in solid state form an extended cooperative network of cations and anions, connected through hydrogen bonds. For the alkyl imidazolium ILs the monomeric unit always consists of one imidazolium cation surrounded by at least three anions (same like in the hybrid), and in turn each anion is surrounded by at least three imidazolium cations. Two major 3D arrangements in the case of imidazolium ILs are then formed: (i) through chains of the imidazolium rings (π -stacking, Figure 5(b) right) with anions accommodated as chains and (ii) by columns consisting of alternating cations and anions (left). In both cases, “free” volumes with high degree of directionality, imitating tunnels, are formed. The analogy found between both materials suggests clearly that the structure organization of the hybrids is governed by that of the ionic liquid. The latter is known as ionic self-assembly (ISA) synthetic strategy and makes use of the electrostatic interactions between the components. It was proposed for the first time for the interactions between surfactants and charged polyelectrolytes. The structure organization results from the incompatibility of the surfactant alkyl tails and the ionic assembly. For these mismatched parts, a phase separation on molecular level could occur thus leading to the structuration of new materials—the ionic self-assemblies [46]. The properties of the resulted hybrids could be tuned then through the variation of the binding factors, namely, the concentration of ionic liquid, its nature ILs (size and hydrophobicity) the nature of the counterions, and so forth. Recently Hill [47] underlined the future necessities of the nanostructured functional POM-based materials for their application in catalysis. Good knowledge and, especially,

the control on several points are needed, such as (i) the role and the nature of the counterion (the surfactant or the IL), (ii) the presence of multiple reactive forms, rearrangement, and isomerization, and (iii) the insight of the electronic properties of the POMs. The principal reaction and hybrids applied in biphasic or heterogeneous catalysis are summarized in Table 1.

The catalytic properties of the hybrids are usually conditioned by its composition and method of preparation. The use of microemulsion was reported as a very useful method of preparation of the hybrids based on surfactants and POMs. The claiming advantage of this method is the production of a relatively monodispersed nanomaterial [48]. The ability to form the emulsion in the case of the hybrids could be used not only for their preparation but also as a good method of product separation in the biphasic catalytic systems. The microemulsion is achieved when a proper balance of attractive and repulsive interactions on the hydrophobic and hydrophilic side of the interface is attained. The water oil biphasic emulsion system with a surfactant type of catalyst designed and synthesized by using a suitable combination of hydrophilic POMs and lipophilic quaternary ammonium cations are reported by Li et al. [49–51] for the oxidative desulfurization of diesel using H_2O_2 as oxidant. All the studied catalysts were based on phosphotungstic POM and a surfactant molecule, such as $[(C_{18}H_{37})_2N^+(CH_3)_2]_3[PW_{12}O_{40}]$, and $[(C_{18}H_{37})N(CH_3)_3]_4[H_2NaPW_{10}O_{40}]$ allowing the autoassembly of the catalysts directly in the emulsion droplets. It was found that the oxidation activity of

