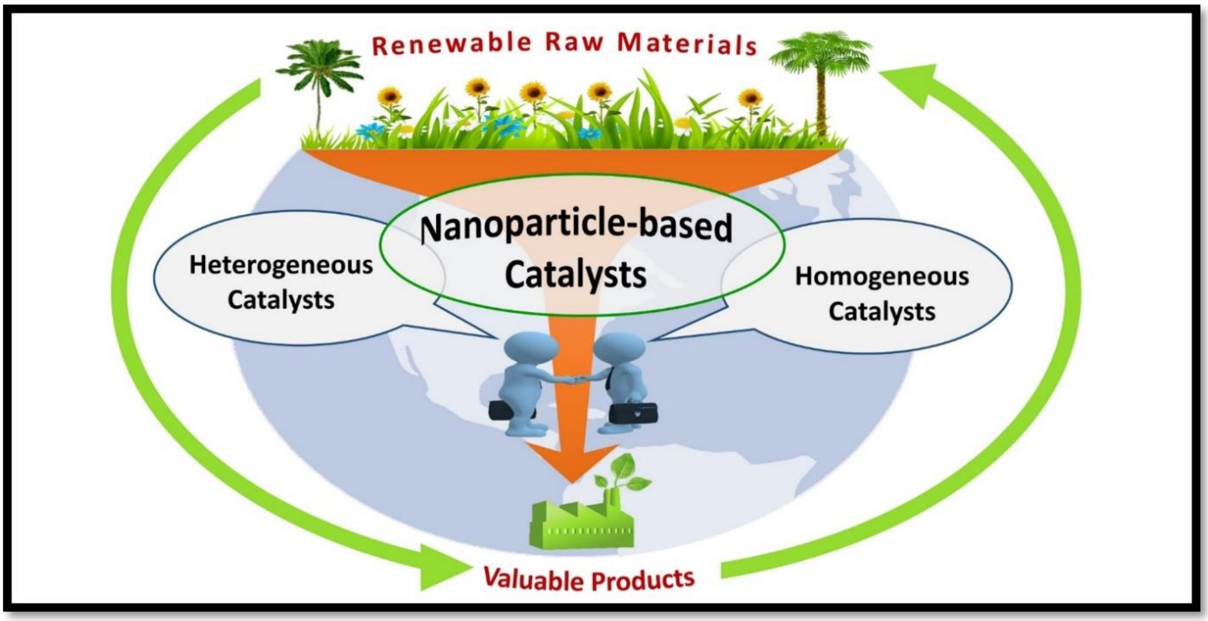
Chapter 2. Chemically catalyzed oxidative cleavage of unsaturated fatty acids and their derivatives



This chapter provides an introduction to the field of oleochemical science. The recent works regarding use of different catalysts in oxidative cleavage of unsaturated fatty acids and their derivatives are reviewed. Furthermore, tungsten-based heteropoly compounds and their applications in organic liquid reactions are discussed.

2.1 Oils and fats as renewable raw materials

Facing with the warning “sorry, out of gas” in near future is one of the most concerning challenges in all around the world nowadays. During the last decades, fossil feedstock derived from oil and gas has always been the most important raw materials for the chemical industry, accounting for more than 90%. Even with this enormous amount, chemical industries have occupied the third position as the user of oil and gas feedstock, after energy generation and transportation [10]. Understandably, the shortage in the petroleum reservoirs in the near future is a worldwide crisis which can be confirmed by Figure 2.1 [11]. It shows the oil and gas production profiles in the past and future for the whole earth which was published in an ASPO[1] Newsletter in 2009. As can be seen, starting from 2010, a downward trend is obvious in the oil and gas production.

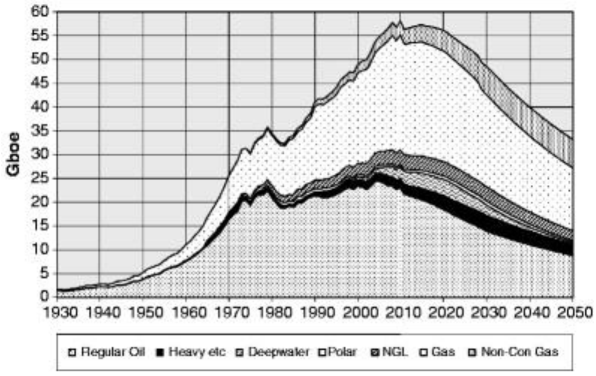


Figure 2.1. Production profiles of oil and gas 2010 base case (Gboe: gigabarrels of oil equivalent) [11]

