






Cite this: *Catal. Sci. Technol.*, 2018, 8, 2257

Heterogeneous catalysis by tungsten-based heteropoly compounds

Amir Enferadi-Kerenkan,  Trong-On Do * and Serge Kaliaguine *

Tungsten, a fascinating metal, has found a variety of catalytic applications in the form of tungsten sulfides, simple tungsten oxides (e.g. tungsten trioxide, tungstate, tungstic acid, tungstite), and polyoxotungstates (POTs). The latter, which have been less industrialized compared to the others, have attracted a great deal of interest recently stemming from reinforcement of uniquely interesting catalytic properties of polyoxometalates (POMs), such as strong acidity, redox capability, and water tolerance, by distinct inherent properties of tungsten such as having very strong Brønsted acid sites. Additionally, the physical and chemical properties of POMs are widely and readily tunable at the molecular level, holding promise for their application in different reactions. However, the water-solubility property of POTs, resulting in lack of recovery in water-involving reactions, is a controversial challenge. To tackle this obstacle, homogeneous POTs have been heterogenized *via* different strategies, classified here into three groups: inorganic cation-substituted solid POTs, organo-solidified POTs, and POTs immobilized onto supports. These strategies have occasionally led to the fabrication of even more efficient catalysts compared to the parent homogeneous POT. A large number of heterogeneous POT-based catalysts have been developed so far, which intriguingly have adjustable catalytically important features such as porosity, hydrophobicity, compatibility toward organic species, chemical composition, admissibility to other elements (with tunable host-guest interactions), and magnetic properties. Such adjustments have enabled size-selective catalysis, enhanced catalytic activity in organic media, prevented poisoning of acid sites by water, rendered bifunctional catalysts, and/or provided facile recovery. We review these breakthroughs in a critical and comparative fashion along with highlighting the most interesting achievements of the reported works. Herein, we have tried to list all the recent works on the heterogeneous catalysis applications of POTs in liquid organic reactions. In doing so, photocatalytic applications of POTs and homogeneous POTs with high recoverability have been excluded.

Received 7th February 2018,
Accepted 20th March 2018

DOI: 10.1039/c8cy00281a

rsc.li/catalysis

1. Introduction

At the end of the 18th century and the dawn of tungsten chemistry, when the charming yellow color of tungsten oxide fascinated the chemists to propose its use as an artist's color and Rudolf Erich Raspe, a German geologist and the famous author of “*The Adventures of Baron Munchausen*”, said that “In beauty it exceeds Turner's well-known yellow by far”,¹ probably they did not think that this pretty colored material would find wide application in industry. Over the years, however, different combinations of tungsten oxide have been developed in a variety of industries, insofar as nowadays tungsten oxide is counted as indispensable to our lives. Besides its application in hydrogen reduction to manufacture elemental tungsten for industries such as electronics, electrical, alloy and steel and for jewellery, biology, sport and leisure equipment, *etc.*, tungsten oxide is used for many purposes in every-



Amir Enferadi-Kerenkan

Amir Enferadi-Kerenkan obtained his BSc and MSc degrees in chemical engineering from Ferdowsi University of Mashhad (Iran, 2007) and Sahand University of Technology (Iran, 2010), respectively. He is currently a PhD candidate (waiting for his upcoming thesis defence) and a professional researcher at the Department of Chemical Engineering, Laval University, Canada, and is working under the supervision of

Prof. Trong-On Do. In his doctoral research project, Amir chiefly focused on the synthesis of advanced organo-functionalized heterogeneous catalysts for liquid-phase oleochemical reactions and development of a sustainable process for production of high-value organic intermediates, diacids, from vegetable oils.

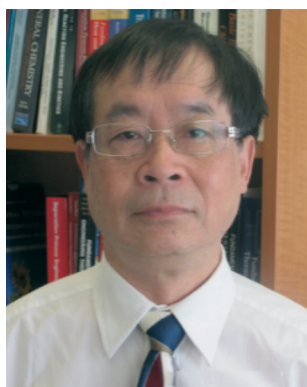
Department of Chemical Engineering, Université Laval, Québec, G1V 0A6, Canada.
E-mail: Trong-On.Do@gch.ulaval.ca, Serge.Kaliaguine@gch.ulaval.ca

day life such as production of smart windows, fireproofing fabrics, and as gas sensors, semiconductors and efficient catalysts and photocatalysts.²

The major modern day use of tungsten oxides is nevertheless in the area of catalysis. The oil industry has been the most striking consumer of tungsten catalysts for the treatment of crude oils since the 1930s.³ Basic reactions such as hydrotreating (hydrodesulphurization, hydrodenitrogenation, and hydrodearomatization), de-NO_x, and reforming are some of the most important reactions catalyzed by tungsten compounds in the chemical industry.^{4,5} Since then, tungsten oxide-based catalysts have received continuous attention because of their increasing advantages in catalysis. First, although tungsten was previously classified as a rare metal, nowadays it is found in most countries, with a lower price and less toxic properties compared to its alternatives from the second and third rows of transition metals for organic reactions (chiefly osmium and ruthenium).^{6,7} Second, tungsten oxides and sulfides exhibit very strong Brønsted acid sites, to which the catalytic activities of transition metals in many reactions are attributed,^{8–10} either as a bulk oxide or when supported.^{11–16} Compared to other metal oxides, tungsten oxide has shown a relatively low point of zero charge (PZC) in the literature,¹⁷ which complies with its high surface acidity. Third, tungsten oxide includes many chemical structures arising from the distinct inherent properties of tungsten, which enable a variety of properties and morphologies for catalytic applications in many chemical reactions. The numerous oxidation states of tungsten from –2 to +6 (ref. 18

and 19) have led to several tungsten oxides WO_x (*x* mainly between 2 and 3) including WO₃ (yellowish), WO_{2.9} or W₂₀O₅₈ (bluish), WO_{2.72} or W₁₈O₄₉ (violet), and WO₂ (brownish).¹ The most common state is tungsten trioxide, which in turn, includes the hydrated (WO₃·*n*H₂O) and anhydrous (WO₃) forms. It has even been shown that the number of water molecules in the structure affects the catalytic activity, particularly in oxidation reactions.²⁰ Furthermore, WO₃ can crystallize in many polymorphs with various crystal structures such as monoclinic, orthorhombic, and tetragonal. Moreover, peroxotungstic acid or hydrated tungsten peroxide is another interesting tungsten oxide-based structure that has shown great potential for catalytic applications.²¹

Applications of tungsten-containing materials in heterogeneous catalytic oxidation reactions have been nicely and recently reviewed.²² However, heteropoly acids (HPAs) or their more often used equivalent, polyoxometalates (POMs) of tungsten, which are another type of tungsten oxide-based material progressively attracting interest particularly in the last decade, have not been included in this reference. The widely tunable physical and chemical properties of POMs at the molecular level have been the subject of extensive research in recent years, giving them promise for applications in various fields such as medicine, materials science, photochromism, electrochemistry, magnetism and catalysis. This considerable diversity in their applications can be traced by looking at the papers published in a special issue of *Chemical Reviews Journal* in 1998 (Volume 98, Issue 1), which exclusively focuses on polyoxometalates. The strong acidity of POMs has



Trong-On Do

Trong-On Do is a full professor in the Department of Chemical Engineering at Laval University, Canada. He received his MSc in 1986 and PhD in 1989 at the University of P. and M. Curie (Paris 6, France). After a period at Brunel University (UK) and the French Catalysis Institute (France), he moved to Laval University in 1990. He then spent two years (1997–1999) at Kanagawa Academy of Science and Technology, Japan, under

the Japanese STA Fellowship Award before joining again Laval University as a professor associated with the NSERC Industrial Chair. Trong-On Do's research is focused on the design and synthesis of innovative and smart materials and their applications in heterogeneous catalysis and renewable energy. He is also a major contributor in the field of zeolite-based materials including controlled-size nanozeolites and hybrid zeolite/mesoporous molecular sieve materials. He has published over 140 papers and review articles in refereed journals and holds 5 international patents. He is the recipient of the 2014/2015 Canadian Catalysis Lectureship Award (CCLA).



Serge Kaliaguine

Professor S. Kaliaguine has worked for more than 40 years in catalysis and surface science research. He has published over 480 papers in refereed journals (over 22 000 citations) and received several prestigious awards. These include Le prix Urgel-Archambaut (ACFAS), the Canadian Catalysis Award (CIC), the Catalysis Lectureship Award (CCF), and the Century of Achievements Award (CSChE).

Professor Kaliaguine has chaired several national and international meetings. He was chairman of the Catalysis Division of the Chemical Institute of Canada, a director of the Canadian Society for Chemical Engineering, president of the International Mesostructured Materials Association and the holder of an NSERC Chair for Industrial Nanomaterials (Adsorbents, Catalysts and Membranes).


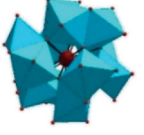
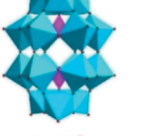
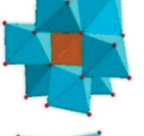

tempted the researchers to examine their efficiency in reactions currently catalyzed by conventional acids (e.g. H_2SO_4 and AlCl_3) such as Friedel–Crafts, esterification, hydration, hydrolysis, and acetalization, where the problems associated with the use of conventional acids like high toxicity, catalyst waste, corrosion, difficulty of separation and recovery have provided a controversial challenge nowadays. On the other hand, POMs are more thermally and oxidatively stable to oxygen donors in comparison with other organometallic complexes.²³

Interestingly and uniquely, the key properties of POMs like acidity, redox capability, and solubility in water or polar solvents can be readily and stably tuned to enhance their efficiency for specific purposes. Such structure modifications are generally carried out at the molecular or atomic level by removing one or more constituent transition metal atoms, giving the parent POM a defected structure, the so-called lacunary structure, and then incorporating another transition metal(s) into the structure. According to this, different metal–oxygen clusters of POMs containing several early transition metals such as tungsten, molybdenum, vanadium, niobium, tantalum, iron, cobalt, nickel, copper, titanium, zinc, manganese and even lanthanoid metals (Gd, Eu, Yb, and Lu (ref. 24)) have been reported up to now in two forms of heterogeneous solid catalysts and homogeneous solution catalysts, which have been widely reviewed for general^{25–29} or specific^{30–35} catalytic applications. In 1983, when the number of known structures of POMs was not even as much as now,

Pope noted in his inspiringly famous book “*Heteropoly and Isopoly Oxometalates*” that POMs have been prepared with more than 65 elements as the central atom (in Pope’s terminology the heteroatom).^{36,37} Therefore, trying to give a complete review of POMs and their synthesis methods has been recommended as neither practical nor appropriate.³⁸

Among all the mentioned transition metals, a great deal of attention has been paid to tungsten, since its heteropoly compounds have shown considerable superiority, especially in the heterogeneous form in terms of acidity, thermal stability, and hydrophobicity, in comparison with the other metals.^{23,39,40} Curiously, W-based heteropoly solid catalysts have not been adequately reviewed exclusively in one paper. Only one review paper,⁴¹ to our knowledge, has focused on heterogeneous catalysis by heteropoly compounds of tungsten, along with molybdenum, which, although preciously informative, dates to three decades ago. Given the wide number of publications that have focused lately on heterogenization of tungsten-based heteropoly catalysts, a review that encompasses their applications as well as currently available synthetic methodologies seems timely. Focusing on tungsten and refraining from discussing other used heteroatoms in this paper, we have tried to review all of the recent works on heterogeneous POM-based catalysts with W as the central atom. In what follows, first the seminal concepts of POMs, which have been extensively reviewed in the literature, with an emphasis on tungsten-containing solid POMs, will be briefly explained in section 2 to bring up the topic. Then,

Table 1 Different structures of POMs

Name	General formula ^a	X (typical examples)	Structure
Keggin	$\text{XM}_{12}\text{O}_{40}^{n-}$	P^{5+} , As^{5+} , Si^{4+} , Ge^{4+}	
Dexter–Silverton	$\text{XM}_{12}\text{O}_{42}^{n-}$	Ce^{4+} , Th^{4+}	
Dawson	$\text{X}_2\text{M}_{18}\text{O}_{62}^{n-}$	P^{5+} , As^{5+}	
Allman–Waugh	$\text{XM}_9\text{O}_{32}^{n-}$	Mn^{4+} , Ni^{4+}	
Anderson (type A)	$\text{XM}_6\text{O}_{24}^{n-}$	Te^{6+} , I^{7+}	

^a M = Mo^{VI} , W^{VI} , $\text{V}^{\text{V,VI}}$, etc.

different solid W-based POM catalysts, classified based on the heterogenization strategy along with their applications in liquid phase organic reactions will be investigated in sections 3–6. In the vast field of heterogeneous W-based POM catalysts, some of the reported works have focused on the synthesis, heterogenization strategies, and characterization of catalytically interesting features (*e.g.* porosity, acidity, stability, *etc.*) only, while some other works have also examined the catalytic efficiency of W-based POMs in some typical reactions. Our focus in this article has been chiefly placed on the latter group, which, although include a variety of liquid organic reactions, can be conveniently categorized into two general groups, acid catalysis and oxidation reactions (please see the recent review by Wang *et al.* for the different organic reactions catalyzed by POMs³⁵). However, some of the interesting and inspiring works from the first group have also been reviewed (especially in section 3). It should be noted that photocatalytic applications of POMs are not covered in this review.

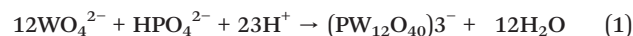
2. Solid heteropoly compounds of tungsten: a primer

Polyoxometalates or their more descriptive synonym, heteropoly oxoanions, are polymeric oxoanions formed by the condensation of more than two different oxoanions, which can give heteropoly acids. In contrast, isopolyanions are composed of one kind of oxoanions, the acid forms of which are called isopoly acids. In fact, although the words POM and HPA are inadvertently being used instead of each other, it should be noticed that a HPA is the acid form of its corresponding POM, and *vice versa*, a POM is the conjugate anion of HPA.

Despite some disagreement over the history of POMs, the majority of the literature cites Berzelius, who reported the preparation of ammonium 12-molybdophosphate in 1826, as

the pioneer of heteropoly compound science. About 40 years later, however, the first tungsten-based heteropoly compound, 12-tungstosilicic acid, was discovered in 1862 by Marignac. The full history of POMs and their progress are available in several reviews and books (*e.g.* ref. 26 and 38) and hence would be redundant here. Over the years, with the better understanding of POM chemistry, various structures were discovered, which are summarized in Table 1. Further information on the details of POM structures is available in numerous papers and books (*e.g.* ref. 36–39, 42 and 43).

Although some POMs with Dawson, Anderson, Allman–Waugh, and less known Preyssler structures have also been examined as catalysts, most of the heteropoly oxometalate catalysts are of Keggin structure, which has been reported for the first time in 1934 by Keggin,⁴⁴ most likely because of the higher thermal stability and ease of synthesis of this structure compared to others.⁴¹ The Keggin cluster of W-based POMs has the general formula $H_nXW_{12}O_{40}$, in which X is the heteroatom (X has been known to be from the p-block of the periodic table (*e.g.*, P, Si, Ge, As) but nowadays is not restricted to them). Hereafter, W-based HPA and POM are designated as heteropoly tungstic acid (HPTA) and polyoxotungstate (POT), respectively (which can be used roughly instead of each other). POTs can be easily prepared and polymerized by dehydration from tungstate and a heteroatom oxoanion in acidified aqueous solution. Eqn (1) indicates the formation of phosphotungstate, the most common POM, from tungstate and phosphate under controlled temperature and pH:



Generally, HPTAs are soluble in water and polar solvents, and thus form homogeneous catalytic systems in many reactions involving such solvents. Although the overwhelming majority of such homogeneous catalytic systems have

Table 2 Inorganic cation-substituted POTs for general catalytic purposes

Entry	Counteranion	IC-substituted POT ^a	Remarks	Ref.
1	Cs ⁺	Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀	Meso- and microporous structures of the POT have been examined The presence of very strong acidic sites on the POT has been indicated	55
2		Cs ₃ PW ₁₂ O ₄₀	Self-organization of the POT nanocrystallites has been successfully controlled by the changes in the synthetic temperatures and counteranions (Cs ⁺ , Ag ⁺ , and NH ₄ ⁺) Formation and growth mechanism of the POT particles have been investigated	62
3	NH ₄ ⁺	(NH ₄) ₃ PW ₁₂ O ₄₀	“Sponge crystals” of the POT have been defined as molecular single crystals including continuous voids originating from series of neighboring vacancies of the constituent large molecules, which have afforded nanospaces in the crystals By changing the synthesis temperature, the POTs with high surface areas, ranging from 65 to 116 m ² g ⁻¹ , have been prepared	63, 64
4		(NH ₄) ₃ PW ₁₂ O ₄₀	Self-organization of the POT nanocrystallites has been successfully controlled by the changes in the synthetic temperature and counteranion (Cs ⁺ , Ag ⁺ , and NH ₄ ⁺) Formation and growth mechanism of the POT particles have been investigated	62
5	Ag ⁺	Ag ₃ PW ₁₂ O ₄₀	Self-organization of the POT nanocrystallites has been successfully controlled by the changes in the synthetic temperature and counteranion (Cs ⁺ , Ag ⁺ , and NH ₄ ⁺) Formation and growth mechanism of the POT particles have been investigated	62

^a IC: inorganic cation.

