

Review

H₂O₂-Based Selective Oxidations Catalyzed by Supported Polyoxometalates: Recent Advances

Nataliya V. Maksimchuk  and Oxana A. Kholdeeva *

Boreskov Institute of Catalysis, Lavrentieva Ave. 5, Novosibirsk 630090, Russia

* Correspondence: khold@catalysis.ru

Abstract: Polyoxometalates (POMs) are transition metal oxygen anionic clusters that are oxidatively and thermally robust due to their inorganic, metal oxide-like nature. The versatility of their structures and compositions ensures tunable acid and redox properties, solubility, and functionality. The potential of POMs as homogeneous catalysts and building blocks for the construction of heterogeneous selective oxidations catalysts is being intensively investigated. POM catalysts immobilized on solid supports have the clear advantages of easy separation and reuse and, thus, better meet the requests of sustainable chemistry, provided that they are leaching-resistant under the reaction conditions. Here, we give a brief overview of recent advances in the field of liquid-phase selective oxidation of organic compounds using supported POMs and the green oxidant–hydrogen peroxide, with a focus on the critical issues of the catalyst stability and reusability. The scope and limitations of various approaches to POM immobilization are discussed.

Keywords: heterogeneous catalysis; hydrogen peroxide; immobilization; liquid-phase selective oxidation; polyoxometalates; supported catalysts



Citation: Maksimchuk, N.V.; Kholdeeva, O.A. H₂O₂-Based Selective Oxidations Catalyzed by Supported Polyoxometalates: Recent Advances. *Catalysts* **2023**, *13*, 360. <https://doi.org/10.3390/catal13020360>

Academic Editor: Jean-François Lamonier

Received: 16 December 2022

Revised: 27 January 2023

Accepted: 2 February 2023

Published: 6 February 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

In the modern chemical industry, the role of liquid-phase selective oxidation in the production of bulk and fine chemicals is permanently increasing [1–3]. The development of cost-effective and environmentally friendly oxidation processes employing safe and readily available oxidants is a challenging goal, as requested by the pursuit of sustainable and green manufacturing of valuable chemicals. In this context, hydrogen peroxide, the molecule that can provide 47% of potentially active oxygen, leaving water as the only byproduct, remains one of the most ecologically and economically attractive oxidants [4–6]. Significant progress achieved on the way to the direct synthesis of H₂O₂ from molecular hydrogen and oxygen contributes to the expansion of interest in this oxidant [7–12].

The use of hydrogen peroxide in oxidation reactions requires catalysts because it is inert toward the majority of organic substrates. Heterogeneous catalysts have clear advantages of facile recovery, recycling, and compatibility with flow reactors and, thus, better meet the needs of sustainable chemistry, provided that the solid catalyst is stable to the leaching of active metal in the reaction medium [2,3].

A serious problem of the currently existing selective oxidation catalysts is their relatively low productivity caused by the damage of active sites under conditions of a large excess of H₂O₂. While catalysts bearing organic and organometallic ligands (both homogeneous and supported) suffer from oxidative degradation, most of metal-containing zeolites and other zeotype solids reveal hydro(solvo)lytic instability in the presence of aqueous H₂O₂, which results in the aggregation of active sites and may be accompanied by metal leaching into the solution. A rare exception among them is the well-known catalyst titanium–silicalite-1 (TS-1), developed by the ENI group in the 1980s [13,14]. The invention of TS-1 appeared to be a real breakthrough in the field of liquid-phase oxidation and greatly expanded interest in the use of aqueous hydrogen peroxide as oxidant. Nowadays, TS-1 is

employed in large-scale industrial processes [15–18], but its scope is limited to small organic substrates capable of penetrating the micropores (0.53×0.56 nm) of the catalyst. Significant scientific efforts have been directed to the development of larger pore analogues of TS-1, in particular, mesoporous Ti-silicates, and several catalytic materials with a fairly good hydro(solvo)lytic stability have been elaborated [19–23]. However, unlike TS-1, these materials are endowed with a hydrophilic nature, and the preferential adsorption of $\text{H}_2\text{O}_2/\text{H}_2\text{O}$, rather than the organic substrate, favors the unproductive H_2O_2 decomposition on the catalyst surface, which results in a large contribution of homolytic oxidation pathways and negative effects on the oxidation selectivity [22,23]. Some limited achievements in this area are related to the partial hydrophobization of the surface of titanium silicate catalysts [24–26] and the introduction of other metals, first of all, niobium, into silicate matrices [27–30]. Meanwhile, the search for alternative types of catalysts capable of heterolytic activation of aqueous hydrogen peroxide remains a challenging goal of oxidation catalysis.

Early transition metal oxygen anionic clusters, also called polyoxometalates (POMs; general formula $[\text{X}_x\text{Y}_y\text{O}_z]^{q-}$ ($x \leq y$), where X is a main group element or transition metal and Y are addenda atoms, most often Mo^{VI} or W^{VI}) have long been attracting the research attention as oxidation catalysts thanks to a unique combination of properties, which includes, first of all, the inorganic nature and metal oxide-like structure, ensuring thermodynamic stability to oxidation along with good thermal and hydro(solvo)lytic stability [31–41]. The obvious structural analogy between POMs and the surface of metal oxides makes it possible to consider POMs as discrete soluble molecular models of heterogeneous catalysts, which can be systematically investigated at the atomic level by experimental and computational techniques [34,42–45].

The solubility, redox, and acid–base properties of POMs and, as a result, their catalytic performance can be finely tuned by choosing the POM structure and chemical composition of both the polyanion and its counter cations. In particular, interesting objects for oxidation catalysis are M-substituted polyoxotungstates that comprise various heterometals (M) strongly bound to the molecular tungsten oxide through multiple M–O–W bonds, which potentially prevents the active site from hydrolysis and di(oligo)merization. In addition, a covalent functionalization of POMs can be used to control the surrounding of the active site, specifically its steric hindrance [46,47]. Some structural types of POMs that will be mentioned in this review, in relation to their use in oxidation catalysis with H_2O_2 , are shown in Figure 1.

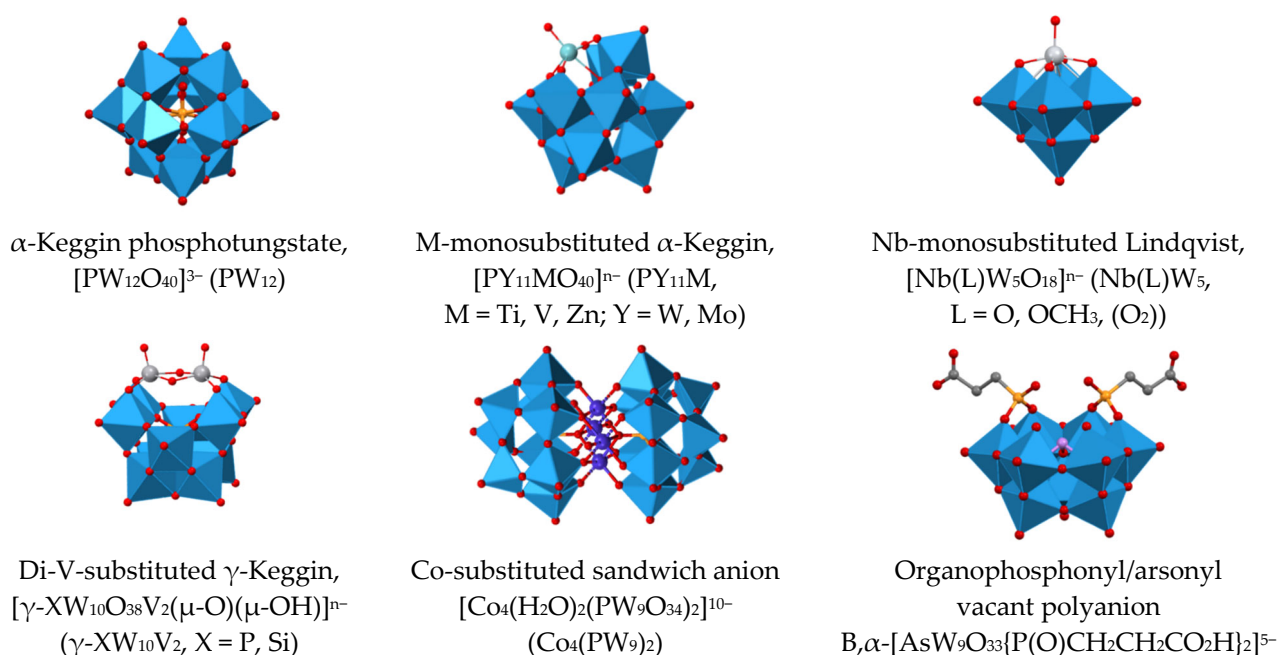


Figure 1. Structures of some POMs used for H_2O_2 -based selective oxidations.

A comprehensive review literature, including several thematic issues and book chapters [32–35,38,48–55], covers different aspects of POM chemistry, in particular, their application in various fields of catalysis [31–33,35–41,49,53–55]. A book chapter of Kholdeeva and Hill covered the literature (until 2012) related to POM immobilization and use in selective oxidations [38]. Wu discussed the progress of using supramolecular interactions for the construction of encapsulated POM catalysts [54]. Enferadi-Kerenkan et al. reviewed catalysis by solidified polyoxotungstates [56], while Evtushok et al. surveyed the POM immobilization on carbon nanotubes and their use in selective oxidations [57]. Some modern trends in the environmentally benign oxidation catalysis by POMs and H_2O_2 , specifically new approaches to biphasic catalysis with POMs and POM immobilization, were touched on in a book chapter of Kholdeeva [55]. However, the topic of selective oxidation using supported POMs has greatly expanded in recent years, and our aim here is to give a brief overview of the new advances in this field, with a focus on the use of hydrogen peroxide as oxidant. Given that the resistance to the leaching of active species under turnover conditions of liquid-phase oxidation is a critical issue for solid catalysts [58], we paid special attention to this problem and singled out those works for which the heterogeneous nature of catalysis was thoroughly validated.

2. Supported POMs as Heterogeneous Catalysts for Selective Oxidations with H_2O_2

To date, a range of different approaches to the immobilization of catalytically active POMs on solid supports have been proposed [38,59–70]. Conventional methodologies include the synthesis of insoluble POM salts (Cs^+ , Ag^+ , K^+ , NH_4^+ , or some organic polycations) [61,68,69,71–75], embedding into silica by means of sol–gel synthesis [59,65,69,76–80], electrostatic attachment via anion exchange with layered double hydroxides [81–84], or modified surface of silica materials [65,68,69,76,80,85–99], anchoring through the formation of dative bonds between POM and surface ligands [100–103], and finally, the covalent binding of organo-functionalized POMs [61,63,66,69,104,105]. In the last decade, some novel approaches that involve combinations of various types of interactions, including supramolecular ones, between the POM and surface, have been developed and successfully employed for the preparation of stable POM-based oxidation catalysts.

2.1. Embedding via Template Synthesis

One of the efficient and convenient approaches to POM heterogenization is encapsulation in an inert matrix during the matrix synthesis. Izumi was the first who suggested inserting a catalytically active POM into silica by means of the sol–gel method [59]. The discovery of ordered mesoporous materials stimulated the further development and modifications of this technique, using various templates as structure-directing agents [38] and references cited therein. However, while microporous POM/ SiO_2 composites could be relatively stable [65,76,77], mesoporous composite materials often showed insufficient stability to POM leaching in polar media.

The evaporation-induced self-assembly (EISA) procedure was employed for a one-pot preparation of a series of ordered meso-macroporous titania–silica–polyoxometalate materials using phosphotungstic acid as a POM and non-ionic surfactant (P123) and monodisperse polystyrene microspheres as co-structure-directing agents [106,107]. Catalysts $\text{PW}_{12}/\text{SiO}_2\text{--TiO}_2$ exhibited a good performance in oxidative desulfurization (ODS) reactions: dibenzothiophene (DBT, 500 ppm S as model fuel), which is considered to be the main sulfide pollutant in fuel oil, was completely removed within 1 h under optimized conditions. The catalytic performance of $\text{PW}_{12}/\text{SiO}_2\text{--TiO}_2$ was superior to that of $\text{PW}_{12}/\text{SiO}_2$, which was explained by the presence of surface Lewis acidic sites in the former [107]. No obvious degradation of the catalytic performance was observed upon catalyst recycling during six runs. The retention of the Keggin structure of PW_{12} was confirmed by FT-IR spectra of the spent catalyst, while XRD measurements and TEM images indicated maintenance of the orderly morphological and microscopic structure. However, the PW_{12} loading

in the reused catalyst, as determined by ICP, dropped from 19.7 to 17.8%, indicating that the leaching of active tungsten species could be possible during the reaction course.

Nogueira and co-workers have suggested the synthesis of core/shell nanoparticles comprising POM as a core encapsulated within silica shell through the hydrolysis of tetraethoxysilane in the presence of POM [108]. Following a similar approach, a $\text{PW}_{12}@ \text{TiO}_2$ core-shell microsphere material was prepared via one-step template synthesis using $\text{K}_3\text{PW}_{12}\text{O}_{40}$ as a core and TiO_2 as a shell [109]. Multiple characterization methods (FT-IR, XRD, XPS, Raman, SEM, and TEM) implicated that PW_{12} was encapsulated into the mesoporous TiO_2 phase as the core. The resultant composite was found to be efficient catalyst for ODS of a model oil using H_2O_2 as an oxidant with 99.9% S removal of DBT after 60 min under the optimum conditions. Additionally, leaching and recycling experiments coupled with catalyst filtration tests confirmed that the $\text{PW}_{12}@ \text{TiO}_2$ is a truly heterogeneous catalyst with excellent recyclability during, at least, seven reuses.

2.2. Electrostatic Binding via Anion-Exchange

Electrostatic binding with NH_3^+ -group of amine-functionalized silica supports continues to be one of the most common methods for POM immobilization. A La-containing POM, $[\text{LaW}_{10}\text{O}_{36}]^{9-} \cdot (\text{LaW}_{10})$ attached to a commercial mesoporous silica functionalized with (3-aminopropyl)triethoxysilane (apt)es [110] and a sandwich-type $[\text{Eu}(\text{PW}_{11}\text{O}_{39})_2]^{11-}$ ($\text{Eu}(\text{PW}_{11})_2$) supported on an aptes-modified SBA-15 [111] behaved as active and recyclable catalysts in ODS of a multicomponent model diesel containing the most refractory sulfur compounds (1-benzothiophene, dibenzothiophene, 4,6-dimethyldibenzothiophene, and 4-methyldibenzothiophene) using H_2O_2 as the oxidant. $\text{Eu}(\text{PW}_{11})_2@ \text{apt} \text{esSBA-15}$ revealed not only a high recycling ability without loss of activity during ten consecutive ODS runs, but also the high robustness and stability of the composite material as confirmed by FT-IR, Raman, ^{31}P MAS NMR, XRD, and SEM/EDS techniques [111].

A PW_{12} -based cross-linked copolymer catalyst was synthesized via the anion exchange of phosphotungstic acid with ionic copolymer obtained through the radical copolymerization of dicationic ($[1,1'-(\text{butane-1,4-diyl})\text{-bis}(3\text{-vinylimidazolium})]\text{Br}_2$) and amine-functionalized ($[3\text{-aminoethyl-1-vinylimidazolium}]\text{Br} \cdot \text{HBr}$) ionic liquids [112]. The resulting hybrid material catalyzed the efficient epoxidation of a range of alkenes (cyclooctene, cyclohexene, 1-hexene, and 1-octene) with up to 100% selectivity to the corresponding epoxides under the conditions of oxidant deficiency. The ICP-AES analysis of the filtrates indicated that ca. 3 wt.% of W leached into the reaction medium during the first operation cycle, while leaching became negligible upon further catalyst reuse. The hot catalyst filtration test confirmed the truly heterogeneous nature of the observed catalysis.

Doherty et al. have used cation-decorated polymeric supports based on ionic liquids (PIILPs) prepared by ring-opening metathesis polymerization of a pyrrolidinium-functionalised norbornene-based monomer with cyclooctene to immobilize the Venturello complex $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]^{3-}$ (PW_4) [113]. The resulting solid was active in the epoxidation of a range of alkenes and allylic alcohols using H_2O_2 with the corresponding epoxides yields up to 94%. The catalyst recovered by centrifugation could be reused at least three times, with a minor reduction in the initial reaction rate. ICP-OES analysis revealed no tungsten in the reaction mixture after the catalyst recovery, while the solid state ^{31}P NMR confirmed stability of the PW_4 structure in the recycled catalyst. However, the TEM images of the reused PW_4 -PIILP have shown some aggregation of the peroxophosphotungstate on the surface. Such aggregation can lead to a reduced accessibility of the active species, which, in turn, may cause decrease in catalytic activity after several reuses.

The Keggin polyanion $[\text{PMo}_{10}\text{V}_2\text{O}_{40}]^{5-}$ ($\text{PMo}_{10}\text{V}_2$) could be successfully immobilized by electrostatic interactions with the positively charged surface of the hydrophilic porous block copolymer membranes on the basis of polystyrene-block-poly(*N,N*-dimethylaminoethyl methacrylate) [114]. The POMbranes thus obtained were active in oxidation of anthracene and 9,10-dihydroanthracene with H_2O_2 , producing anthraquinone with 71–100% yields, as well as oxidized tetrahydrothiophene (THT), to a mixture of sulfoxide and sulfone. Despite

the fact that no POM leaching was observed under the turnover conditions, the recycling experiments have shown a steady loss of catalytic activity. The catalyst deactivation could be explained by a strong adsorption of the reaction products on the catalyst surface. Indeed, the reactivation by drying the membrane in a vacuum improved the catalytic performance upon reuse in THT oxidation.