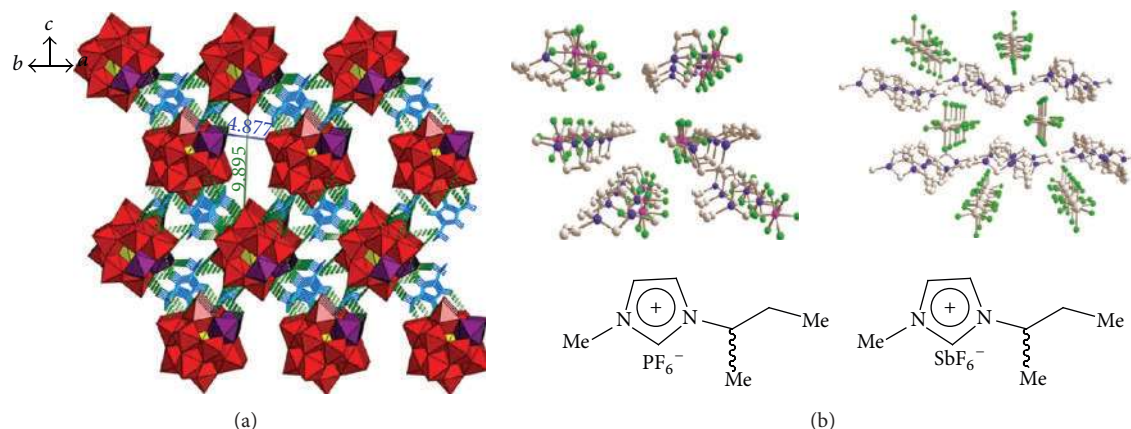


FIGURE 5: (a) The 3D packing structure of $[\text{Dmim}]_2\text{Na}_3[\text{SiW}_{11}\text{O}_{39}\text{Fe}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ viewed along the $[1, 1, 0]$ reprinted from [45]. (b) Illustration of the two major 3-D arrangements of imidazolium ILs, reprinted from [25].

the catalysts depends on the proper quaternary ammonium cation and its ability to form metastable emulsions in diesel with the H_2O_2 . The higher the ability to form a metastable emulsion, higher the oxidation activity and the better the separation after reaction either by demulsification or by decantation. Zhu et al. [52, 53] also report the preparation and application of various metal-based surfactant type ionic liquids peroxomolybdates and peroxotungstates for the oxidative desulfurization of fuel in oil/water mixture. The role of the quaternary ammonium cation was suggested to be the transfer of the catalytically active compounds to the sulfur containing aromatics thus enhancing the oxidation rate. Successful reusability up to 10 cycles for the hybrids was observed. Although very good results were obtained in the catalytic oxidation by POMs of the sulfur containing compounds in diesel or fuel, the use of biphasic system implies a mass transfer across the interface of aqueous and oil phases, which could be improved by the use of the hybrids but the last separation step is still challenging in a large-scale application. The use of a solid hybrid could be then envisaged as the next logical step. Very recently Zhang et al. [54] proposed the use of the $[\text{Bmim}]_3[\text{PMo}_{12}\text{O}_{40}]$ for the oxidation of benzothiophenes (BT), dibenzothiophenes (DBT), and 4–6 dimethyldibenzothiophene (4,6-DMDBT). Together with the bare hybrid, its immobilized homologues (supported on SiO_2 , Al_2O_3 or TiO_2) were prepared for comparison purposes. The supported hybrids present higher oxidation activities than the bulk catalysts. Diminution of the rate of the undesired parallel reaction of thermal decomposition of H_2O_2 in presence of nitrogen containing compound (carbazole and quinolone) was also found. The activity decreases in the order $\text{DBT} > 4,6\text{-DMDBT} > \text{BT}$. The same trend was reported by Li et al. [55] for the same reaction using different POM-IL hybrid $[\text{Hmim}]_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]$ —catalytic system very effective under mild conditions and recyclable up to 6 times without significant decrease in activity. The Keggin based POM-IL hybrid materials $[\text{MIMPS}]_3\text{PW}_{12}\text{O}_{40}\cdot 2\text{H}_2\text{O}$ (1-(3-sulfonic group) propyl-3-methyl imidazolium phosphotungstate), $[\text{Bmim}]_3\text{PW}_{12}\text{O}_{40}$ (1-butyl 3-methyl imidazolium

phosphotungstate), $[\text{Bmim}]_3\text{PMo}_{12}\text{O}_{40}$ (1-butyl 3-methyl imidazolium phosphomolybdate) and $[\text{Bmim}]_4\text{SiW}_{12}\text{O}_{40}$ (1-butyl-3-methyl imidazolium silicotungstate) were applied by Zhu et al. [56] in the oxidative desulfurization of fuels using H_2O_2 as oxidant, and ionic liquid as solvent. The best found catalyst was $[\text{MIMPS}]_3\text{PW}_{12}\text{O}_{40}\cdot 2\text{H}_2\text{O}$ with 100% S-removal at 30°C within one hour. Moreover, the reaction system also exhibited high activity in real diesel oil, in which the S content was reduced from 1113 ppm to 198 ppm. In 2013, Chen et al. [57] using the activity of those kinds of hybrids in the desulfurization reaction developed a very elegant catalytic system—phosphotungstic acid containing ionic liquid immobilized on magnetic mesoporous silica. The magnetic component was added in order to supply an additional advantage of the system—facile separation of the catalyst by applying an external magnetic field. The oxidation of dibenzothiophene in mild conditions leads to almost 100% conversion to DBTO and DBTO_2 in very short time (2–8 h) and high degree of recyclability (up to 5). This study showed that with an appropriate knowledge of the system, especially its inconvenience, one could innovate betting on new systems with additionally improved properties.