Table 3 Inorganic cation-substituted POTs for acid catalysis reactions

Entry	Counteranion	IC-substituted POT	Reaction	Remarks	Ref.
1	Cs ⁺	Cs _{2.2} H _{0.8} PW ₁₂ O ₄₀	Decomposition of ester, dehydration of alcohol, and alkylation of aromatics	Pore size of the POT was precisely controlled by Cs ⁺ content This POT was reported as the first example of shape-selective catalysis by a solid superacid in liquid organic reaction	56
2		Cs _x H _{4-x} SiW ₁₂ O ₄₀	Transesterification of C ₄ and C ₈ triglycerides and esterification of palmitic acid	Changing the homogeneous properties of the POT to heterogeneous properties by increasing the Cs ⁺ content has been investigated	61
3		Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀	Microwave-assisted transesterification of yellow horn oil	Optimizing the reaction conditions, the POT has been shown to be an efficient catalyst for production of biodiesel fuel by means of microwave irradiation	65
4		Cs _x H _{3-x} PW ₁₂ O ₄₀ (x = 1, 1.5, 2, 2.5, 3)	Ultrasound-assisted transesterification of crude jatropha oil	Changes in the POT properties and catalytic activity have been investigated	66
5		Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀	Cycloaddition of crotonaldehyde to monoterpenic alkenes	The catalytic activity of the POT has been compared with that of silica-supported HTPA (H ₃ PW ₁₂ O ₄₀)	67
6		Cs ₃ PW ₁₂ O ₄₀	Conversions of cellobiose and cellulose into sorbitol in water	Ru nanoparticles have been supported on the POT, which despite not having strong acidity, was an efficient catalyst	58
7		Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀	Glycerol acetalization with formaldehyde	The catalytic activity of the POT has been compared with that of periodic mesoporous organosilicas, zeolite ZSM-5, and commercial catalyst Amberlyst-15, which showed superiority	68
8		Cs ₂ HPW ₁₂ O ₄₀ Cs ₃ HSiW ₁₂ O ₄₀	Carbonylation of dimethyl ether to methyl acetate	The POT was modified by adding Rh to its structure, which greatly increased the conversion because a multiplier effect occurred between Rh and the POT	59
9		Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀	Synthesis of xanthenedione derivatives from aldehydes	CS _{2.5} has been employed for the first time for the synthesis of 1,8-dioxo-octahydroxanthenes by the reaction of aldehydes with 1,3-cyclohexanedione/dimedone and exhibited high yields of products and short reaction time	69
10		Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀	Thioacetalization and transthoacetalization reactions	The POT was an effective catalyst with high selectivity	70
11		Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀ Cs _{3.5} H _{0.5} SiW ₁₂ O ₄₀	Production of methyl <i>tert</i> -butyl ether (MTBE) from methanol and <i>tert</i> -butyl alcohol	The Cs-substituted POTs exhibited higher activity compared to the parent POTs and activated carbon-supported POTs, which was discussed from kinetic viewpoints	60
12		Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀ Cs _{1.87} H _{1.13} PW ₁₂ O ₄₀	Esterification of oleic acid with polyethylene glycol	By optimizing the reactants' molar ratio and the reaction temperature, the synthesized acid catalysts were active and selective	71
13	Ag ⁺	Ag _x H _{4-x} SiW ₁₂ O ₄₀ x = 0, 1, 2, 3, and 4	Transformation of alkynoxyranes to furan	Ag content was optimized to reach good catalytic efficiency	72
14		Ag ₃ PW ₁₂ O ₄₀	Conversion of fructose and glucose into 5-hydroxymethylfurfural	The POT was tolerant to high-concentration feedstock and showed environmentally benign properties with double acidity	73
15		Ag ₃ PW ₁₂ O ₄₀	Intermolecular hydroamination of olefins	Compared to the parent HPTA, the synthesized POT exhibited lower catalytic efficiency	74
16	Na ⁺	H ₁₄ [NaP ₅ W ₂₉ MoO ₁₁₀]	Different functional group protective reactions such as tetrahydropyranylation of phenol and alcohols, acetylation of alcohols, phenols, amines and thiols with Ac ₂ O, trimethylsilylation of phenols and alcohols	The Mo-substituted Preyssler structure POT has shown higher activity than Keggin or Wells–Dawson heteropolyacids due to its higher number of acidic protons	75
17		Na ₈ H[PW ₉ O ₃₄]	Knoevenagel condensation and cyanosilylation of various aldehydes and ketones and the synthesis of benzoxazole derivatives	The POT could catalyze the reactions at 25 °C under mild conditions in chloride-free solvents	76

Table 3 (continued)

Entry	Counteraction	IC-substituted POT	Reaction	Remarks	Ref.
18	K ⁺	K _{2.2} H _{0.8} PW ₁₂ O ₄₀	Esterification of 2-keto-1-gulonic acid	The POT showed good catalytic activity (slightly lower than that of homogeneous HPTA)	77
19		K _x H _{3-x} PW ₁₂ O ₄₀ (x = 2 and 2.5)	Dehydration of ethanol	The POTs have exhibited higher reactivity than HPTA Thermal stability of the POTs in x = 2.5 is higher than in x = 2	78
20	NH ₄ ⁺	(NH ₄) ₃ PW ₁₂ O ₄₀	Intermolecular hydroamination of olefins	Compared to PTA, the POT exhibited lower catalytic efficiency	74
21		(NH ₄) ₂ HPW ₁₂ O ₄₀	Thioacetalization and transtioacetalization reactions	The POT was an effective catalyst with high selectivity	70
22	Sn ²⁺	Sn _x [H ₃ PW ₁₂ O ₄₀] (x = 0.5, 1, and 1.5)	Benzylation of arenes with benzyl alcohol	Dependency of the catalytic activity on Sn ²⁺ content has been investigated	79
23	Zn ²⁺	Zn _{1.2} H _{0.6} PW ₁₂ O ₄₀	Esterification of palmitic acid and transesterification of waste cooking oil	The POT has shown superior catalytic activity compared to HTPA due to introduction of Lewis acid sites by partial exchange of H ⁺ by Zn ²⁺ , high acid strength by Lewis site-assisted Brønsted sites, a high surface area, and nanostructure	80
24	Bi ³⁺	BiPW ₁₂ O ₄₀	Esterification of oleic acid with <i>n</i> -butanol	In addition to BiPW, other metal salts of PTA were synthesized including LaPW, CuPW, AlPW, FePW, and SnPW; however, the most efficient catalyst was bismuth salt of PTA	81

Table 4 Inorganic cation-substituted POTs for oxidation reactions

Entry	Counteraction	IC-substituted POT	Reaction	Remarks	Ref.
1	K ⁺	K ₆ [PW ₉ V ₃ O ₄₀]	Ammoximation of different ketones and aldehydes	The V-substituted POT has been proved to be heterogeneous in iso-propanol and recyclable	82
2	Mn ²⁺ Co ²⁺ Cu ²⁺	{[M ₂ (H ₂ O) ₆][Mn ₄ (H ₂ O) ₁₆][WZn(Mn(H ₂ O)) ₂ (ZnW ₉ O ₃₄) ₂]}·10H ₂ O (M = Co ^{II} and Cu ^{II})	Oxidative aromatization of Hantzsch 1,4-dihydropyridines	The POT-based solid was prepared by using {Mn ₂ Zn ₃ W ₁₀ } as a building block and Mn ^{II} cation as a connecting node. Induced by Co ²⁺ and Cu ²⁺ and solvent molecules, this solid was transformed into the final interesting 3D solid framework	83

demonstrated better efficiency than their heterogeneous counterparts, especially in organic transformations where heterogeneous systems possess poor reactant/catalyst contact arising from pore diffusion limitations and mass transfer resistance, the use of homogeneous systems in large-scale reactions may not be in line with sustainable chemistry due to lack of catalyst reusability. This gave rise to the rapid development of heterogenization of originally homogenous W-based heteropoly compounds. Interestingly, solid POT catalysts have exhibited unique pseudo-liquid phase properties in liquid organic reactions, particularly in the presence of highly polar and small size substrates, which enables them with good catalytic efficiency despite their generally non-porous structures.^{45–47} Moreover, compared to the other solid acids, heterogeneous HPTAs have shown excellent water-tolerant properties,²³ which hold a promise for their application in reactions involving water such as hydrolysis, hydration, esterification, and acetalization where a major problem in the use of solid acids is the poisoning of acid sites by water resulting in loss of their catalytic activities. Additionally,

the relatively low thermal stability of HTPAs leading to a difficult catalyst regeneration process, which had influenced their application to some extent, has been overcome by offering some approaches such as developing novel HTPAs with high thermal stability, modification of HTPAs to enhance coke combustion, preventing coke formation on HTPAs during the reaction, employing supercritical fluids as the reaction medium and cascade reactions using multifunctional HTPA catalysis.⁴⁸

So far, solidification of HPTAs has been done mainly *via* substitution of some protons of their structure by inorganic cations, grafting functional organic species to POTs, and immobilization of HPTAs on supports, which will be explained in sections 3–5, respectively. Such strategies and particularly the synthesis approaches have been recently reviewed by Rafiee and Eavani.⁴⁹ Occasionally, these strategies have been exploited simultaneously to fabricate a heterogeneous POT, in which it is difficult to clearly determine which part shoulders the responsibility for heterogenization (inorganic cation or organic species or support); the POTs heterogenized by

Table 5 Organo-solidified POTs for acid catalysis reactions

Entry	Organic source	POT-organic hybrid	Reaction	Remarks	Ref.
1	Amino acid: lysine	$(ly)_xH_{3-x}PW_{12}O_{40}$ $x = 1, 2$	Transesterification of triglycerides and esterification of free fatty acids	The POT is an acid-base bifunctional nanocatalyst, which allowed acid-base tandem conversions in one pot The acidic or basic strength could be modulated by changing the ratio of HTPA anion to amino acid	107
2	Organosulfate surfactant: dodecyl sulfate	$Cr[(DS)H_2PW_{12}O_{40}]_3$ (DS: $OSO_3C_{12}H_{25}$ dodecyl sulfate)	Conversion of cellulose into HMF	Good catalytic activity of the POT was mainly attributed to double Brønsted and Lewis acidities and the micellar structured catalytic system with hydrophobic groups	108
3	Quaternary ammonium surfactant: CTAB	$[C_{16}H_{33}N(CH_3)_3]H_2PW_{12}O_{40}$	Hydrolysis of polysaccharides into glucose	The POT was designed to form a micellar catalytic system, which gave good efficiency toward production of glucose	109
4	Ionic liquid	$[MIMPS]_3PW_{12}O_{40}$ $[PyPS]_3PW_{12}O_{40}$ $[TEAPS]_3PW_{12}O_{40}$	Esterification of free fatty acids	The POT showed high catalytic activity, self-separation, and easy reuse Good solubility in reactants, nonmiscibility with ester product, and high melting point of the POT enable the reaction-induced switching from homogeneous to heterogeneous with subsequent precipitation of the catalyst	104, 110
5	Ionic liquid	$[TPSP]_3PW_{12}O_{40}$	Esterification of free fatty acids	High efficiency of the POT came from its pseudo-liquid phase behavior, phase transfer phenomena, and stabilization effect of the heteropolyanion on carbonium ion intermediates	111
6	Ionic liquid	$[MIM-PSH]_xH_{3-x}PW_{12}O_{40}$ $x: 1 \text{ to } 3$	Esterification of palmitic acid	Superior catalytic efficiency of the POT arose from better super-acidity and lower molecular transport resistance of catalyst	112
7	Ionic liquid	$[NMP]_3PW_{12}O_{40}$	Prins cyclization of styrene with formalin	Excellent catalytic performance of the POT was due to its pseudo-liquid behavior and stabilization effect of carbonyl in amide on protonated formaldehyde of the reaction intermediate, together with its solid nature and insolubility	113
8	Ionic liquid	$[MIMPS]_3PW_{12}O_{40}$	Beckmann rearrangements of ketoximes	Using $ZnCl_2$ as cocatalyst, the POT was highly efficient and recoverable	114
9	Ionic liquid	$[DPySO_3H]_{1.5}PW_{12}O_{40}$	Beckmann rearrangement of cyclohexanone oxime	In the absence of environmentally harmful cocatalyst $ZnCl_2$, the POT was highly efficient and recoverable	115
10	Ionic liquid	$[PyBS]_3PW_{12}O_{40}$ $[TEABS]_3PW_{12}O_{40}$ $[MIMBS]_3PW_{12}O_{40}$ $[PyBS]_4SiW_{12}O_{40}$ $[TEABS]_4SiW_{12}O_{40}$ $[MIMBS]_4SiW_{12}O_{40}$	Transesterifications of trimethylolpropane	The $[PyBS]_3PW_{12}O_{40}$ POT acted as a homogeneous catalyst during the reaction which upon cooling at the end of the reaction became solid, enabling self-separation performance	116
11	Ionic liquid	$[MIMBS]_3PW_{12}O_{40}$	Conversion of furfuryl alcohol into alkyl levulinates	The POT was highly efficient and recoverable	117
12	Ionic liquid	$[TMEDASO_3H]_{1.5}PW_{12}O_{40}$	Conversion of fructose into 5-hydroxymethylfurfural (HMF) and alkyl levulinate	The POT could perform one-pot conversion of fructose into HMF and alkyl levulinate Catalytic activities of the POTs followed the order of their acid strength	118
13	Ionic liquid	$[PySalM]_3PW_{12}O_{40}$	Knoevenagel condensation	The acid-base bifunctional POT provided a controlled nearby position for the acid-base dual sites	119
14	Ionic liquid	PEG-2000 chain-functionalized alkylimidazolium $H_3PW_{12}O_{40}$	Esterification of alcohols and aldehydes	Emulsion was formed between the POT and substrates during the reaction promoting the catalytic process, which, after reaction, was broken by addition of a weakly polar organic solvent to facilitate separation of the POT	120
15	Organozirconium complexes	$[(n-C_4H_9)_4N]_6[\alpha-PW_{11}Al(OH)O_3ZrCp_2]_2$ $[(n-C_4H_9)_4N]_6[\alpha-SiW_{11}Al(OH)_2O_3ZrCp_2]_2 \cdot 2H_2O$ ($Cp = \eta^5-C_5H_5^-$)	Esterification of fatty acids with methanol	The P-containing POT exhibited higher activity than the Si-containing one due to its Lewis acidity; fatty acids interacted with the Lewis acid sites in the catalysts	121
16	Cationic Al(III)-Schiff base complex (Al(III)-salphen)	$[Al(salphen)(H_2O)_2]_3[\alpha-PW_{12}O_{40}]_mC_8H_{10} \cdot nCH_3COCH_3$	Pinacol rearrangement	The organo-modified POT exhibited higher activity than its parent components, arising from the synergistic effect of Al(III)-salphen and POT in a porous framework	122

TPSP: triphenyl(3-sulfopropyl)phosphonium. MIM-PS: zwitterion 3-(1-methylimidazolium-3-yl) propane-1-sulfonate. NMP: *N*-methyl-pyrrolidonium. DPySO₃: *N,N'*-di(3-sulfopropyl) 4,4'-dipyridinium. MIMBS: methylimidazolebutylsulfate. PySalM: 1-(2-salicylaldehyde)pyridinium. Salphen = *N,N'*-phenylenebis(salicylideneimine).

such a combination of strategies are discussed in section 6. In order to enable a better comparison and outlook, the reported works in the literature have been tabulated in Tables 2–9. In these tables, the “Remarks” columns list the most important features of the reported works with emphasis on the catalyst’s structure and not the reaction, to fit the scope of this review article. It should be noted that HPTAs, in their free form, are sometimes either insoluble in the reaction medium or easily separable from the reaction mixture and hence can act as heterogeneous catalysts (e.g. ref. 50–52) and are not covered in Tables 2–9 because our focus in this paper has been placed on heterogenization of originally homogeneous HPTAs *via* modification of their structures.

3. Inorganic cation-substituted solid POTs

Substitution of protons by a cation with appropriate size, amount, charge, and hydrophobicity could result in insoluble solids provided that the substituted cation can make strong ionic interactions with POT. About three decades ago, Moffat *et al.* reported the synthesis of microporous POT catalysts using salts of heteropoly compounds with different monovalent cations.⁵³ To date, cations such as Cs⁺, Na⁺, K⁺, NH₄⁺, Ag⁺, Sn²⁺, Zn²⁺, Bi³⁺, Mn²⁺, Co²⁺, and Cu²⁺ have successfully substituted protons of the homogeneous POTs to heterogenize them. They are listed in Tables 2–4. Although the synthesis of solid POT catalysts would attract more scientific and industrial attention when associated with a practical application in a typical reaction, tuning the properties of solidified POTs with inorganic cations has been the sole subject of several articles for many years (Table 2). Tables 3 and 4 list the works in this field, including applications in acid catalysis and oxidation reactions, respectively.

Extensive researches have focused particularly on the caesium cation, most likely because of its unique effects not only on the solubility but also on the surface area, pore structure and surface acidity of the resultant POT.²³ Professors Okuhara, Mizuno and Misono and their colleagues have thoroughly investigated the changes in catalytically important aspects of Cs⁺ substituted phosphotungstic acid (PTA) in their inspiring works;^{23,54–56} water-soluble PTA was converted to a water-tolerant acid catalyst (Cs_xH_{3–x}PW₁₂O₄₀), the hydrophobicity of which is even higher than those of silica–alumina and some zeolites²³ and, interestingly, its catalytic features could be well tuned *via* varying the amount of Cs⁺ cations. Changing the pore structure from ultramicroporous (pore width 0.43 to 0.50 nm) in Cs_{2.1}H_{0.9}PW₁₂O₄₀ to mesoporous in Cs_{2.5}H_{0.5}PW₁₂O₄₀ enables shape-selective catalysis properties. More importantly, upon incorporation of Cs⁺ in PTA, the surface area slightly decreased from 6 m² g^{–1} at $x = 0$ to 1 m² g^{–1} at $x = 2$, but further increasing the Cs⁺ content to $x = 3$ surprisingly increased the surface area to 156 m² g^{–1}.⁵⁵ Fig. 1 shows the surface area as well as the surface concentration of acid sites of Cs_xH_{3–x}PW₁₂O₄₀ as a function of Cs⁺ content.^{23,56}

As Fig. 1 shows, the surface acidity (number of protons on the surface), which was determined by IR spectroscopy studies of CO adsorption at 110 K, reached a maximum at $x = 2.5$. This remarkably high surface acidity along with the reported higher acid strength of Cs_{2.5}H_{0.5}PW₁₂O₄₀ (abbreviated as Cs2.5), measured by microcalorimetry of NH₃ adsorption and TPD of NH₃, compared to the common solid acid catalysts (e.g. H-ZSM-5 and SiO₂–Al₂O₃)^{55,57} has proposed Cs2.5 as a superior solid acid catalyst. Recently, a great deal of attention has been paid to catalytic applications of Cs2.5, particularly in acid catalysis reactions (Table 3). Cs3, in spite of its weaker acidity compared to the better known Cs2.5, has also been investigated as a support for Ru nanoparticles in the conversion of cellobiose and cellulose into sorbitol in aqueous medium.⁵⁸

Silicotungstic acid is another POT that has been heterogenized by substitution of Cs⁺ cations.^{59–61} For example, Pesaresi *et al.* have reported the synthesis of Cs_xH_{4–x}SiW₁₂O₄₀ and its application for C₄ and C₈ triglyceride transesterification and palmitic acid esterification with methanol.⁶¹ The degree of heterogenization strongly depends on the amount of caesium cations: at lower Cs content ($x \leq 0.8$) these catalysts showed partially homogeneous properties, while at higher Cs loading they exhibited entirely heterogeneous properties.