Lindqvist-type $\text{Na}_9\text{LaW}_{10}\text{O}_{36} \cdot 32\text{H}_2\text{O}$ intercalated into layered double hydroxides modified with ionic liquids (ILs) demonstrated high activity and selectivity in the epoxidation of a range of allylic alcohols with H_2O_2 [115]. The highest activity was exhibited by a $\text{Mg}_3\text{Al-ILs-C}_8\text{-LaW}_{10}$ material based on $[\text{Mg}_{0.75}\text{Al}_{0.25}(\text{OH})_2](\text{NO}_3)_{0.25} \cdot 2\text{H}_2\text{O}$ ($\text{Mg}_3\text{Al-NO}_3$) modified with 1-octyl-3-(3-triethoxy-silylpropyl)-4,5-dihydroimidazolium hexafluorophosphate ($(\text{EtO})_3\text{Si-ILs-C}_8$). The oxidation of trans-2-hexen-1-ol in the presence of $\text{Mg}_3\text{Al-ILs-C}_8\text{-LaW}_{10}$ showed 99% epoxide selectivity at 96% substrate conversion after 2.5 h at 25 °C. The catalyst could be readily isolated from the reaction mixture by centrifugation and reused for, at least, five times without a loss of the initial catalytic activity. The stability of the $\text{Mg}_3\text{Al-ILs-C}_8\text{-LaW}_{10}$ structure under turnover conditions was confirmed by FTIR, ^{29}Si NMR CP/MAS, and XPS measurements, while the heterogeneous nature of the catalysis was verified by the catalyst filtration test performed during the reaction course.

2.3. Inclusion in Metal–Organic Frameworks

In recent years, the immobilization of POMs into the cages of metal–organic frameworks (MOFs) has attracted much research attention [70,116–126]. Férey and co-workers were the first who demonstrated that POM molecules can penetrate MOF, and a large cage (3.4 nm diameter with windows of 1.2 and 1.6 nm) of the mesoporous chromium terephthalate MIL-101 can accommodate up to five Keggin-type POMs [127]. The subsequent studies by Maksimchuk et al. revealed that only one polyanion per cage is strongly attached to the MIL-101(Cr) surface (Figure 2), and the POM attachment occurs through anion exchange with nitrate anions present in the MIL-101 framework, while all extra POM molecules easily leach into solution [118,128,129]. The binding between polyanion and MIL-101 is, therefore, electrostatic, and POM can be re-extracted by an anion exchange procedure, for example, using a solution of a perchlorate or nitrate salt [118,128,129].

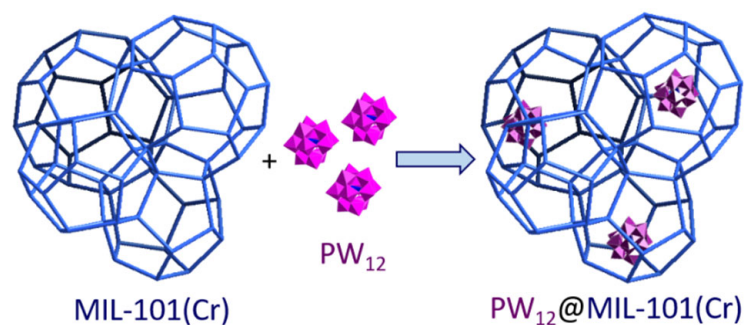


Figure 2. Incorporation of Keggin POM into the cages of MIL-101(Cr).

The combination of MIL-101 and a POM capable of activating H_2O_2 has made it possible to use hydrogen peroxide as oxidant in a range of selective oxidations (Table 1). Specifically, Figure 3 demonstrates the application of $\text{PW}_{12}@\text{MIL-101(Cr)}$ in the epoxidation of various alkenes [118,129]. Fairly good yields of epoxides could be obtained for monoterpenes, the substrates prone to various rearrangements, using equimolar amount of H_2O_2 . Although the activity of the $\text{PW}_{12}/\text{H}_2\text{O}_2$ catalytic system is commonly attributed to the lower nuclearity peroxotungstates (first of all, PW_4 and PW_2) formed in situ under the conditions of H_2O_2 excess [130–133], the ^{31}P NMR MAS spectrum of the $\text{PW}_{12}/\text{MIL-101(Cr)}$ catalyst remained practically unchanged after five runs of cyclohexene oxidation. This implies that immobilization on MIL-101(Cr) could increase the stability of the polyanion, even if the transformation of the MIL-included PW_{12} to low-nuclearity species occurs in the presence of H_2O_2 , such transformation is apparently reversible.

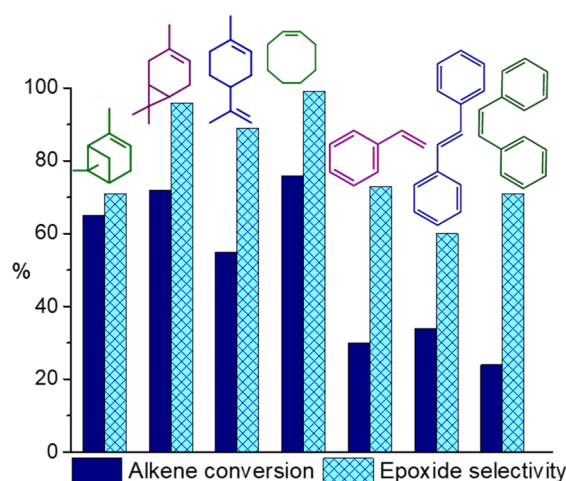


Figure 3. Alkene epoxidation with equimolar amount of H_2O_2 catalyzed by $\text{PW}_{12}\text{@MIL-101}(\text{Cr})$.

Interestingly, the hybrid materials POM@MIL-101 ($\text{POM} = [\text{PW}_{11}\text{TiO}_{40}]^{5-}$ (PW_{11}Ti) or PW_{12}) demonstrated a pronounced improvement of both epoxidation selectivity and alkene conversion upon enlarging concentration of the oxidant (Figure 4), despite the increasing water concentration in the system (H_2O_2 was taken as a 30% aqueous solution) [118,128,129]. The reverse trend was observed for the corresponding homogeneous POMs, which is what one would expect, given that the increased concentration of H_2O_2 (H_2O) is favorable for epoxide ring opening and overoxidation processes. The unusual behavior of the POM@MIL-101 catalysts in alkene epoxidation with aqueous H_2O_2 was explained by the specific sorption properties of the MOF support [118,120]. It was suggested that the hydrophobic part of the terephthalate linker favors adsorption of nonpolar hydrocarbons and, oppositely, disfavors the adsorption of water. This suggestion is supported by the character of the water adsorption isotherm reported for MIL-101, which shows that H_2O uptake by MIL-101 starts at high relative pressures ($p/p_0 = 0.4$) [134], indicating that the MOF surface behaves as a hydrophobic one when the concentration of water in the organic solvent is low [120].

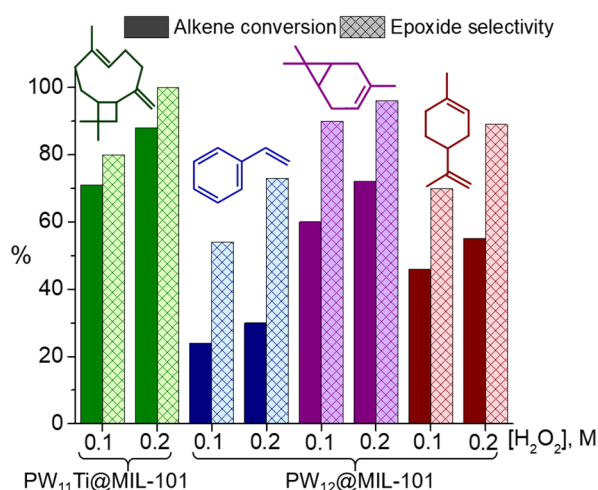


Figure 4. Effect of H_2O_2 concentration on alkene epoxidation catalyzed by $\text{POM@MIL-101}(\text{Cr})$.

Following these first works, a large number of papers concerning POM immobilization within MOFs have been published [55,70,120,121,124–126]. Hatton and co-workers reported a one-pot synthesis of MIL-101(Cr)-immobilized phosphotungstic acid, which was active in the epoxidation of caryophyllene with H_2O_2 (Table 1), behaved as truly heterogeneous catalyst, and could be recycled without loss of activity [135]. Nonetheless, the $\text{PW}_{12}\text{@MIL-101}$ material showed a reduction of the POM content upon the re-

cycling. Balula and co-workers inserted a range of POMs (Tb-substituted Keggin-type dimer $[\text{Tb}(\text{PW}_{11}\text{O}_{39})_2]^{11-}$ ($\text{Tb}(\text{PW}_{11})_2$) [136], sandwich-type $\text{Co}_4(\text{PW}_9)_2$ (see Figure 1 for the structure) [137], trivacant $[\text{A-PW}_9\text{O}_{34}]^{9-}$ (PW_9), [138], Venturolo peroxotungstate PW_4 [139], and europium-substituted Lindqvist dimer $[\text{Eu}(\text{W}_5\text{O}_{18})_2]^{9-}$ (EuW_{10}) [140]) by post-synthetic impregnation of MOF (MIL-101(Cr) or ZIF-8) with a POM solution. PW_9 @MIL-101 revealed catalytic activity in oxidation of monoterpenes and S-compounds with H_2O_2 . Most of the hybrid materials exhibited high activity in the oxidative desulfurization [124,137–140] (Table 2), whereas $\text{Co}_4(\text{PW}_9)_2$ @MIL-101 also catalyzed oxidation of alkenes (geraniol, limonene, styrene) and cyclooctane with H_2O_2 (Table 1) [137]. While the oxidation of geraniol gave only 1,2-epoxygeraniol, limonene was transformed mainly to 1,2-epoxide and the corresponding 1,2-diol, whereas benzaldehyde was the main product obtained from styrene [137]. Although the structure of both POM (confirmed by EDX, FT-IR, and Raman measurements) and MOF (confirmed by XRD and SEM) was retained, the catalyst kept its activity during at least three consecutive runs, and some POM leaching was documented [137].

A one-pot mechanochemical synthesis was suggested as an efficient strategy to insert PMoV heteropolyacids $\text{H}_{3+n}\text{PMo}_{12-n}\text{V}_n\text{O}_{40}$ ($n = 2-4$) into the large cavities of a metastable MOF, rho-ZIF [141]. The PMoV@rho-ZIF composites were effective catalysts for the selective oxidation of a series of organic sulfides to sulfoxides with aqueous H_2O_2 (Table 1). The heterogeneous nature of the catalysis was confirmed by the catalyst filtration experiment, and the PMoV@rho-ZIF materials could be recycled at least four times without a significant loss of activity, with retention of the POM and MOF structures. Wang et al. immobilized an ionic liquid–phosphotungstate inside the cages of pre-activated MIL-101(Cr) with unsaturated Cr^{3+} active sites via formation of Cr–N dative bonds [142]. The catalytic material was active in the H_2O_2 -based oxidation of cyclohexene to produce adipic acid (AA) and maintained activity for at least six reuses. Yields of AA up to 78% under solvent-free conditions have been claimed (Table 1). Unfortunately, the absence of leaching and the nature of the catalysis were not addressed by the authors.

In order to suppress the leaching of immobilized POM, Qiu and co-workers proposed an encapsulation strategy based on an ionic liquid bridging [143,144]. Thus, phosphotungstic acid was successfully encapsulated into the Zr-based MOF UiO-66 by (i) in situ solvothermal procedure using carboxyl-functionalized methylimidazole as bridging molecule [143] or (ii) manual grinding technique using 4-aminopyridine as bridging compound [144]. A range of physicochemical methods (XRD, EDS, and XPS) confirmed the successful introduction and high dispersion of POM. The PW_{12} @UiO-66 composites exhibited high activity in oxidative desulfurization of DBT (as 1000 ppm S model oil) with H_2O_2 (Table 2). The authors suggested that such activity is attributed to the high dispersion of the active component on the surface of UiO-66 and synergy between the Zr(IV) open sites in the MOF and active W(VI) sites in the POM. Indeed, IL-functionalized PW_{12} , POM-free UiO-66, and even a mixture of POM and MOF showed lower activity in DBT desulfurization, as compared to the composite catalyst [143].

Phosphotungstic and phosphomolybdic (PMo_{12}) heteropolyacids were encapsulated within the MOF-808 by in situ synthesis based on a ‘ship-in-a-bottle’ approach [145,146]. Lin et al. used MOF-808X with tunable window diameters [145]. Both PMo_{12} @MOF-808 and PW_{12} @MOF-808X revealed high activity and stability in ODS of model fuels and could be used repeatedly without a loss of catalytic properties (Table 2). A few UiO-66(67)-incorporated hybrid materials with a range of POMs (PW_{12} or PMo_{12} heteropolyacids and salts), and they were synthesized via a direct solvothermal reaction [147–149]. A composite PW_{12} @UiO-66 with 35 wt% of POM was highly active in the selective oxidation of cyclopentene to glutaraldehyde with H_2O_2 (78% yield at 95% substrate conversion, see Table 1), did not suffer active metal leaching, and could be used repeatedly [147].

Table 1. H₂O₂-based oxidations over MOF-included POMs.

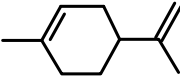
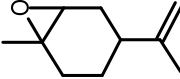
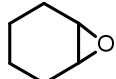
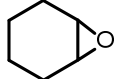
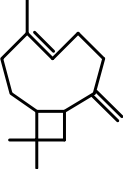
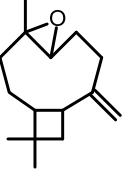
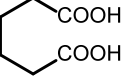
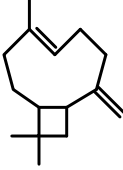
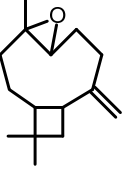
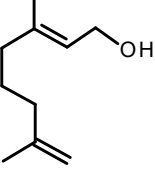
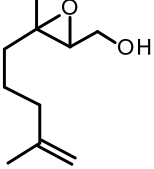
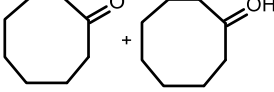
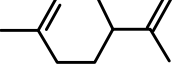
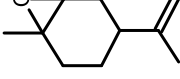
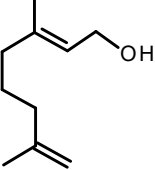
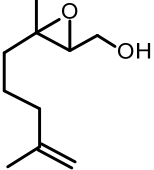
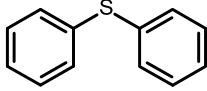
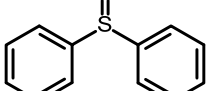
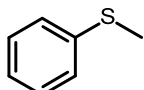
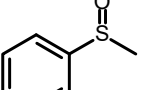
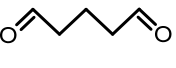
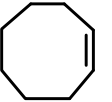
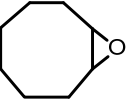
POM	MOF	Synthesis Method	Substrate/Conv. %		Product/ Selectivity, %		Nature of Catalysis ^a	Ref.
PW ₁₂	MIL-101(Cr)	Ads. ^b		55		89	Heterog.	[129]
				50		61		
				72		76		
PW ₄	MIL-101(Cr)	Ads.		75		77	Heterog.	[129]
PW ₁₂	MIL-101(Cr)	Solv. ^c		n.d. ^d		92 ^e	Heterog.	[135]
IL-PW ₁₂	MIL-101(Cr)	Post-synth. ^f		n.d.		78 ^e	n.d.	[142]
PW ₁₁ Ti	MIL-101(Cr)	Ads.		88		100	Heterog. ^g	[128]
Co ₄ (PW ₉) ₂	MIL-101(Cr)	Ads.		>99		>99	n.d.	[137]
				57		>99		
PW ₉	MIL-101(Cr)	Imp. ⁱ		93		50 ^h	Heterog.	[138]
				>99		>99		

Table 1. Cont.

POM	MOF	Synthesis Method	Substrate/Conv. %	Product/ Selectivity, %	Nature of Catalysis ^a	Ref.
PMo ₁₁ V	rho-ZIF	Mechanochem.	 83	 89	Heterog.	[141]
			 97	 96		
PW ₁₂	UiO-66	Solv.	 95	 83	n.d.	[147]
Co-PMo ₁₂ ^j	UiO-67	Solv.	82	>99	Heterog.	[149]
PMo ₁₂	UiO-67	Solv.	 75	 >99	n.d.	

^a Nature of catalysis (truly heterogeneous catalysis was confirmed by hot catalyst filtration tests). ^b Synthesis by adsorption of POM from acetonitrile. ^c Solvothermal one-pot synthesis. ^d Not determined. ^e Isolated yield. ^f Immobilization by post-synthetic strategy through a Cr–N dative bond. ^g Depended on the reaction conditions. ^h Diepoxide and 1,2-diol were also formed. ⁱ Impregnation of MOF with aqueous solution of PW₉. ^j Presumably CoHPMo₁₂O₄₀.

Table 2. H₂O₂-based ODS over MOF-immobilized POMs.

POM	MOF	Synthesis Method	O/S, mol. Ratio	Sulfur Content, ppm	Desulfurization %	Nature of Catalysis ^a	Ref.
Tb(PW ₁₁) ₂	MIL-101(Cr)	Imp. ^b	21	1500	>99	Heterog.	[136]
PW ₉	MIL-101(Cr)	Imp.	21	1700	>99	Heterog.	[138]
PW ₄	MIL-101(Cr)	Imp.	5	2000	>99	n.d. ^c	[139]
EuW ₁₀	ZIF-8	Imp.	1500	1500	95	n.d.	[140]
PW ₁₂	MOF-808	Solv. ^d	5	1000 ^e	100	Heterog.	[145]
PMo ₁₂	MOF-808	Solv.	21	1500	92	n.d.	[146]
PMo ₁₂	UiO-66	Solv.	3	500	100	n.d.	[150]
(mim(CH ₂) ₃ COO)-PW ₁₂ ^f	UiO-66	Solv.	5	1000 ^e	100	n.d.	[143]
PW ₁₂	UiO-66-D ^g	Solv.	7	800	100	n.d.	[151]
PW ₁₂	UiO-66	Mechanochem.	5	1000 ^e	100	Heterog.	[144]
PW ₁₂	UiO-67	Solv.	13	1000	100	Heterog.	[148]
BMIM-PMo ₁₂ ^h	ZIF-8	Solv.	16	2000	92	n.d.	[152]

^a Nature of catalysis (truly heterogeneous catalysis was confirmed by hot catalyst filtration tests). ^b Synthesis by impregnation of MOF with solution of POM. ^c Not determined. ^d Solvothermal one-pot synthesis. ^e DBT was used as model fuel. ^f 1-Carboxypropyl-3-methyl imidazolium phosphotungstate [mim(CH₂)₃COOH]₃[PW₁₂O₄₀]. ^g UiO-66 with defects. ^h 1-Butyl-3-methylimidazolium phosphomolybdate [BMIM]₃[PMo₁₂O₄₀].