In addition, global concerns for environmental pollutions associated with petroleum materials have propelled the attention of researchers to the renewable raw materials. Among feedstock from renewable resources, oils and fats of vegetable and animal origin could become one of the major players in the chemical industry in near future, due to not only the economic reasons, but also environmental ones [8,12]. Oils and fats have chemical structures giving them a potential for the industrial development in the field of feedstock materials [13]. On one hand, their structures are similar to petroleum materials with long hydrocarbon chains. On the other hand, they include several functional sites for chemical modifications. Moreover, they are abundant in nature, biodegradable, and have nontoxic properties that make them promising candidates for replacing petrochemical materials.

---

[1] The association for the study of peak oil and gas

2.1.1 Globalization of oils and fats

Oils and fats differ in the state of material; oils are often liquid at ambient temperature, but fats are solid. They are derived from vegetable origins such as palm, soybean, rapeseed (canola), sunflower seed (so-called four major vegetable oils), palm kernel, coconut and olive, or animal origins such as butter, lard, tallow, and fish oil. There is no widely-accepted definition for lipid, but the one which is presented by AOCS[2] would be the best [14]: “Lipids are fatty acids and their derivatives, and substances related biosynthetically or functionally to these compounds.”

Nowadays, extraction of oils and fats from bio-based materials is being rapidly globalized. Oilseeds are obtained in all over the world, under all sorts of climates, in both northern and southern hemispheres and from a variety of plants. In the recent 30 years, production of oilseeds has dramatically increased (see Figure 2.2). Rising from about 190 million tons in 1985 to more than 453 million tons in 2011 shows a 136% increase in the production of the major 10 oilseeds (soybeans, cotton seed, rapeseed, sunflower seed, groundnuts (shelled), sesame seed, palm kernels, copra, linseed and castor seed) in a period of 26 years. It makes more sense when compared with the “grains” (wheat, coarse grains and rice) with only 34% increase in production in the same period. In addition, the area of harvest of oilseeds rose from 160 million hectares to 260 million hectares during the same period, which in turn confirms the increase in productivity from 1.19 tons/hectare in 1985 to 1.74 tons/hectare in 2011 [15].

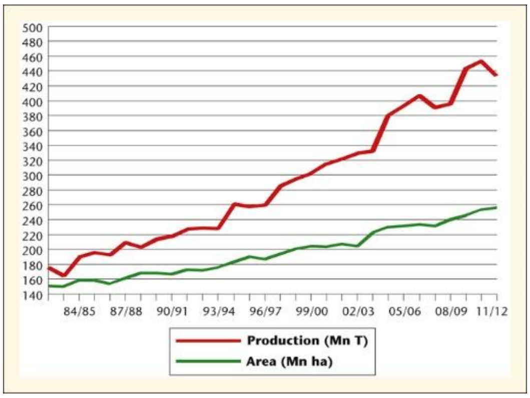


Figure 2.2. World area and production of the major 10 oilseeds (soybeans, cotton seed, rapeseed, sunflower seed, groundnuts (shelled), sesame seed, palm kernels, copra, linseed and castor seed) [15].

---

[2] The American oil chemists’ society

From the total production of about 450 million tons in 2011, more than 57% of all oilseeds were produced in the Americas continent, as Figure 2.3 shows [15]. However, Figure 2.4 indicates that in terms of consumption, Asia continent had a higher rank than Americas [15]. In addition, despite the fact that overall world consumption had about 99% growth in the period of 1996 to 2012, the portion of the Americas continent decreased from 22.8% to 19.5%. One reason would refer to the use of oils and fats as human foods and higher populations increase rate in Asia, because the majority of yearly produced oils and fats are, these days, used in food industries [6].

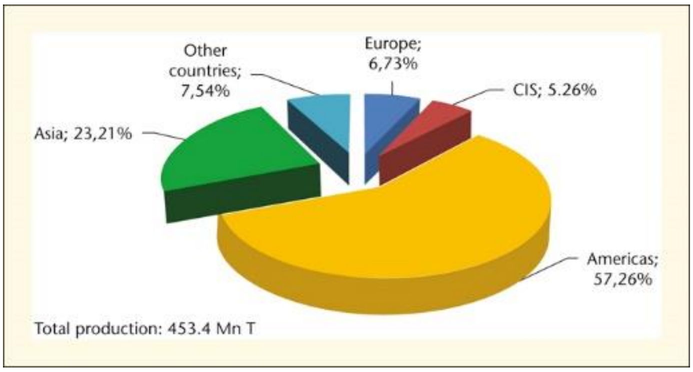


Figure 2.3. World production of oilseeds by main regions (Year 2011) [15].