The substitution of some other inorganic cations including Na⁺, K⁺, NH₄⁺, Ag⁺, Sn²⁺, Zn²⁺, Bi³⁺, Mn²⁺, Co²⁺, and Cu²⁺ into POT structures in order to heterogenize them have been also documented, but not as much as caesium (please see Tables 3 and 4). As these tables show, this class of solidified POT catalysts is more interesting for acid catalysis reactions compared to oxidation reactions, most probably because of their high and tunable acidity.

4. Organo-solidified POTs

Parallel to the intrinsically interesting properties of POMs, succinctly summarized in section 1, their potential for functionalization *via* organic compounds is a tremendous impetus that has pushed research on POMs in the last ten years. Such functionalization has been found compulsory for implementation of POMs to some, mainly new, applications, since organo-modified POMs render several opportunities for facile integration of POMs into functional architectures and devices that original POMs cannot.⁸⁴ This gives an additional firm rise to push the essentially attractive area of organic–inorganic hybrid materials to be applied in POM preparation.

In the field of catalysis, employing hybrid organic–inorganic polyoxometalate-based catalysts is currently a hot topic being enthusiastically and rapidly explored, not only for heterogenization purposes but also for their versatility in liquid organic reactions arising from the wide variety of organic groups and proper adjustment of the surface state. Indisputable merits of exploiting organic species in POT structures are increasing catalyst hydrophobicity and thus preventing (i) aggregation of catalyst particles and (ii) poisoning of acid sites by H₂O in water-involving reactions. On the other hand, functionalization and even post-functionalization of POTs

Table 6 Organo-solidified POTs for oxidation reactions

Entry	Organic source	POT–organic hybrid	Reaction	Remarks	Ref.
1	Quaternary ammonium surfactant: tetra- <i>n</i> -butylammonium	$[(n\text{-C}_4\text{H}_9)_4\text{N}]_4[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$	Size-selective oxidation of various organic substrates, including olefins, sulfides, and silanes, with H_2O_2	The nonporous POT has been synthesized <i>via</i> a bottom-up approach, which gave good catalytic activity because of high mobility of the catalyst in the solid bulk and easy cosorption of the substrate and oxidant	106
2	Quaternary ammonium surfactant: Tetra methylammonium Tetra- <i>n</i> -propylammonium Tetra- <i>n</i> -butylammonium Tetra- <i>n</i> -pentylammonium	$[(\text{CH}_3)_4\text{N}]_4[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2]$ $[(n\text{-C}_3\text{H}_7)_4\text{N}]_4[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2]$ $[(n\text{-C}_4\text{H}_9)_4\text{N}]_4[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2]$ $[(n\text{-C}_5\text{H}_{11})_4\text{N}]_4[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2]$	Epoxidation of alkenes (propene and 1-hexene)	High catalytic activity of the POT arises from flexibility of crystal structures of the POT and high mobility of alkylammonium cations, resulting in uniform distribution of reactant and oxidant molecules throughout the solid bulk of the catalyst. Not only atomic structures of the active sites but also the structures and dynamics of the surroundings are important for the design and synthesis of highly active POT	123
3	Quaternary ammonium surfactants with varying alkyl chain length: DDA, TDA, HAD, and ODA	$(\text{DDA})_3\text{PW}_{12}\text{O}_{40}$ $(\text{TDA})_3\text{PW}_{12}\text{O}_{40}$ $(\text{HDA})_3\text{PW}_{12}\text{O}_{40}$ $(\text{ODA})_3\text{PW}_{12}\text{O}_{40}$	Oxidative desulphurization of dibenzothiophene with H_2O_2	The mesostructured POT was highly efficient due to the presence of long alkyl chains on its surface that provided suitable hydrophobic–hydrophobic properties and polarity resulting in better adsorption of the substrate sulfide molecules and desorption of the product sulfones	124
4	Quaternary ammonium surfactant: CTAB	$[\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N}]_4\text{H}_2\text{SiV}_2\text{W}_{10}\text{O}_{40}$	Catalytic wet peroxide oxidation (CWPO) of phenol	High performance of the POT catalyst was attributed to (i) micellar structure formed by surfactant and (ii) catalytic center $\text{H}_2\text{SiV}_2\text{W}_{10}\text{O}_{40}^{4-}$	125
5	Quaternary ammonium surfactants with varying alkyl chain length: DA, DDA, and TDA	$[\text{C}_n]_3\text{PW}_{12}\text{O}_{40}$ $n = 10, 12, 14$	Epoxidation of olefins with H_2O_2	The $(\text{DDA})_3\text{PW}_{12}\text{O}_{40}$ POT formed a Pickering emulsion in the presence of water and an aromatic solvent, which is particularly efficient for the epoxidation of olefins	105
6	Quaternary ammonium surfactants with varying alkyl chain length: DDA, TSA, and DODA	$(\text{DDA})_9\text{LaW}_{10}\text{O}_{36}$ $(\text{TSA})_9\text{LaW}_{10}\text{O}_{36}$ $(\text{DODA})_9\text{LaW}_{10}\text{O}_{36}$	Oxidative desulphurization of dibenzothiophene with H_2O_2	Alkyl chains on the surface of the amphiphilic POT adsorbed weakly polar sulfide by hydrophobic–hydrophobic interactions, where they were oxidized to sulfones by active POT species	126
7	Quaternary ammonium surfactants: ODA	$(\text{ODA})_7\text{PW}_{11}\text{O}_{39}$	Oxidative desulphurization of a model diesel with H_2O_2	The heterogeneous catalyst has shown a superior desulfurization performance when compared with the homogeneous quaternary ammonium TBAPW ₁₁ catalyst	127
8	Quaternary ammonium surfactants: TPA and TBA	$(\text{TPA})_{2.75}[\text{H}_{5.25}\text{W}_{12}\text{O}_{40}]\cdot 7.42\text{H}_2\text{O}$ $(\text{TBA})_{3.31}[\text{H}_{4.69}\text{W}_{12}\text{O}_{40}]\cdot 1.08\text{H}_2\text{O}$	Oxidative cleavage of oleic acid	Employing heterogeneous Keggin clusters of tungsten oxide in the oxidative cleavage of UFAs was reported for the first time, which showed excellent activity	128
9	Ionic liquid	$[\text{PSPy}]_3\text{PW}_{12}\text{O}_{40}$	Oxidative desulphurization of dibenzothiophene (DBT), 4,6-dimethyldibenzothiophene	Catalytic oxidation activity of the sulfur-containing compounds occurred in the	129

Table 6 (continued)

Entry	Organic source	POT-organic hybrid	Reaction	Remarks	Ref.
10	Ionic liquid	[BuPyPS] ₃ PW ₁₂ O ₄₀ [PhPyPS] ₃ PW ₁₂ O ₄₀ [BzPyPS] ₃ PW ₁₂ O ₄₀	(4,6-DMDBT), and benzothiophene (BT) with H ₂ O ₂ Oxidation of thioethers and thiophenes and desulfurization of model fuels	following order: DBT > 4,6--DMDBT > BT The POTs showed thermoregulated phase-separable behavior in the reaction Temperature-dependent solubility of the POTs as a function of the organic cation in water was studied	130
11	Ionic liquid	[HDIm] ₂ {[W=O(O ₂) ₂] ₂ (μ-O)} [HHIm] ₂ {[W=O(O ₂) ₂] ₂ (μ-O)}	Epoxidation of olefins	Efficient reaction-induced phase-separation POT has been developed in this work. The reaction system switched from triphase to emulsion and then to biphasic and finally to all the POT self-precipitating at the end of the reaction	131
12	Ionic liquid	PEG chain-functionalized N-dodecylimidazolium POT	Epoxidation of olefins with H ₂ O ₂	The highly efficient POT was also a self-separation catalyst	132
13	Ionic liquid	[PEG-300-C ₁₂ MIM] {[W=O(O ₂) ₂] ₂ (μ-O)} [PEG-800-C ₁₂ MIM] {[W=O(O ₂) ₂] ₂ (μ-O)}	Epoxidation of olefins with H ₂ O ₂	Although the POT was dissolved considerably by increasing the temperature during the reaction, it was recovered well by a thermoregulated-phased separation after the reaction	133
14	Ionic liquid	MimAM(H)-PW	Epoxidation of alkenes with H ₂ O ₂	The POT exhibited advantages of convenient recovery, steady reuse, simple preparation, and flexible composition	134
15	Ionic liquid	DPyAM(H)-PW	Oxidation of benzyl alcohol with H ₂ O ₂	The POT gave high conversion and selectivity in the heterogeneous solvent-free catalytic system	135
16	Ionic liquid	[Dmim] _{1.5} PW	Oxidation of alcohols with H ₂ O ₂	The POT was an efficient solid catalyst with easy recovery and good reusability	136
17	Ionic liquid	[C ₄ mim] ₃ PW ₁₂ O ₄₀ [C ₄ mim] ₄ SiW ₁₂ O ₄₀	Oxidation of sulfides with H ₂ O ₂	Excellent performance of the POT was attributed to its promoted redox property arising from neighboring functionalized ionic liquid cations	137
18	Ionic liquid	[TMGDH] _{2.3} H _{0.7} PW [TMGDH] ₃ PW [TMGOH] _{2.2} H _{0.8} PW [TMG] ₃ PW	Epoxidation of <i>cis</i> -cyclooctene with H ₂ O ₂	The mesostructured POT exhibited superior activity because of controllable introduction of hydroxyl groups into its structure resulting in promotion of unusual morphology and pore structure, together with a hydrogen-bonding-enriched microenvironment surrounding the POT anion	138
19	Ionic liquid	[TMGHA] _{2.4} H _{0.6} PW	Oxidation of benzyl alcohol with H ₂ O ₂	High activity of the POT was ascribed to its mesoporosity and dual wettability for water and alcohols	139
20	Ionic liquid	Dicationic ionic liquids/PW ₁₂ O ₄₀	Oxidation of cyclohexene with molecular oxygen	Using two dicationic ionic liquids, different hybrid catalysts were prepared which showed excellent activity in a solvent-free reaction system	140
21	Amine: hexamethylenetetramine	[C ₆ H ₁₃ N ₄] ₂ [HPW ₁₂ O ₄₀]-2H ₂ O	Oxidative desulfurization of sulfur-containing model fuel	The hybrid POT was highly active and recoverable	141

Table 6 (continued)

Entry	Organic source	POT-organic hybrid	Reaction	Remarks	Ref.
22	Tripodal organic triammonium cation: BTE	BTE-PW ₁₁ O ₃₉	with H ₂ O ₂ Epoxidation of olefins with H ₂ O ₂	The hybrid POT catalyzed olefin epoxidation efficiently	142
23	Quaternary ammonium surfactant: DA	DA ₁₁ [La(PW ₁₁ O ₃₉) ₂]	Oxidation of alkenes, alkenols, sulfides, silane and alcohol with H ₂ O ₂	The catalyst played a dual trapping role for both substrate and oxidant	143
24	C ₁₂ mim CTA TBA	[C ₁₂ mim] ₅ PTiW ₁₁ O ₄₀ [CTA] ₅ PTiW ₁₁ O ₄₀ [TBA] ₅ PTiW ₁₁ O ₄₀	Epoxidation of olefins with H ₂ O ₂	Organic counteractions greatly affected catalytic activity	144
25	Tripodal polyammonium cations	[ZnWZn ₂ (H ₂ O) ₂ (ZnW ₉ O ₃₄) ₂] ¹²⁻	Epoxidation of allylic alcohols and oxidation of secondary alcohols with H ₂ O ₂	Mesoporosity of the synthesized catalyst enabled oxidation of many organic substrates irrespective of molecular shape, with efficiency similar to that of the corresponding homogeneous catalyst The catalyst showed three-dimensional perforated coral-shaped amorphous materials with the organic cations surrounding the POT anions	145
26	Coordination polymers	[Cu ^{II} ₂ (C ₅ H ₅ NCOO) ₂ (4-bpo) ₂ (H ₂ O) ₂ SiW ₁₂ O ₄₀ ·H ₂ O (1) [Cu ^I ₄ (4-bpo) ₆ SiW ₁₂ O ₄₀ ·3H ₂ O (2) [Cu ^I ₄ (3-bpo) ₄ SiW ₁₂ O ₄₀ ·3H ₂ O (3)	Epoxidation of styrene with <i>tert</i> -butyl hydroperoxide	Geometry and coordination mode of bpo ligands played important roles in the formation of the hybrid solidified POT	146
27	Coordination polymers	{[Cu(en) ₂] ₃ [TeW ₆ O ₂₄]}·6H ₂ O	Epoxidation of cyclohexene and styrene by <i>tert</i> -butyl hydroperoxide	One of the rare examples of Anderson structure of the POTs, which gave high catalytic efficiency and suggested that Anderson POTs can be further explored as a template for generation of ladder architecture	147
28	Metalloporphyrins	{[Cd(DMF) ₂ Mn ^{III} (DMF) ₂ TPyP](PW ₁₂ O ₄₀)}·2DMF·5H ₂ O	Selective oxidation of alkylbenzenes	The POT-porphyrin hybrid combined multiple functional groups in a single structure, which resulted in excellent activity and size selectivity of the catalyst in accordance with its pore dimensions	148

Decyltrimethylammonium bromide (DA-Br), dodecyltrimethylammonium bromide (DDA-Br), tetradecyltrimethylammonium bromide (TDA-Br), hexadecyltrimethylammonium bromide (HDA-Br), and octadecyltrimethylammonium bromide (ODA-Br). Dodecyltrimethylammonium bromide (DDA-Br), trimethylstearyl ammonium bromide (TSA-Br), and dimethyldioctadecyl ammonium bromide (DODA-Br). (DDA = dimethyldioctadecyl ammonium, omim = 1-octyl-3-methyl-imidazolium) DIm: protic *N*-dodecylimidazolium. HIm: *N*-hexylimidazolium. MimAM: 1-aminoethyl-3-methylimidazolium. DPyAM: amino-attached 4,4-bipyridine. Dmim: 1,1'-(butane-1,4-diyl)-bis(3-methylimidazolium). C₄mim: 1-*n*-butyl-3-methylimidazolium. TMGDH: dihydroxy-tethered tetramethylguanidinium. TMGOH: monohydroxy-tethered tetramethylguanidinium. TMG: tetramethylguanidinium. BTE: benzene-1,3,5-[tris(phenyl-4-carboxylic acid)] tris(2-trimethyl-ammonium ethyl) ester. C₁₂mim: 1-dodecyl-3-methylimidazolium. CTA: cetyltrimethylammonium. TBA: tetrabutylammonium. *n*-bpo: (2,5-bis(*n*-pyridyl))-1,3,4-oxadiazole. en: ethylene-diamine. DMF: *N,N*-dimethylformamide; TPyP: tetrapyridylporphyrin. DA: dodecyltrimethylammonium bromide.

with organic moieties are currently performed under either hydrothermal conditions benefiting from a simple, often one-pot, procedure or mild synthetic conditions complying with the principles of “chimie douce”.^{85–87} Given the aforementioned positive features and comparatively huge number of recent publications in this domain, the incorporation of organic groups into the structure of POMs has been the sole subject of several recent review papers.^{84,86,88–95}

Different techniques developed for the design and synthesis of organic-inorganic hybrid POM compounds have been widely

investigated. Briefly, they have been categorized into two classes based on the nature of interactions between organic and inorganic parts: non-covalent and covalent POT-organic hybrids. In these two classes, many organic compounds have been encapsulated into POT structures to modify its heterogeneous catalytic properties such as surfactants, especially nitrogen-containing ones, amines, ionic liquids, *etc.* With the aid of crystal engineering and supramolecular cooperation, although the first group has been more deeply investigated^{96–98} most probably due to its comparatively convenient fabrication,

Table 7 POTs solidified with immobilization on supports for acid catalysis reactions

Entry	Support	POT	Reaction	Remarks	Ref.	
1	Silica	C ₈ -AP grafted SBA-15	H ₃ PW ₁₂ O ₄₀	Hydrolysis of ester	The supported POT was surrounded by hydrophobic alkyl groups in channels of nanostructured mesoporous silica, which afforded paths for the efficient approach of reactant molecules and water to the active sites	166
2		AP grafted SBA-15	H ₃ PW ₁₂ O ₄₀	Acid–base tandem reaction	The supported POT could be easily tuned: predominantly basic, or predominantly acidic, or equally acidic and basic by changing the ratio of polyacid and amine groups	167
3		SiO ₂	H ₃ PW ₁₂ O ₄₀	Polymerization of β-pinene	The supported POT had no poison to hydrogenation catalysts and had low corrosion to polymerization and hydrogenation equipment	168
4		SiO ₂	H ₃ PW ₁₂ O ₄₀	Esterification of camphene with carboxylic acids	The supported POT exhibited very good activity, high turnover number, and steady reuse without loss of activity and selectivity	169
5		SiO ₂	H ₃ PW ₁₂ O ₄₀	Isomerization of α-pinene and longifolene	The catalyst was very active in small amounts, exhibiting high turnover numbers, good stability and steady reuse without loss of activity	170
6		SiO ₂	H ₃ PW ₁₂ O ₄₀	Conversion of citronellal to menthol	Adding Pd to the supported POT's structure, a bifunctional catalyst was developed that directs the reaction <i>via</i> acid-catalyzed cyclization followed by Pd-catalyzed hydrogenation	171
7		SiO ₂	H ₄ SiW ₁₂ O ₄₀	Esterification of oleic acid with methanol	The supported POT showed high catalytic activity close to that of the unsupported one; however, leaching of active sites resulted in gradual deactivation of the catalyst	172
8	Transition metal oxides	Mesoporous ZrO ₂ Mesoporous ZrO ₂ -ethane-bridged organosilica	H ₃ PW ₁₂ O ₄₀	Transesterification of Eruca Sativa Gars oil	The ethane-containing supported POT exhibited higher catalytic activity due to combination of strong Brønsted acidity, 3D interconnected mesostructure, and enhanced hydrophobicity	173
9		Mesoporous ZrO ₂ Mesoporous ZrO ₂ -benzene/ethane-bridged organosilica	H ₃ PW ₁₂ O ₄₀	Esterification of levulinic acid	The alkyl-containing supported POT exhibited higher catalytic activity due to the combination of strong Brønsted acidity, well-defined ordered mesostructure, homogeneous dispersion of active sites, and enhanced surface hydrophobicity of the hybrid catalysts	174, 175
10		Ta ₂ O ₅	H ₃ PW ₁₂ O ₄₀	Esterification of acetic acid with ethanol	The POT kept its Keggin structure after immobilization and micro- or micro-meso porosities and nanometer sizes. It showed higher activity than the parent PTA	176
11		Hydrous ZrO ₂	H ₃ PW ₁₂ O ₄₀	Condensation of dimesones, urea, aryl aldehydes, enolizable ketones, and acetyl chlorides	Structural integrity and good dispersion of the POT in the support were responsible for the high catalytic efficiency	177
12		ZrO ₂	H ₃ PW ₁₂ O ₄₀	Regioselective monobromination of aromatic substrates	The supported POT exhibited excellent yields and efficient recovery	178
13		Nano-TiO ₂ -NH ₂	H ₃ PW ₁₂ O ₄₀	Synthesis of 2,4,5-triaryl substituted imidazoles	The optimal synthesis conditions were achieved by the combination of response surface methodology and central composite design	179
14	MOFs	MIL-101 (Cr)	H ₃ PW ₁₂ O ₄₀	Knoevenagel condensation of benzaldehyde, esterification of acetic acid, dehydration of methanol	The supported POT was a bifunctional porous solid with outstanding catalytic performance in base- and acid-catalyzed reactions, which was obtained by direct	180