Another method of immobilization is related to the use of POMs as building blocks for the construction of POM-based frameworks (so-called POMOFs) [119,153]. The family of diverse POMOF materials combines the advantages of POM chemistry with the specific MOF's properties; however, just a few of these materials were assessed as catalysts for aerobic- or ^tBuOOH-based oxidations [154–158], and no H₂O₂-based oxidation was reported.

The main limitation for the use of MOF-supported POMs in oxidation catalysis, especially in H₂O₂-based oxidations, is related to the stability of the chosen framework. For example, in the case of MIL-101-supported POMs, the reaction conditions have a great impact on the catalyst stability. At temperatures below 50 °C and [H₂O₂] = 0.2 M or lower, POM/MIL-101 composites behave as true heterogeneous catalysts and can be recycled with a retention of the catalytic properties, while at higher H₂O₂ concentrations and/or temper-

atures, the MIL-101 matrix starts to destroy, leading to deactivation of the POM/MIL-101 catalysts [128].

2.4. Covalent Anchoring in Hybrid Materials

The covalent approach to the immobilization of active complexes offers the obvious advantage of improved stability of the hybrid material. To perform the covalent post-functionalization of POMs, the appropriate organic functions need to be grafted on the polyanion. Proust and co-workers elaborated a synthetic approach applicable to the functionalization of catalytically active vacant Keggin-type POMs with organo-silyl or organo-phosphonyl moieties [62,66,159]. Later on, Villanneau and co-workers have proposed an efficient strategy for the covalent linkage of POM via functionalization by complementary organic functions of both vacant polyoxometalate species and mesoporous silica support (Figure 5) [160]. A few combinations of functional groups have been tested, including carboxylic acid or alkylamine/amine functions for either vacant POM or silica support modification [160,161]. This strategy allowed for an excellent nanostructuration of the POMs shell at the surface of silica support to be created, as determined by HR-TEM (Figure 5). The resulting hybrid materials exhibited a high resistance to leaching in ionic and polar solvent mixtures [160] and, moreover, in oxidative reaction medium of H_2O_2 -based liquid-phase oxidations [161]. The main limitation of this approach was the low control of the quantity of POM grafted, which hardly corresponded to the amount of POM engaged during the preparation.

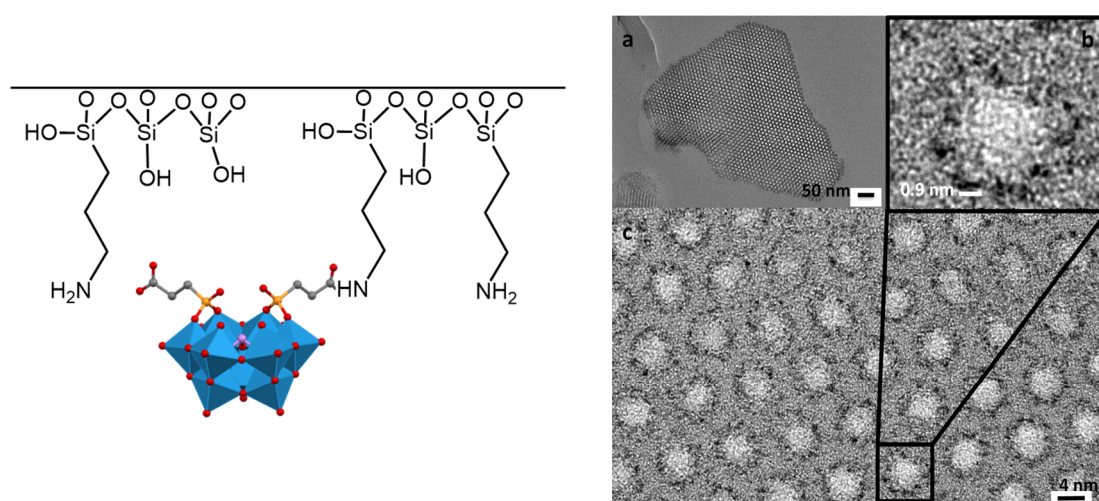
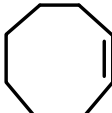


Figure 5. Covalent grafting of phosphonate derivatives of vacant POMs onto the walls of NH_2 -functionalized SBA-15 silica (**left**) and HR-TEM micrographs of $\text{POM-CO}_2\text{H@SBA-NH}_2$ at different (**a–c**) magnifications (**right**). Reprinted with permission from ref. [161]. Copyright 2015 American Chemical Society.

The catalytic performance of $\text{POM-CO}_2\text{H@SBA-NH}_2$, $\text{POM-CO}_2\text{H@MCF-NH}_2$, and $\text{POM-NH}_2\text{@SBA-CO}_2\text{H}$ materials ($\text{POM} = (\text{}^t\text{Bu}_4\text{N})_3\text{NaH}[\text{As}^{\text{III}}\text{W}_9\text{O}_{33}\{\text{P}(\text{O})(\text{CH}_2\text{CH}_2\text{CO}_2\text{H})_2\}]$ ($\text{AsW}_9\text{-P}(\text{O})\text{COOH}$) or $(\text{}^t\text{Bu}_4\text{N})_4\text{H}[\text{PW}_9\text{O}_{34}\{\text{As}(\text{O})(\text{C}_6\text{H}_4\text{NH}_2)_2\}]$ ($\text{PW}_9\text{-As}(\text{O})\text{NH}_2$)) was assessed in cyclooctene epoxidation with H_2O_2 at room temperature, and the resulting substrate conversions varied in the range of 19–76% (Table 3) [161]. The material with the most regular distribution of POM inside the support channels ($\text{POM-CO}_2\text{H@SBA-NH}_2$) showed the best activity among others, although the reaction rate was lower than in homogeneous conditions. This catalyst was also active in cyclohexene epoxidation, but similarly to cyclooctene oxidation, a significant decrease in the initial reaction rate was observed, as compared to the corresponding homogeneous catalyst. Meanwhile, the final conversion was at the same level (ca. 75%), and the selectivity to epoxy cyclohexane

was even higher for the immobilized POM than with the homogeneous one (94 vs. 81%, Table 3).

Table 3. Alkene epoxidation with H_2O_2 over $AsW_9-P(O)COOH$ - and $PW_9-As(O)NH_2$ -based catalysts.

Catalyst	Substrate/Conversion, %	Epoxide Selectivity, %
$AsW_9-P(O)COOH$		96
$AsW_9-P(O)COOH@SBA-NH_2$		>99
$PW_9-As(O)NH_2$		76
$PW_9-As(O)NH_2@SBA-COOH$		97
$AsW_9-P(O)COOH@MCF-NH_2$		>99
$AsW_9-P(O)COOH$		19
$AsW_9-P(O)COOH@SBA-NH_2$		41
$AsW_9-P(O)COOH$		73
$AsW_9-P(O)COOH@SBA-NH_2$		81
		75
		94

The covalent immobilization methodology was further amended using cross-linking agents that are able to form specific covalent bonds with both a surface and the desired molecule. The hybrid derivative of a heteropolytungstate with two aniline groups, $(Bu_4N)_3[NaHPW_9O_{34}\{As(O)C_6H_4-p-NH_2\}_2]$ was post-functionalized by 1,4-phenylene diisothiocyanate and then covalently grafted onto the surface of an amino-functionalized SBA-15 via formation of thiourea bonds [162]. The formation of thiourea link was confirmed by ^{13}C CP-MAS NMR spectroscopy, whereas the dispersion of POM along the channels of the SBA-15 support, without the formation of large aggregates, was corroborated by HR-TEM. The catalytic behavior of the grafted catalyst was tested in a model reaction of cyclooctene epoxidation with H_2O_2 . However, the immobilization of POM has led to a deterioration of the catalytic performance, most likely caused by the steric hindrance around the active site.

Kozhevnikov and co-workers elaborated an immobilization technique of POM binding onto the surface of a phosphazene (RPN, R = benzyl, iso-butyl, or iso-propyl) functionalized silica via alkylaminocyclophosphazene tethers, which could potentially prevent POM from leaching [163]. The POM/RPN- SiO_2 (POM = $[PW_{12}O_{40}]^{3-}$ or $[PMo_{12}O_{40}]^{3-}$) catalysts were active in the oxidative desulfurization of benzothiophenes with H_2O_2 in a heptane- H_2O reaction medium, and $PMo_{12}/BzPN-SiO_2$ exhibited higher activity than homogeneous $PMo-BzPN$ counterpart.

Liu et al. grafted poly(glycidyl methacrylate) (PGMA) onto the surface of SiO_2 to prepare ‘hairy’ PGMA/ SiO_2 particles, which were further used for the covalent binding of the amino-modified vacant Wells-Dawson POM $[\alpha-P_2W_{17}O_{61}]^{10-}$ (P_2W_{17}) [164]. The resulting P_2W_{17} -PGMA/ SiO_2 material catalyzed oxidative desulfurization of tetrahydrothiophene with H_2O_2 (100% conversion after 60 min) behaved as a truly heterogeneous catalyst, according to the filtration experiment, and could be reused at least five times with the retention of its activity and structure.

While covalently bound POMs usually reveal superior stability to leaching, their activity is typically lower, relative to the homogeneous counterparts. Another shortcoming is associated with synthetic difficulties of covalent derivatization of many catalytically interesting POMs.

2.5. Encapsulation within Supramolecular Complexes

Surfactant-encapsulated polyoxometalates (SEPs) can be formed by exchanging counterions in POMs with cationic surfactants. Depending on the surfactant nature, the resulting SEPs can be soluble in traditional organic solvents acting as homogeneous catalysts or behave as heterogeneous catalysts. Amphiphilic POM-based, well-defined, and robust nanowires and nanotubes (the assembly shape depends on the nature of the encapsulating molecules) constructed by self-assembly of units consisting of POMs encapsulated by

single-chain surfactant molecules (Figure 6) can provide an optimal catalytic environment, acting as a dual trapping catalyst [165]. The hydrophobic long alkyl chains on the surface of POM cluster adsorb the weakly polar sulfide molecules, where they are oxidized to sulfones by an active peroxo-POM-complex and then easily escape because of their polarity. The POM–amphiphile units constructed of phosphotungstic acid and a series of surfactants varying in alkyl chain length (dodecyltrimethylammonium (DDA), tetradecyltrimethylammonium, hexadecyltrimethylammonium, and octadecyltrimethylammonium) catalyzed oxidation of dibenzothiophene into corresponding sulfone with 100% selectivity at complete conversions (20–40 min, 50 °C) [165]. After the oxidation reaction, the catalyst could be recovered by filtration or centrifugation and reused with retention of the mesomorphology and catalytic properties. The ^{31}P NMR investigations of the reaction solutions indicated no leaching of the active species.

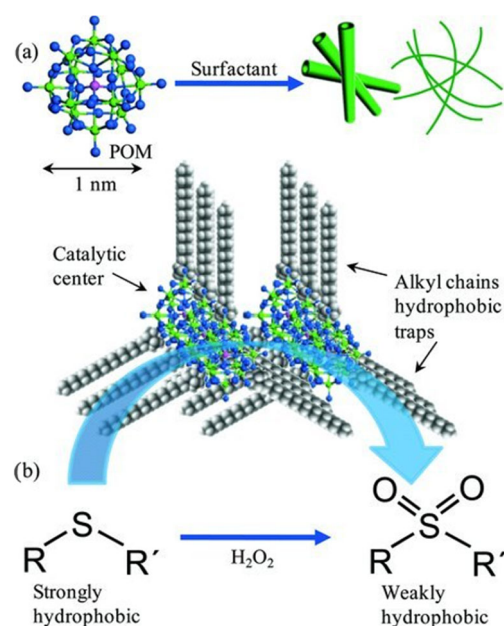


Figure 6. Schematic representation of preparation of (a) surfactant-encapsulated POM semitube and wire assemblies and (b) oxidation of sulfides to sulfones. Reproduced from ref. [165] with permission of WILEY-VCH Verlag GmbH and Co. KGaA, Weinheim. Copyright 2011.

Song and co-workers have prepared a series of amphiphilic lanthanide-containing POMs ($[\text{LnW}_{10}\text{O}_{36}]^{9-}$, Ln = La, Ce, Y, Nd, Sm, Eu, Gd, Tb, Yb) by surfactant encapsulation using surfactants varying in alkyl chain lengths (DDA, trimethylstearylammmonium, and dimethyldioctadecylammmonium (DODA)) and tested the catalytic activity of the new SEPs in ODS reactions using H_2O_2 [166]. $(\text{DDA})_9\text{LaW}_{10}$ in combination with $[\text{omim}]\text{PF}_6$ (omim = 1-octyl-3-methyl-imidazolium) as a sulfone extractant exhibited 100% DBT conversion in 14 min under mild conditions (30 °C, O/S = 5).

An interesting POM immobilization strategy involving both covalent and non-covalent interactions has been developed by Wu and co-workers [54,167–170]. The concept involves the surfactant encapsulation of POM via replacing its counter ions by quaternary ammonium cations (di(11-hydroxyundecyl)dimethylammmonium (DOHDA), DODA, or didodecyldimethylammmonium) through electrostatic interactions, thus forming a structure similar to that of a reverse micelle system (Figure 7).

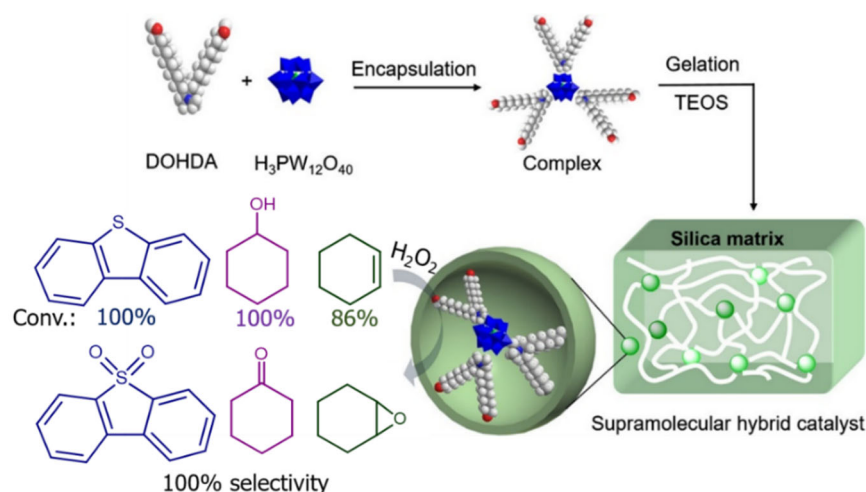


Figure 7. Schematic representation of preparation of supramolecular hybrid catalyst assembled on the basis of PW_{12} and DOHDA and its catalytic performance in H_2O_2 -based oxidations. Adapted from ref. [54] with permission of Elsevier Inc. Copyright 2017.

The resulting hybrid species can then be covalently fixed within a silica gel matrix through sol–gel condensation with tetraethyl orthosilicate. Such immobilized supramolecular hybrid catalysts possess a defined hydrophobic environment to capture the organic substrate, which could potentially maximize the catalytic efficiency. The supramolecular hybrid catalyst based on PW_{12} polyanion and DOHDA cation was active in a range of H_2O_2 -based selective oxidations [169]. Thus, DBT gave the corresponding sulfone as the sole product. By analyzing 1H NMR spectra of DBT in the presence of pure silica, surfactant-encapsulated POM species, and the resulting hybrid catalyst, the authors have concluded that hydrophobic nano-environments around the POM in the catalyst tend to capture the substrates of low polarity (sulfides) and release the polar oxidized product–sulfone. The structural integrity of the developed hybrid material under turnover conditions was confirmed by ^{31}P NMR, IR, and XPS measurements along with elemental analysis data. Moreover, the catalytic activity of the recovered catalyst was as high as that of the freshly prepared one for at least five consecutive runs. The elaborated hybrid catalyst was also active in epoxidation of cyclohexene with nearly 100% selectivity to the corresponding epoxide at 86% substrate conversion and revealed the complete oxidation of cyclohexanol to cyclohexanone [169].

Following the same methodology, Wu and co-workers synthesized chiral complexes via the electrostatic interaction of a catalytically efficient sandwich POM, $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ and a new cationic surfactant bearing chiral head, which were further covalently immobilized into the silica matrix using a sol–gel procedure [171]. The supramolecular chirality around the POM made possible kinetic resolution of racemic alcohols via catalytic oxidation with H_2O_2 .

Nogueira et al. prepared a composite material based on a cross-linked organic/inorganic hybrid core composed by the mono-substituted POM $[PW_{11}Zn(H_2O)O_{39}]^{5-}$ ($PW_{11}Zn$) and amine-organosilane (aptes) surrounded by a silica shell [172]. The resulting $PW_{11}Zn$ -aptes@ SiO_2 composite catalyzed the selective epoxidation of cyclooctene and geraniol, as well as oxidative desulfurization of a model oil with H_2O_2 , and the catalytic performance of the immobilized POM was similar to that of homogeneous $PW_{11}Zn$ counterpart. Despite the fact that elemental analysis has shown the leaching of ca. 6% of the initial POM amount during an ODS run, the experiment with catalyst filtration confirmed the true heterogeneous nature of the observed catalysis.