The ionic liquids are often used for immobilization of POMs on silica surface, thus producing hybrids directly on the support surface. The active species may be linked by two main strategies on its support, either by ionic interactions (ionic bonds, van der Waals) or by covalent bonds. The choice of the support depends generally on the desired reaction and could be organic as resin or inorganic as silica. Yamaguchi et al. [58] reported a few years ago the immobilization of the peroxotungstate catalyst on dihydroimidazolium-based ionic liquid modified SiO_2 . The immobilized catalyst presents the same activity in the liquid phase epoxidation of various olefins by H_2O_2 as its homogeneous analogue. This system diminishes also the problems with the tungsten leaching and allows the separation and reutilization. Tan et al. [59] used almost the same strategy to immobilize the $\text{H}_3\text{PW}_{12}\text{O}_{40}$ on 1-(3-aminopropyl)-3-propylimidazolium bromine modified SBA 15. They use the ability of the SBA-15 supported ionic liquid to carry out the anionic exchange in order to load the

TABLE I: Summary of the principal reaction and hybrids applied in biphasic and heterogeneous catalysis.

Reaction	Model compound	Hybrid	References
Oxidative desulfurization	Benzothiophene (BT), 5-methylbenzothiophenes (5-MBT) dibenzothiophenes (DBT) 4-6 dimethyldibenzothiophene (4,6-DMDBT) + H ₂ O ₂ and real diesel	Quaternary ammonium POMs complexes; [(C ₁₈ H ₃₇) ₂ N ⁺ (CH ₃) ₃][PW ₁₂ O ₄₀] and [(C ₁₈ H ₃₇)N(CH ₃) _{3,4}][H ₂ NaPW ₁₀ O ₄₀]	[49–51]
	DBT + H ₂ O ₂	Surfactant type POMs [(n-C ₈ H ₁₇) ₂ N(CH ₃) ₃][PO ₄ [XO(O) ₂] ₂] ₄ , [(n-C ₁₂ H ₂₅) ₃ NCH ₃] ₃ [PO ₄ [XO(O) ₂] ₂] ₄ , X = Mo and W	[52, 53]
	BT, DBT, 4,6-DMDBT + H ₂ O ₂	[Bmim] ₃ [PMo ₁₂ O ₄₀] (1-butyl 3-methyl imidazolium phosphomolybdate)	[54]
	BT, DBT and 4,6-DMDBT + H ₂ O ₂	[Hmim] ₅ [PMo ₁₀ V ₂ O ₄₀]	[55]
	Real diesel oil	[MIMPS] ₃ PW ₁₂ O ₄₀ ·2H ₂ O (1-(3-sulfonic group) propyl-3-methyl imidazolium phosphotungstate), [Bmim] ₃ PW ₁₂ O ₄₀ (1-butyl 3-methyl imidazolium phosphotungstate), [Bmim] ₃ PMo ₁₂ O ₄₀ [Bmim] ₄ SiW ₁₂ O ₄₀ . Phosphotungstic acid containing ionic liquid immobilized on magnetic mesoporous silica	[56]
DBTO + H ₂ O ₂		[57]	
Epoxidation	Olefins + H ₂ O ₂	Peroxotungstate dihydroimidazolium-based hybrid on modified SiO ₂	[58]
	Methyl-9,10, octadecenoate + H ₂ O ₂ + O ₂	Peroxotungstate immobilized on amphiphilic resin using the methylimidazole and imidazole based ionic liquids with different alkyl substitutes (from C ₆ to C ₁₂) as a linkers	[63]
	Cyclooctene + H ₂ O ₂	[[n-C ₁₆ H ₃₃ N(CH ₃) ₃] ₄ Na ₃ PW ₁₁ O ₃₉] Venturello's anion coupled with alkylimidazolium cations, heteropolytungstate-ionic liquid modified silica magnetite particles	[72] [77] [78]
Alcohols oxidation	Oleic acid + H ₂ O ₂	Q ₃ [PO ₄ [WO(O) ₂] ₂] ₄ {Q = quaternary ammonium}	[76]
	benzyl alcohol + H ₂ O ₂	H ₃ PW ₁₂ O ₄₀ on 1-(3-aminopropyl)-3-propylimidazolium bromine modified SBA 15	[59]
	Variety of benzylic alcohols + H ₂ O ₂	Phosphotungstic based ionic liquid complex immobilized on mesoporous silica	[61]
	Variety of benzylic and aliphatic secondary alcohols	1-methyl-3-butylimidazolium decatungstate [bmim][W ₁₀ O ₂₃]	[64]
	Benzene oxidation + O ₂ + ascorbic acid	[(C ₄ H ₉) ₄ N] _m [XW ₁₁ YO ₃₉ H ₅ O] where X = P ⁵⁺ , Si ⁴⁺ , Ge ⁴⁺ , B ³⁺ and Y = Ti ⁴⁺ , V ⁵⁺ , Cr ³⁺ , Mn ²⁺ , Fe ³⁺ , Co ²⁺ , Ni ²⁺ , Cu ²⁺ , Zn ²⁺	[65]
Hydroxylation	Methanol + O ₂	Bmim ₃ PMo ₁₂ O ₄₀ and Bmim ₃ PW ₁₂ O ₄₀	[91, 92]
Esterification	Benzene + H ₂ O ₂	Dicationic (dimethyl diimidazolium) PMo ₁₀ V ₂ O ₄₀ ⁵⁻	[66, 67]
	Palmitic acid to biodiesel	Keggin tungstophosphate complex SO ₃ H functionalized zwitterion	[68]
Transesterification	Variety of monocarboxylic acids with monohydric alcohols	Imidazolium based [MIMPS] ₃ PW ₁₂ O ₄₀ , pyridinium based-[PyPS] ₃ PW ₁₂ O ₄₀ and alkyl ammonium [TEAPS] ₃ PW ₁₂ O ₄₀	[69, 70]
	Trimethylolpropane + various fatty acid methyl esters	Imidazolium based [MIMPS] ₃ PW ₁₂ O ₄₀ , pyridinium based-[PyPS] ₃ PW ₁₂ O ₄₀ , and alkyl ammonium [TEAPS] ₃ PW ₁₂ O ₄₀	[71]