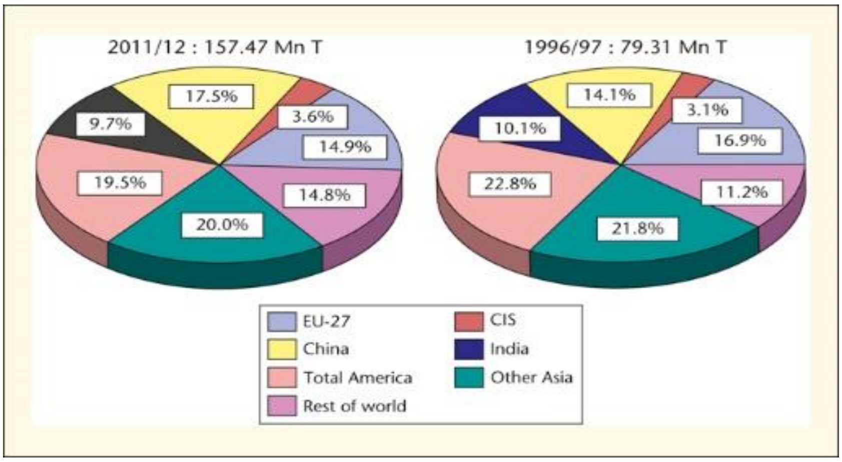


Figure 2.4. Consumption of vegetable oils by major countries (MnT) (year 2011/12 vs. 1996/97) [15].

Presenting some statistical data about the different industrial users of oils and fats in the world, would give a better outlook. In addition to the food industry, oils and fats are used as the basis of the oleochemical industry, as well as a very small portion for animal feeds. Interestingly, a significant growth in the portion of non-food uses is obvious in the data presented in Table 2.1 [16]. It shows the distribution of nine major vegetable oils (coconut, cottonseed, olive, palm, palm kernel, peanut, rapeseed, soybean, and sunflower) between non-food and food use over the last recent years. Since the year 1999 to 2012, the non-food portion has increased from 10.5 to 23.9%. This increase is particularly remarkable from 2003/04 onwards.

Table 2.1. Food and non-food consumptions (million tons and %) of nine major vegetable oils between 1999/00 and 2011/12 [16].

	TOTAL	FOOD	NON-FOOD	NON-FOOD %
1999/00	82.9	74.2	8.7	10.5
2000/01	88.8	78.6	10.2	11.5
2001/02	91.1	80.2	10.9	12.0
2002/03	95.1	82.9	12.2	12.8
2003/04	100.7	86.9	13.8	13.7
2004/05	108.2	91.5	16.7	15.4
2005/06	114.7	94.2	20.5	17.9
2006/07	119.4	95.9	23.5	19.7
2007/08	125.1	98.8	26.3	21.0
2008/09	129.7	101.4	28.3	21.8
2009/10	137.8	106.4	31.4	22.8
2010/11	144.6	110.9	33.7	23.3
2011/12	150.0	114.2	35.8	23.9

According to what was mentioned above, it can be concluded that a significant growth in the production of oils and fats in the recent years is clear in all around the world. One reason would be the human food use of oils and fats and growing populations of the world. Data in Table 2.1, however, confirms the increasing rate of non-food use of oils and fats in the world, in particular during the last decade. This makes it highly desirable to conduct extensive researches in this field in the region of the Americas continent.

2.1.2 Oleochemical industries

Oleochemical industries are those which exploit oils and fats to produce valuable materials. They are being rapidly developed as a result of the rapid globalization of such feedstock. In order to use oils and fats in the advanced chemical industries, it is necessary to split them into the so-called oleochemical base materials [17]. The lipids are made from triglyceride, which, in turn, consists of glycerine and three fatty acids (Figure 2.5) [7]. The triglycerides which form animal fats, typically have more saturated fatty acids while those triglycerides constitute vegetable oils, have more unsaturated fatty acids [18] (for more information about saturated and unsaturated fatty acids see section 2.2.1).