If a charge transfer (CT) complex is employed for POM encapsulation, the resulting composite material can exhibit properties of a photothermal catalyst. Wu and co-workers synthesized a series of on-site heating catalytic composites through the electrostatic complexation of a cationic CT-complex with 3,3',5,5'-tetramethylbenzidine (TMB) bearing

strong NIR absorption and a range of Keggin polyanions ($\text{PMo}_{10}\text{V}_2$, PMo_{11}V , PW_{11}V , and PMo_{12}) [173]. The resulting assembled materials displayed an integrated NIR photothermal effect and enhanced catalytic activity in the mild oxidation of toluene and its derivatives, as well as alkenes and organic sulfides with H_2O_2 [173]. Under NIR radiation, a substrate conversion increased ca. 25%, relative to the external heating. The CT complex plays the role of a local heater attaching to the POM catalyst, which enhances the catalytic reaction efficiency, while itself does not join the catalytic process. Filtration tests confirmed heterogeneous nature of the catalysis over $\text{PMo}_{10}\text{V}_2@\text{TMB}_{\text{CT}}$, and besides, no increased conversion was detected in the filtrate, even under the external heating to 55 °C. The $\text{PMo}_{10}\text{V}_2@\text{TMB}_{\text{CT}}$ catalyst could be successfully recycled with retention of its structure, as confirmed by FT-IR and UV-Vis-NIR spectroscopy.

2.6. Immobilization on Carbon Materials

The entrapping of POMs inside the pores of activated carbons was first reported by Izumi and Urabe [174]. Later on, Van Bekkum et al. showed that the carbon nature and the activation method strongly affect the strength of adsorption and amount of adsorbed heteropolyacids [175]. A summary of the early literature on this topic can be found in the book chapter by Hill and Kholdeeva [38].

The mesoporous carbon Sibunit was found to be one of the best carbon supports that enabled strong irreversible adsorption of catalytically active POMs with retention of their structure and catalytic properties [65]. The use of Sibunit as a carrier made it possible to prepare catalysts that remained stable toward POM leaching, even if highly polar products, such as carboxylic acids, were formed in the reaction [65]. However, the main disadvantage of POM/Sibunit catalysts was their poor reusability caused by strong adsorption of oxidation products, which cannot be removed from the catalyst surface by washing, extraction, or evacuation [65,176].

In recent years, carbon nanomaterials (CNMs) have received great attention for the preparation of hybrid inorganic materials for energy storage and conversion, electronic and optic sensors, and catalysis [177–180]. The immobilization of POM on CNMs was accomplished using electrostatic [181–184] and π - π [185] interactions, as well as covalent binding [180,186].

Hybrid materials based on POMs and CNMs have been widely used in electrocatalysis and energy storage applications [181,182,184–190]. In recent years, such materials have also attracted attention as selective oxidation catalysts [176,183,191–196]. Salavati et al. reported POM immobilization by a one-step solid-state reaction of a sodium salt of $\text{PMo}_{10}\text{V}_2$ with multiwall carbon nanotubes (MWCNTs) [192]. The resulting materials catalyzed oxidation of a range of alkenes by H_2O_2 with selectivity to the corresponding epoxides of 58–100% at 47–80% conversions. The catalyst maintained its catalytic properties for at least four reuses, despite some leaching of vanadium during the reaction. A catalyst prepared by the deposition of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ on CNTs was used for the oxidative removal of DBT, with a desulfurization efficiency of up to 100%; however, no information on POM leaching was provided [193].

The functionalization of CNMs provides additional opportunities for the immobilization of active complexes, including POMs. Hajian and Alghour have developed a hybrid catalyst, following a sequence of MWCNT modifications [191]. Carboxylic acid-tailored MWCNTs (MWCNT-COOH) were first functionalized with thionyl chloride and then with 1-(3-aminopropyl) imidazole, followed by the reaction with 1-bromobutan (APIB) and the subsequent addition of tetrabutylammonium salt of $[\text{PZnMo}_2\text{W}_9\text{O}_{39}]^{5-}$ (ZnMo_2W_9). Imidazolium (Im) groups present on the support bound the POM electrostatically. The resulting hybrid $\text{ZnMo}_2\text{W}_9/\text{MWCN-APIB}$ exhibited high activity and selectivity in the oxidation of various alcohols, with H_2O_2 producing corresponding aldehydes. Although noticeable leaching was observed only during the first two reuses, catalytic activity staidly decreased during seven consecutive runs. Another group used Im-based ionic liquids to modify the surface of amphiphilic graphene oxide (GO) for the immobilization of PW_{12}

via anion exchange [197]. The Im-PW₁₂/GO material catalyzed oxidation of a range of alcohols with H₂O₂, while the hot catalyst filtration test confirmed the heterogeneous nature of catalysis.

Masteri-Farahani and Modarres immobilized PW₄ through electrostatic interaction with the surface of graphene oxide modified with cysteamine hydrochloride as a linking agent [198]. The resulting PW₄/GO catalyst was active in H₂O₂-based oxidation of alkenes and allylic alcohols with selectivity to the corresponding epoxides >99%. Moreover, the catalyst could be readily recovered by centrifugation and reused for at least five runs, without a significant decrease in activity. The catalyst filtration experiment exhibited almost no activity in the filtrate after the separation of the catalyst from the reaction mixture, approving the high stability of the PW₄/GO catalyst to leaching and heterogeneous nature of catalysis. No PW₄ species were detected in the solution by means of ICP-OES.

Gan et al. modified carbonized cellulose nanofiber (CCNF) with polyethyleneimine and γ -(2,3-epoxypropoxy)propyltrimethoxysilane, in order to load it with K₄[β -SiMo₃W₉O₄₀] $\cdot$ 5H₂O [199]. The resulting POM/CCNF material was active in ODS reactions: the removal efficiency of DBT, benzothiophene, and 4,6-dimethyldibenzothiophene was 99, 89, and 100%, respectively, while using model oils with the initial sulfur concentration of 2000 ppm. Recycling experiments have shown that the POM/CCNF catalyst kept its activity for at least three consecutive runs.

Wang and co-workers used a 'click reaction' between the azido group of K_{1.5}Cs_{5.5}[γ -SiW₁₀O₃₉Cu₂(N₃)₂] (SiW₁₀Cu₂(N₃)₂) and the alkynyl groups on functionalized graphene for covalent immobilization of POM [200]. The SiW₁₀Cu₂/GO catalyst exhibited excellent activity in the oxidation of toxic 2-chloroethyl ethyl sulfide (mustard simulant) to much less toxic sulfoxide, with 100% selectivity at complete conversion, and it could be reused at least 10 times without losing catalytic properties. Experiment with catalyst filtration during the course of the reaction confirmed the heterogeneous nature of catalysis, while ²⁹Si MAS NMR along with TEM measurements corroborated retention of the catalyst original structure and morphology after the oxidation reaction.

The doping of carbon nanomaterials with nitrogen in the process of their synthesis leads to the formation of different types of surface N-species (pyridine-like, pyrrole-like, or quaternary ones), which afford supplementary opportunities for immobilization of catalytically active complexes and may also affect the hydrophilic properties of the supported catalysts [201–203]. Evtushok et al. first reported the use of N-CNMs for immobilization of POM [176]. The di-V-substituted γ -Keggin phosphotungstate [γ -PW₁₀O₃₈V₂(μ O)(μ -OH)]^{4−} (γ -PW₁₀V₂) was immobilized on bamboo-like N-doped carbon nanotubes (N-CNTs) [176] and N-doped carbon nanofibers (N-CNFs) having herring-bone packing of graphite layers [195] by adsorption from acetonitrile. Undoped CNTs were also used for comparison. It was shown that the presence of nitrogen is necessary to ensure the strong attachment and quasi-molecular dispersion of the POM on the carbon surface, which, in turn, affects the catalytic behavior and catalyst stability under turnover conditions. Other key factors that favor the successful and maximum adsorption of POM are pre-drying of the supports and addition of mineral acid. The addition of acid makes possible irreversible binding of γ -PW₁₀V₂ to the surface with retention of the POM structure and catalytic properties. Using an optimal catalyst PW₁₀V₂/N-CNTs (15 wt.% POM, 1.8 at.% N), 2,3,6-trimethylphenol (TMP) was oxidized with H₂O₂ to afford trimethyl-*p*-benzoquinone (TMBQ, vitamin E precursor) in a nearly quantitative yield and with 80% oxidant utilization efficiency, retaining characteristics of homogeneous γ -PW₁₀V₂ (Figure 8). It is noteworthy that γ -PW₁₀V₂ requires retention of its structure and protonation state to perform heterolytic activation of H₂O₂ [204]. The first attempts of the immobilization of γ -PW₁₀V₂ onto commercially available Fe₂O₃ led to catalysts that were stable in a 1:1 mixture of EtOAc/*t*BuOH, but lost POMs in CH₃CN [205]. Immobilization using other approaches, such as embedding into silica, electrostatic attachment to amine-modified SiO₂ or MIL-101, and adsorption on Sibunit, resulted in a pronounced decrease in catalytic activity and selectivity of γ -PW₁₀V₂ (Figure 8), which demonstrated the significant leach-

ing of POM, leading to high contribution of homogeneous catalysis (γ -PW₁₀V₂@SiO₂), or revealed poor recyclability (γ -PW₁₀V₂/Sibunit). The confined space inside nanotube tangles endowed the catalyst with superior activity (TOF = 500 h^{−1}) and space–time yield (450 g L^{−1} h^{−1}) [176,206]. Moreover, the catalyst did not suffer POM leaching under the turnover conditions and showed excellent recycling performance, in contrast to γ -PW₁₀V₂ immobilized on N-free CNTs.

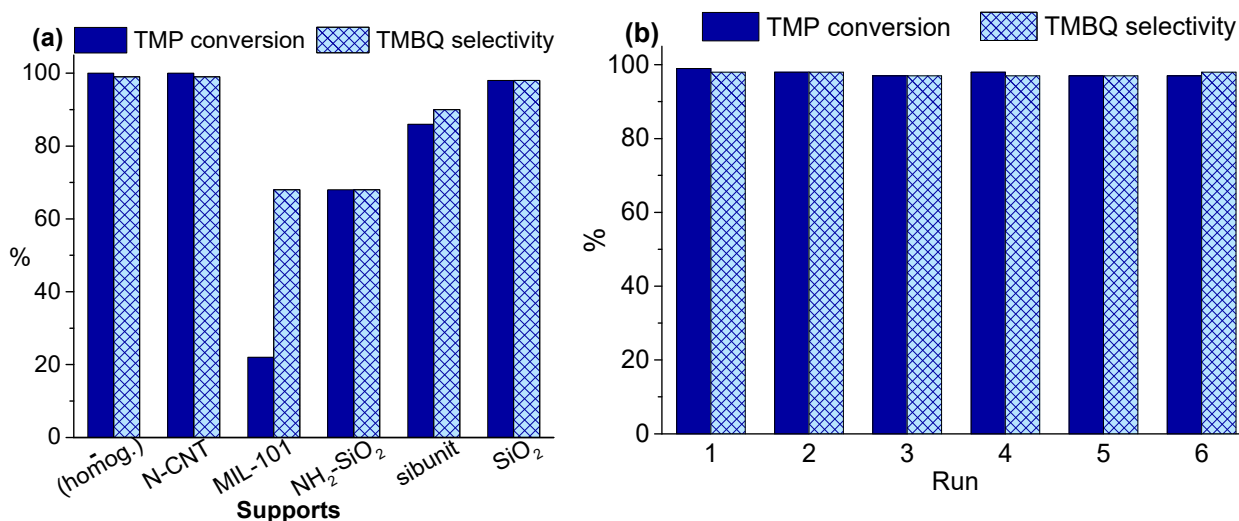
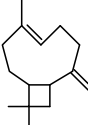


Figure 8. (a) Oxidation of TMP to TMBQ with H₂O₂ over γ -PW₁₀V₂-based catalysts. In case of POM encapsulation within SiO₂ significant POM leaching was observed. (b) Recycling of 15 wt% γ -PW₁₀V₂/N-CNTs in TMP oxidation. Adapted with permission from ref. [176]. Copyright 2018, American Chemical Society.

The scope of N-free and N-doped CNTs as supports was also explored in the immobilization of the Venturello complex PW₄ [194] and Nb-substituted Lindqvist tungstates [Nb(L)W₅O₁₈]^{n−} (Nb(L)W₅, L = O, OCH₃, (O)₂ or OOH) and [(NbW₅O₁₈)₂O]^{4−} ((NbW₅)₂O) [196]. In contrast to the immobilization of γ -PW₁₀V₂, neither N-doping nor acid additives were imperative to providing strong binding and quasi-molecular dispersion of PW₄ on the surface of CNTs. Moreover, N-free CNTs have proven to be even more preferable than N-CNTs as a support for PW₄ and the Lindqvist Nb-POM because, in contrast to N-CNTs, they are inert for H₂O₂ unproductive decomposition and, thus, enable a higher oxidant utilization efficiency. The addition of acid during the immobilization process allows the POM content in the catalyst and catalytic activity to be increased, but acidity may be objectionable for product selectivity. In the oxidation of cyclohexene and other acid-sensitive alkenes, acidity deteriorates epoxide selectivity because of epoxide-ring opening and overoxidation processes, whereas selectivity to the sum of heterolytic oxidation products remains high (Table 4). On the contrary, a marked improvement in sulfoxide selectivity and yield is observed for the thioether oxidation (Figure 9), most likely due to an increased electrophilicity of the active peroxy species, which favors sulfoxidation and disfavors subsequent oxidation to sulfone [57,194,207,208]. The catalyst 15 wt.% PW₄/CNTs prepared using 2 equiv. of HClO₄ was effective and truly heterogeneous for the epoxidation of cyclooctene, which is not an acid-sensitive substrate, and sulfoxidation of various thioethers, but the catalytic activity gradually decreased during recycling. The deactivation was, most likely, caused by the loss of catalyst acidity and/or diffusion of PW₄ inside the inner channels of CNT (the latter could be observed in HR-TEM images [194]). The scope of the acid-free catalyst 5 wt.% PW₄/CNTs for alkene epoxidation was broader (Table 4), and it did not lose activity after reuse. Dimethyl carbonate was the solvent of choice in terms of catalyst activity and stability to POM leaching.

Table 4. Alkene oxidation with H₂O₂ in the presence of CNT-supported POMs.

POM	Support	H ⁺ Added, Equiv. ^a	Substrate	Substrate Conv. %	Epoxide Selectivity, % ^b	Ref.
PW ₄	CNTs	0.2		66	79	[194]
PW ₁₀ V ₂ ^c	CNTs	0		82	79 (100)	[195]
HNb(O ₂)W ₅	CNTs	0		32	39 (93)	[196]
HNb(O ₂)W ₅	CNTs	2		59	15 (90)	[196]
HNb(O ₂)W ₅	N-CNTs	2		30	23 (81)	[196]
PW ₄	CNTs	2		93	97	[194]
HNb(O ₂)W ₅	CNTs	2		94	98	[196]
HNb(O ₂)W ₅	N-CNTs	2		70	97	[196]
PW ₄	CNTs	2		100	65	[194]
HNb(O ₂)W ₅	CNTs	2		100	55 (100)	[196]
HNb(O ₂)W ₅	CNTs	0		100	60 (99)	[196]
PW ₄	CNTs	0		50	80	[194]
HNb(O ₂)W ₅	CNTs	2		80	25 (77)	[196]
PW ₄	CNTs	0		85	85	[194]
HNb(O ₂)W ₅	CNTs	0		80	67 (94)	[196]

^a The amount of HClO₄ relative to POM added during the catalyst preparation. ^b In parentheses, total selectivity for heterolytic oxidation products (corresponding epoxide+diol and products of their further oxidation, diepoxide and ketol). ^c Hot catalyst filtration test along with ICP-OES analysis of the filtrate indicated some leaching of the active vanadium species.

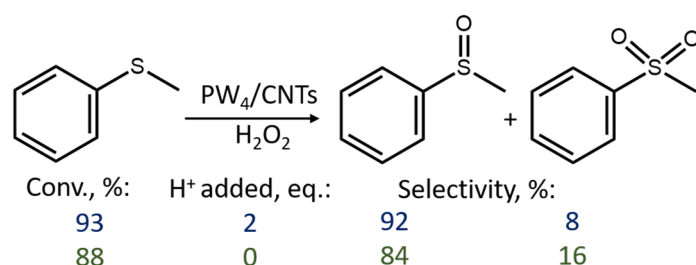


Figure 9. Oxidation of methyl phenyl sulfide with H₂O₂ in the presence of PW₄/CNTs catalysts differed in the amount of HClO₄ added during the catalyst preparation. Adapted from ref. [194]. Copyright 2019, Creative Commons Attribution License (CC BY).

The immobilization of the Lindqvist-type Nb-POM onto the surface of both CNTs and N-CNT enabled stabilization of the most reactive monomeric form Nb(OH)W₅, thus preventing its dimerization and subsequent deactivation [196]. As a result, (N)-CNTs-supported Nb(L)W₅ exhibited higher catalytic activity than their homogeneous counterparts. The addition of acid upon the immobilization increased the Nb-POM loading [196] and, moreover, facilitated the formation of active hydroperoxo species Nb(OOH)W₅ responsible for the heterolytic oxygen transfer to C=C bond of alkene [207]. Similar to γ-PW₁₀V₂, N-doping facilitated a quasi-molecular dispersion of Nb(L)W₅ on the surface, but it also favored unproductive decomposition of H₂O₂, thereby leading to the worsening of the catalytic performance in terms of alkene conversion and epoxide selectivity (see Table 4). Therefore, the use of undoped CNTs for the preparation of epoxidation catalysts seems to be advantageous.

Importantly, CNT-supported PW₄ and Nb(L)W₅ did not suffer from POM leaching if dimethylcarbonate was employed as solvent and demonstrated a truly heterogeneous nature of the catalysis and excellent recycling performance [57,194,196].

3. Conclusions

Polyoxometalates have great potential as catalysts for the liquid-phase selective oxidation of organic compounds using green oxidants, in particular, dilute hydrogen peroxide. During the last decade, some new highly active and selective POM catalysts have been discovered, and various approaches have been proposed for POM immobilization on solid supports to make easy catalyst separation and recycling possible. The most developed and prospective methodologies that enable the strong binding of POM to the surface and preventing leaching into the solution involve POM immobilization by means of different types of chemical bonding and supramolecular interactions. The proper choice of the POM, support, and immobilization method depends on the type of oxidative transformation and may also depend on the nature of the organic substrate and target oxidation product.