$\text{PW}_{12}\text{O}_{40}^{3-}$ anion on the surface, as well as partly protonated amino groups as accelerators to the catalytic process. The amino modified catalysts resulted to be much more active than the unpromoted ones with 92% of benzyl alcohol conversion with 91% selectivity to benzaldehyde in the selective oxidation of benzyl alcohol with H_2O_2 . The same approach was used by Cuan and Yan [60] to achieve the multicomponent assembly of novel kinds of photofunctional hybrids with polyoxometalates ($\text{Na}_9\text{EuW}_{10}\text{O}_{36}\cdot 32\text{H}_2\text{O}$) and benzoate (4-aminobenzoate, 4-hydroxybenzoate, 4-mercaptobenzoate) modified silica through imidazolium ionic liquid (1-methyl-3-trimethoxysilylpropyl) compound as double functional linkage. This study combines more than two functionalities to the search of luminescent mesoporous material. The new material presents especially strong characteristic Eu^{3+} luminescence with long decay time and large radiative transition areas to contribute high quantum efficiency.

Instead of employing the anion exchange to charge the POMs on the IL modified silica surface, Zhao et al. [61] newly proposed the preparation of the immobilized hybrid by one pot synthesis, encapsulating directly the hybrid during the SBA-15 formation. The resulting material showed a good catalytic efficiency as a function of alcohol type ranging from 30 to 98% of conversion with selectivity to aldehydes oscillating between 50 and 99%. The reusability up to 5 times with negligible loss of activity was also reported. It was found that the location of imidazolium cation in the mesoporous silica is one of the key factors impacting the catalytic performance. The catalyst with POM linked to bridging organic moieties located in the channel walls between Si centers presented superior TOF and selectivity to aldehydes compared to the catalyst with terminal organic moieties.