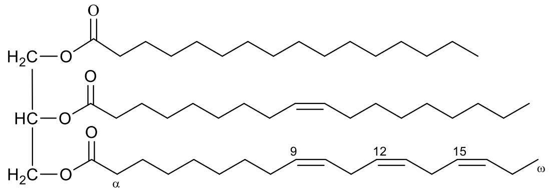


Figure 2.5. Typical example of a lipid structure with glycerol and three fatty acids (palmitic acid, oleic acid, and alpha-linolenic acid, from top to bottom) [7].

Decomposition of the triglycerides results in the release of oleochemical base materials which are shown in Figure 2.6. They mainly include fatty acids (ca. 52%), fatty acid methyl esters (ca. 11%), fatty amines (ca. 9%), and fatty alcohols (ca. 25%) [6] [19].

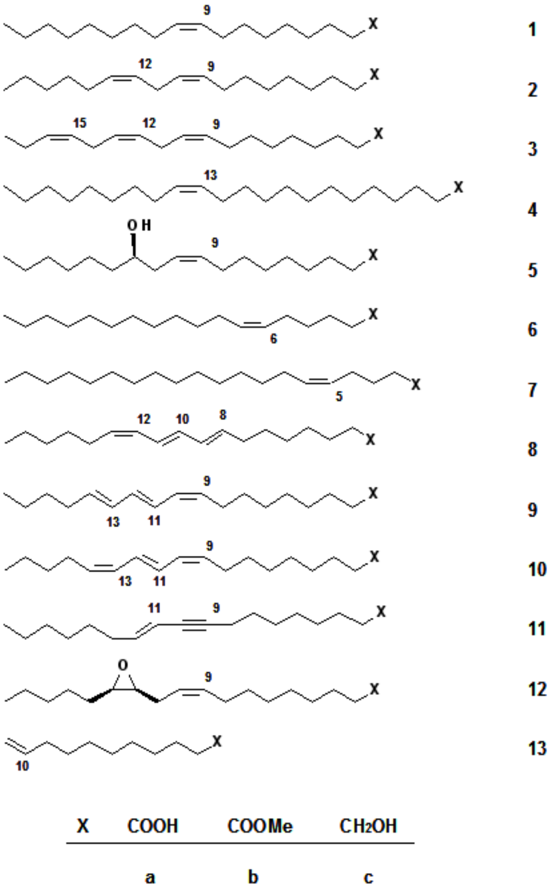


Figure 2.6. Oleochemical base materials as starting materials for chemical industries: oleic acid (1a), linoleic acid (2a), linolenic acid (3a), erucic acid (4a), ricinoleic acid (5a), petroselinic acid (6a), 5-eicosenoic acid (7a), calendic acid (8a), α-eleostear acid (9a), punicic acid (10a), santalbic acid (11a), vernolic acid (12a), 10-undecenoic acid (13a), and the respective methyl esters (1b-13b) and alcohols (1c-13c) [20].

The oleochemical base materials have a variety of chemical applications that is scarcely less than that of petrochemicals [6,17]. Table 2.2 summarizes these applications. Polymer is one of the most important industries which can exploit lipids and convert them into valuable products. Next section will be detailed on this.

Table 2.2. Summary of the applications of basic oleochemicals.

Oleochemical base materials	Applications
Fatty acids and derivatives (52 %)	Plastics; metal soaps; washing and cleaning agents; soaps; alkyd resins; dyestuffs; textile, leather and paper industries; rubbers; lubricants
Fatty acid methyl esters (11 %)	Cosmetics; toothpastes; pharmaceuticals; foodstuffs; lacquers; plastics; synthetic resins; tobacco; explosives; cellulose processing
Fatty alcohols and derivatives (25 %)	Washing and cleaning agents; cosmetics; textile, leather and paper industries; mineral oil additives
Fatty amines and derivatives (9 %)	Fabric conditioners; mining; road-making; biocides; textile and fiber industries; mineral oil additives
Neutral oils and derivatives	Lacquers; dyestuffs; varnishes; linoleum, soaps

2.1.2.1 Polymer industry

Oils and fats have been employed in polymer industry for many years, either in the form of triglycerides or oleochemical base materials. The main applications are categorized in three groups in Table 2.3 including polymer materials (linseed oil and soybean oil as drying oils), polymer additives (epoxidized soybean oil as plasticizer), and building blocks for polymer (dicarboxylic acids for polyesters or polyamides) [9]. Such applications are currently undergoing rapid development to extend scope of the specialty and commodity products. One of the most important applications is preparing building blocks for polymers. Long-chain dicarboxylic acids required for this purpose, are the major product of complete oxidation of unsaturated fatty acids. There are numerous reactions in which unsaturated fatty acids could be involved and form a variety of products (more information in section 2.2.2). In these reactions, carboxylic groups or the carbon-carbon double bonds of unsaturated fatty acids can take part. The oxidation of unsaturated fatty acids includes partial or complete cleavage of the carbon-carbon double bond(s). The latter results in obtaining mono- and dicarboxylic acids.