MOFs are ‘smart’ supports that can enhance catalytic properties of POMs by different synergetic effects; however, the reaction conditions, especially in the case of oxidation with aqueous H_2O_2 , should be properly controlled, in order to keep the structure of MOF within its stability limit. The organic/inorganic hybrid derivatives of POMs are a new class of catalysts that offer an undisputable advantage of ability to covalent bonding using different linking strategies with an excellent dispersion along the surface of an inorganic support and with the retention of the catalytic properties. However, synthetic difficulties for derivatization of some POMs may be a shortcoming of this approach. Encapsulation within the supramolecular complexes may provide an optimized catalytic environment based on dual polar properties. Moreover, if a charge transfer complex is employed for POM encapsulation, the resulting composite material can exhibit properties of a photothermal catalyst. For those POMs, which require retention of the structure coupled with the specific protonation state to keep catalytic activity, the best choice might be use of carbon-based nanomaterials, in particular, carbon nanotubes. A blend of electrostatic forces and hydrogen bonding ensures the excellent stability and recyclability of the CNTs-supported POM catalysts, while a balance between the activity and selectivity can be tuned through the careful control of the amount of acid added during the POM immobilization.

So far, most of the elaborated supported POM catalysts were evaluated for the selective oxidation of S-compounds, olefins, phenols, and alcohols to produce sulfoxides, sulfones, epoxides, diols, quinones, aldehydes, ketones, and a few highly efficient catalyst systems have been suggested. However, the potential of immobilized POMs for the selective oxidation of alkanes and aromatics still remains very little explored. The development of supported POM catalysts for oxidative cleavage of C=C and C–C bonds and production of highly polar products—carboxylic and dicarboxylic acids—continues to be a challenge for oxidation catalysis researchers and POM chemists.

Author Contributions: Writing—review and editing, O.A.K. and N.V.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research was partially funded by the Ministry of Science and Higher Education of the Russian Federation within the governmental order for the Boreskov Institute of Catalysis (project AAAA-A21-121011390008-4).

Data Availability Statement: Not applicable. Refer to the original papers for data availability.

Acknowledgments: The authors thank all co-authors of the joint papers published on H_2O_2 -based selective oxidation catalysis by supported polyoxometalates.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

AA: adipic acid; APIB, 1-bromobutan; aptes, (3-aminopropyl)triethoxysilane; AsW9-P(O)COOH, $(^t\text{Bu}_4\text{N})_3\text{NaH}[\text{As}^{\text{III}}\text{W}_9\text{O}_{33}\{\text{P}(\text{O})(\text{CH}_2\text{CH}_2\text{CO}_2\text{H})_2\}_2]$; BMIM, 1-butyl-3-methylimidazolium; CCNF, carbonized cellulose nanofiber; CNMs, carbon nanomaterials; Co-PMo₁₂, CoHPMo₁₂O₄₀; Co₄(PW₉)₂, $[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$; CT, charge

transfer; DBT, dibenzothiophene; DDA, dodecyltrimethylammonium; DODA, dimethyldioctadecylammonium; DOHDA, di(11-hydroxyundecyl)dimethylammonium; EISA, evaporation-induced self-assembly; (EtO)₃Si-ILs-C₈, 1-octyl-3-(3-triethoxy-silylpropyl)-4,5-dihydroimidazolium hexafluorophosphate; EuW₁₀, [Eu(W₅O₁₈)₂]^{9−}; Eu(PW₁₁)₂, [Eu(PW₁₁O₃₉)₂]^{11−}; GO, graphene oxide; Im, imidazolium; LaW₁₀, [LaW₁₀O₃₆]^{9−}; Mg₃Al-NO₃, [Mg_{0.75}Al_{0.25}(OH)₂](NO₃)_{0.25}·2H₂O; mim, 3-methyl imidazolium; MOFs, metal-organic frameworks; MWCNTs, multiwall carbon nanotubes; Nb(L)W₅, [Nb(L)W₅O₁₈]^{n−}; (NbW₅)₂O, [(NbW₅O₁₈)₂O]^{4−}; N-CNFs, N-doped carbon nanofibers; N-CNTs, N-doped carbon nanotubes; ODS, oxidative desulfurization; omim, 1-octyl-3-methyl-imidazolium; PGMA, poly(glycidyl methacrylate); PIILPs, polymer immobilized ionic liquid phase; PMo₁₂, [PMo₁₂O₄₀]^{3−}; PMo₁₀V₂, [PMo₁₀V₂O₄₀]^{5−}; PMo₁₁V, [PMo₁₁VO₄₀]^{4−}; POMs, polyoxometalates; PW₄, [PO₄{WO(O₂)₂}]₄^{3−}; PW₉, [A-PW₉O₃₄]^{9−}; PW₉-As(O)NH₂, (tBu₄N)₄H[PW₉O₃₄{As(O)(C₆H₄NH₂)₂}]₂; PW₁₁Ti, [PW₁₁TiO₄₀]^{5−}; PW₁₁Zn, [PW₁₁Zn(H₂O)O₃₉]^{5−}; PW₁₂, [PW₁₂O₄₀]^{3−}; P₂W₁₇, [α-P₂W₁₇O₆₁]^{10−}; PY₁₁M, [PY₁₁MO₄₀]^{n−}; RPN (R = benzyl, iso-butyl or iso-propyl), phosphazene; SEPs, surfactant-encapsulated polyoxometalates; SiW₁₀Cu₂(N₃)₂, K_{1.5}Cs_{5.5}[γ-SiW₁₀O₃₉Cu₂(N₃)₂]; Tb(PW₁₁)₂, [Tb(PW₁₁O₃₉)₂]^{11−}; THT, tetrahydrothiophene; TMB, 3,3',5,5'-tetramethylbenzidine; TMP, 2,3,6-trimethylphenol; TMBQ, trimethyl-*p*-benzoquinone; γ-XW₁₀V₂ (X = P, Si), [γ-XW₁₀O₃₈V₂(μ-O)(μ-OH)]^{n−}; ZnMo₂W₉, [PZnMo₂W₉O₃₉]^{5−}.

References

- Sheldon, R.; Arends, I.W.C.E.; Hanefeld, U. *Green Chemistry and Catalysis*; Wiley VCH: Weinheim, Germany, 2007.
- Clerici, M.G.; Kholdeeva, O.A. (Eds.) *Liquid Phase Oxidation via Heterogeneous Catalysis: Organic Synthesis and Industrial Applications*; Wiley: Hoboken, NJ, USA, 2013.
- Duprez, D.; Cavani, F. (Eds.) *Handbook of Advanced Methods and Processes in Oxidation Catalysis*; Imperial College Press: London, UK, 2014.
- Jones, C.W. *Application of Hydrogen Peroxide and Derivatives*; Royal Society of Chemistry: Cambridge, UK, 1999.
- Strukul, G. (Ed.) *Catalytic Oxidations with Hydrogen Peroxide as Oxidant*; Kluwer: Dordrecht, The Netherlands, 1992.
- Strukul, G.; Scarso, A. Environmentally benign oxidants. In *Liquid Phase Oxidation via Heterogeneous Catalysis: Organic Synthesis and Industrial Applications*; Clerici, M.G., Kholdeeva, O.A., Eds.; Wiley: Hoboken, NJ, USA, 2013; pp. 1–20.
- Strukul, G.; Menegazzo, F. (Eds.) Catalysts 2019, Special Issue on Direct Synthesis of Hydrogen Peroxide. Available online: https://www.mdpi.com/si/catalysts/hydrogen_peroxide (accessed on 10 December 2022).
- Campos-Martin, J.M.; Blanco-Brieva, G.; Fierro, J.L.G. Hydrogen peroxide synthesis: An outlook beyond the anthraquinone process. *Angew. Chem. Int. Ed.* **2006**, *45*, 6962–6984. [CrossRef] [PubMed]
- Edwards, J.K.; Freakley, S.J.; Lewis, R.J.; Pritchard, J.C.; Hutchings, G.J. Advances in the direct synthesis of hydrogen peroxide from hydrogen and oxygen. *Catal. Today* **2015**, *248*, 3–9. [CrossRef]
- Ciriminna, R.; Albanese, L.; Meneguzzo, F.; Pagliaro, M. Hydrogen peroxide: A key chemical for today's sustainable development. *ChemSusChem* **2016**, *9*, 3374–3381. [CrossRef]
- Ranganathan, S.; Sieber, V. Recent advances in the direct synthesis of hydrogen peroxide using chemical catalysis—A review. *Catalysts* **2018**, *8*, 379. [CrossRef]
- Menegazzo, F.; Signoretti, M.; Ghedini, E.; Strukul, G. Looking for the “dream catalyst” for hydrogen peroxide production from hydrogen and oxygen. *Catalysts* **2019**, *9*, 251. [CrossRef]
- Taramasso, M.; Perego, G.; Notari, B. Preparation of Porous Crystalline Synthetic Material Comprised of Silicon and Titanium Oxides. US Patent Application 4 410 501, 18 December 1983.
- Clerici, M.G.; Domine, M.E. Oxidation reactions catalyzed by transition-metal-substituted zeolites. In *Liquid Phase Oxidation via Heterogeneous Catalysis: Organic Synthesis and Industrial Applications*; Clerici, M.G., Kholdeeva, O.A., Eds.; Wiley: Hoboken, NJ, USA, 2013; pp. 21–126.
- Romano, U.; Ricci, M. The hydroxylation of phenol to hydroquinone and catechol. In *Liquid Phase Oxidation via Heterogeneous Catalysis: Organic Synthesis and Industrial Applications*; Clerici, M.G., Kholdeeva, O.A., Eds.; Wiley: Hoboken, NJ, USA, 2013; pp. 451–462.
- Rivetti, F.; Buzzoni, R. The greening of nylon: The ammoximation process. In *Liquid Phase Oxidation via Heterogeneous Catalysis: Organic Synthesis and Industrial Applications*; Clerici, M.G., Kholdeeva, O.A., Eds.; Wiley: Hoboken, NJ, USA, 2013; pp. 462–474.
- Forlin, A.; Bergamo, M.; Lindner, J. Production of propylene oxide. In *Liquid Phase Oxidation via Heterogeneous Catalysis: Organic Synthesis and Industrial Applications*; Clerici, M.G., Kholdeeva, O.A., Eds.; Wiley: Hoboken, NJ, USA, 2013; pp. 474–496.
- Cavani, F.; Teles, J.H. Sustainability in catalytic oxidation: An alternative approach or a structural evolution? *ChemSusChem* **2009**, *2*, 508–534. [CrossRef] [PubMed]

19. Xiao, F.-S. Ordered mesoporous materials with improved stability and catalytic activity. *Top. Catal.* **2005**, *35*, 9–24. [[CrossRef](#)]
20. Kholdeeva, O.A.; Mel'gunov, M.S.; Shmakov, A.N.; Trukhan, N.N.; Kriventsov, V.V.; Zaikovskii, V.I.; Malyshev, M.E.; Romannikov, V.N. A new mesoporous titanium-silicate Ti-MMM-2: A highly active and hydrothermally stable catalyst for H₂O₂-based selective oxidations. *Catal. Today* **2004**, *91–92*, 205–209. [[CrossRef](#)]
21. Ivanchikova, I.D.; Kovalev, M.K.; Mel'gunov, M.S.; Shmakov, A.N.; Kholdeeva, O.A. User-friendly synthesis of highly selective and recyclable mesoporous titanium-silicate catalysts for the clean production of substituted p-benzoquinones. *Catal. Sci. Technol.* **2014**, *4*, 200–207. [[CrossRef](#)]
22. Kholdeeva, O.A. Selective oxidations catalyzed by mesoporous metal silicates. In *Liquid Phase Oxidation via Heterogeneous Catalysis: Organic Synthesis and Industrial Applications*; Clerici, M.G., Kholdeeva, O.A., Eds.; Wiley: Hoboken, NJ, USA, 2013; pp. 127–219.
23. Kholdeeva, O.A. Recent developments in liquid-phase selective oxidation using environmentally benign oxidants and mesoporous metal silicates. *Catal. Sci. Technol.* **2014**, *4*, 1869–1889. [[CrossRef](#)]
24. Bisio, C.; Carniato, F.; Guidotti, M. The control of the coordination chemistry for the genesis of heterogeneous catalytically active sites in oxidation reactions. *Angew. Chem. Int. Ed.* **2022**, *61*, e202209894. [[CrossRef](#)] [[PubMed](#)]
25. Guidotti, M.; Batonneau-Gener, I.; Gianotti, E.; Marchese, L.; Mignard, S.; Psaro, R.; Sgobba, M.; Ravasio, N. The effect of silylation on titanium-containing silica catalysts for the epoxidation of functionalised molecules. *Micropor. Mesopor. Mater.* **2008**, *111*, 39–47. [[CrossRef](#)]
26. Guidotti, M.; Psaro, R.; Batonneau-Gener, I.; Gavrilo, E. Heterogeneous catalytic epoxidation: High limonene oxide yields by surface silylation of Ti-MCM-41. *Chem. Eng. Technol.* **2011**, *34*, 1924–1927. [[CrossRef](#)]
27. Gallo, A.; Tiozzo, C.; Psaro, R.; Carniato, F.; Guidotti, M. Niobium metallocenes deposited onto mesoporous silica via dry impregnation as catalysts for selective epoxidation of alkenes. *J. Catal.* **2013**, *298*, 77–83. [[CrossRef](#)]
28. Ivanchikova, I.D.; Maksimchuk, N.V.; Skobelev, I.Y.; Kaichev, V.V.; Kholdeeva, O.A. Mesoporous niobium-silicates prepared by evaporation-induced self-assembly as catalysts for selective oxidations with aqueous H₂O₂. *J. Catal.* **2015**, *332*, 138–148. [[CrossRef](#)]
29. Kholdeeva, O.A.; Ivanchikova, I.D.; Maksimchuk, N.V.; Skobelev, I.Y. H₂O₂-based selective oxidations: Nb(V) versus Ti(IV). *Catal. Today* **2019**, *333*, 63–70. [[CrossRef](#)]
30. Thornburg, N.E.; Thompson, A.B.; Notestein, J.M. Periodic trends in highly dispersed groups IV and V supported metal oxide catalysts for alkene epoxidation with H₂O₂. *ACS Catal.* **2015**, *5*, 5077–5088. [[CrossRef](#)]
31. Hill, C.L.; Prosser-McCarthy, C.M. Homogeneous catalysis by transition metal oxygen anion clusters. *Coord. Chem. Rev.* **1995**, *143*, 407–455. [[CrossRef](#)]
32. Neumann, R. Polyoxometalates as catalysts for oxidation with hydrogen peroxide and molecular oxygen. In *Transition Metals for Organic Synthesis*, 2nd ed.; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, Germany, 2004; Volume 2, pp. 415–426.
33. Hill, C.L. Polyoxometalates: Reactivity. In *Comprehensive Coordination Chemistry II*; Wedd, A.G., Ed.; Elsevier Science: New York, NY, USA, 2004; Volume 4, pp. 679–759.
34. Pope, M.T. Polyoxo anions: Synthesis and structure. In *Comprehensive Coordination Chemistry II*; Wedd, A.G., Ed.; Elsevier Science: New York, NY, USA, 2004; Volume 4, pp. 635–678.
35. Mizuno, N.; Kamata, K.; Uchida, S.; Yamaguchi, K. Liquid-phase oxidations with hydrogen peroxide and molecular oxygen catalyzed by polyoxometalate-based compounds. In *Modern Heterogeneous Oxidation Catalysis: Design, Reactions and Characterization*; Mizuno, N., Ed.; WILEY-VCH Verlag GmbH & Co., KGaA: Weinheim, Germany, 2009; pp. 185–216.
36. Neumann, R. Activation of molecular oxygen, polyoxometalates, and liquid-phase catalytic oxidation. *Inorg. Chem.* **2010**, *49*, 3594–3601. [[CrossRef](#)]
37. Mizuno, N.; Yamaguchi, K.; Kamata, K. Epoxidation of olefins with hydrogen peroxide catalyzed by polyoxometalates. *Coord. Chem. Rev.* **2005**, *249*, 1944–1956. [[CrossRef](#)]
38. Hill, C.L.; Kholdeeva, O.A. Selective liquid phase oxidations in the presence of supported polyoxometalates. In *Liquid Phase Oxidation via Heterogeneous Catalysis: Organic Synthesis and Industrial Applications*; Clerici, M.G., Kholdeeva, O.A., Eds.; Wiley: Hoboken, NJ, USA, 2013; pp. 263–319.
39. Sun, M.; Zhang, J.; Putaj, P.; Caps, V.; Lefebvre, F.; Pelletier, J.; Basset, J.-M. Catalytic oxidation of light alkanes (C1–C4) by heteropoly compounds. *Chem. Rev.* **2014**, *114*, 981–1019. [[CrossRef](#)] [[PubMed](#)]
40. Wang, S.-S.; Yang, G.-Y. Recent advances in polyoxometalate-catalyzed reactions. *Chem. Rev.* **2015**, *115*, 4893–4962. [[CrossRef](#)] [[PubMed](#)]
41. Weinstock, I.A.; Schreiber, R.E.; Neumann, R. Dioxygen in polyoxometalate mediated reactions. *Chem. Rev.* **2018**, *118*, 2680–2717. [[CrossRef](#)]
42. Carabineiro, H.; Villanneau, R.; Carrier, X.; Herson, P.; Lemos, F.; Ribeiro, F.R.; Proust, A.; Che, M. Zirconium-substituted isopolytungstates: Structural models for zirconia-supported tungsten catalysts. *Inorg. Chem.* **2006**, *45*, 1915–1923. [[CrossRef](#)]
43. Kholdeeva, O.A. Titanium-monosubstituted polyoxometalates: Relation between homogeneous and heterogeneous Ti-single-site-based catalysis. *Top. Catal.* **2006**, *40*, 229–243. [[CrossRef](#)]
44. Kholdeeva, O.A.; Maksimovskaya, R.I. Titanium- and Zirconium-monosubstituted polyoxometalates as molecular models for studying mechanisms of oxidation catalysis. *J. Mol. Catal. A Chem.* **2007**, *262*, 7–24. [[CrossRef](#)]
45. Kholdeeva, O.A. Hydrogen peroxide activation over Ti(IV): What have we learned from studies on Ti-containing polyoxometalates? *Eur. J. Inorg. Chem.* **2013**, *2013*, 1595–1605. [[CrossRef](#)]