Table 7 (continued)

Entry	Support	POT	Reaction	Remarks	Ref.
15	MIL-101 (Cr)	H ₃ PW ₁₂ O ₄₀	Dehydration of fructose and glucose to HMF	and one-pot encapsulation of POT into the support Different loadings of POT were investigated resulting in highly active and recyclable solid acid catalysts	181
16	MIL-101 (Cr)	Ru-H ₃ PW ₁₂ O ₄₀	Conversion of cellulose and cellobiose into sorbitol	The ratio of acid site density (comes from the POT) to the number of Ru surface atoms in the Ru-POT/MIL-100(Cr) was optimized to reach the highest reaction efficiency	182
17	MIL-101 (Cr)	H ₃ PW ₁₂ O ₄₀	Baeyer condensation of benzaldehyde and 2-naphthol and epoxidation of caryophyllene by H ₂ O ₂	Under microwave-assisted heating reaction, the supported POT was highly active and exceptionally stable	183
18	MIL-101 (Cr)	H ₃ PW ₁₂ O ₄₀	Alcoholysis of styrene oxide	Probing the acid sites using <i>in situ</i> FTIR showed generation of additional hydroxyl groups and Lewis acid sites, which were responsible for the high efficiency of the supported POT in a short reaction time	184
19	Polymers	Polymeric ionic liquid: Poly(VMPS)	Esterification of alcohols	Both the polymeric framework and large heteropolyanion were responsible for the solid nature of the catalyst Excellent catalytic activity came from acidic SO ₃ H functional groups in the hybrid catalyst	185
20	Povidone (PVP)	H ₃ PW ₁₂ O ₄₀	Azidation of alcohols	Higher surface area of the PVP-POT (10.5 m ² g ⁻¹) compared to PTA was responsible for enhancing the catalytic activity	186
21	PDVC (poly(<i>p</i> -divinylbenzene, 4-vinylbenzyl chloride))	H ₃ PW ₁₂ O ₄₀	Acetylation of glycerol	Ethylenediamine was used as a soft linker between polymer and PTA. The POT showed hybrid characteristic of heterogeneous and homogeneous catalysts, resulting in superior activity compared to that in the literature	187
22	Magnetic NPs	Organo-functionalized SiO ₂ (shell)-iron oxide (core)	Friedel-Crafts reactions of indoles	The first report on non-covalent immobilization of POT on MNPs	188
23		Organo-functionalized SiO ₂ (shell)-iron oxide (core)	Esterification of free fatty acid	The first-time application of MNP-supported POTs in esterification reactions	189
24		Poly(glycidyl methacrylate) (PGMA) (shell)-iron oxide (core)	Esterification of free fatty acids and transesterification of triglycerides	Good catalytic performance was ascribed to the high acidity and nano-size of the catalyst Firm attachment of POT on MNPs <i>via</i> covalent binding, stable PGMA shell, and superparamagnetic properties of MNPs led to high stability and recyclability of the catalyst	190
25		Diamine-functionalized silica-coated magnetite (Fe ₃ O ₄)	Synthesis of tetrahydrobenzo[<i>b</i>]pyrans and Knoevenagel condensation	The catalyst had relatively uniform spherical nanoparticles with a 60 nm average size and offered high reaction efficiency, recyclability, and avoidance of organic solvent	191
26	Zeolites	Zeolite imidazolate framework (ZIF-67)	Friedel-Crafts acylation of anisole with benzoyl chloride	Excellent dispersion of the POT over ZIF-67 was achieved, with different amounts of PTA encapsulated in the support structure resulting in high activity, stability and reusability	192
27	Carbon materials	Activated carbon	Polymerization of β-pinene	The POT could interact strongly with surface oxygen-containing groups on activated carbon, resulting in stable immobilization of POT, which led to a decrease in the specific surface area of the activated carbon	193
28	Other	Mineral clay: bentonite (BNT)	Hydroxyalkylation of	Optimized amount of the POT	194

Table 7 (continued)

Entry	Support	POT	Reaction	Remarks	Ref.
	supports		phenol	supported on BNT showed higher product yield and selectivity than those of parent POT and BNT, mainly due to excellent dispersion of the POT on BNT resulting in redistribution of Brønsted and Lewis acid sites on BNT	
29	Clay: K10 and KSF montmorillonite	H ₃ PW ₁₂ O ₄₀	Condensation of 1,2-phenylenediamines and ketones	The supported POT was highly active, non-hygroscopic, non-corrosive, and efficiently recyclable	195
30	Magnesium fluoride (MgF ₂)	H ₃ PW ₁₂ O ₄₀	Esterification of oleic acid and simultaneous esterification and transesterification of jatropha oil	A series of catalysts with different acidity and dispersion of active sites were prepared and compared to each other	196

AP: 3-aminopropyl. VMPS: 1-vinyl-3-propane sulfonate imidazolium.

the second group is currently undergoing a rapid development not only because of some unavoidable drawbacks of the first group (e.g. catalyst leaching despite appreciable stability in the reaction media) but also because of the undisputed advantages of covalently linked hybrids such as fine control of the interaction between the components resulting in enhancement of synergistic effects, better dispersion of POMs in matrices, and, most importantly, higher and more lasting stability of the assembly.

The first class, non-covalent hybrids, encompasses those hybrids with electrostatic interactions, hydrogen bonds or van der Waals forces. The most distinguished example of this group is organic cation-substituted POMs; the anionic character of POMs renders the exchange of their countercations feasible. As mentioned above, POTs are originally soluble in water and polar solvents, while generally metal oxides are not. Since complete dissolution and solvolysis of the components to give charged species are required for formation of ionic bonding, POTs, unlike the metal oxides, are capable of electrostatically interacting with positively charged solutes, resulting in facile incorporation of inorganic (discussed in section 3) and organic cations into the structures of POTs. Organic cations in ionic liquids have attracted large attention to act as countercations pairing with POT anions since 2004.^{99,100} This attention arises not only from the ease of synthesis procedure but also from increasing interest in ionic liquids due to their unique properties such as low melting point, non-volatility and flammability, and ionic conductivity. These interesting features, firstly, rendered the resultant POT-organic hybrid efficiently applicable in electrochemical processes and practically applicable in surface and interface science through fabrication of self-assembled films (e.g. layer-by-layer (LbL) or Langmuir-Blodgett (LB) films).^{95,101} Many studies were then done on the preparation of catalytically active solid POT-organic hybrids out of ionic liquids. Hydrogen bonding in the fabrication of POM-organic hybrids based on non-covalent interactions has also been reported, similar to what was obtained in linking proteins to POMs;^{102,103} however, the overwhelming majority of the non-covalent interactions involve ionic bonding.

The second class contains those hybrids in which organic and inorganic parts are connected *via* strong covalent or ionic-covalent bonds. These hybrids are usually formed either by substitution of an oxo group of the POMs by an organic ligand or by electrophilic organic components approaching the nucleophilic surface oxygen atoms of POMs. Undoubtedly, this class of organo-modified POTs is more stable due to the stronger interactions between the organic and the inorganic parts. However, fabrication of their assemblies often involves sophisticated functionalization. The first step is removing one or more addenda atoms and their attendant oxide ions from the structure, giving a lacunary structure. Then, organic moieties can be grafted to the organometallic compounds of lacunary POT clusters (Fig. 2). Different strategies for the second step have been employed based on functionalization and/or post-functionalization of POTs (Fig. 3), which have been nicely investigated and compared in a critical review paper presented by Proust *et al.*⁸⁴

Some of the previously mentioned review papers on organo-modification techniques of POMs have covered their catalytic aspects also as a subsection; however, particular focus that thoroughly covers the catalytic applications of POM-based organic-inorganic hybrids has been less documented;^{88,92,93} Nlate and Jahire presented a microreview on dendritic POM-based hybrid catalysts for oxidation reactions, which although efficient and recoverable, are categorized under homogeneous catalysis,⁹² while the other two references addressed heterogeneous catalysis by organic-inorganic hybrid POMs.^{88,93} Herein, we have listed the catalytic applications of organo-solidified W-based POMs (POTs) to encourage exploiting the inherently interesting properties of tungsten, succinctly mentioned in the Introduction section, and heterogeneous organo-modified POMs simultaneously, which could be advantageous to be employed in several organic liquid reactions. Tables 5 and 6 summarize the organo-modified POT catalysts with their applications in acid catalysis and oxidation reactions, respectively. It should be noted that the reported homogeneous POT-organic hybrids used with a phase transfer agent, despite sometimes being efficient in terms of recyclability, are not included in these tables.

Table 8 POTs solidified with immobilization on supports for oxidation reactions

Entry	Support	POT	Reaction	Remarks	Ref.
1	Silica	Ionic liquid-modified SiO ₂ [W(=O)(O ₂) ₂ (H ₂ O)] ₂ (μ-O)] ²⁻	Epoxidation of olefins with H ₂ O ₂	Activity of the supported POT was comparable to that of the homogeneous analogue, confirming successful heterogenization No leaching of active sites was obtained	197
2	Ionic liquid-modified SBA-15	H ₃ PW ₁₂ O ₄₀	Oxidation of alcohols with H ₂ O ₂	The supported POT exhibited high catalytic activity and selectivity and reusability without leaching in solvent-free catalytic reaction	198
3	Ionic liquid-modified SBA-15	H ₃ PW ₁₂ O ₄₀	Oxidation of alcohols with H ₂ O ₂	The supported POT prepared <i>via</i> one-pot procedure Occasion of adding POT as well as location of the organic cations in the mesostructure played a crucial role in catalytic performance	199
4	Ionic liquid-modified SBA-15	H ₃ PW ₁₂ O ₄₀	Oxidative desulfurization of fuels	The hybrid POT possessed an ordered mesoporous structure and high specific surface area. Due to the introduction of imidazole-based ionic liquid, the catalyst exhibited good wettability for model oil, which had a significant contribution to desulfurization activity	200
5	Mesoporous SBA-16	H ₆ P ₂ W ₁₈ O ₆₂	Epoxidation of olefins and oxidation of alcohols with H ₂ O ₂	Pore entrance size of the SBA-16 was modified by silylation reaction to enable trapping the POT	201
6	Transition metal oxides	Ordered mesoporous ZrO ₂ H ₃ PW ₁₂ O ₄₀ H ₄ SiW ₁₂ O ₄₀	Oxidation of alkenes with H ₂ O ₂	The supported POT exhibited higher catalytic activity compared to its parents: ZrO ₂ and heteropoly acids	202
7	MOFs	MIL-101	Oxidation of alkenes with H ₂ O ₂	The supported POTs demonstrated good activity comparable to that of homogeneous heteropoly acids In contrast to homogeneous systems, use of a higher H ₂ O ₂ /alkene molar ratio allowed increasing both alkene conversion and epoxide selectivity arising from specific sorption properties of the support	203
8	MIL-101 (Cr)	[PW ₁₁ O ₃₉] ⁷⁻ [SiW ₁₁ O ₃₉] ⁸⁻	Oxidation of alkenes with H ₂ O ₂	The supported POTs were highly active, selective (comparable to homogeneous ones) and recyclable catalysts	204
9	rht-MOF-1	H ₃ PW ₁₂ O ₄₀	Oxidation of alkylbenzene	The Keggin POT could be immobilized into the β-cage of rht-MOF-1 by a solvothermal method with a highly ordered and porous structure, resulting in good dispersion of POT in the reaction and enhancement of catalytic activity	205
10	Cu ₃ (BTC) ₂ MOF (HKUST-1)	H ₃ PW ₁₂ O ₄₀ H ₄ SiW ₁₂ O ₄₀	Oxidative desulfurization of model fuels	The POT encapsulated in MOF showed selective oxidation of sulfides to corresponding sulfones or sulfoxides with efficient reusability	206
11	Copper organic frameworks with pyrazine derivatives	H ₃ PW ₁₂ O ₄₀ H ₄ SiW ₁₂ O ₄₀	Epoxidation of alkenes with H ₂ O ₂	The heterogenized POT showed higher catalytic activity compared to the corresponding	207

Table 8 (continued)

Entry	Support	POT	Reaction	Remarks	Ref.
12	Metal-organic coordination network (MOCN): (1) Co(BBTZ) _{1.5} (HBBTZ)(H ₂ O) ₂ (2) Co _{2.5} (BBTZ) ₄ (H ₂ O) ₂ (3) Cu(BBTZ) ₂	PW ₁₂ O ₄₀ BW ₁₂ O ₄₀	Oxidative desulfurization of dibenzothiophene	homogeneous POT A new non-porous POT-based MOCN was synthesized, which showed good catalytic activity in contrast to the parent POT, due to monodispersion of POT units in the MOCN at the molecular level, exposing more active POT sites	208
13	[Cu(4,4'-bipy) ₂ (H ₂ O) ₂] _n ²ⁿ⁺ (bipy = bipyridine)	H ₃ PW ₁₂ O ₄₀ H ₄ SiW ₁₂ O ₄₀	Oxidation of ethylbenzene	Oxidation of the substrate occurred in the pore of the framework, and the valence of the metal ion in the POTs significantly influenced the catalytic activity of the 3D framework	209
14	MIL-101 (Cr)	[PW ₁₁ CoO ₃₉] ⁵⁻ [PW ₁₁ TiO ₄₀] ⁵⁻	Oxidation of alkenes with molecular oxygen and H ₂ O ₂	The POTs were electrostatically attached to the surfaces of the support, which showed good stability and no leaching under mild conditions (<i>T</i> < 50 °C)	210
15	MIL-101 (Cr)	[Ln(PW ₁₁ O ₃₉) ₂] ¹¹⁻ Ln = Eu ³⁺ and Sm ³⁺	Oxidation of styrene with H ₂ O ₂	The supported POTs exhibited higher activity than that of homogeneous parent POTs, which was further increased by microwave-assisted oxidative reactions	211
16	MIL-101 (Cr)	[Tb(PW ₁₁ O ₃₉) ₂] ¹¹⁻	Oxidative desulfurization of fuels	Higher desulfurization efficiency was obtained by the supported POT compared to the homogeneous parent POT	212
17	Polymers Ionic copolymer: AM-BM	H ₃ PW ₁₂ O ₄₀	Epoxidation of alkenes with H ₂ O ₂	Peroxo-W active sites in the POT promoted by the amino groups in the polymer matrix was responsible for the catalyst's excellent performance. Stable structure of the catalyst came from cross-linked structure of the copolymer cations	213
18	Ionic copolymer: DIM-CIM	H ₃ PW ₄ O ₁₆	Epoxidation of alkenes with H ₂ O ₂	Amphiphilic structure of the supported POT acted as a "trapping agent" for both hydrophobic alkene substrates and hydrophilic H ₂ O ₂ , promoting catalytic activity	214
19	Ionic copolymer: NDMAM-AVIM	H ₃ PW ₁₂ O ₄₀	Oxidation of alcohols with H ₂ O ₂	Excellent performance of the supported POT comes from the featured structure of the polymeric framework giving the catalyst a solid nature and stimuli-responsive behavior	215
20	Ionic copolymer: AVIM-DVB and PDIM-DVB	H ₃ PW ₁₂ O ₄₀	Oxidation of benzyl alcohol with H ₂ O ₂	High activity of the catalyst arose from amino functional groups and high BET surface area of polymeric framework	216
21	Poly(ethylene oxide-pyridinium)	H ₃ PW ₁₂ O ₄₀	Oxidation of alcohols with H ₂ O ₂	Using the supported POT, chemoselective oxidation of sterically hindered secondary alcohols in the presence of primary alcohols was achieved	217
22	Amphiphilic resins	H ₃ PW ₁₂ O ₄₀	Epoxidation of unsaturated fatty esters with H ₂ O ₂	Catalytic properties of the supported POT varied with hydrophilic/lipophilic balance (carbon chain number, spacer arm between benzene cycle and imidazole group, <i>N</i> -substitution of imidazole ring)	218

Table 8 (continued)