Another type of stabilization and immobilization of organic compounds through host-guest interactions was recently summarized in an extensive review [62]. Concerning the hybrids, Poli et al. [63] presented a very complete and interesting study on the peroxotungstate catalyst immobilization on amphiphilic resin by ion exchange using the methylimidazole and imidazole based ionic liquids with different alkyl substitutes (from C_6 to C_{12}) as linkers. They found that the imidazolium group resulted to be the most appropriate quaternary ammonium group for supporting the peroxophosphotungstate anion. In addition, if both N atoms in the imidazole are substituted the delocalization of the total charge which occurs in the ring increases the total positive charge and stabilizes in greater extent the POM anion. The catalytic activities of the hybrids in the epoxidation of methyl-9-10-octadecenoate with H_2O_2 under O_2 flow were found to vary with the hydrophilic/lipophilic balance (carbon chain number, spacers, and N-substitution of imidazolium ring). The hybrids resulted in 50% conversion of the fatty acid with 60% of selectivity to epoxide and a good stability and recyclability in 2 cycles.

Immobilized or bulk, the POM-IL hybrids are applied successfully in a number of organic transformations, especially when a good separation and reuse of the catalyst are needed. For example, Chhikara et al. [64] developed a simple and efficient protocol for the oxidation in mild

conditions of a variety of benzylic and aliphatic secondary alcohols by hydrogen peroxide catalyzed by 1-methyl-3-butylimidazolium decatungstate $[\text{bmim}][\text{W}_{10}\text{O}_{23}]$ in ionic liquid $[\text{bmim}][\text{BF}_4]$. An easy recovery of the catalytic system, excellent yield of the products (89 to 97% of the desired ketones or aldehydes), and recycling of the catalytic system without much decreasing the yield of the product were also reported. The benzene oxidation by molecular oxygen to phenol with ascorbic acid as a reducing agent was reported to be effectively catalyzed by the transition metal exchanged phosphotungstate stabilized with quaternary ammonium salt $[(\text{C}_4\text{H}_9)_4\text{N}]_m[\text{XW}_{11}\text{YO}_{39}\text{H}_2\text{O}]$ where $\text{X} = \text{P}^{5+}, \text{Si}^{4+}, \text{Ge}^{4+}, \text{B}^{3+}$ and $\text{Y} = \text{Ti}^{4+}, \text{V}^{5+}, \text{Cr}^{3+}, \text{Mn}^{2+}, \text{Fe}^{3+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}$ [65]. The activity of the POM was positively influenced by the presence of the transition metal, being its nature the most important factor. The presence of ascorbic acid was judged indispensable for the benzene oxidation by molecular oxygen, which partial pressure increase enhances the conversion but not the selectivity to phenol. The phenol could be obtained from benzene as well by the hydroxylation of the latter with H_2O_2 . Some recent studies of Leng et al. [66, 67] were devoted to this reaction in which they proposed the application of a dicationic (dimethyl diimidazolium) and a polymeric ionic liquid to the $\text{PMo}_{10}\text{V}_2\text{O}_{40}^{5-}$ anion in order to improve the resistance of the hybrid in excess of H_2O_2 . The satisfactory results in the case of the dicationic ionic liquid lead to the application of the polymeric one for which high efficient heterogeneous performance was observed (100% selectivity with 23% phenol yield) and attributed to the promotion of the redox properties of the POM by the intramolecular charge transfer from the π -electron enriched cross-linked polymeric IL framework.

Series of hybrids based on TPAs ionic liquid coupled with SO_3H functionalized zwitterion and Keggin tungstophosphate were applied in the esterification of palmitic acid to biodiesel and the optimum conditions were established. The use of optimum parameters gave a maximum of 91.8% yield of biodiesel and easy recycling of the catalyst after a simple treatment [68]. The performance of a series of polyoxometalate hybrids based on organic cations containing either imidazolium $[\text{MIMPS}]_3\text{PW}_{12}\text{O}_{40}$, pyridinium $[\text{PyPS}]_3\text{PW}_{12}\text{O}_{40}$, or alkyl ammonium $[\text{TEAPS}]_3\text{PW}_{12}\text{O}_{40}$ was used as "reaction-induced self-separation catalysts" for various esterification reactions [69, 70]. The good solubility in the polycarboxylic acid or polyol, immiscibility with ester product, and high melting points of the heteropolyanion-based IL catalysts result in the switching from homogeneous to heterogeneous conditions with good results and recovery and reuse of this kind of catalysts. The ether yield varies between 69 and 95% depending on the reactants, with around 7 cycles of reusability with negligible loss of activity. The same series of catalysts together with their phosphomolybdic analogues were applied in the transesterification of trimethylolpropane with various fatty acid methyl esters [71]. The $[\text{PyBS}]_3\text{PW}_{12}\text{O}_{40}$ catalyst showed several advantages over the traditional catalysts such as high catalytic activity, easy separation, and high yield of desired product. It was found that this catalyst acted as homogeneous catalyst at the reaction temperature and converts to a solid state upon