46. Zhang, T.; Mazaud, L.; Chamoreau, L.-M.; Paris, C.; Guillemot, G.; Proust, A. Unveiling the active surface sites in heterogeneous titanium-based silicalite epoxidation catalysts: Input of silanol-functionalized polyoxotungstates as soluble analogues. *ACS Catal.* **2018**, *8*, 2330–2342. [\[CrossRef\]](#)
47. Solé-Daura, A.; Zhang, T.; Fouilloux, H.; Robert, C.; Thomas, C.M.; Chamoreau, L.-M.; Carbó, J.J.; Proust, A.; Guillemot, G.; Poblet, J.M. Catalyst design for alkene epoxidation by molecular analogues of heterogeneous titanium-silicalite catalysts. *ACS Catal.* **2020**, *10*, 4737–4750. [\[CrossRef\]](#)
48. Pope, M.T.; Müller, A. (Eds.) *Polyoxometalate Chemistry: From Topology via Self-Assembly to Applications*; Kluwer: Dordrecht, The Netherlands, 2001.
49. Kozhevnikov, I.V. *Catalysis by Polyoxometalates*; Wiley: Chichester, UK, 2002.
50. Hill, C.L. (Ed.) Special Issue on Polyoxometalates in Catalysis. *J. Mol. Catal. A Chem.* **2007**, *262*, 1–242.
51. Weinstock, I.A. (Ed.) Thematic issue on Frontiers in Metal Oxide Cluster Science. *Isr. J. Chem.* **2011**, *51*, 169–302.
52. Cronin, L.; Müller, A. (Eds.) Themed collection on Polyoxometalate Cluster Science. *Chem. Soc. Rev.* **2012**, *41*, 7325–7648.
53. Carraro, M.; Fiorani, G.; Sartorel, A.; Bonchio, M. Polyoxometalates catalysts for sustainable oxidations and energy applications. In *Handbook of Advanced Methods and Processes in Oxidation Catalysis*; Duprez, D., Cavani, F., Eds.; Imperial College Press: London, UK, 2014; pp. 586–630.
54. Wu, L. Organically encapsulated polyoxometalate catalysts: Supramolecular composition and synergistic catalysis. In *Encapsulated Catalysts*; Sadjadi, S., Ed.; Elsevier: Amsterdam, The Netherlands, 2017; pp. 1–33.
55. Kholdeeva, O.A. Recent progress in selective oxidations with hydrogen peroxide catalyzed by polyoxometalates. In *Frontiers of Green Catalytic Selective Oxidations. Green Chemistry and Sustainable Technology*; Bryliakov, K.P., Ed.; Springer: Singapore, 2019; pp. 61–91.
56. Enferadi-Kerenkan, A.; Do, T.-O.; Kaliaguine, S. Heterogeneous catalysis by tungsten-based heteropoly compounds. *Catal. Sci. Technol.* **2018**, *8*, 2257–2284. [\[CrossRef\]](#)
57. Evtushok, V.Y.; Lopatkin, V.A.; Podyacheva, O.Y.; Kholdeeva, O.A. Immobilization of polyoxometalates on carbon nanotubes: Tuning catalyst activity, selectivity and stability in H₂O₂-based oxidations. *Catalysts* **2022**, *12*, 472. [\[CrossRef\]](#)
58. Sheldon, R.A.; Wallau, M.; Arends, I.W.C.E.; Schuchardt, U. Heterogeneous catalysts for liquid-phase oxidations: Philosophers' stones or Trojan horses? *Acc. Chem. Res.* **1998**, *31*, 485–493. [\[CrossRef\]](#)
59. Izumi, Y. Recent advances in immobilization of heteropolycarboxylic acids. *Res. Chem. Intermediat.* **1998**, *24*, 461–471. [\[CrossRef\]](#)
60. Vazylyev, M.; Sloboda-Rozner, D.; Haimov, A.; Maayan, G.; Neumann, R. Strategies for oxidation catalyzed by polyoxometalates at the interface of homogeneous and heterogeneous catalysis. *Top. Catal.* **2005**, *34*, 93–99. [\[CrossRef\]](#)
61. Mizuno, N.; Kamata, K.; Yamaguchi, K. Liquid-phase oxidations catalyzed by polyoxometalates. In *Surface and Nanomolecular Catalysis*; Richards, R., Ed.; CRC Press LLC: Boca Raton, FL, USA, 2006; pp. 463–492.
62. Proust, A.; Thouvenot, R.; Gouzerh, P. Functionalization of polyoxometalates: Towards advanced applications in catalysis and materials science. *Chem. Commun.* **2008**, *2008*, 1837–1852. [\[CrossRef\]](#)
63. Mizuno, N.; Kamata, K.; Yamaguchi, K. Green oxidation reactions by polyoxometalate-based catalysts: From molecular to solid catalysts. *Top. Catal.* **2010**, *53*, 876–893. [\[CrossRef\]](#)
64. Dolbecq, A.; Dumas, E.; Mayer, C.R.; Mialane, P. Hybrid organic–inorganic polyoxometalate compounds: From structural diversity to applications. *Chem. Rev.* **2010**, *110*, 6009–6048. [\[CrossRef\]](#)
65. Kholdeeva, O.A.; Maksimchuk, N.V.; Maksimov, G.M. Polyoxometalate-based heterogeneous catalysts for liquid phase selective oxidations: Comparison of different strategies. *Catal. Today* **2010**, *157*, 107–113. [\[CrossRef\]](#)
66. Proust, A.; Matt, B.; Villanneau, R.; Guillemot, G.; Gouzerh, P.; Izzet, G. Functionalization and post-functionalization: A step towards polyoxometalate-based materials. *Chem. Soc. Rev.* **2012**, *41*, 7605–7622. [\[CrossRef\]](#)
67. Song, Y.F.; Tsunashima, R. Recent advances on polyoxometalate-based molecular and composite materials. *Chem. Soc. Rev.* **2012**, *41*, 7384–7402. [\[CrossRef\]](#)
68. Zhou, Y.; Chen, G.; Long, Z.; Wang, J. Recent advances in polyoxometalate-based heterogeneous catalytic materials for liquid-phase organic transformations. *RSC Adv.* **2014**, *4*, 42092–42113. [\[CrossRef\]](#)
69. Rafiee, E.; Eavani, S. Heterogenization of heteropoly compounds: A review of their structure and synthesis. *RSC Adv.* **2016**, *6*, 46433–46466. [\[CrossRef\]](#)
70. Cherevan, A.S.; Nandan, S.P.; Roger, I.; Liu, R.; Streb, C.; Eder, D. Polyoxometalates on functional substrates: Concepts, synergies, and future perspectives. *Adv. Sci.* **2020**, *7*, 1903511. [\[CrossRef\]](#) [\[PubMed\]](#)
71. Rhule, J.T.; Neiwert, W.A.; Hardcastle, K.I.; Do, B.T.; Hill, C.L. Ag₅PMo₁₀V₂O₄₀, a heterogeneous catalyst for air-based selective oxidation at ambient temperature. *J. Am. Chem. Soc.* **2001**, *123*, 12101–12102. [\[CrossRef\]](#) [\[PubMed\]](#)
72. Okuhara, T. Water-tolerant solid acid catalysts. *Chem. Rev.* **2002**, *102*, 3641–3666. [\[CrossRef\]](#) [\[PubMed\]](#)
73. Plault, L.; Hauseler, A.; Nlate, S.; Astruc, D.; Ruiz, J.; Gatard, S.; Neumann, R. Synthesis of dendritic polyoxometalate complexes assembled by ionic bonding and their function as recoverable and reusable oxidation catalysts. *Angew. Chem. Int. Ed.* **2004**, *43*, 2924–2928. [\[CrossRef\]](#)
74. Mizuno, N.; Uchida, S.; Kamata, K.; Ishimoto, R.; Nojima, S.; Yonehara, K.; Sumida, Y. A flexible nonporous heterogeneous catalyst for size-selective oxidation through a bottom-up approach. *Angew. Chem. Int. Ed.* **2010**, *49*, 9972–9976. [\[CrossRef\]](#)
75. Mirante, F.; Dias, L.; Silva, M.; Ribeiro, S.O.; Corvo, M.C.; de Castro, B.; Granadeiro, C.M.; Balula, S.S. Efficient heterogeneous polyoxometalate-hybrid catalysts for the oxidative desulfurization of fuels. *Catal. Commun.* **2018**, *104*, 1–8. [\[CrossRef\]](#)

76. Kholdeeva, O.A.; Vanina, M.P.; Timofeeva, M.N.; Maksimovskaya, R.I.; Trubitsina, T.A.; Melgunov, M.S.; Burgina, E.B.; Mrowiec-Bialon, J.; Jarzebski, A.B.; Hill, C.L. Co-containing polyoxometalate-based heterogeneous catalysts for the selective aerobic oxidation of aldehydes under ambient conditions. *J. Catal.* **2004**, *226*, 363–371. [\[CrossRef\]](#)
77. Maksimchuk, N.V.; Melgunov, M.S.; Mrowiec-Białoń, J.; Jarzebski, A.B.; Kholdeeva, O.A. H₂O₂-based allylic oxidation of α -pinene over different single site catalysts. *J. Catal.* **2005**, *235*, 175–183. [\[CrossRef\]](#)
78. Dufaud, V.; Lefebvre, F.; Niccolai, G.P.; Aouine, M. New insights into the encapsulation and stabilization of heteropolyacids inside the pore walls of mesostructured silica materials. *J. Mater. Chem.* **2009**, *19*, 1142–1150. [\[CrossRef\]](#)
79. Sousa, J.L.C.; Santos, I.C.M.S.; Simões, M.M.Q.; Cavaleiro, J.A.S.; Nogueira, H.I.S.; Cavaleiro, A.M.V. Iron(III)-substituted polyoxotungstates immobilized on silica nanoparticles: Novel oxidative heterogeneous catalysts. *Catal. Commun.* **2011**, *12*, 459–463. [\[CrossRef\]](#)
80. Jalkh, C.; Ghazaly, C.; El-Rassy, H. Entrapment vs. immobilization of polyoxometalates into silica and titania aerogels: Application in heterogeneous oxidation catalysis. *Mater. Chem. Phys.* **2020**, *252*, 123296. [\[CrossRef\]](#)
81. Yun, S.K.; Pinnavaia, T.J. Layered double hydroxides intercalated by polyoxometalate anions with Keggin (α -H₂W₁₂O₄₀^{6−}), Dawson (α -P₂W₁₈O₆₂^{6−}), and Finke (Co₄(H₂O)₂(PW₉O₃₄)₂^{10−}) structures. *Inorg. Chem.* **1996**, *35*, 6853–6860. [\[CrossRef\]](#)
82. Jana, S.K.; Kubota, Y.; Tatsumi, T. Cobalt-substituted polyoxometalate pillared hydrotalcite: Synthesis and catalysis in liquid-phase oxidation of cyclohexanol with molecular oxygen. *J. Catal.* **2008**, *255*, 40–47. [\[CrossRef\]](#)
83. Omwoma, S.; Chen, W.; Tsunashima, R.; Song, Y.F. Recent advances on polyoxometalates intercalated layered double hydroxides: From synthetic approaches to functional material applications. *Coord. Chem. Rev.* **2014**, *258–259*, 58–71. [\[CrossRef\]](#)
84. Li, T.; Miras, H.N.; Song, Y.-F. Polyoxometalate (POM)-layered double hydroxides (LDH) composite materials: Design and catalytic applications. *Catalysts* **2017**, *7*, 260. [\[CrossRef\]](#)
85. Neumann, R.; Miller, H.J. Alkene oxidation in water using hydrophobic silica particles derivatized with polyoxometalates as catalysts. *J. Chem. Soc. Chem. Commun.* **1995**, *1995*, 2277–2278. [\[CrossRef\]](#)
86. Kamada, M.; Kominami, H.; Kera, Y. Deposition and interaction of phosphododecatungstate on a silica gel surface modified with a silane coupling agent having anilino groups. *J. Colloid Interface Sci.* **1996**, *182*, 297–300. [\[CrossRef\]](#)
87. Okun, N.M.; Anderson, T.M.; Hill, C.L. [(Fe^{III}(OH)₂)₃(A- α -PW₉O₃₄)₂]^{9−} on cationic silica nanoparticles, a new type of material and efficient heterogeneous catalyst for aerobic oxidations. *J. Am. Chem. Soc.* **2003**, *125*, 3194–3195. [\[CrossRef\]](#) [\[PubMed\]](#)
88. Kasai, J.; Nakagawa, Y.; Uchida, S.; Yamaguchi, K.; Mizuno, N. [γ -1,2-H₂SiV₂W₁₀O₄₀] immobilized on surface-modified SiO₂ as a heterogeneous catalyst for liquid-phase oxidation with H₂O₂. *Chem. Eur. J.* **2006**, *12*, 4176–4184. [\[CrossRef\]](#) [\[PubMed\]](#)
89. Bordoloi, A.; Lefebvre, F.; Halligudi, S.B. Selective oxidation of anthracene using inorganic–organic hybrid materials based on molybdovanadophosphoric acids. *J. Catal.* **2007**, *247*, 166–175. [\[CrossRef\]](#)
90. Yamaguchi, K.; Yoshida, C.; Uchida, S.; Mizuno, N. Peroxotungstate immobilized on ionic liquid-modified silica as a heterogeneous epoxidation catalyst with hydrogen peroxide. *J. Am. Chem. Soc.* **2005**, *127*, 530–531. [\[CrossRef\]](#)
91. Kato, C.N.; Tanabe, A.; Negishi, S.; Goto, K.; Nomiya, K. An efficient PMo₁₁V^{VO}₄₀^{4−}/silica material having cationic ammonium moiety: Synthesis, characterization, and catalytic performance for oxidation of alcohols with dioxygen. *Chem. Lett.* **2005**, *34*, 238–239. [\[CrossRef\]](#)
92. Maksimchuk, N.V.; Melgunov, M.S.; Chesalov, Y.A.; Mrowiec-Białoń, J.; Jarzebski, A.B.; Kholdeeva, O.A. Aerobic oxidations of α -pinene over cobalt-substituted polyoxometalate supported on amino-modified mesoporous silicates. *J. Catal.* **2007**, *246*, 241–248. [\[CrossRef\]](#)
93. Inumaru, K.; Ishihara, T.; Kamiya, Y.; Okuhara, T.; Yamanaka, S. Water-tolerant, highly active solid acid catalysts composed of the Keggin-type polyoxometalate H₃PW₁₂O₄₀ immobilized in hydrophobic nanospaces of organomodified mesoporous silica. *Angew. Chem. Int. Ed.* **2007**, *46*, 7625–7676. [\[CrossRef\]](#)
94. Chen, L.; Zhu, K.; Bi, L.-H.; Suchopar, A.; Reicke, M.; Mathys, G.; Jaensch, H.; Kortz, U.; Richards, R.M. Solvent-free aerobic oxidation of *n*-alkane by iron(III)-substituted polyoxotungstates immobilized on SBA-15. *Inorg. Chem.* **2007**, *46*, 8457–8459. [\[CrossRef\]](#)
95. Panchenko, V.N.; Borbáth, I.; Timofeeva, M.N.; Góbbölös, S. Amine-modified silica NH₂–(CH₂)_x–SiO₂ (*x* = 0, 2, 3) as support for cobalt-substituted polyoxometalate TBA₄HPW₁₁CoO₃₉: Effect of the nature of the support on the oxidation activity. *J. Mol. Catal. A Chem.* **2010**, *319*, 119–125. [\[CrossRef\]](#)
96. Kovalchuk, T.V.; Sfihi, H.; Zaitsev, V.N.; Fraissard, J. Preparation and characterization of catalysts based on oniumsilica-immobilized Keggin acids. *Catal. Today* **2011**, *169*, 138–149. [\[CrossRef\]](#)
97. Balula, S.S.; Cunha-Silva, L.; Santos, I.C.M.S.; Estrada, A.C.; Fernandes, A.C.; Cavaleiro, J.A.S.; Pires, J.; Freire, C.; Cavaleiro, A.M.V. Mono-substituted silicotungstates as active catalysts for sustainable oxidations: Homo- and heterogeneous performance. *New J. Chem.* **2013**, *37*, 2341–2350. [\[CrossRef\]](#)
98. Mirante, F.; Ribeiro, S.O.; de Castro, B.; Granadeiro, C.M.; Balula, S.S. Sustainable desulfurization processes catalyzed by titanium-polyoxometalate@TM-SBA-15. *Top. Catal.* **2017**, *60*, 1140–1150. [\[CrossRef\]](#)
99. Ribeiro, S.O.; Granadeiro, C.M.; Almeida, P.L.; Pires, J.; Valença, R.; Campos-Martin, J.M.; Ribeiro, J.C.; de Castro, B.; Balula, S.S. Effective zinc-substituted Keggin composite to catalyze the removal of sulfur from real diesels under a solvent-free system. *Ind. Eng. Chem. Res.* **2019**, *58*, 18540–18549. [\[CrossRef\]](#)
100. Johnson, B.J.S.; Stein, A. Surface modification of mesoporous, macroporous, and amorphous silica with catalytically active polyoxometalate clusters. *Inorg. Chem.* **2001**, *40*, 801–808. [\[CrossRef\]](#)