Entry	Support	POT	Reaction	Remarks	Ref.	
23	Polymer-immobilised ionic liquid phase	$[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]^{3-}$	Epoxidation of allylic alcohols and alkenes with H_2O_2	A new polymeric support with tunable surface properties and microstructure has been prepared by ring-opening metathesis polymerisation	219	
24	Poly(divinylbenzene)	$[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]^{3-}$	Epoxidation of olefins with H_2O_2	High catalytic activity and epoxide selectivity was attributed to an optimized hydrophilicity/hydrophobicity balance in the mesoporous environment as well as facile diffusion of the reactants and products	220	
25	Poly(methyl methacrylate)	$[(\text{CH}_2=\text{CH}(\text{CH}_2)_6\text{Si})_x\text{O}_y\text{SiW}_w\text{O}_z]^{4-}$ (1) $x = 2, w = 11, y = 1, z = 39$ (2) $x = 2, w = 10, y = 1, z = 36$ (3) $x = 4, w = 9, y = 3, z = 34$	Oxidation of organic sulfides with H_2O_2	Catalytic efficiency was affected by fine-tuning of the polymer composition, including tailored design of the POT-based monomers	221	
26	A modified porous resin	$(\text{NBu}_4)_6[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}(\text{SiC}_6\text{H}_4\text{CH}_2\text{N}_3)_2\text{O}]$	Oxidation of tetrahydrothiophene	The POT was functionalized and the resin was modified prior to immobilization to be able to have strong covalent bonding between the POT clusters and the macroporous resin surface	222	
27	Biopolymer: chitosan	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	Degradation of chitosan with H_2O_2	The POT was easy to separate from chitosan at the end of the reaction, improving the purity of the products	223	
28	Magnetic NPs	Ferromagnetic nanocrystals (iron oxide)	$(\text{DODA})_3\text{PW}_{12}\text{O}_{40}$	Oxidation of sulfides to sulfones	Nanospaces and increased surfactant alkyl chain density around the POT in the nanocones provided enhanced catalytic performance	224
29	Poly(ionic liquid) coated iron oxide	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	Epoxidation of bio-derived olefins with H_2O_2	Catalytically active centers were amino-functionalized W species, while the amphiphilic catalyst structure acted as a "trapping agent" for both hydrophobic olefin substrates and H_2O_2 molecules in the aqueous phase	225	
30	Alumina	Au/ Al_2O_3	$\text{K}_8[\text{BW}_{11}\text{O}_{39}\text{H}]\cdot n\text{H}_2\text{O}$	Epoxidation of cyclooctene with molecular oxygen	By adding Au NPs and combining catalytic activities of the POT and gold, an efficient and recoverable catalyst was developed	226
31	Other supports	Layered double hydroxides (LDHs)	$[\text{WZn}_3(\text{ZnW}_9\text{O}_{34})_2]^{12-}$	Epoxidation of allylic alcohols with aqueous H_2O_2	The first report of direct immobilization of a self-assembled POT in LDH, which showed excellent activity, high dispersion and good hydrothermal stability	227
32	$\text{Mg}_3\text{Al-NO}_3$	$[\text{WZn}_3(\text{H}_2\text{O})_2(\text{ZnW}_9\text{O}_{34})_2]^{12-}$	Oximation of aldehydes by H_2O_2	Selectivity of oximation of various aldehydes was increased under mild conditions by using the supported POT	228	
33	$\text{Mg}_3\text{Al-ionic liquid}$	$\text{La}(\text{PW}_{11})$	Selective sulfoxidation of sulfides and epoxidation of olefins	The catalyst exhibited high efficiency for both reactions and scaled-up experiments revealed that the catalyst retained its efficiency and robustness	229	

DODA = dimethyldioctadecylammonium. BBTZ = 1,4-bis-(1,2,4-triazol-1-ylmethyl)benzene.

One of the most common and unique advantages of organo-solidified POTs is their improved compatibility with the liquid medium of organic reactions, resulting in not only

comparable and even sometimes superior, catalytic efficiencies to the corresponding homogeneous POTs but also self-separation performance at the end of the reaction.

Table 9 POTs heterogenized via combined strategies

Entry	POT	Inorganic cation	Organic part	Support	Reaction	Remarks	Ref.
1	Fe ^{III} AspPW ₁₂	Fe ³⁺	Amino acid: aspartic acid (Asp)	—	Fenton-like degradation of 4-chlorophenol with H ₂ O ₂	Adding Fe to the POT's structure, the catalyst showed superior catalytic performance from acidic to neutral pH values	234
2	Na ₇ H ₂ LaW ₁₀ O ₃₆ ·32H ₂ O	Na ⁺	—	Ionic liquid-modified SiO ₂	Desulfurization of DBT, BT, and 4,6-DMDBT	The POT was highly dispersed in the support resulting in good activity of the catalyst	235
3	(TBA) ₂ H ₃ [Co ₄ (H ₂ O) ₂ (PW ₆ O ₃₄) ₂]	—	Quaternary ammonium surfactant: TBA	MOF: MIL-101	Oxidation of olefins with H ₂ O ₂	Immobilization of this sandwich-type POT on MOF was reported for the first time, which showed high activity for oxidation of various hydrocarbons	236
4	[Cu ₂ (BTC) _{4/3} (H ₂ O) ₂] ₆ [H ₂₄ XW ₁₂ O ₄₀] ₄ ·(C ₄ H ₁₂ N) ₂ (X = Si, Ge, P, As)	—	Quaternary ammonium surfactant: TMA	Cu-BTC-based MOF	Hydrolysis of esters	The catalysts exhibited (i) good dispersion of POTs at the molecular level, prohibiting conglomeration, (ii) high immobilization of POTs, preventing catalyst leaching, and (iii) a highly stable crystalline framework, allowing for catalyst recycling	237
5	H ₃ [(Cu ₄ Cl) ₃ (BTC) ₈] ₂ [PW ₁₂ O ₄₀] ₄ ·(C ₄ H ₁₂ N) ₆ ·3H ₂ O	—	Quaternary ammonium surfactant: TMA	Cu-BTC-based MOF	Adsorption and decomposition of dimethyl methylphosphonate	A novel POT/MOF with sodalite topology was obtained by a simple hydrothermal method, which showed excellent activity and stability	238
6	[Cu ₃ (C ₆ H ₃ O ₆) ₂] ₄ [(CH ₃) ₄ N] ₃ CuPW ₁₁ O ₃₉ H	—	Quaternary ammonium surfactant: TMA	MOF-199 (HKUST-1)	Aerobic oxidation	The supported POT exploited attractive features of both POT and MOF and exhibited mutual enhancement of stability by each component and high efficiency in detoxification of various sulfur compounds	239
7	PYI-Ni ₂ H[BW ₁₂ O ₄₀]	Ni ²⁺	Asymmetric organocatalytic group: <i>l</i> - or <i>d</i> -pyrrolidin-2-ylimidazole (PYI)	Chiral MOF	Asymmetric dihydroxylation of aryl olefins with H ₂ O ₂	Hydrophilic/hydrophobic properties of channels of the enantiomorphs POT-MOF were modulated to adsorb oxidant and olefins, resulting in excellent stereoselectivity	240
8	[Cu ₃ (4,4'-bpy) ₃][HSiW ₁₂ O ₄₀] ₄ ·(C ₃ H ₄ N ₂) ₂ ·[Cu(Phen)(4,4'-bpy)(H ₂ O)] ₂ [PW ₁₂ O ₄₀] ₄ ·(4,4'-bpy)	—	Imidazole and bipyridine	MOF	Oxidation of alcohols with H ₂ O ₂	The synthesized POT exhibited higher activity compared to the corresponding Mo-based POMs	241
9	TBA ₄ ·2H _{0,8} [PW ₁₁ Zn(H ₂ O)O ₃₉]	—	Quaternary ammonium surfactant: TBA	MOF: MIL-101 (Cr)	Oxidative desulfurization of fuels	The POT was homogeneously encapsulated within cages of the support without affecting its crystal structure and morphology	242
10	K ₆ P ₂ W ₁₈ O ₆₂ K _{1,4} [NaP ₅ W ₃₀ O ₁₁₀]	K ⁺	—	Silica: MCM-48, SBA-3, SBA-15 and NH ₃ ⁺ functionalized SiO ₂	Oxidation of thioethers with H ₂ O ₂	The Preyssler complex was more active compared to its Dawson analog. Characteristics of the support also affect the catalytic activity	243
11	TBA ₄ HPW ₁₁ CoO ₃₉ TBA ₃ PW ₁₁ CoO ₃₉	—	Quaternary ammonium surfactant: TBA	NH ₃ ⁺ and NH ₃ ⁺ -modified mesoporous silica	Aerobic oxidation of aldehydes	Catalytic activities of the supported POTs were comparable to those of homogeneous parent POTs; however, they showed leaching of active sites after the 3rd cycle	244
12	Cs _{2,5} H _{0,5} PW ₁₂ O ₄₀ /CTAB	Cs ⁺	Quaternary ammonium surfactant: CTAB	—	Regioselective bromination of aromatic compounds	The catalyst exhibited high yields in regioselective bromination of phenol and phenol derivatives and some other aromatic compounds with molecular bromine at room temperature.	245
13	MoO ₂ (acac)-K ₈ [SiW ₁₁ O ₃₉]	K ⁺	Molybdenylacetylacetonate complex	—	Epoxydation of alkenes with	Catalytic activity of MoO ₂ (acac) ₂ was modified by incorporation of the POT <i>via</i> covalent bonding	246

Table 9 (continued)

Entry	POT	Inorganic cation	Organic part	Support	Reaction	Remarks	Ref.
14	$\text{Pd}(\text{salen})\text{-K}_8[\text{SiW}_{11}\text{O}_{39}]$	K^+	Palladium (salen)	—	<i>tert</i> -BuOOH Suzuki cross-coupling reactions	because of the charge-transfer role of the resultant complex The resultant hybrid POT showed greatly improved activity and much higher yields of coupling products compared to its parent organic and inorganic components, even with low catalyst loading	247
15	$\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$	Cs^+	—	Silica: 2D (SBA-15) and 3D (KIT-6 and SBA-16) Silica	Acetalization of glycerol with formaldehyde	The activity of the supported nanoparticles was superior to that of the bulk one. The effect of tuning the 2D/3D architecture of the mesoporous silica supports was investigated	248
16	$\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$	Cs^+	—	Silica	Acetalization of glycerol with acetone and paraformaldehyde	For the reaction with acetone, the supported $\text{Cs}_{2.5}$ showed higher activity than the bulk one, while the supported $\text{Cs}_{2.5}$ gave a lower conversion compared to the bulk for the reaction with paraformaldehyde	249

DBT: dibenzothioephene. BT: benzothioephene. 4,6-DMDBT: 4,6-dimethylidibenzothioephene. TBA: tetrabutylammonium. BTC: benzotriethylammonium. TMA: tetramethylammonium. Bpy: bipyridine. Phen = 1,10-phenanthroline. salen = *N,N'*-bis(salicylidene)ethylenediamine.

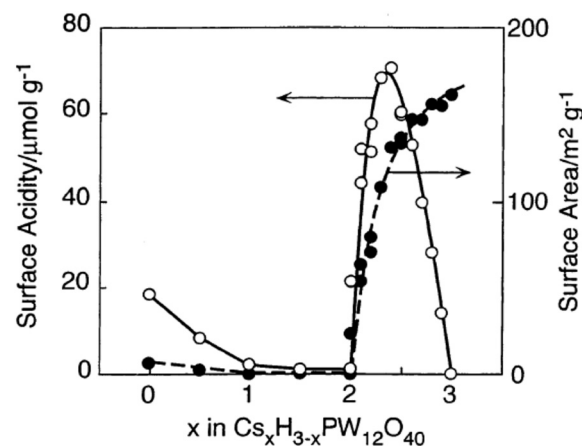


Fig. 1 Surface area and acidity of $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ as a function of Cs^+ content.^{23,56} Reprinted with permission from ref. 23. Copyright 2018 American Chemical Society.

Intriguingly, the organic-POT hybrid catalyst is capable of changing its heterogeneous behavior during liquid-phase organic reactions; at the beginning of the reaction, it is obviously a solid catalyst in the reaction mixture, which would then turn into a pseudo-homogeneous system during the reaction, often upon heating. Afterwards, the reaction mixture keeps a pseudo-liquid phase until the end of the reaction, when the catalyst starts to precipitate, often upon cooling to room temperature (Fig. 4). This enables self-separation and easy recovery of the organo-solidified POT catalyst.

Leclercq *et al.* have stabilized Pickering emulsion medium for oxidation reactions by using $[\text{C}_{12}]_3\text{PW}_{12}\text{O}_{40}$ in the presence of water and an aromatic solvent (Fig. 5). Combining the advantages of biphasic catalysis and heterogeneous catalysis in such catalytic emulsions made separation of the products easy and prevented catalyst leaching.¹⁰⁵ Mizuno *et al.* have reported preparation of a size-selective catalyst *via* organo-modification of the POT silicodectungstate by tetrabutylammonium, which was synthesized through a bottom-up approach. The resultant hybrid gave excellent catalytic activity because of the high mobility of the catalyst in the solid bulk and easy cosorption of the substrate and oxidant, H_2O_2 (Fig. 6).¹⁰⁶

5. POTs solidified *via* immobilization onto supports or into matrixes

The most conventional method to prepare heterogeneous POT-based catalysts is deposition of POTs onto supports or into matrixes.¹⁴⁹ Depending on the nature of the POTs and type of support, different strategies have been developed for immobilization of POTs on supports. Examples mainly include impregnation, ion exchange, adsorption, encapsulation, covalent linkage, *etc.* Different supports have been introduced as immobilizers: graphite (HOPG),^{150–152} carbon nanotubes (CNTs),^{153–160} and metal surfaces such as Au (ref. 161 and 162) and Ag (ref. 163) have been employed as

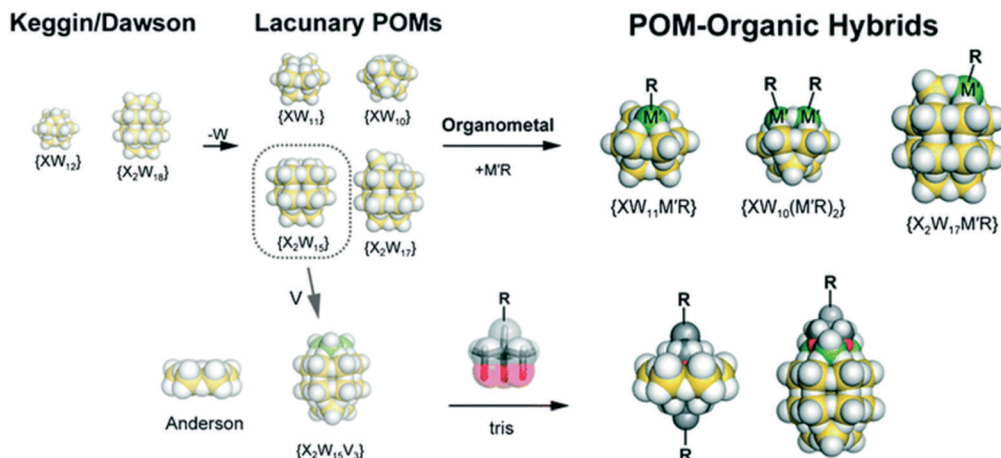


Fig. 2 Schematic view of the preparation of covalent POT-organic hybrids.⁹⁵ Reproduced from ref. 95 with permission from the Royal Society of Chemistry.

support for several applications like microscopy imaging, electrodes and electro-assisted catalysis and sensing.

Focusing on catalysis applications, employing porous (often meso) supports such as silica, alumina, transition metal oxides, metal-organic frameworks (MOFs), magnetic nanoparticles (MNPs), zeolites, carbons, *etc.*, as well as polymeric matrixes to host POTs has been reported. Roughly speaking, most of the reported immobilized POTs on the support encompass non-covalent interactions between POTs and support, which has provoked a criticism that such solid catalysts leach into the liquid medium of the reaction due to the weak interactions between active species and support, eventually causing deactivation of the catalysts. To address this matter, efforts on covalently linking POTs to supports, which often requires advanced functionalization prior to or during the immobilization, are rapidly under way today. These efforts have chiefly focused on using polymeric and MOF-made supports due to their capability of covalently encapsulating POTs arising from their organic frameworks. This is most probably

the reason for many more reported works on these two supports to carry catalytically active POMs compared to the other types of supports and, consequently, for presenting review papers exclusively on POM-MOF¹⁶⁴ and POM-polymer^{98,165} hybrids.

In general, owing to the intrinsic properties of the supports, the immobilized POTs have exhibited enhanced catalytically important features compared to their bulk forms. The most striking feature is porosity; larger surface area and pore volume as well as narrower pore size distribution have been obtained by employing mesoporous silica, alumina, transition metal oxides, polymers, zeolites, MOFs, and carbon materials. Hydrophilic-hydrophobic properties have been adjusted by employing MOFs and polymers. Intriguingly, for liquid organic reactions, the catalyst can be compatibilized toward organic substrates with the aid of the organic framework of the polymers. By employing transition metal oxides as a support, strong host-guest interactions as well as tunable chemical composition and active sites can be obtained. MNP-supported POTs have been endowed with a feasible magnetic separation and recovery, which is industrially applicable and fascinating. Further details about these different types of supports as well as immobilization strategies and catalytic applications have been elegantly reviewed by Kholdeeva *et al.* in 2010 (ref. 30) and Zhou *et al.* in 2014.¹⁰⁰ Herein we try to cover all of the recent works dealing exclusively with tungsten-based POMs immobilized on supports and their catalytic applications. This was neither practical nor possible in those review papers focusing on POM-based catalysts in general, and not exclusively POT-based ones, because of too many publications on POM-based catalysts. Tables 7 and 8 show the reported POT/support catalytic systems along with their applications in acid catalysis and oxidation reactions.

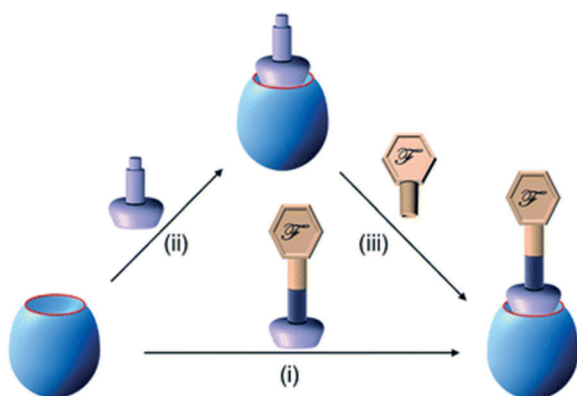


Fig. 3 Schematic overall view of the different strategies for the preparation of covalent POT-organic hybrids. Path (i): direct functionalization, paths (ii) and (iii): post-functionalization (blue: the lacunary POM, lilac: the anchoring tether, beige: the added functional moiety).⁸⁴ Reproduced from ref. 84 with permission from the Royal Society of Chemistry.