cooling which allows its full recovery and reuse up to 8 times without any significant change of the catalytic activity. The combination of a certain zwitterion and sodium phosphotungstate $[\text{n-C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3]_4\text{Na}_3\text{PW}_{11}\text{O}_{39}$ resulted in an excellent catalyst, for the epoxidation of cyclooctene with H_2O_2 , and high TON was reported even in solvent-less conditions at low temperatures 0°C . A strong cooperative role between zwitterion and sodium phosphotungstate salt was found and, in addition, the hybrid material showed high structural stability during the reaction. The simple method of preparation and the high catalytic activity were reported as principle advantages pointing practical applications [72].

The organics stabilized POMs (the as-called Venturolo anion $\{\text{PO}_4[(\text{WO}(\text{O}_2)_2)_4]^{3-}\}$) were extensively applied in the reaction of epoxidation of alkenes in the late 80s in biphasic system in the presence of quaternary ammonium cation ($\text{C}_6\text{--}\text{C}_{18}$) whose role was to transfer the products from one phase to another [73–75]. The same approach was later used by Kozhevnikov et al. [76] in the epoxidation of oleic acid by H_2O_2 in mild conditions. The employed peroxy phosphotungstate yielded 84% of epoxide at 95% of oleic acid conversion without using a chlorocarbon solvent. It was also suggested that in the reaction conditions various peroxophosphotungstate species coexist which could increase the rate of the reaction. Recently the Venturolo anion was coupled with alkylimidazolium cation to form self-separation catalyst in the epoxidation of olefins [77]. Various olefins were transformed efficiently to epoxides with conversion varying between 86 and 98% in ethyl acetate media with high selectivity neighboring 99% and up to 5 cycles viability. Going to a new level, Bagheri et al. [78] immobilized heteropolytungstate-ionic liquid hybrids on the surface of silica coated magnetite particles aiming to ease the separation and recycling of the material by adding the superparamagnetic properties of the magnetite. The resulting material showed an excellent activity (84% conversion with 99% of selectivity) in the epoxidation of cyclooctene with advantages in the separation and thermal stability compared to IL-POM bare systems.

The synthesis of β -keto enol ethers was selected by Rafiee and Eavani [79] as the reaction of application of the POM-IL hybrids. They study the activities of the hybrids as a function of the IL cation and found that the activity was little influenced by the cation contrary to the solubility of the hybrids. Depending on the polarity of the cations and of the reaction mixture, a “self-separation” or heterogeneous catalysis was observed. Regardless of the separation process, the catalyst could be easily recycled and reused several times without significant loss of activity.

Rostami et al. [80] synthesized di[1,6-bis(3-methylimidazolium-1-yl)hexane] decatungstate dehydrate ($[\text{C}_6(\text{MIm})_2]_2\text{W}_{10}\text{O}_{32}\cdot 2\text{H}_2\text{O}$) hybrid as a novel heterogeneous catalyst in the synthesis of 4-arylidene-2-phenyl-5(4)-oxazolones (azlactones) under ultrasound-assisted solvent-free conditions. The novelty of this work lies in the operational and experimental simplicity (easy hybrid synthesis and easy separation and use), enhanced reaction rates, and the existence of options for further

transformations of the resulting 4-arylidene-2-phenyl-5(4)-oxazolones into synthetically interesting biologically active compounds. The same group continued in the field of azlactones by the application of 1-butyl-3-methylimidazolium phosphotungstates and phosphomolybdates in the synthesis of 4-benzylidene-2-phenyloxazoline-5-ones [81]. The corresponding azlactones were obtained with good to excellent yields and catalyst reusability via Erlenmeyer synthesis by the reaction of different aldehydes with hippuric acid and acetic anhydride.