101. Yang, Y.; Guo, Y.; Hu, C.; Wang, Y.; Wang, E. Preparation of surface modifications of mesoporous titania with monosubstituted Keggin units and their catalytic performance for organochlorine pesticide and dyes under UV irradiation. *Appl. Catal. A General* **2004**, *273*, 201–210. [[CrossRef](#)]
102. Errington, R.J.; Petkar, S.S.; Horrocks, B.R.; Houlton, A.; Lie, L.H.; Patole, S.N. Covalent immobilization of a TiW_5 polyoxometalate on derivatized silicon surfaces. *Angew. Chem. Int. Ed.* **2005**, *44*, 1254–1257. [[CrossRef](#)]
103. Zhou, Y.; Bao, R.; Yue, B.; Gu, M.; Pei, S.; He, H. Synthesis, characterization and catalytic application of SBA-15 immobilized rare earth metal sandwiched polyoxometalates. *J. Mol. Catal. A Chemical* **2007**, *270*, 50–55. [[CrossRef](#)]
104. Joo, N.; Renaudineau, S.; Delapierre, G.; Bidan, G.; Chamoreau, L.-M.; Thouvenot, R.; Gouzerh, P.; Proust, A. Organosilyl/-germyl polyoxotungstate hybrids for covalent grafting onto silicon surfaces: Towards molecular memories. *Chem. Eur. J.* **2010**, *16*, 5043–5051. [[CrossRef](#)]
105. Luo, X.; Yang, C. Photochromic ordered mesoporous hybrid materials based on covalently grafted polyoxometalates. *Phys. Chem. Chem. Phys.* **2011**, *13*, 7892–7902. [[CrossRef](#)] [[PubMed](#)]
106. Du, Y.; Zhou, L.; Guo, Z.; Du, X.; Lei, J. Preparation of ordered meso/macroporous HPW/titania-silica catalyst for efficient oxidative desulfurization of model fuel. *J. Porous Mater.* **2019**, *26*, 1069–1077. [[CrossRef](#)]
107. Yan, X.-M.; Mei, P.; Xiong, L.; Gao, L.; Yang, Q.; Gong, L. Mesoporous titania-silica-polyoxometalate nanocomposite materials for catalytic oxidation desulfurization of fuel oil. *Catal. Sci. Technol.* **2013**, *3*, 1985–1992. [[CrossRef](#)]
108. Granadeiro, C.M.; Ferreira, R.A.S.; Soares-Santos, P.C.R.; Carlos, L.D.; Trindade, T.; Nogueira, H.I.S. Lanthanopolyoxotungstates in silica nanoparticles: Multi-wavelength photoluminescent core/shell materials. *J. Mater. Chem.* **2010**, *20*, 3313–3318. [[CrossRef](#)]
109. Gao, H.; Wu, X.; Sun, D.; Niu, G.; Guan, J.; Meng, X.; Liu, C.; Xia, W.; Song, X. Preparation of core-shell $\text{PW}_{12}/\text{TiO}_2$ micro-spheres and oxidative desulfurization performance. *Dalton Trans.* **2019**, *48*, 5749–5755. [[CrossRef](#)]
110. Chen, Y.; Zhao, S.; Song, Y.-F. An efficient heterogeneous catalyst based on highly dispersed $\text{Na}_7\text{H}_2\text{LaW}_{10}\text{O}_{36} \cdot 32\text{H}_2\text{O}$ nanoparticles on mesoporous silica for deep desulfurization. *Appl. Catal. A Gen.* **2013**, *466*, 307–314. [[CrossRef](#)]
111. Ribeiro, S.O.; Nogueira, L.S.; Gago, S.; Almeida, P.L.; Corvd, M.C.; de Castro, B.; Granadeiro, C.M.; Balula, S.S. Desulfurization process conciliating heterogeneous oxidation and liquid extraction: Organic solvent or centrifugation/water? *Appl. Catal. A Gen.* **2017**, *542*, 359–367. [[CrossRef](#)]
112. Leng, Y.; Zhang, W.; Wang, J.; Jiang, P. A novel heteropolyanion-based amino-containing cross-linked ionic copolymer catalyst for epoxidation of alkenes with H_2O_2 . *Appl. Catal. A Gen.* **2012**, *445–446*, 306–311. [[CrossRef](#)]
113. Doherty, S.; Knight, J.G.; Ellison, J.R.; Weekes, D.; Harrington, R.W.; Hardacre, C.; Many, H. An efficient recyclable peroxometalate-based polymer-immobilised ionic liquid phase (PIILP) catalyst for hydrogen peroxide-mediated oxidation. *Green Chem.* **2012**, *14*, 925–929. [[CrossRef](#)]
114. Romanenko, I.; Lechner, M.; Wendler, F.; Horenz, C.; Streb, C.; Schacher, F.H. POMbranes: Polyoxometalate-functionalized block copolymer membranes for oxidation catalysis. *J. Mater. Chem. A* **2017**, *5*, 15789–15796. [[CrossRef](#)]
115. Li, T.; Wang, Z.; Chen, W.; Miras, H.N.; Song, Y.-F. Rational design of a polyoxometalate intercalated layered double hydroxide: Highly efficient catalytic epoxidation of allylic alcohols under mild and solvent-free conditions. *Chem. Eur. J.* **2017**, *23*, 1069–1077. [[CrossRef](#)] [[PubMed](#)]
116. Hwang, Y.K.; Férey, G.; Lee, U.H.; Chang, J.S. Liquid phase oxidation of organic compounds by metal-organic frameworks. In *Liquid Phase Oxidation via Heterogeneous Catalysis: Organic Synthesis and Industrial Applications*; Clerici, M.G., Kholdeeva, O.A., Eds.; Wiley: Hoboken, NJ, USA, 2013; pp. 371–409.
117. Yu, R.; Kuang, X.-F.; Wua, X.-Y.; Lua, C.-Z.; Donahue, J.P. Stabilization and immobilization of polyoxometalates in porous coordination polymers through host-guest interactions. *Coord. Chem. Rev.* **2009**, *253*, 2872–2890. [[CrossRef](#)]
118. Maksimchuk, N.V.; Kholdeeva, O.A.; Kovalenko, K.A.; Fedin, V.P. MIL-101 Supported polyoxometalates: Synthesis, characterization, and catalytic applications in selective liquid-phase oxidation. *Isr. J. Chem.* **2011**, *51*, 281–289. [[CrossRef](#)]
119. Du, D.Y.; Qin, J.S.; Li, S.L.; Su, Z.M.; Lan, Y.Q. Recent advances in porous polyoxometalate based metal-organic framework materials. *Chem. Soc. Rev.* **2014**, *43*, 4615–4632. [[CrossRef](#)]
120. Kholdeeva, O.A. Liquid-phase selective oxidation catalysis with metal-organic frameworks. *Catal. Today* **2016**, *278*, 22–29. [[CrossRef](#)]
121. Freire, C.; Fernandes, D.M.; Nunes, M.; Abdelkader, V.K. POM & MOF-based electrocatalysts for energy-related reactions. *Chem. Cat. Chem.* **2018**, *10*, 1703–1730.
122. Samaniyan, M.; Mirzaei, M.; Khajavian, R.; Eshtiagh-Hosseini, H.; Streb, C. Heterogeneous catalysis by polyoxometalates in metal-organic frameworks. *ACS Catal.* **2019**, *9*, 10174–10191. [[CrossRef](#)]
123. Buru, C.T.; Farha, O.K. Strategies for incorporating catalytically active polyoxometalates in metal-organic frameworks for organic transformations. *ACS Appl. Mater. Interfaces* **2020**, *12*, 5345–5360. [[CrossRef](#)]
124. Piscopo, C.G.; Granadeiro, C.M.; Balula, S.S.; Bošković, D. Metal-organic framework-based catalysts for oxidative desulfurization. *ChemCatChem* **2020**, *12*, 4721–4731. [[CrossRef](#)]
125. Sun, J.; Abednatanzi, S.; Van Der Voort, P.; Liu, Y.-Y.; Leus, K. POM@MOF hybrids: Synthesis and applications. *Catalysts* **2020**, *10*, 578. [[CrossRef](#)]
126. Mialane, P.; Mellot-Draznieks, C.; Gairola, P.; Duguet, M.; Benseghir, Y.; Oms, O.; Dolbecq, A. Heterogenisation of polyoxometalates and other metal-based complexes in metal-organic frameworks: From synthesis to characterisation and applications in catalysis. *Chem. Soc. Rev.* **2021**, *50*, 6152–6220. [[CrossRef](#)] [[PubMed](#)]

127. Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surblé, S.; Margiolaki, I. A chromium terephthalate-based solid with unusually large pore volumes and surface area. *Science* **2005**, *309*, 2040–2042. [CrossRef] [PubMed]
128. Maksimchuk, N.V.; Timofeeva, M.N.; Melgunov, M.S.; Shmakov, A.N.; Chesalov, Y.A.; Dybtsev, D.N.; Fedin, V.P.; Kholdeeva, O.A. Heterogeneous selective oxidation catalysts based on coordination polymer MIL-101 and transition metal substituted polyoxometalates. *J. Catal.* **2008**, *257*, 315–323. [CrossRef]
129. Maksimchuk, N.V.; Kovalenko, K.A.; Arzumanov, S.S.; Chesalov, Y.A.; Stepanov, A.G.; Fedin, V.P.; Kholdeeva, O.A. Hybrid polyoxotungstate/MIL-101 materials: Synthesis, characterization, and catalysis of H₂O₂-based alkene epoxidation. *Inorg. Chem.* **2010**, *49*, 2920–2930. [CrossRef] [PubMed]
130. Aubry, C.; Chottard, G.; Platzter, N.; Bregeault, J.-M.; Thouvenot, R.; Chauveau, F.; Huet, C.; Ledon, H. Reinvestigation of epoxidation using tungsten-based precursors and hydrogen peroxide in a biphasic medium. *Inorg. Chem.* **1991**, *30*, 4409–4415. [CrossRef]
131. Duncan, D.C.; Chambers, R.C.; Hecht, E.; Hill, C.L. Mechanism and dynamics in the H₃[PW₁₂O₄₀]-catalyzed selective epoxidation of terminal olefins by H₂O₂. Formation, reactivity, and stability of {PO₄[WO(O₂)₂]₄}^{3−}. *J. Am. Chem. Soc.* **1995**, *117*, 681–691. [CrossRef]
132. Bailey, A.J.; Griffith, W.P.; Parkin, B.C.; Bailey, A.J.; Griffith, W.P.; Parkin, B.C. Heteropolyperoxo- and isopolyperoxo-tungstates and-molybdates as catalysts for the oxidation of tertiary amines, alkenes and alcohols. *J. Chem. Soc. Dalton Trans.* **1995**, *1995*, 1833–1837. [CrossRef]
133. Bregeault, J.-M. Transition-metal complexes for liquid-phase catalytic oxidation: Some aspects of industrial reactions and of emerging technologies. *Dalton Trans.* **2003**, *2003*, 3289–3302. [CrossRef]
134. Küsgens, P.; Rose, M.; Senkovska, I.; Fröde, H.; Henschel, A.; Siegle, S.; Kaskel, S. Characterization of metal-organic frameworks by water adsorption. *Micropor. Mesopor. Mater.* **2009**, *120*, 325–330. [CrossRef]
135. Bromberg, L.; Diao, Y.; Wu, H.; Speakman, T.A.; Hatton, S.A. Chromium(III) terephthalate metal organic framework (MIL-101): HF-free synthesis, structure, polyoxometalate composites, and catalytic properties. *Chem. Mater.* **2012**, *24*, 1664–1675. [CrossRef]
136. Ribeiro, S.; Granadeiro, C.M.; Silva, P.; Paz, F.A.A.; de Biani, F.F.; Cunha-Silva, L.; Balula, S.S. An efficient oxidative desulfurization process using terbium-polyoxometalate@MIL-101(Cr). *Catal. Sci. Technol.* **2013**, *3*, 2404–2414. [CrossRef]
137. Balula, S.S.; Granadeiro, C.M.; Barbosa, A.D.S.; Santos, I.C.M.S.; Cunha-Silva, L. Multifunctional catalyst based on sandwich-type polyoxotungstate and MIL-101 for liquid phase oxidations. *Catal. Today* **2013**, *210*, 142–148. [CrossRef]
138. Granadeiro, C.M.; Barbosa, A.D.S.; Ribeiro, S.; Santos, I.C.M.S.; de Castro, B.; Cunha-Silva, L.; Balula, S.S. Oxidative catalytic versatility of a trivacant polyoxotungstate incorporated into MIL-101(Cr). *Catal. Sci. Technol.* **2014**, *4*, 1416–1425. [CrossRef]
139. Gao, Y.; Mirante, F.; de Castro, B.; Zhao, J.; Cunha-Silva, L.; Balula, S.S. An effective hybrid heterogeneous catalyst to desulfurize diesel: Peroxotungstate@metal-organic framework. *Molecules* **2020**, *25*, 5494. [CrossRef] [PubMed]
140. Fernandes, S.; Flores, D.; Silva, D.; Santos-Vieira, I.; Mirante, F.; Granadeiro, C.M.; Balula, S.S. Lindqvist@nanoporous MOF-based catalyst for effective desulfurization of fuels. *Nanomaterials* **2022**, *12*, 2887. [CrossRef] [PubMed]
141. Zhao, X.; Duan, Y.; Yang, F.; Wei, W.; Xu, Y.; Hu, C. Efficient mechanochemical synthesis of polyoxometalate@ZIF complexes as reusable catalysts for highly selective oxidation. *Inorg. Chem.* **2017**, *56*, 14506–14512. [CrossRef]
142. Wang, L.; Lub, J.; Wang, Y.; Wang, H.; Wang, J.; Ren, T. Preparation and characterization of novel cyclohexene-to-adipic acid catalyst with ionic liquid phosphotungstate immobilized on MIL-101 nanocages based on Cr-N coordination. *J. Mol. Struct.* **2023**, *1271*, 133973. [CrossRef]
143. Qi, Z.; Huang, Z.; Wang, H.; Li, L.; Ye, C.; Qiu, T. In situ bridging encapsulation of a carboxyl-functionalized phosphotungstic acid ionic liquid in UiO-66: A remarkable catalyst for oxidative desulfurization. *Chem. Eng. Sci.* **2020**, *225*, 115818. [CrossRef]
144. Wu, C.; Sun, Z.; Ye, C.; Qi, Z.; Chen, J.; Huang, Z.; Qiu, T. Encapsulation of HPW and preparation of composites rich in Zr-defects by manual grinding: Synergistic catalysis for efficient oxidative desulfurization at room temperature. *Chem. Eng. J.* **2023**, *451*, 138906. [CrossRef]
145. Lin, Z.-J.; Zheng, H.-Q.; Chen, J.; Zhuang, W.-E.; Lin, Y.-X.; Su, J.-W.; Huang, Y.-B.; Cao, R. Encapsulation of phosphotungstic acid into metal-organic frameworks with tunable window sizes: Screening of PTA@MOF catalysts for efficient oxidative desulfurization. *Inorg. Chem.* **2018**, *57*, 13009–13019. [CrossRef]
146. Fernandes, S.C.; Viana, A.M.; de Castro, B.; Cunha-Silva, L.; Balula, S.S. Synergistic combination of the nanoporous system of MOF-808 with a polyoxomolybdate to design an effective catalyst: Simultaneous oxidative desulfurization and denitrogenation processes. *Sustain. Energy Fuels* **2021**, *5*, 4032–4040. [CrossRef]
147. Yang, X.-L.; Qiao, L.-M.; Dai, W.-L. Phosphotungstic acid encapsulated in metal-organic framework UiO-66: An effective catalyst for the selective oxidation of cyclopentene to glutaraldehyde. *Micropor. Mesopor. Mater.* **2015**, *211*, 73–81. [CrossRef]
148. Peng, Y.-L.; Liu, J.; Zhang, H.-F.; Luo, D.; Li, D. A size-matched POM@MOF composite catalyst for highly efficient and recyclable ultra-deep oxidative fuel desulfurization. *Inorg. Chem. Front.* **2018**, *5*, 1563–1569. [CrossRef]
149. Song, X.; Hu, D.; Yang, X.; Zhang, H.; Zhang, W.; Li, J.; Jia, M.; Yu, J. Polyoxomolybdic cobalt encapsulated within Zr-based metal-organic frameworks as efficient heterogeneous catalysts for olefins epoxidation. *ACS Sustain. Chem. Eng.* **2019**, *7*, 3624–3631. [CrossRef]
150. Zhang, X.; Zhang, Z.; Zhang, B.; Yang, X.; Chang, X.; Zhou, Z.; Wang, D.-H.; Zhang, M.-H.; Bu, X.-H. Synergistic effect of Zr-MOF on phosphomolybdic acid promotes efficient oxidative desulfurization. *Appl. Catal. B Environ.* **2019**, *256*, 117804. [CrossRef]