6. POTs heterogenized *via* combined strategies

Combining the three heterogenization strategies discussed in sections 3–5 offers some additional advantages in the design

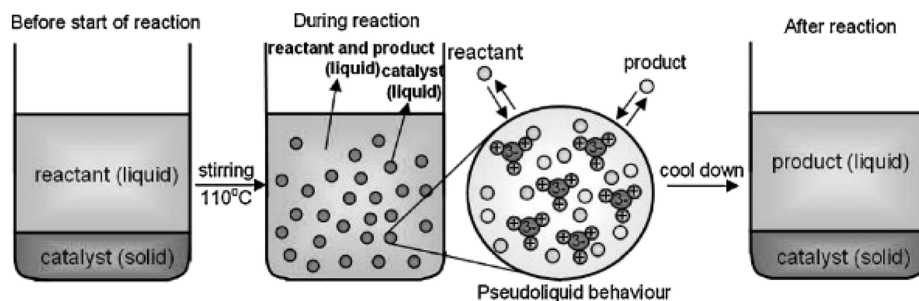


Fig. 4 Schematic diagram of a typical organic liquid-phase reaction over organic-POT hybrids with self-separation performance.¹⁰⁴ Reproduced from ref. 104 with permission from Elsevier.

of heterogeneous catalysts, making the resultant solid POT catalysts more fascinating. In the case of supported POTs, organo-modification of the surfaces (of the POTs, the supports or both) can be employed prior to immobilization in order to either enhance the stability of the supported POTs or improve the dispersion of the POT active sites into the support's structure. For example, Villanneau *et al.* have reported successful covalent immobilization of the hybrid POT $[\text{AsW}_9\text{O}_{33}\{\text{P}(\text{O})(\text{CH}_2\text{CH}_2\text{CO}_2\text{H})_2\}_2]^{5-}$ onto NH_2 -functionalized

mesoporous SBA-15, which obviously resulted in better stability of the supported catalyst and less leaching of active sites compared to common electrostatic interaction-based supported POTs. They prepared anchored homogeneous catalysts retaining important mesoporosity, in which the POT would play the role of a polydentate inorganic ligand for active centers.²³⁰ Furthermore, such hybridization of polyoxometalates *via* an organic-inorganic association has been exploited to develop a heterogeneous catalyst with tunable

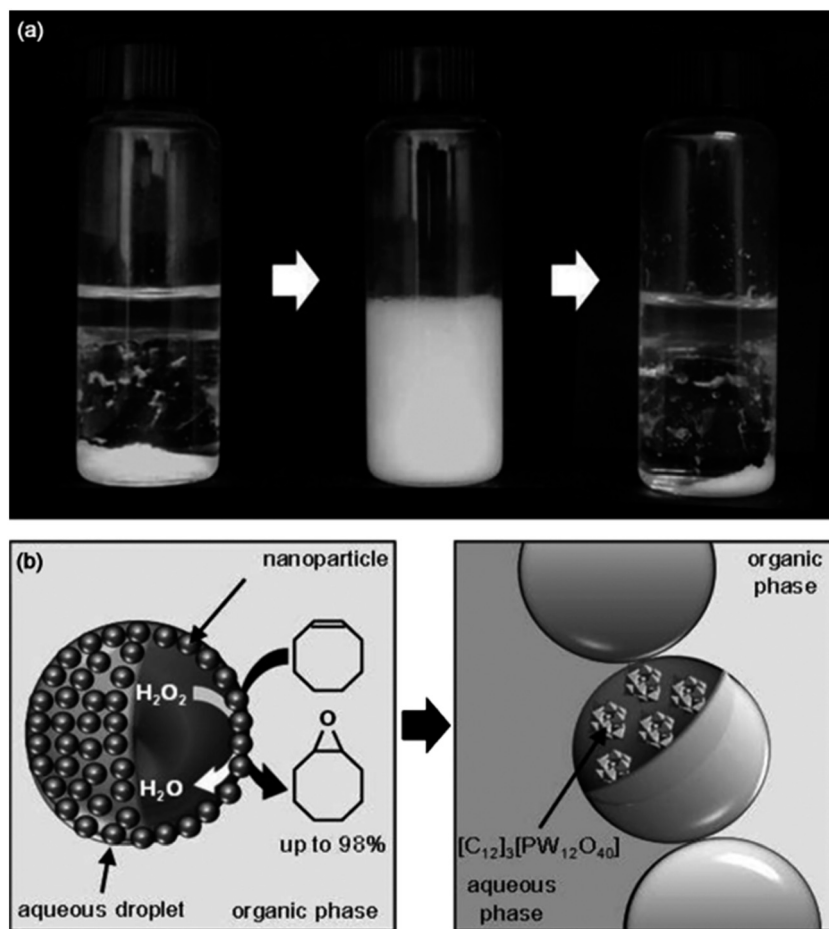


Fig. 5 (a) Macroscopic views of the water/toluene/ $[\text{C}_{12}]_3[\text{PW}_{12}\text{O}_{40}]$ system before emulsification, during the reaction, and after centrifugation (from left to right). (b) Schematic representation of the catalytic epoxidation of olefins inside this emulsion.¹⁰⁵ Reproduced from ref. 105 with permission from John Wiley and Sons.

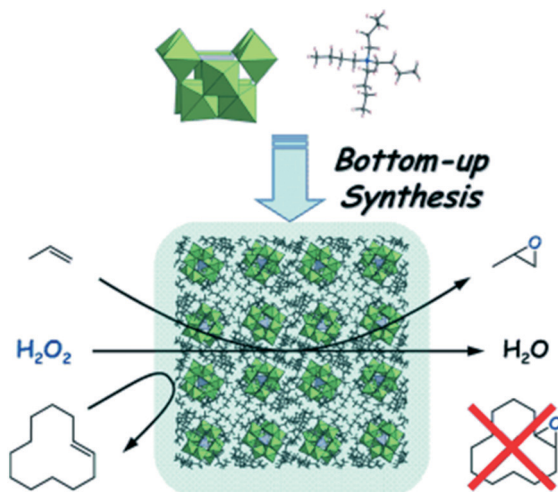


Fig. 6 Size-selective oxidation of olefins over $[(n-C_4H_9)_4N]_4[\gamma-SiW_{10}O_{34}(H_2O)_2] \cdot H_2O$ synthesized via a bottom-up approach.¹⁰⁶ Reproduced from ref. 106 with permission from John Wiley and Sons.

functionality imparted through supramolecular assembly.²³¹ Employing two hydrophilic (mica) and hydrophobic supports (highly oriented pyrolytic graphite), Raj *et al.* have investigated the role of surface hydrophilicity/hydrophobicity in determining supramolecular organization of the POT ($[PW_{12}O_{40}]^{3-}$) support. They have also demonstrated that organo-functionalization of the POT with dimethyldioctadecylammonium bromide is an efficient strategy to control the final product morphology and obtain highly dispersed POT active species on various hydrophilic and hydrophobic supports (Fig. 7).²³² Uchida *et al.* reported complexation of $[SiW_{12}O_{40}]^{4-}$ (ca. 1.0 nm in size) and a large macro cation of $[Cr_3O(OOCH)_6(H_2O)_3]^+$ (ca. 0.7 nm in size) in the presence of K^+ , which left nanosized channels in the lattice of the produced complex, $K_3[Cr_3O(OOCH)_6(H_2O)_3]SiW_{12}O_{40} \cdot 12H_2O$, resulting in catalytically interesting properties.²³³ Table 9 lists the reported solid POTs which have exploited a combination of the three strategies to enhance their catalytic efficiencies in various liquid-phase organic reactions.

7. Conclusion

Nowadays, although tungsten-based heterogeneous catalysts are used in industry with high efficiency for several reactions, research in this area is still increasingly exciting. A great deal of this excitement arises from W-based heteropoly compounds, whose excellent versatility, like other POMs, holds promise for application in various organic reactions chiefly including oxidation and acid catalysis reactions. Advantageously toward the other POMs, the POTs, especially in heterogeneous form, have generally shown higher acidity, thermal stability, and hydrophobicity. However, POTs are originally soluble in water and polar solvents, resulting in lack and/or difficulty of recovery, which often involved poisoning of their acid sites with water. Therefore, to push the use of W-based heteropoly acid catalysts to practical applications, it is imperative to develop efficiently recoverable catalytic systems *via* heterogenization of homogeneous POT-based catalysts. A variety of solid POTs has been reported so far with tuned interesting features individualized for the target organic reaction. They mainly include the Keggin structure with a few examples of Dawson, Anderson, Allman-Waugh, and less known Preyssler structures in the form of normal, lacunary, transition metal substituted lacunary, and sandwich-type POMs.

Partial or complete substitution of protons of polyoxotungstates by a cation with the appropriate size, amount, charge, hydrophobicity, and ability to make strong ionic interactions with POT has led to insoluble solids. Cations such as Na^+ , K^+ , NH_4^+ , Ag^+ , Sn^{2+} , Zn^{2+} , Bi^{3+} , Mn^{2+} , Co^{2+} , Cu^{2+} , and

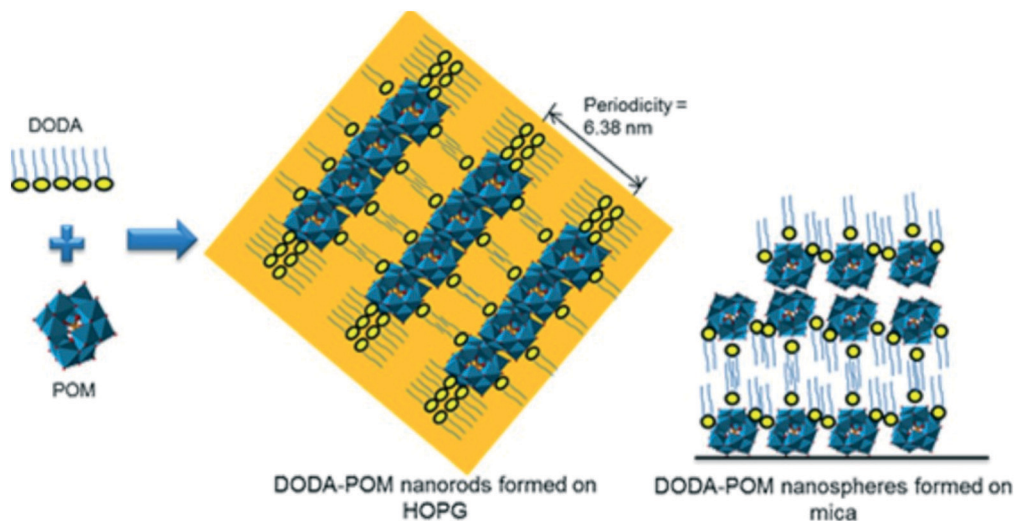


Fig. 7 Controlling the morphology and dispersion of supported POT heterogeneous catalysts *via* organo-modification of the POT.²³² Reproduced from ref. 232 with permission from PubMed Central.

Cs⁺, with dramatically more emphasis on the latter due to the unique effects of cesium on tuning the surface area, pore structure and surface acidity, have been substituted to the protons of the homogeneous POTs to heterogenize them. Easy adjustment of the surface acidity of the POTs *via* incorporation of inorganic cations justifies the larger application of this class of solid POTs in acid catalysis reaction compared to oxidation reaction.

The fabrication of hybrid organic–inorganic POT-based catalysts is currently a hot topic being enthusiastically explored, not only for heterogenization purposes but also for their versatility in liquid organic reactions arising from the wide variety of organic groups and proper adjustment of the surface state. The obtained advantages of organo-solidified POTs can be succinctly listed as (i) formation of a pseudo-homogeneous phase and/or stabilization of the Pickering emulsion medium resulting in enhancement of catalyst efficiency, (ii) increasing catalyst hydrophobicity which results in prevention of catalyst particle aggregation and poisoning of acid sites by water, (iii) enabling self-separation of the catalyst at the end of the reaction, and even (iiii) preparation of size-selective catalysts to selectively allow the desired molecule ingress and egress.

Immobilization of POTs onto supports such as polymers, silica, alumina, transition metal oxides, MOFs, magnetic nanoparticles, zeolites, and carbon materials has been reported as a conventional method for anchoring homogeneous POTs. Tuning of porosity, hydrophilic–hydrophobic properties, chemical composition, active sites, and magnetic properties has been achieved by employing supports with different functionalities. However, leaching of catalyst active sites has always been the associated problem of supported catalysts, which is currently being addressed by efforts on covalently linking POTs to the supports, chiefly polymers and MOFs due to their capability of covalently encapsulating POTs arising from their organic frameworks. Organo-functionalization of the POT or support surface prior to or during the immobilization has been recommended as an efficient approach to not only enhance the stability of supported POTs *via* covalent bonding but also improve dispersion of the POT active sites into the support.

Although POTs have shown higher thermal stability compared to the other POMs, the generally difficult regeneration (decoking) process of POM-based catalysts despite the reported efforts in this field, still calls for further work. Moreover, immobilization of POTs onto some materials (*e.g.* silica, MOFs) is occasionally associated with some undesired consequences (*e.g.* reducing their acid strength, impairing their oxidation resistance). Efforts to minimize these effects should be encouraged. Considering the widely tunable properties of POTs, their vast versatility, and fast pace of progress in heterogeneous POT-based catalysis, it is definitely only a matter of time before application of solid POTs in different organic reactions is industrialized. Hopefully, this review will help the researchers to drive further development in this currently challenging field.

Conflicts of interest

There are no conflicts to declare.

References

- 1 W.-D. S. Matthias Weil, *Newsletter of International Tungsten Industry Association*, June 2013, 2013.
- 2 H. Zheng, J. Z. Ou, M. S. Strano, R. B. Kaner, A. Mitchell and K. Kalantar-zadeh, *Adv. Funct. Mater.*, 2011, **21**, 2175–2196.
- 3 J. Christian, R. P. Singh Gaur, T. Wolfe and J. R. L. Trasorras, *Newsletter of International Tungsten Industry Association*, June 2011, 2011.
- 4 J. Song, Z.-F. Huang, L. Pan, J.-J. Zou, X. Zhang and L. Wang, *ACS Catal.*, 2015, **5**, 6594–6599.
- 5 B. A. Wasmi, A. A. Al-Amiery, A. A. H. Kadhum and A. B. Mohamad, *J. Nanomater.*, 2014, **2014**, 7.
- 6 P. Spanning, P. C. A. Bruijninx, B. M. Weckhuysen and R. J. M. Klein Gebbink, *Catal. Sci. Technol.*, 2014, **4**, 2182–2209.
- 7 A. Enferadi Kerenkan, F. Beland and T.-O. Do, *Catal. Sci. Technol.*, 2016, **6**, 971–987.
- 8 D. G. Barton, M. Shtein, R. D. Wilson, S. L. Soled and E. Iglesia, *J. Phys. Chem. B*, 1999, **103**, 630–640.
- 9 D. G. Barton, S. L. Soled and E. Iglesia, *Top. Catal.*, 1998, **6**, 87–99.
- 10 D. G. Barton, S. L. Soled, G. D. Meitzner, G. A. Fuentes and E. Iglesia, *J. Catal.*, 1999, **181**, 57–72.
- 11 V. M. Benitez, C. A. Querini, N. S. Fiigoli and R. A. Comelli, *Appl. Catal., A*, 1999, **178**, 205–218.
- 12 J. Bernholc, J. A. Horsley, L. L. Murrell, L. G. Sherman and S. Soled, *J. Phys. Chem.*, 1987, **91**, 1526–1530.
- 13 G. Busca, *Phys. Chem. Chem. Phys.*, 1999, **1**, 723–736.
- 14 P. Carniti, A. Gervasini and A. Auroux, *J. Catal.*, 1994, **150**, 274–283.
- 15 C. Martín, P. Malet, G. Solana and V. Rives, *J. Phys. Chem. B*, 1998, **102**, 2759–2768.
- 16 R. Thomas, E. M. van Oers, V. H. J. de Beer, J. Medema and J. A. Moulijn, *J. Catal.*, 1982, **76**, 241–253.
- 17 M. Kosmulski, *J. Colloid Interface Sci.*, 2014, **426**, 209–212.
- 18 P. M. Morse, Q. D. Shelby, D. Y. Kim and G. S. Girolami, *Organometallics*, 2008, **27**, 984–993.
- 19 H. S. C. O'Neill, A. J. Berry and S. M. Eggins, *Chem. Geol.*, 2008, **255**, 346–359.
- 20 Y. Lu, H. Yin, H. Wu, H. Liu, T. Jiang and Y. Wada, *Catal. Commun.*, 2006, **7**, 832–838.
- 21 A. Enferadi-Kerenkan, A. S. Ello and T.-O. Do, *Ind. Eng. Chem. Res.*, 2017, **56**, 10639–10647.
- 22 W.-L. Dai, J. Ding, Q. Zhu, R. Gao and X. Yang, in *Catalysis Volume 28*, The Royal Society of Chemistry, 2016, vol. 28, pp. 1–27.
- 23 T. Okuhara, *Chem. Rev.*, 2002, **102**, 3641–3666.
- 24 R. Sato, K. Suzuki, M. Sugawa and N. Mizuno, *Chem. – Eur. J.*, 2013, **19**, 12982–12990.
- 25 C. L. Hill and C. M. Prosser-McCartha, *Coord. Chem. Rev.*, 1995, **143**, 407–455.