Another reaction, in which the POM-IL hybrids were reported as efficient, inexpensive, and recyclable green catalyst, is the solvent-free synthesis of 1,8-dioxodecahydroacridines. The used hybrid was tetrabutylammonium hexatungstate which catalyzes the one pot synthesis of 1,8-dioxodecahydroacridines by the reaction of dimedone with aromatic or aliphatic aldehydes in the presence of a nitrogen source (ammonium acetate or aromatic amines). When compared to the classical Hantzsch synthetic procedure, the use of this catalyst and reaction path resulted in diminution of the reaction time (7–14 min), higher yields (> 90%), facile setup, and minimal environmental impact [82].

Tetraalkylammonium salts of transition metal substituted polyoxometalates, such as $[(\text{n-C}_7\text{H}_{15})_4\text{N}]_6[\alpha\text{-SiW}_{11}\text{O}_{39}\text{Co}]$ and $[(\text{n-C}_7\text{H}_{15})_4\text{N}]_6[\alpha\text{-SiW}_{11}\text{O}_{39}\text{Mn}]$, were reported to efficiently catalyze cyclic carbonate synthesis from carbon dioxide and epoxide [83]. The catalytic activity is significantly influenced by the nature of the transition metal substituent and/or counteranion ($\text{Co}^{2+} \approx \text{Mn}^{2+} > \text{Ni}^{2+} > \text{Fe}^{3+} \gg \text{Cu}^{2+}$; $(\text{n-C}_7\text{H}_{15})_4\text{N}^+ > (\text{n-C}_4\text{H}_9)_4\text{N}^+ \gg \text{K}^+$). Especially valuable catalysts are Co- or Mn-substituted ones which do require neither additional organic solvents nor additives. POM-IL ($[\text{Hmim}]_3\text{PW}_{12}\text{O}_{40}$) hybrid among others was employed in the acetalization of carbonyl compounds [84]. During the reaction, the hybrids and the reaction medium formed a temperature-dependent phase separation system, which eased the product transfer and catalyst separation. The high activity of the hybrids (92–97% yields) was maintained up to 10 cycles of reaction with a negligible loss of activity.

Inside the large spectrum of reactions catalyzed by the POM-IL hybrids, an emerging field is the reaction of alcohols oxidation. The oxidation in mild conditions by H_2O_2 over polytungstates stabilized with quaternary ammonium cations was broadly reported [85–88]. However, the use of volatile organic solvents and, in most cases, the loss of catalyst were not avoided. A few years ago, Chhikara et al. [89] proposed to use the imidazolium based phosphotungstate complex in ionic liquid for the alcohols oxidation to the corresponding carbonyl groups. This oxidation presented the advantage of a homogeneous reaction mixture, easy recovery of the catalyst, excellent yields, and low degree of solvent consumption. In the field of alcohols oxidation, the oxidation of methanol attracted recently a renewed interest pointing to the on-site generation of H_2 for the fuel cells. A selective oxidation can lead to valuable oxygenated products such as formaldehyde, methyl formate, dimethyl ether, and dimethoxymethane and in addition can be used as a model reaction to characterize acid-base and redox properties of the materials [90].

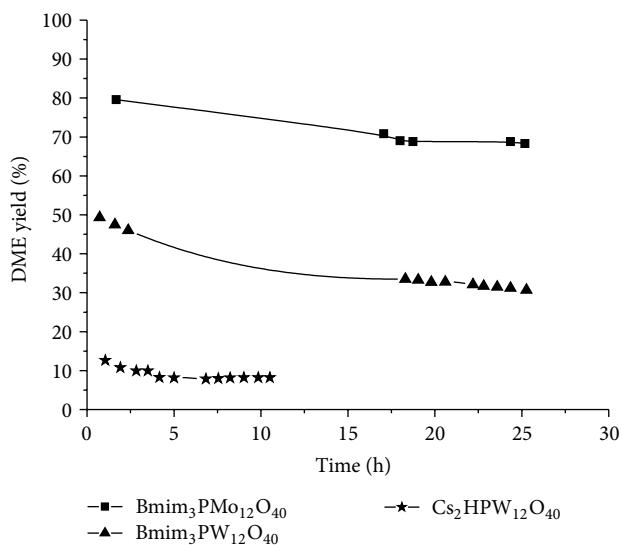


FIGURE 6: Dimethyl ether yield over POM-IL hybrids in gas phase dehydration of methanol from [92].