2.1.2.1.1 Long-chain dicarboxylic acids

Dicarboxylic acids, HOOC(CH2)nCOOH (n represents the number of methylene groups and their derivatives, see Figure 2.7), are industrially important chemicals due to their potential in the production of various intermediates [21]. As mentioned in Table 2.3, long-chain dicarboxylic acids are used as polymer intermediates in polyamides, polyesters, and alkyd resins. One of the most striking polymers obtained from dicarboxylic acids is nylon 1313 (produced from brassylic acid) which interestingly shows enhanced properties in comparison with common nylons (a lower melting point, lower density, and more hydrophobicity than nylon-11 and nylon-12) [22]. Furthermore, the esters of dicarboxylic acids are used as lubricants and hydraulic fluids over a wide temperature range [21], as well as plasticizers for polyvinyl chloride [21,20].

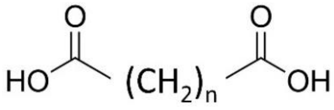


Figure 2.7. A dicarboxylic acid with two carboxyl groups as a valuable chemical in the polymer industry.

Dicarboxylic acids are produced from petrochemical feedstock (e.g., production of adipic acid from the multistage butadiene oxidation [23]). Also, ring-opening oxidation of cyclic compounds is another route to produce these chemicals [1]. Biotechnology techniques have been also developed for this purpose [24]. Until recently, the production of only two of these dicarboxylic acids from oleochemical base materials has been commercialized, including sebacic acid which is obtained by alkaline cleavage of castor oil [1] and azelaic acid which is produced from oxidation of oleic acid through ozonolysis [25]. Surprisingly, these oleochemically derived dicarboxylic acids can simplify condensation of the polymers, as a result of their special properties such as high impact strength, hydrolytic stability, hydrophobicity, lower glass transition temperatures, and flexibility [26,9].

Table 2.3. Examples of applications of oils and fats in polymer industry [9].

Raw materials (oleochemical base or triglycerides)	Product	Application	Category
Castor and soybean oils Linseed oil	Polymerized castor and soybean oils Polymerized linseed oil	Drying oils Linoleum	Polymer materials
Soybean oil Rapeseed oil Stearic acid	Epoxides Fatty acid esters and amides Soaps	Stabilizers and plasticizers Lubricants, Stabilizers	Polymer additives
Castor, soybean, sunflower, linseed, and tall oils and oleic acid	Dicarboxylic acids and ether/ester polyols	Polyamides, polyesters, alkyd resins, and polyurethanes	Building blocks for polymers

2.2 Fatty acids and their reactions

2.2.1 Fatty acids: a primer

As mentioned earlier, the constituents of lipids are fatty acids. A general definition of fatty acids is a carboxylic acid with a long hydrocarbon chain, which consists of two parts: hydrophilic carboxyl group and hydrophobic alkane chain (Figure 2.8).

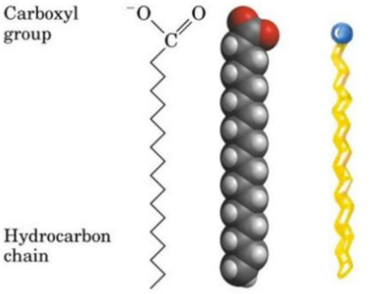


Figure 2.8. Fatty acids structure.

In the most generic classification, fatty acids are divided into saturated (without carbon-carbon double bond) and unsaturated (with carbon-carbon double bond(s)) types. UFAs can, in turn, be categorized in mono-unsaturated (with one double bond) and poly-unsaturated (with more than one double bonds). The two carbon atoms just near the double bond can occur in *cis* or *trans* configurations. However, most of naturally UFAs have *cis* configuration [27].