151. Ma, Y.; Li, A.; Wang, C.; Ge, X. Preparation of HPW@UiO-66 catalyst with defects and its application in oxidative desulfurization. *Chem. Eng. J.* **2021**, *404*, 127062. [\[CrossRef\]](#)
152. Silva, D.F.; Viana, A.M.; Santos-Vieira, I.; Balula, S.S.; Cunha-Silva, L. Ionic liquid-based polyoxometalate incorporated at ZIF-8: A sustainable catalyst to combine desulfurization and denitrogenation processes. *Molecules* **2022**, *27*, 1711. [\[CrossRef\]](#)
153. Miras, H.N.; Vilá-Nadal, L.; Cronin, L. Polyoxometalate based open-frameworks (POM-OFs). *Chem. Soc. Rev.* **2014**, *43*, 5679–5699. [\[CrossRef\]](#)
154. Song, J.; Luo, Z.; Britt, D.K.; Furukawa, H.; Yaghi, O.M.; Hardcastle, K.I.; Hill, C.L. A multiunit catalyst with synergistic stability and reactivity: A polyoxometalate-metal organic framework for aerobic decontamination. *J. Am. Chem. Soc.* **2011**, *133*, 6839–16846. [\[CrossRef\]](#)
155. Zou, C.; Zhang, Z.; Xu, X.; Gong, Q.; Li, J.; Wu, C.-D. A multifunctional organic–inorganic hybrid structure based on Mn^{III}–porphyrin and polyoxometalate as a highly effective dye scavenger and heterogeneous catalyst. *J. Am. Chem. Soc.* **2012**, *134*, 87–90. [\[CrossRef\]](#)
156. Han, Q.; He, C.; Zhao, M.; Qi, B.; Niu, J.; Duan, C. Engineering chiral polyoxometalate hybrid metal–organic frameworks for asymmetric dihydroxylation of olefins. *J. Am. Chem. Soc.* **2013**, *135*, 10186–10189. [\[CrossRef\]](#) [\[PubMed\]](#)
157. Li, D.; Xu, Q.; Li, Y.; Qiu, Y.; Ma, P.; Niu, J.; Wang, J. A stable polyoxometalate-based metal–organic framework as highly efficient heterogeneous catalyst for oxidation of alcohols. *Inorg. Chem.* **2019**, *58*, 4945–4953. [\[CrossRef\]](#) [\[PubMed\]](#)
158. Wang, Q.; Xu, B.; Wang, Y.; Wang, H.; Hu, X.; Ma, P.; Niu, J.; Wang, J. Polyoxometalate-incorporated framework as a heterogeneous catalyst for selective oxidation of C–H bonds of alkylbenzenes. *Inorg. Chem.* **2021**, *60*, 7753–7761. [\[CrossRef\]](#) [\[PubMed\]](#)
159. Gouzerh, P.; Proust, A. Main-group element, organic, and organometallic derivatives of polyoxometalates. *Chem. Rev.* **1998**, *98*, 77–112. [\[CrossRef\]](#) [\[PubMed\]](#)
160. Villanneau, R.; Marzouk, A.; Wang, Y.; Djamaa, A.B.; Laugel, G.; Proust, A.; Launay, F. Covalent grafting of organic–inorganic polyoxometalates hybrids onto mesoporous SBA-15: A key step for new anchored homogeneous catalysts. *Inorg. Chem.* **2013**, *52*, 2958–2965. [\[CrossRef\]](#)
161. Bentaleb, F.; Makrygenni, O.; Brouri, D.; Diogo, C.C.; Mehdi, A.; Proust, A.; Launay, F.; Villanneau, R. Efficiency of polyoxometalate-based mesoporous hybrids as covalently anchored catalysts. *Inorg. Chem.* **2015**, *54*, 7607–7616. [\[CrossRef\]](#)
162. Makrygenni, O.; Brouri, D.; Proust, A.; Launay, F.; Villanneau, R. Immobilization of polyoxometalate hybrid catalysts onto mesoporous silica supports using phenylene diisothiocyanate as a cross-linking agent. *Micropor. Mesopor. Mater.* **2019**, *278*, 314–321. [\[CrossRef\]](#)
163. Cravena, M.; Xiao, D.; Kunstmann-Olsen, C.; Kozhevnikova, E.F.; Blanca, F.; Steiner, A.; Kozhevnikov, I.V. Oxidative desulfurization of diesel fuel catalyzed by polyoxometalate immobilized on phosphazene-functionalized silica. *Appl. Catal. B Environ.* **2018**, *231*, 82–91. [\[CrossRef\]](#)
164. Liu, Y.; Zuo, P.; Wang, R.; Liu, Y.; Jiao, W. Covalent immobilization of Dawson polyoxometalates on hairy particles and its catalytic properties for the oxidation desulfurization of tetrahydrothiophene. *J. Cleaner Production* **2020**, *274*, 122774. [\[CrossRef\]](#)
165. Nisar, A.; Zhuang, J.; Wang, X. Construction of amphiphilic polyoxometalate mesostructures as a highly efficient desulfurization catalyst. *Adv. Mater.* **2011**, *23*, 1130–1135. [\[CrossRef\]](#)
166. Xu, J.; Zhao, S.; Ji, Y.; Song, Y.-F. Deep desulfurization by amphiphilic lanthanide-containing polyoxometalates in ionic-liquid emulsion systems under mild conditions. *Chem. Eur. J.* **2013**, *19*, 709–715. [\[CrossRef\]](#) [\[PubMed\]](#)
167. Qi, W.; Li, H.; Wu, L. A novel, luminescent, silica-sol-gel hybrid based on surfactant-encapsulated polyoxometalates. *Adv. Mater.* **2007**, *19*, 1983–1987. [\[CrossRef\]](#)
168. Qi, W.; Wu, L. Polyoxometalate/polymer hybrid materials: Fabrication and properties. *Polym. Int.* **2009**, *58*, 1217–1225. [\[CrossRef\]](#)
169. Qi, W.; Wang, Y.; Li, W.; Wu, L. Surfactant-encapsulated polyoxometalates as immobilized supramolecular catalysts for highly efficient and selective oxidation reactions. *Chem. Eur. J.* **2010**, *16*, 1068–1078. [\[CrossRef\]](#)
170. Yan, Y.; Wu, L. Polyoxometalate-incorporated supramolecular self assemblies: Structures and functional properties. *Isr. J. Chem.* **2011**, *51*, 181–190. [\[CrossRef\]](#)
171. Shi, L.; Wang, Y.Z.; Li, B.; Wu, L.X. Polyoxometalate complexes for oxidative kinetic resolution of secondary alcohols: Unique effects of chiral environment, immobilization and aggregation. *Dalton Trans.* **2014**, *43*, 9177–9188. [\[CrossRef\]](#)
172. Nogueira, L.S.; Ribeiro, S.; Granadeiro, C.M.; Pereira, E.; Feio, G.; Cunha-Silva, L.; Balula, S.S. Novel polyoxometalate silica nano-sized spheres: Efficient catalysts for olefin oxidation and the deep desulfurization process. *Dalton Trans.* **2014**, *43*, 9518–9528. [\[CrossRef\]](#)
173. Chen, X.; Yang, A.; Wang, G.; Wei, M.; Liu, N.; Li, B.; Wu, L. Reinforced catalytic oxidation of polyoxometalate@charge transfer complex by on-site heating from photothermal conversion. *Chem. Eng. J.* **2022**, *446*, 137134. [\[CrossRef\]](#)
174. Izumi, Y.; Urabe, K. Catalysis of heteropoly acids entrapped in activated carbon. *Chem. Lett.* **1981**, *10*, 663–666. [\[CrossRef\]](#)
175. Schwegler, M.A.; Vinke, P.; van der Eijk, M.; van Bekkum, H. Activated carbon as a support for heteropolyanion catalysts. *Appl. Catal.* **1992**, *80*, 41–57. [\[CrossRef\]](#)
176. Evtushok, V.Y.; Suboch, A.N.; Podyacheva, O.Y.; Stonkus, O.A.; Zaikovskii, V.I.; Chesalov, Y.A.; Kibis, L.S.; Kholdeeva, O.A. Highly efficient catalysts based on divanadium-substituted polyoxometalate and N-doped carbon nanotubes for selective oxidation of alkylphenols. *ACS Catal.* **2018**, *8*, 1297–1307. [\[CrossRef\]](#)
177. Eder, D. Carbon nanotube–inorganic hybrids. *Chem. Rev.* **2010**, *110*, 1348–1385. [\[CrossRef\]](#)

178. Shearer, C.J.; Cherevan, A.; Eder, D. Application of functional hybrids incorporating carbon nanotubes or graphene. In *Carbon Nanotubes and Graphene*; Tanaka, K., Iijima, S., Eds.; Elsevier Ltd.: Amsterdam, The Netherlands, 2014; Chapter 16; pp. 387–433.
179. Shearer, C.J.; Cherevan, A.; Eder, D. Application and future challenges of functional nanocarbon hybrids. *Adv. Mater.* **2014**, *26*, 2295–2318. [[CrossRef](#)] [[PubMed](#)]
180. Ji, Y.; Huang, L.; Hu, J.; Streb, C.; Song, Y.F. Polyoxometalate-functionalized nanocarbon materials for energy conversion, energy storage and sensor systems. *Energy Environ. Sci.* **2015**, *8*, 776–789. [[CrossRef](#)]
181. Toma, F.M.; Sartorel, A.; Iurlo, M.; Carraro, M.; Parisse, P.; Maccato, C.; Rapino, S.; Gonzalez, B.R.; Amenitsch, H.; Da Ros, T.; et al. Efficient water oxidation at carbon nanotube–polyoxometalate electrocatalytic interfaces. *Nat. Chem.* **2010**, *2*, 826–831. [[CrossRef](#)]
182. Akter, T.; Hu, K.; Lian, K. Investigations of multilayer polyoxometalates-modified carbon nanotubes for electrochemical capacitors. *Electrochim. Acta* **2011**, *56*, 4966–4971. [[CrossRef](#)]
183. Gao, Y.; Gao, R.; Zhang, G.; Zheng, Y.; Zhao, J. Oxidative desulfurization of model fuel in the presence of molecular oxygen over polyoxometalate based catalysts supported on carbon nanotubes. *Fuel* **2018**, *224*, 261–270. [[CrossRef](#)]
184. Jawale, D.V.; Fossard, F.; Miserque, F.; Geertsen, V.; Teillout, A.L.; de Oliveira, P.; Mbomekalle, I.M.; Gravel, E.; Doris, E. Carbon nanotube–polyoxometalate nanohybrids as efficient electro-catalysts for the hydrogen evolution reaction. *Carbon* **2022**, *188*, 523–532. [[CrossRef](#)]
185. Ma, D.; Liang, L.; Chen, W.; Liu, H.; Song, Y.F. Covalently tethered polyoxometalate–pyrene hybrids for noncovalent side-wall functionalization of single-walled carbon nanotubes as high-performance anode material. *Adv. Funct. Mater.* **2013**, *23*, 6100–6105. [[CrossRef](#)]
186. Chen, W.; Huang, L.; Hu, J.; Li, T.; Jia, F.; Song, Y.F. Connecting carbon nanotubes to polyoxometalate clusters for engineering high-performance anode materials. *Phys. Chem. Chem. Phys.* **2014**, *16*, 19668–19673. [[CrossRef](#)]
187. Kawasaki, N.; Wang, H.; Nakanishi, R.; Hamanaka, S.; Kitaura, R.; Shinohara, H.; Yokoyama, T.; Yoshikawa, H.; Awaga, K. Nanohybridization of polyoxometalate clusters and single-wall carbon nanotubes: Applications in molecular cluster batteries. *Angew. Chem. Int. Ed.* **2011**, *50*, 3471–3474. [[CrossRef](#)]
188. Ji, Y.; Hu, J.; Huang, L.; Chen, W.; Streb, C.; Song, Y.F. Covalent attachment of Anderson-type polyoxometalates to single-walled carbon nanotubes gives enhanced performance electrodes for lithium ion batteries. *Chem. Eur. J.* **2015**, *21*, 6469–6474. [[CrossRef](#)]
189. Chen, H.-Y.; Al-Oweini, R.; Friedl, J.; Lee, C.Y.; Li, L.; Kortz, U.; Stimming, U.; Srinivasan, M. A novel SWCNT–polyoxometalate nanohybrid material as an electrode for electrochemical supercapacitors. *Nanoscale* **2015**, *7*, 7934–7941. [[CrossRef](#)]
190. Hu, J.; Ji, Y.; Chen, W.; Streb, C.; Song, Y.F. “Wiring” redox-active polyoxometalates to carbon nanotubes using a sonication-driven periodic functionalization strategy. *Energy Environ. Sci.* **2016**, *9*, 1095–1101. [[CrossRef](#)]
191. Hajian, R.; Alghour, Z. Selective oxidation of alcohols with H₂O₂ catalyzed by zinc polyoxometalate immobilized on multi-wall carbon nanotubes modified with ionic liquid. *Chin. Chem. Lett.* **2017**, *28*, 971–975. [[CrossRef](#)]
192. Salavati, H.; Tangestaninejad, S.; Moghadam, M.; Mirkhani, V.; Mohammadpoor-Baltork, I. Sonocatalytic epoxidation of alkenes by vanadium-containing polyphosphomolybdate immobilized on multi-wall carbon nanotubes. *Ultrason. Sonochemistry* **2010**, *17*, 453–459. [[CrossRef](#)] [[PubMed](#)]
193. Wang, R.; Yu, F.; Zhang, G.; Zhao, H. Performance evaluation of the carbon nanotubes supported Cs_{2.5}H_{0.5}PW₁₂O₄₀ as efficient and recoverable catalyst for the oxidative removal of dibenzothiophene. *Catal. Today* **2010**, *150*, 37–41. [[CrossRef](#)]
194. Evtushok, V.Y.; Ivanchikova, I.D.; Podyacheva, O.Y.; Stonkus, O.A.; Suboch, A.N.; Chesalov, Y.A.; Zalomaeva, O.V.; Kholdeeva, O.A. Carbon Nanotubes modified by Venturello complex as highly efficient catalysts for alkene and thioethers oxidation with hydrogen peroxide. *Front. Chem.* **2019**, *7*, 858. [[CrossRef](#)]
195. Evtushok, V.Y.; Podyacheva, O.Y.; Suboch, A.N.; Maksimchuk, N.V.; Stonkus, O.A.; Kibis, L.S.; Kholdeeva, O.A. H₂O₂-based selective oxidations by divanadium-substituted polyoxotungstate supported on nitrogen-doped carbon nanomaterials. *Catal. Today* **2020**, *354*, 196–203. [[CrossRef](#)]
196. Evtushok, V.Y.; Ivanchikova, I.D.; Lopatkin, V.A.; Maksimchuk, N.V.; Podyacheva, O.Y.; Suboch, A.N.; Stonkus, O.A.; Kholdeeva, O.A. Heterolytic alkene oxidation with H₂O₂ catalyzed by Nb-substituted Lindqvist tungstates immobilized on carbon nanotubes. *Catal. Sci. Technol.* **2021**, *11*, 3198–3207. [[CrossRef](#)]
197. Zhang, W.-H.; Shen, J.-J.; Wu, J.; Liang, X.-Y.; Xu, J.; Liu, P.; Xue, B.; Li, Y.-X. An amphiphilic graphene oxide-immobilized polyoxometalate-based ionic liquid: A highly efficient triphase transfer catalyst for the selective oxidation of alcohols with aqueous H₂O₂. *Mol. Catal.* **2017**, *443*, 262–269. [[CrossRef](#)]
198. Masteri-Farahani, M.; Modarres, M. Clicked graphene oxide supported Venturello catalyst: A new hybrid nanomaterial as catalyst for the selective epoxidation of olefins. *Mater. Chem. Phys.* **2017**, *199*, 522–527. [[CrossRef](#)]
199. Gan, M.; Yang, G.; Wang, Z.; Sui, X.; Hou, Y. Highly efficient oxidative desulfurization catalyzed by a polyoxometalate/carbonized cellulose nanofiber composite. *Energy Fuels* **2020**, *34*, 778–786. [[CrossRef](#)]
200. Zhang, X.; Li, Y.; Li, Y.; Wang, S.; Wang, X. Polyoxometalate immobilized on graphene via click reaction for simultaneous dismutation of H₂O₂ and oxidation of sulfur mustard simulant. *ACS Appl. Nano Mater.* **2019**, *2*, 6971–6981. [[CrossRef](#)]
201. Podyacheva, O.Y.; Ismagilov, Z.R. Nitrogen-doped carbon nanomaterials: To the mechanism of growth, electrical conductivity and application in catalysis. *Catal. Today* **2015**, *249*, 12–22. [[CrossRef](#)]
202. Arrigo, R.; Schuster, M.E.; Xie, Z.; Yi, Y.; Wowsnick, G.; Sun, L.L.; Hermann, K.E.; Friedrich, M.; Kast, P.; Hävecker, M.; et al. Nature of the N–Pd interaction in nitrogen-doped carbon nanotube catalysts. *ACS Catal.* **2015**, *5*, 2740–2753. [[CrossRef](#)]

203. Cao, Y.; Mao, S.; Li, M.; Chen, Y.; Wang, Y. Metal/porous carbon composites for heterogeneous catalysis: Old catalysts with improved performance promoted by N-doping. *ACS Catal.* **2017**, *7*, 8090–8112. [[CrossRef](#)]
204. Skobelev, I.Y.; Evtushok, V.Y.; Kholdeeva, O.A.; Maksimchuk, N.V.; Maksimovskaya, R.I.; Ricart, J.M.; Poblet, J.M.; Carbó, J.J. Understanding the regioselectivity of aromatic hydroxylation over divanadium-substituted γ -Keggin polyoxotungstate. *ACS Catal.* **2017**, *7*, 8514–8523. [[CrossRef](#)]
205. Wang, Y.; Kamata, K.; Ishimoto, R.; Ogasawara, Y.; Suzuki, K.; Yamaguchi, K.; Mizuno, N. Composites of $[\gamma\text{-H}_2\text{PV}_2\text{W}_{10}\text{O}_{40}]^{3-}$ and $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$ supported on Fe_2O_3 as heterogeneous catalysts for selective oxidation with aqueous hydrogen peroxide. *Catal. Sci. Technol.* **2015**, *5*, 2602–2611. [[CrossRef](#)]
206. Kholdeeva, O.A.; Zalomaeva, O.V. Recent advances in transition-metal-catalyzed selective oxidation of substituted phenols and methoxyarenes with environmentally benign oxidants. *Coord. Chem. Rev.* **2016**, *306*, 302–330. [[CrossRef](#)]
207. Maksimchuk, N.V.; Maksimov, G.M.; Evtushok, V.Y.; Ivanchikova, I.D.; Chesalov, Y.A.; Maksimovskaya, R.I.; Kholdeeva, O.A.; Sole-Daura, A.; Poblet, J.M.; Carbo, J.J. Relevance of protons in heterolytic activation of H_2O_2 over Nb(V): Insights from model studies on Nb-substituted polyoxometalates. *ACS Catal.* **2018**, *8*, 9722–9737. [[CrossRef](#)]
208. Zalomaeva, O.V.; Maksimchuk, N.V.; Maksimov, G.M.; Kholdeeva, O.A. Thioether oxidation with H_2O_2 catalyzed by Nb-substituted polyoxotungstates: Mechanistic insights. *Eur. J. Inorg. Chem.* **2019**, *2019*, 410–416. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.