Pure heterogeneous gas phase dehydration/oxidation of methanol over 1-butyl, 3-methyl imidazolium based POM hybrids (Bmim₃PMO₁₂O₄₀ and Bmim₃PW₁₂O₄₀) was reported by Ivanova et al. [91, 92]. The fresh hybrids do not catalyze the dehydration of methanol but after some activation procedure showed a high activity in the harsh range of selected reaction conditions (activation at 400°C in methanol/air mixture and 275°C for the dehydration) in comparison to the analogues metal salt Cs₂HPW₁₂O₄₀ (Figure 6).

Special attention in these works was paid to the stability and corresponding activity of the hybrids as a function of the temperature. In the activation conditions a full oxidation of methanol was obtained and, at the temperature of dehydration, dimethyl ether was produced with selectivity exceeding 95%. A close relationship between the nature of the POM anion and the thermal stability range was observed. The Mo based POM seems to catalyze the oxidation of the imidazolium cation and the destruction of the hybrid during the activation, contrary to the W-based POM which active site seems to be the imidazolium deficient hybrid. The differences between the acidic and redox properties of both hybrids are responsible for their different behavior. Both types of properties can be controlled either by the POM part or by the IL modification. Those studies open the door to the direct application of the POM-IL materials in the gas phase heterogeneous catalysis. In this area a lot of work has to be done. Recently Dermeche et al. [93] found that the product distribution of the selective oxidation of methanol depends on the polyanion composition and on the framework symmetry. The different heteroatom introduced in the Dawson structure based polyoxometalates allows the control of the dehydration oxidation products.

Where Is the Future?

The increasing development of hybrid systems in the last decade indicates by itself that they are a class of forthcoming

and promising materials. The extensive use of the polyoxometalates in the acid catalysis and especially their ability to activate H₂O₂ [94] opened the possibility for their application in the acid and oxidation catalysis in mild conditions. The diversity of the polyoxometalate structures and the good knowledge of their structure/properties relationship provide the necessary foundation in the field, but their synergism with the ionic liquids still remains underexplored. The majority of the reports in the literature deal with the imidazolium or quaternary ammonium based family organic cations and the inorganic part is mainly based on Keggin structures. The diversity in both inorganic and organic families could result in an extensive development of the application targeted hybrids. Their special photochromic and electrochromic behavior should not be forgotten, opening a large field of possible application in the materials science. The application of these hybrids in the gas phase medium temperature reactions still has not revealed its truly potential, but the first step is made; good productivity in the methanol dehydration reaction was found.

The field of biofuels production and natural products valorization is one of the newest fields in catalysis, aiming at the replacement of the limited fossil fuels and the decreasing of the environmental impact. Among the current renewable and sustainable alternatives, the 5-hydroxymethylfurfural (HMF) converted from sugars in biofuel and petroleum chemistry [95, 96]. The ionic liquids have been already reported for the production of HMF [97–99] and very recently the application of the polyacids based catalyst with excellent efficiency and very good selectivity was reported [100]. The combination of both catalysts seems to be the next logical step, targeting higher stability and more importantly higher productivity by applying it in heterogeneous in-flow reactions.

Regardless of the field of application, material science, catalysis, or medicine, the polyoxometalate derivatives were, are, and will be always one of the top materials for research and developing.

Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

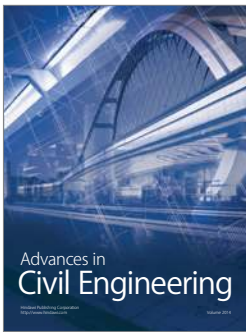
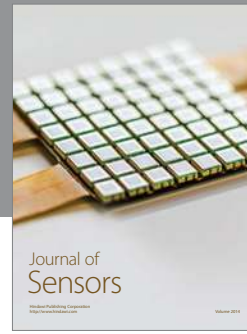
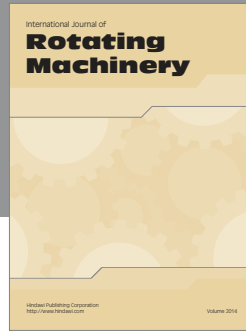
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