The common UFAs derived from vegetable oils, have 16 to 18 carbons in their hydrocarbon chain with up to three double bonds. Animal fats, in addition to these UFAs, contain other even carbon numbered fatty acids, such as C_{20} and C_{22}, and up to six double bonds (in fish oils) [14]. Table 2.4 shows the common fatty acids extracted from animal and plant origins with their structures and different nomenclature systems [14,28]. In nature, the most abundant saturated fatty acid is palmitic acid (C_{16}) and the most abundant monounsaturated fatty acid is oleic acid (C_{18}) [29]. The C_{18} polyunsaturated fatty acids like linoleic or *cis*-9, *cis*-12-octadecadienoic acid (18:2(*n*-6)) and α-linolenic or *cis*-9, *cis*-12, *cis*-15-octadecatrienoic acid (18:3(*n*-3)), are also of the main components of most plant lipids, including many of the commercially important vegetable oils. The structures of these C_{18} unsaturated fatty acids are shown in Figure 2.9.

Table 2.4. Common fatty acids of animal and plant origins; structures and nomenclature systems [28,4].

Systematic name	Common name	Chemical structure	Shorthand
Saturated fatty acids			
Ethanoic	Acetic	CH_3COOH	2:0
Butanoic	Butyric	$CH_3(CH_2)_2COOH$	4:0
Hexanoic	Caproic	$CH_3(CH_2)_4COOH$	6:0
Octanoic	Caprylic	$CH_3(CH_2)_6COOH$	8:0
Decanoic	Capric	$CH_3(CH_2)_8COOH$	10:0
Dodecanoic	Lauric	$CH_3(CH_2)_{10}COOH$	12:0
Tetradecanoic	Myristic	$CH_3(CH_2)_{12}COOH$	14:0
Hexadecanoic	Palmitic	$CH_3(CH_2)_{14}COOH$	16:0
Octadecanoic	Stearic	$CH_3(CH_2)_{16}COOH$	18:0
Eicosanoic	Arachidic	$CH_3(CH_2)_{18}COOH$	20:0
Docosanoic	behenic	$CH_3(CH_2)_{20}COOH$	22:0
Monounsaturated fatty acids			
cis-9-hexadecenoic	Palmitoleic	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$	16:1(n-7)
cis-6-octadecenoic	Petroselinic	$CH_3(CH_2)_{10}CH=CH(CH_2)_4COOH$	18:1(n-12)
cis-9-octadecenoic	Oleic	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	18:1(n-9)
cis-11-octadecenoic	*cis-vaccenic*	$CH_3(CH_2)_5CH=CH(CH_2)_9COOH$	18:1(n-7)
cis-13-docosenoic	Erucic	$CH_3(CH_2)_7CH=CH(CH_2)_{11}COOH$	22:1(n-9)
cis-15-tetracosenoic	Nervonic	$CH_3(CH_2)_7CH=CH(CH_2)_{13}COOH$	24:1(n-9)
Polyunsaturated fatty acids			
9,12-octadecadienoic	linoleic	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$	18:2(n-6)
9,12,15-octadecatrienoic	α-linolenic	$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$	18:3(n-3)
6,9,12-octadecatrienoic	γ-linolenic	$CH_3(CH_2)_4CH=CHCH_2CH=CHCH_2CH=CH\ (CH_2)_4COOH$	18:3(n-6)
5,8,11,14-eicosatetraenoic	arachidonic	$CH_3(CH_2)_4CH=CHCH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_3COOH$	20:4(n-6)
5,8,11,14,17-eicosapentaenoic	EPA	$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_3COOH$	20:5(n-3)
4,7,10,13,16,19-docosahexaenoic	DHA	$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CHCH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_2COOH$	22:6(n-3)

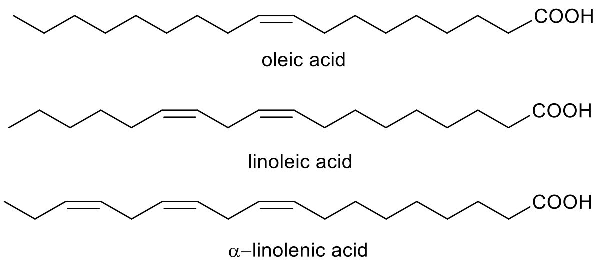


Figure 2.9. Different C18 mono and poly-UFAs.