- 26 A. Patel, N. Narkhede, S. Singh and S. Pathan, *Catal. Rev.: Sci. Eng.*, 2016, **58**, 337–370.
- 27 R. Yu, X.-F. Kuang, X.-Y. Wu, C.-Z. Lu and J. P. Donahue, *Coord. Chem. Rev.*, 2009, **253**, 2872–2890.
- 28 S.-T. Zheng and G.-Y. Yang, *Chem. Soc. Rev.*, 2012, **41**, 7623–7646.
- 29 N. Mizuno, K. Yamaguchi and K. Kamata, *Catal. Surv. Asia*, 2011, **15**, 68–79.
- 30 O. A. Kholdeeva, N. V. Maksimchuk and G. M. Maksimov, *Catal. Today*, 2010, **157**, 107–113.
- 31 N. Mizuno and K. Kamata, *Coord. Chem. Rev.*, 2011, **255**, 2358–2370.
- 32 N. Mizuno, K. Yamaguchi and K. Kamata, *Coord. Chem. Rev.*, 2005, **249**, 1944–1956.
- 33 N. Narkhede, S. Singh and A. Patel, *Green Chem.*, 2015, **17**, 89–107.
- 34 I. V. Kozhevnikov, *Chem. Rev.*, 1998, **98**, 171–198.
- 35 S.-S. Wang and G.-Y. Yang, *Chem. Rev.*, 2015, **115**, 4893–4962.
- 36 R. Mattes, *Angew. Chem.*, 1984, **96**, 730–730.
- 37 M. Pope, *Inorganic Chemistry Concepts Vol. 8: Heteropoly and Isopoly Oxometalates*, Springer, 1983.
- 38 J. B. Moffat, *Metal-Oxygen Clusters: The Surface and Catalytic Properties of Heteropoly Oxometalates*, Springer, 2001.
- 39 I. V. Kozhevnikov, *J. Mol. Catal. A: Chem.*, 2007, **262**, 86–92.
- 40 N. Mizuno and M. Misono, *Chem. Rev.*, 1998, **98**, 199–218.
- 41 M. Misono, *Catal. Rev.: Sci. Eng.*, 1987, **29**, 269–321.
- 42 I. Kozhevnikov, *Catalysts for fine chemical synthesis, catalysis by polyoxometalates*, Wiley, 2002.
- 43 T. Okuhara, N. Mizuno and M. Misono, in *Advances in Catalysis*, ed. D. D. Eley, W. O. Haag and B. Gates, Academic Press, 1996, vol. 41, pp. 113–252.
- 44 J. F. Keggin, *Proc. R. Soc. London, Ser. A*, 1934, **144**, 75.
- 45 M. Misono, *Chem. Commun.*, 2001, 1141–1152, DOI: 10.1039/B102573M.
- 46 N. M. Makoto Misono, K. Katamura, A. Kasai, Y. Konishi, K. Sakata, T. Okuhara and Y. Yoneda, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 400–406.
- 47 M. Misono, *Catal. Lett.*, 1992, **12**, 63–71.
- 48 I. V. Kozhevnikov, *J. Mol. Catal. A: Chem.*, 2009, **305**, 104–111.
- 49 E. Rafiee and S. Eavani, *RSC Adv.*, 2016, **6**, 46433–46466.
- 50 R. Hekmatshoar, S. Sadjadi, S. Sadjadi, M. M. Heravi, Y. S. Beheshtiha and F. F. Bamoharram, *Synth. Commun.*, 2010, **40**, 1708–1716.
- 51 A. C. Chaskar, A. A. Yadav, B. P. Langi, A. Murugappan and C. Shah, *Synth. Commun.*, 2010, **40**, 2850–2856.
- 52 K. Lan and Z. X. Shan, *Synth. Commun.*, 2007, **37**, 2171–2177.
- 53 J. B. Moffat, J. B. McMonagle and D. Taylor, *Solid State Ionics*, 1988, **26**, 101–108.
- 54 T. Okuhara and T. Nakato, *Catal. Surv. Asia*, 1998, **2**, 31–44.
- 55 T. Okuhara, H. Watanabe, T. Nishimura, K. Inumaru and M. Misono, *Chem. Mater.*, 2000, **12**, 2230–2238.
- 56 O. Toshio, N. Toru and M. Makoto, *Chem. Lett.*, 1995, **24**, 155–156.
- 57 T. Okuhara, T. Nishimura, H. Watanabe and M. Misono, *J. Mol. Catal.*, 1992, **74**, 247–256.
- 58 M. Liu, W. Deng, Q. Zhang, Y. Wang and Y. Wang, *Chem. Commun.*, 2011, **47**, 9717–9719.
- 59 Y. Liu, K. Murata and M. Inaba, *React. Kinet., Mech. Catal.*, 2016, **117**, 223–238.
- 60 M. Matouq, T. Tagawa and S. Goto, *J. Chem. Eng. Jpn.*, 1993, **26**, 254–258.
- 61 L. Pesaresi, D. R. Brown, A. F. Lee, J. M. Montero, H. Williams and K. Wilson, *Appl. Catal., A*, 2009, **360**, 50–58.
- 62 K. Okamoto, S. Uchida, T. Ito and N. Mizuno, *J. Am. Chem. Soc.*, 2007, **129**, 7378–7384.
- 63 K. Inumaru, *Catal. Surv. Asia*, 2006, **10**, 151–160.
- 64 T. Ito, K. Inumaru and M. Misono, *J. Phys. Chem. B*, 1997, **101**, 9958–9963.
- 65 S. Zhang, Y.-G. Zu, Y.-J. Fu, M. Luo, D.-Y. Zhang and T. Efferth, *Bioresour. Technol.*, 2010, **101**, 931–936.
- 66 A. S. Badday, A. Z. Abdullah and K.-T. Lee, *Energy*, 2013, **60**, 283–291.
- 67 V. V. Costa, K. A. da Silva Rocha, R. A. Mesquita, E. F. Kozhevnikova, I. V. Kozhevnikov and E. V. Gusevskaya, *ChemCatChem*, 2013, **5**, 3022–3026.
- 68 L. Chen, B. Nohair and S. Kaliaguine, *Appl. Catal., A*, 2016, **509**, 143–152.
- 69 A. Thakur, A. Sharma and A. Sharma, *Synth. Commun.*, 2016, **46**, 1766–1771.
- 70 H. Firouzabadi, N. Iranpoor and K. Amani, *Synthesis*, 2002, **2002**, 0059–0062.
- 71 F. Z. Abdullah, A. Ma amor, N. A. Daud and S. B. A. Hamid, *Quim. Nova*, 2017, **40**, 506–512.
- 72 S. Borghese, B. Louis, A. Blanc and P. Pale, *Catal. Sci. Technol.*, 2011, **1**, 981–986.
- 73 C. Fan, H. Guan, H. Zhang, J. Wang, S. Wang and X. Wang, *Biomass Bioenergy*, 2011, **35**, 2659–2665.
- 74 L. Yang, L.-W. Xu and C.-G. Xia, *Tetrahedron Lett.*, 2008, **49**, 2882–2885.
- 75 G. Romanelli, D. Ruiz, P. Vázquez, H. Thomas and J. C. Autino, *Chem. Eng. J.*, 2010, **161**, 355–362.
- 76 S. Zhao, Y. Chen and Y.-F. Song, *Appl. Catal., A*, 2014, **475**, 140–146.
- 77 T. H. T. Vu, H. T. Au, T. M. T. Nguyen, M. T. Pham, T. T. Bach and H. N. Nong, *Catal. Sci. Technol.*, 2013, **3**, 699–705.
- 78 L. Matachowski, A. Drelinkiewicz, E. Lalik, M. Ruggiero-Mikołajczyk, D. Mucha and J. Kryściak-Czerwenka, *Appl. Catal., A*, 2014, **469**, 290–299.
- 79 C. Ramesh Kumar, K. T. V. Rao, P. S. Sai Prasad and N. Lingaiah, *J. Mol. Catal. A: Chem.*, 2011, **337**, 17–24.
- 80 J. Li, X. Wang, W. Zhu and F. Cao, *ChemSusChem*, 2009, **2**, 177–183.
- 81 J. Wang, G. Luo, C. Liu and J. Lai, *Energy Sources, Part A*, 2014, **36**, 479–488.
- 82 X. Xue, F. Song, B. Ma, Y. Yu, C. Li and Y. Ding, *Catal. Commun.*, 2013, **33**, 61–65.
- 83 L.-X. Shi, W.-F. Zhao, X. Xu, J. Tang and C.-D. Wu, *Inorg. Chem.*, 2011, **50**, 12387–12389.

- 84 A. Proust, B. Matt, R. Villanneau, G. Guillemot, P. Gouzerh and G. Izzet, *Chem. Soc. Rev.*, 2012, **41**, 7605–7622.
- 85 F. Ribot and C. Sanchez, *Comments Inorg. Chem.*, 1999, **20**, 327–371.
- 86 A. Dolbecq, E. Dumas, C. R. Mayer and P. Mialane, *Chem. Rev.*, 2010, **110**, 6009–6048.
- 87 D. A. Loy and K. J. Shea, *Chem. Rev.*, 1995, **95**, 1431–1442.
- 88 S. Ivanova, *ISRN Chem. Eng.*, 2014, **2014**, 13.
- 89 D. Li, P. Yin and T. Liu, *Dalton Trans.*, 2012, **41**, 2853–2861.
- 90 M. Mirzaei, H. Eshtiagh-Hosseini, M. Alipour and A. Frontera, *Coord. Chem. Rev.*, 2014, **275**, 1–18.
- 91 A. Nisar and X. Wang, *Dalton Trans.*, 2012, **41**, 9832–9845.
- 92 S. Nlate and C. Jahier, *Eur. J. Inorg. Chem.*, 2013, **2013**, 1606–1619.
- 93 Y. Ren, M. Wang, X. Chen, B. Yue and H. He, *Materials*, 2015, **8**, 1545.
- 94 M.-P. Santoni, G. S. Hanan and B. Hasenknopf, *Coord. Chem. Rev.*, 2014, **281**, 64–85.
- 95 Y.-F. Song and R. Tsunashima, *Chem. Soc. Rev.*, 2012, **41**, 7384–7402.
- 96 E. Coronado, C. Giménez-Saiz and C. J. Gómez-García, *Coord. Chem. Rev.*, 2005, **249**, 1776–1796.
- 97 C. Sanchez, G. J. d. A. A. Soler-Illia, F. Ribot, T. Lalot, C. R. Mayer and V. Cabuil, *Chem. Mater.*, 2001, **13**, 3061–3083.
- 98 H. Wu, H.-K. Yang and W. Wang, *New J. Chem.*, 2016, **40**, 886–897.
- 99 A. B. Bourlinos, K. Raman, R. Herrera, Q. Zhang, L. A. Archer and E. P. Giannelis, *J. Am. Chem. Soc.*, 2004, **126**, 15358–15359.
- 100 Y. Zhou, G. Chen, Z. Long and J. Wang, *RSC Adv.*, 2014, **4**, 42092–42113.
- 101 S. Liu and Z. Tang, *Nano Today*, 2010, **5**, 267–281.
- 102 G. Zhang, B. Keita, C. T. Craescu, S. Miron, P. de Oliveira and L. Nadjo, *J. Phys. Chem. B*, 2007, **111**, 11253–11259.
- 103 Y. Zhou, L. Zheng, F. Han, G. Zhang, Y. Ma, J. Yao, B. Keita, P. de Oliveira and L. Nadjo, *Colloids Surf., A*, 2011, **375**, 97–101.
- 104 Y. Leng, J. Wang, D. Zhu, Y. Wu and P. Zhao, *J. Mol. Catal. A: Chem.*, 2009, **313**, 1–6.
- 105 L. Leclercq, A. Mouret, A. Proust, V. Schmitt, P. Bauduin, J.-M. Aubry and V. Nardello-Rataj, *Chem. – Eur. J.*, 2012, **18**, 14352–14358.
- 106 N. Mizuno, S. Uchida, K. Kamata, R. Ishimoto, S. Nojima, K. Yonehara and Y. Sumida, *Angew. Chem., Int. Ed.*, 2010, **49**, 9972–9976.
- 107 Q. Zhao, H. Wang, H. Zheng, Z. Sun, W. Shi, S. Wang, X. Wang and Z. Jiang, *Catal. Sci. Technol.*, 2013, **3**, 2204–2209.
- 108 S. Zhao, M. Cheng, J. Li, J. Tian and X. Wang, *Chem. Commun.*, 2011, **47**, 2176–2178.
- 109 M. Cheng, T. Shi, H. Guan, S. Wang, X. Wang and Z. Jiang, *Appl. Catal., B*, 2011, **107**, 104–109.
- 110 Y. Leng, J. Wang, D. Zhu, X. Ren, H. Ge and L. Shen, *Angew. Chem., Int. Ed.*, 2009, **48**, 168–171.
- 111 W. Zhang, Y. Leng, D. Zhu, Y. Wu and J. Wang, *Catal. Commun.*, 2009, **11**, 151–154.
- 112 X.-X. Han, Y.-F. He, C.-T. Hung, L.-L. Liu, S.-J. Huang and S.-B. Liu, *Chem. Eng. Sci.*, 2013, **104**, 64–72.
- 113 W. Zhang, Y. Leng, P. Zhao, J. Wang, D. Zhu and J. Huang, *Green Chem.*, 2011, **13**, 832–834.
- 114 X. Zhang, D. Mao, Y. Leng, Y. Zhou and J. Wang, *Catal. Lett.*, 2013, **143**, 193–199.
- 115 D. Mao, Z. Long, Y. Zhou, J. Li, X. Wang and J. Wang, *RSC Adv.*, 2014, **4**, 15635–15641.
- 116 K. Li, L. Chen, H. Wang, W. Lin and Z. Yan, *Appl. Catal., A*, 2011, **392**, 233–237.
- 117 Z. Zhang, K. Dong and Z. Zhao, *ChemSusChem*, 2011, **4**, 112–118.
- 118 J. Chen, G. Zhao and L. Chen, *RSC Adv.*, 2014, **4**, 4194–4202.
- 119 M. Zhang, P. Zhao, Y. Leng, G. Chen, J. Wang and J. Huang, *Chem. – Eur. J.*, 2012, **18**, 12773–12782.
- 120 H. Li, Y. Qiao, L. Hua, Z. Hou, B. Feng, Z. Pan, Y. Hu, X. Wang, X. Zhao and Y. Yu, *ChemCatChem*, 2010, **2**, 1165–1170.
- 121 C. N. Kato, T. Ogasawara, A. Kondo and D. Kato, *Catal. Commun.*, 2017, **96**, 41–45.
- 122 R. Kawahara, R. Osuga, J. N. Kondo, N. Mizuno and S. Uchida, *Dalton Trans.*, 2017, **46**, 3105–3109.
- 123 S. Uchida, K. Kamata, Y. Ogasawara, M. Fujita and N. Mizuno, *Dalton Trans.*, 2012, **41**, 9979–9983.
- 124 A. Nisar, J. Zhuang and X. Wang, *Adv. Mater.*, 2011, **23**, 1130–1135.
- 125 H. Li, X. Yu, H. Zheng, Y. Li, X. Wang and M. Huo, *RSC Adv.*, 2014, **4**, 7266–7274.
- 126 J. Xu, S. Zhao, Y. Ji and Y.-F. Song, *Chem. – Eur. J.*, 2013, **19**, 709–715.
- 127 F. Mirante, L. Dias, M. Silva, S. O. Ribeiro, M. C. Corvo, B. de Castro, C. M. Granadeiro and S. S. Balula, *Catal. Commun.*, 2018, **104**, 1–8.
- 128 A. Enferadi-Kerenkan, A. Gandon and T. O. Do, *Dalton Trans.*, 2018, **47**, 1214–1222.
- 129 W. Huang, W. Zhu, H. Li, H. Shi, G. Zhu, H. Liu and G. Chen, *Ind. Eng. Chem. Res.*, 2010, **49**, 8998–9003.
- 130 E. Rafiee and S. Eavani, *J. Mol. Catal. A: Chem.*, 2013, **380**, 18–27.
- 131 Y. Qiao, Z. Hou, H. Li, Y. Hu, B. Feng, X. Wang, L. Hua and Q. Huang, *Green Chem.*, 2009, **11**, 1955–1960.
- 132 H. Li, Z. Hou, Y. Qiao, B. Feng, Y. Hu, X. Wang and X. Zhao, *Catal. Commun.*, 2010, **11**, 470–475.
- 133 J. Chen, L. Hua, W. Zhu, R. Zhang, L. Guo, C. Chen, H. Gan, B. Song and Z. Hou, *Catal. Commun.*, 2014, **47**, 18–21.
- 134 Y. Leng, J. Wang, D. Zhu, M. Zhang, P. Zhao, Z. Long and J. Huang, *Green Chem.*, 2011, **13**, 1636–1639.
- 135 Y. Leng, P. Zhao, M. Zhang and J. Wang, *J. Mol. Catal. A: Chem.*, 2012, **358**, 67–72.
- 136 Y. Leng, P. Zhao, M. Zhang, G. Chen and J. Wang, *Sci. China: Chem.*, 2012, **55**, 1796–1801.
- 137 P. Zhao, M. Zhang, Y. Wu and J. Wang, *Ind. Eng. Chem. Res.*, 2012, **51**, 6641–6647.
- 138 G. Chen, Y. Zhou, P. Zhao, Z. Long and J. Wang, *ChemPlusChem*, 2013, **78**, 561–569.

- 139 G. Chen, Y. Zhou, Z. Long, X. Wang, J. Li and J. Wang, *ACS Appl. Mater. Interfaces*, 2014, **6**, 4438–4446.
- 140 F. Nezampour, M. Ghiaci and H. Farrokhpour, *Appl. Catal., A*, 2017, **543**, 104–114.
- 141 H. Mirhoseini and M. Taghdiri, *Fuel*, 2016, **167**, 60–67.
- 142 Z. Zhang, W. Zhao, B. Ma and Y. Ding, *Catal. Commun.*, 2010, **12**, 318–322.
- 143 S. Zhao, Y. Jia and Y.-F. Song, *Appl. Catal., A*, 2013, **453**, 188–194.
- 144 L. Hua, Y. Qiao, Y. Yu, W. Zhu, T. Cao, Y. Shi, H. Li, B. Feng and Z. Hou, *New J. Chem.*, 2011, **35**, 1836–1841.
- 145 M. V. Vasylyev and R. Neumann, *J. Am. Chem. Soc.*, 2004, **126**, 884–890.
- 146 Y. Ren, C. Du, S. Feng, C. Wang, Z. Kong, B. Yue and H. He, *CrystEngComm*, 2011, **13**, 7143–7148.
- 147 D. Dutta, A. D. Jana, M. Debnath, A. Bhaumik, J. Marek and M. Ali, *Dalton Trans.*, 2010, **39**, 11551–11559.
- 148 C. Zou, Z. Zhang, X. Xu, Q. Gong, J. Li and C.-D. Wu, *J. Am. Chem. Soc.*, 2012, **134**, 87–90.
- 149 Y. Izumi, R. Hasebe and K. Urabe, *J. Catal.*, 1983, **84**, 402–409.
- 150 M. S. Alam, V. Dremov, P. Müller, A. V. Postnikov, S. S. Mal, F. Hussain and U. Kortz, *Inorg. Chem.*, 2006, **45**, 2866–2872.
- 151 M. S. Kaba, I. K. Song, D. C. Duncan, C. L. Hill and M. A. Barteau, *Inorg. Chem.*, 1998, **37**, 398–406.
- 152 I. K. Song, M. S. Kaba, K. Nomiya, R. G. Finke and M. A. Barteau, *J. Mol. Catal. A: Chem.*, 2007, **262**, 216–226.
- 153 M. A. AlDamen, J. M. Clemente-Juan, E. Coronado, C. Martí-Gastaldo and A. Gaita-Ariño, *J. Am. Chem. Soc.*, 2008, **130**, 8874–8875.
- 154 J.-D. Compain, P. Mialane, A. Dolbecq, I. M. Mbomekallé, J. Marrot, F. Sécheresse, E. Rivière, G. Rogez and W. Wernsdorfer, *Angew. Chem., Int. Ed.*, 2009, **48**, 3077–3081.
- 155 A. Giusti, G. Charron, S. Mazerat, J.-D. Compain, P. Mialane, A. Dolbecq, E. Rivière, W. Wernsdorfer, R. Ngo Biboum, B. Keita, L. Nadjo, A. Filoramo, J.-P. Bourgoïn and T. Mallah, *Angew. Chem., Int. Ed.*, 2009, **48**, 4949–4952.
- 156 M. Orlandi, R. Argazzi, A. Sartorel, M. Carraro, G. Scorrano, M. Bonchio and F. Scandola, *Chem. Commun.*, 2010, **46**, 3152–3154.
- 157 F. Puntoriero, G. La Ganga, A. Sartorel, M. Carraro, G. Scorrano, M. Bonchio and S. Campagna, *Chem. Commun.*, 2010, **46**, 4725–4727.
- 158 F. Puntoriero, A. Sartorel, M. Orlandi, G. La Ganga, S. Serroni, M. Bonchio, F. Scandola and S. Campagna, *Coord. Chem. Rev.*, 2011, **255**, 2594–2601.
- 159 C. Ritchie, A. Ferguson, H. Nojiri, H. N. Miras, Y.-F. Song, D.-L. Long, E. Burkholder, M. Murrie, P. Kögerler, E. K. Brechin and L. Cronin, *Angew. Chem., Int. Ed.*, 2008, **47**, 5609–5612.
- 160 F. M. Toma, A. Sartorel, M. Iurlo, M. Carraro, P. Parris, C. Maccato, S. Rapino, B. R. Gonzalez, H. Amenitsch, T. Da Ros, L. Casalis, A. Goldoni, M. Marcaccio, G. Scorrano, G. Scoles, F. Paolucci, M. Prato and M. Bonchio, *Nat. Chem.*, 2010, **2**, 826–831.
- 161 Z. Tang, S. Liu, E. Wang and S. Dong, *Langmuir*, 2000, **16**, 4946–4952.
- 162 D. Zhong, F. L. Sousa, A. Müller, L. Chi and H. Fuchs, *Angew. Chem., Int. Ed.*, 2011, **50**, 7018–7021.
- 163 J. Kim and A. A. Gewirth, *Langmuir*, 2003, **19**, 8934–8942.
- 164 D.-Y. Du, J.-S. Qin, S.-L. Li, Z.-M. Su and Y.-Q. Lan, *Chem. Soc. Rev.*, 2014, **43**, 4615–4632.
- 165 M. Carraro and S. Gross, *Materials*, 2014, **7**, 3956.
- 166 K. Inumaru, T. Ishihara, Y. Kamiya, T. Okuhara and S. Yamanaka, *Angew. Chem., Int. Ed.*, 2007, **46**, 7625–7628.
- 167 N. R. Shiju, A. H. Alberts, S. Khalid, D. R. Brown and G. Rothenberg, *Angew. Chem.*, 2011, **123**, 9789–9793.
- 168 Z. Liu, S. Cao, S. Wang, W. Zeng and T. Zhang, *React. Kinet., Mech. Catal.*, 2014, **111**, 577–590.
- 169 A. L. P. de Meireles, K. A. da Silva Rocha, I. V. Kozhevnikov and E. V. Gusevskaya, *Appl. Catal., A*, 2011, **409**, 82–86.
- 170 K. A. da S. Rocha, P. A. Robles-Dutenhefner, I. V. Kozhevnikov and E. V. Gusevskaya, *Appl. Catal., A*, 2009, **352**, 188–192.
- 171 K. A. da Silva Rocha, P. A. Robles-Dutenhefner, E. M. B. Sousa, E. F. Kozhevnikova, I. V. Kozhevnikov and E. V. Gusevskaya, *Appl. Catal., A*, 2007, **317**, 171–174.
- 172 B. Zhen, H. Li, Q. Jiao, Y. Li, Q. Wu and Y. Zhang, *Ind. Eng. Chem. Res.*, 2012, **51**, 10374–10380.
- 173 F. Su, L. Ma, Y. Guo and W. Li, *Catal. Sci. Technol.*, 2012, **2**, 2367–2374.
- 174 F. Su, L. Ma, D. Song, X. Zhang and Y. Guo, *Green Chem.*, 2013, **15**, 885–890.
- 175 F. Su, Q. Wu, D. Song, X. Zhang, M. Wang and Y. Guo, *J. Mater. Chem. A*, 2013, **1**, 13209–13221.
- 176 L. Xu, Y. Guo, H. Ma and J. Guan, *J. Wuhan Univ. Technol., Mater. Sci. Ed.*, 2013, **28**, 580–585.
- 177 M. A. Naik, S. Samantaray and B. G. Mishra, *J. Cluster Sci.*, 2011, **22**, 295–307.
- 178 R. Rajagopal, S. A. Siddiqui, T. Daniel, R. J. Lahoti and K. V. Srinivasan, *J. Mol. Catal. A: Chem.*, 2004, **210**, 165–169.
- 179 T. Shamsi, A. Amoozadeh, E. Tabrizian and S. M. Sajjadi, *React. Kinet., Mech. Catal.*, 2017, **121**, 505–522.
- 180 J. Juan-Alcañiz, E. V. Ramos-Fernandez, U. Lafont, J. Gascon and F. Kapteijn, *J. Catal.*, 2010, **269**, 229–241.
- 181 Y. Zhang, V. Degirmenci, C. Li and E. J. M. Hensen, *ChemSusChem*, 2011, **4**, 59–64.
- 182 J. Chen, S. Wang, J. Huang, L. Chen, L. Ma and X. Huang, *ChemSusChem*, 2013, **6**, 1545–1555.
- 183 L. Bromberg, Y. Diao, H. Wu, S. A. Speakman and T. A. Hatton, *Chem. Mater.*, 2012, **24**, 1664–1675.
- 184 L. H. Wee, F. Bonino, C. Lamberti, S. Bordiga and J. A. Martens, *Green Chem.*, 2014, **16**, 1351–1357.
- 185 Y. Leng, P. Jiang and J. Wang, *Catal. Commun.*, 2012, **25**, 41–44.
- 186 S. Kamble, S. More and C. Rode, *New J. Chem.*, 2016, **40**, 10240–10245.

- 187 M. A. Betiha, H. M. A. Hassan, E. A. El-Sharkawy, A. M. Al-Sabagh, M. F. Menoufy and H. E. M. Abdelmoniem, *Appl. Catal., B*, 2016, **182**, 15–25.
- 188 X. Zheng, L. Zhang, J. Li, S. Luo and J.-P. Cheng, *Chem. Commun.*, 2011, **47**, 12325–12327.
- 189 X. Duan, Y. Liu, Q. Zhao, X. Wang and S. Li, *RSC Adv.*, 2013, **3**, 13748–13755.
- 190 T. Zillillah, A. Ngu and Z. Li, *Green Chem.*, 2014, **16**, 1202–1210.
- 191 F. Shahbazi and K. Amani, *Catal. Commun.*, 2014, **55**, 57–64.
- 192 M. Ammar, S. Jiang and S. Ji, *J. Solid State Chem.*, 2016, **233**, 303–310.
- 193 Z. Liu, S. Cao, S. Wang, W. Zeng, T. Zhang, P. Li and F. Lei, *J. Chem. Eng. Jpn.*, 2015, **48**, 29–34.
- 194 R. Liu, X. Xia, X. Niu, G. Zhang, Y. Lu, R. Jiang and S. He, *Appl. Clay Sci.*, 2015, **105**, 71–77.
- 195 R. Fazaeli and H. Aliyan, *Appl. Catal., A*, 2007, **331**, 78–83.
- 196 K.-L. Yang, S. Huang, H. Pan, H. Zhang, X.-F. Liu and S. Yang, *RSC Adv.*, 2017, **7**, 33335–33343.
- 197 K. Yamaguchi, C. Yoshida, S. Uchida and N. Mizuno, *J. Am. Chem. Soc.*, 2005, **127**, 530–531.
- 198 R. Tan, C. Liu, N. Feng, J. Xiao, W. Zheng, A. Zheng and D. Yin, *Microporous Mesoporous Mater.*, 2012, **158**, 77–87.
- 199 H. Zhao, L. Zeng, Y. Li, C. Liu, B. Hou, D. Wu, N. Feng, A. Zheng, X. Xie, S. Su and N. Yu, *Microporous Mesoporous Mater.*, 2013, **172**, 67–76.
- 200 J. Xiong, W. Zhu, W. Ding, L. Yang, Y. Chao, H. Li, F. Zhu and H. Li, *Ind. Eng. Chem. Res.*, 2014, **53**, 19895–19904.
- 201 M. Masteri-Farahani, G. R. Najafi, M. Modarres and M. Taghvaei-Nakhjiri, *J. Porous Mater.*, 2016, **23**, 285–290.
- 202 E. Skliri, I. N. Lykakis and G. S. Armatas, *RSC Adv.*, 2014, **4**, 8402–8409.
- 203 N. V. Maksimchuk, K. A. Kovalenko, S. S. Arzumanov, Y. A. Chesalov, M. S. Melgunov, A. G. Stepanov, V. P. Fedin and O. A. Kholdeeva, *Inorg. Chem.*, 2010, **49**, 2920–2930.
- 204 C. M. Granadeiro, A. D. S. Barbosa, P. Silva, F. A. A. Paz, V. K. Saini, J. Pires, B. de Castro, S. S. Balula and L. Cunha-Silva, *Appl. Catal., A*, 2013, **453**, 316–326.
- 205 J.-W. Sun, P.-F. Yan, G.-H. An, J.-Q. Sha, G.-M. Li and G.-Y. Yang, *Sci. Rep.*, 2016, **6**, 25595.
- 206 E. Rafiee and N. Nobakht, *J. Mol. Catal. A: Chem.*, 2015, **398**, 17–25.
- 207 H. Haddadi, S. M. Hafshejani, M. R. Farsani and A. K. Babahydari, *New J. Chem.*, 2015, **39**, 9879–9885.
- 208 Y.-Y. Ma, H.-Q. Tan, Y.-H. Wang, X.-L. Hao, X.-J. Feng, H.-Y. Zang and Y.-G. Li, *CrystEngComm*, 2015, **17**, 7938–7947.
- 209 F. Yu, P.-Q. Zheng, Y.-X. Long, Y.-P. Ren, X.-J. Kong, L.-S. Long, Y.-Z. Yuan, R.-B. Huang and L.-S. Zheng, *Eur. J. Inorg. Chem.*, 2010, **2010**, 4526–4531.
- 210 N. V. Maksimchuk, M. N. Timofeeva, M. S. Melgunov, A. N. Shmakov, Y. A. Chesalov, D. N. Dybtsev, V. P. Fedin and O. A. Kholdeeva, *J. Catal.*, 2008, **257**, 315–323.
- 211 C. M. Granadeiro, P. Silva, V. K. Saini, F. A. A. Paz, J. Pires, L. Cunha-Silva and S. S. Balula, *Catal. Today*, 2013, **218**, 35–42.
- 212 S. Ribeiro, C. M. Granadeiro, P. Silva, F. A. Almeida Paz, F. F. de Biani, L. Cunha-Silva and S. S. Balula, *Catal. Sci. Technol.*, 2013, **3**, 2404–2414.
- 213 Y. Leng, W. Zhang, J. Wang and P. Jiang, *Appl. Catal., A*, 2012, **445–446**, 306–311.
- 214 Y. Leng, J. Wu, P. Jiang and J. Wang, *Catal. Sci. Technol.*, 2014, **4**, 1293–1300.
- 215 Y. Leng, J. Liu, P. Jiang and J. Wang, *RSC Adv.*, 2012, **2**, 11653–11656.
- 216 Y. Leng, J. Wang and P. Jiang, *Catal. Commun.*, 2012, **27**, 101–104.
- 217 Y. M. A. Yamada, C. K. Jin and Y. Uozumi, *Org. Lett.*, 2010, **12**, 4540–4543.
- 218 E. Poli, J.-M. Clacens and Y. Pouilloux, *Catal. Today*, 2011, **164**, 429–435.
- 219 S. Doherty, J. G. Knight, J. R. Ellison, D. Weekes, R. W. Harrington, C. Hardacre and H. Manyar, *Green Chem.*, 2012, **14**, 925–929.
- 220 S. P. Maradur, C. Jo, D.-H. Choi, K. Kim and R. Ryoo, *ChemCatChem*, 2011, **3**, 1435–1438.
- 221 M. Carraro, G. Fiorani, L. Mognon, F. Caneva, M. Gardan, C. Maccato and M. Bonchio, *Chem. – Eur. J.*, 2012, **18**, 13195–13202.
- 222 Y. Xiao, D. Chen, N. Ma, Z. Hou, M. Hu, C. Wang and W. Wang, *RSC Adv.*, 2013, **3**, 21544–21551.
- 223 Q. Z. Huang, L. H. Zhuo and Y. C. Guo, *Carbohydr. Polym.*, 2008, **72**, 500–505.
- 224 A. Nisar, Y. Lu, J. Zhuang and X. Wang, *Angew. Chem.*, 2011, **123**, 3245–3250.
- 225 Y. Leng, J. Zhao, P. Jiang and J. Wang, *ACS Appl. Mater. Interfaces*, 2014, **6**, 5947–5954.
- 226 U. Jameel, M.-q. Zhu, X.-z. Chen, Y. Liu and Z.-f. Tong, *J. Zhejiang Univ., Sci., A*, 2016, **17**, 1000–1012.
- 227 P. Liu, H. Wang, Z. Feng, P. Ying and C. Li, *J. Catal.*, 2008, **256**, 345–348.
- 228 S. Zhao, L. Liu and Y.-F. Song, *Dalton Trans.*, 2012, **41**, 9855–9858.
- 229 T. Li, W. Zhang, W. Chen, H. N. Miras and Y.-F. Song, *ChemCatChem*, 2018, **10**, 188–197.
- 230 R. Villanneau, A. Marzouk, Y. Wang, A. B. Djamaa, G. Laugel, A. Proust and F. Launay, *Inorg. Chem.*, 2013, **52**, 2958–2965.
- 231 G. Raj, C. Swalus, A. Guillet, M. Devillers, B. Nysten and E. M. Gaigneaux, *Langmuir*, 2013, **29**, 4388–4395.
- 232 G. Raj, C. Swalus, E. Arendt, P. Eloy, M. Devillers and E. M. Gaigneaux, *Beilstein J. Nanotechnol.*, 2014, **5**, 1749–1759.
- 233 S. Uchida, S. Sakamoto and N. Mizuno, *Res. Chem. Intermed.*, 2002, **28**, 389–396.
- 234 L. Zhang, H. Zeng, Y. Zeng, Z. Zhang and X. Zhao, *J. Mol. Catal. A: Chem.*, 2014, **392**, 202–207.
- 235 Y. Chen and Y.-F. Song, *ChemPlusChem*, 2014, **79**, 304–309.
- 236 S. S. Balula, C. M. Granadeiro, A. D. S. Barbosa, I. C. M. S. Santos and L. Cunha-Silva, *Catal. Today*, 2013, **210**, 142–148.

- 237 C.-Y. Sun, S.-X. Liu, D.-D. Liang, K.-Z. Shao, Y.-H. Ren and Z.-M. Su, *J. Am. Chem. Soc.*, 2009, **131**, 1883–1888.
- 238 F.-J. Ma, S.-X. Liu, C.-Y. Sun, D.-D. Liang, G.-J. Ren, F. Wei, Y.-G. Chen and Z.-M. Su, *J. Am. Chem. Soc.*, 2011, **133**, 4178–4181.
- 239 J. Song, Z. Luo, D. K. Britt, H. Furukawa, O. M. Yaghi, K. I. Hardcastle and C. L. Hill, *J. Am. Chem. Soc.*, 2011, **133**, 16839–16846.
- 240 Q. Han, C. He, M. Zhao, B. Qi, J. Niu and C. Duan, *J. Am. Chem. Soc.*, 2013, **135**, 10186–10189.
- 241 A. K. Babahydari, R. Fareghi-Alamdari, S. M. Hafshejani, H. A. Rudbari and M. R. Farsani, *J. Iran. Chem. Soc.*, 2016, **13**, 1463–1470.
- 242 D. Julião, A. C. Gomes, M. Pillinger, L. Cunha-Silva, B. de Castro, I. S. Gonçalves and S. S. Balula, *Fuel Process. Technol.*, 2015, **131**, 78–86.
- 243 Z. Karimi and A. R. Mahjoub, *Catal. Commun.*, 2011, **12**, 984–988.
- 244 O. A. Kholdeeva, M. P. Vanina, M. N. Timofeeva, R. I. Maksimovskaya, T. A. Trubitsina, M. S. Melgunov, E. B. Burgina, J. Mrowiec-Bialon, A. B. Jarzebski and C. L. Hill, *J. Catal.*, 2004, **226**, 363–371.
- 245 H. Firouzabadi, N. Iranpoor and K. Amani, *J. Mol. Catal. A: Chem.*, 2003, **195**, 289–294.
- 246 M. Moghadam, V. Mirkhani, S. Tangestaninejad, I. Mohammadpoor-Baltork and M. M. Javadi, *Inorg. Chem. Commun.*, 2010, **13**, 244–249.
- 247 J. Tong, H. Wang, X. Cai, Q. Zhang, H. Ma and Z. Lei, *Appl. Organomet. Chem.*, 2014, **28**, 95–100.
- 248 L. Chen, B. Nohair, D. Zhao and S. Kaliaguine, *Appl. Catal., A*, 2018, **549**, 207–215.
- 249 L. Chen, B. Nohair, D. Zhao and S. Kaliaguine, *ChemCatChem*, DOI: 10.1002/cctc.201701656.