Presence of the rigid double bond(s) in *cis*-unsaturated fatty acids causes the chain to bend. The increase in such double bonds decreases the flexibility of the chain and results in more curved shape of the chain. As can be seen in Figure 2.10, oleic acid with one double bond, has a “kink” in it, whereas the curvatures in linoleic acid, with two double bonds, and α-linolenic acid, with three double bonds, are more intense [30]. The direct result is that the presence of *cis* bonds prevents tight packing of fatty acids in the molecules of triglycerides, and therefore the lipids formed by such acids, usually have liquid state at ambient temperature (so-called oils). By contrast, saturated fatty acids can tightly attach to form a solid-state lipid (so-called fats) (see Figure 2.11).

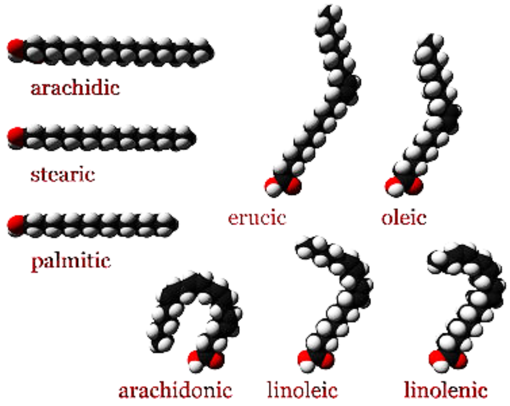
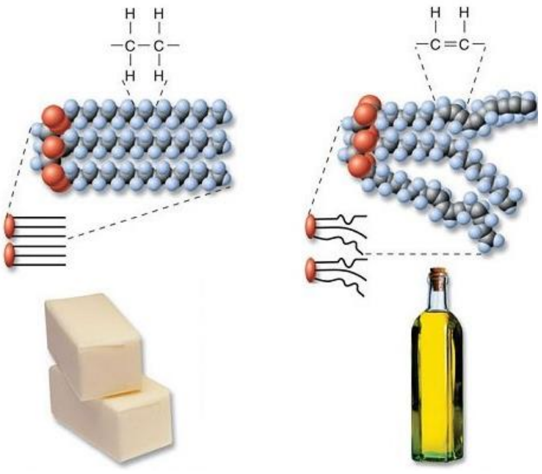


Figure 2.10. 3-D models of different fatty acid types. Arachidic, stearic, and palmitic acids are saturated. Erucic and oleic acids are monounsaturated, and linolenic, linoleic and arachidonic are polyunsaturated fatty acids [30].

2.2.1.1 Oleic acid

The most abundant mono-UFA in nature is oleic acid (C_{18}) [29], which exists in various vegetable and animal oils and fats. Its systematic name is *cis*-9-octadecenoic acid with shorthand form 18:1 (n-9) that shows it has 18 carbon atoms with one carbon-carbon double bond on the ninth carbon atom (chemical formula $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$) [31]. Oleic acid, like other fatty acids, mainly emerges in the form of triglycerides, and these oleic acid containing triglycerides constitute the majority of olive oils [32]. That is why it has been called "oleic" which means come from oil or olive. It is worth pointing out that these triglycerides are also available in relatively large amounts in pecan, peanut, macadamia, sunflower, grape seed, sea buckthorn, sesame, wild apricot seed, rapeseed, and poppyseed oils [33-35]. In addition, they are abundantly present in many animal fats such as chicken and turkey fat and lard [36].

Currently, although oleic acid has a variety of industrial applications like, as a component of human diet (in triglyceride form), major component of soaps (in sodium salt form), and in pharmaceuticals [31], the most important one is production of dicarboxylic acids via ozonolysis [25], which will be discussed further in section 2.2.2.1.2.



(a) Hard fat (saturated): Fatty acids with single bonds between all carbon pairs

(b) Oil (unsaturated): Fatty acids that contain double bonds between one or more pairs of carbon atoms

Figure 2.11. Effect of C=C in the packing of saturated and unsaturated fatty acids.

2.2.2 Reactions of unsaturated fatty acids

According to what was explained in the previous section, there are various functional sites in the structure of fatty acids. The differences between the length of aliphatic chain, geometry of the molecule (*cis* or *trans* configurations) and the number and position of C-C double bond(s), play a crucial role in biological processes, and consequently, lead to the possibility for variety of products even more than petrochemistry products [7].

The reactive sites in the structure of a fatty acid can be categorized in two parts; the double bond(s) in the chain and the acidic group. The majority of industrial reactions is carried out at the carboxylic group (>90%, in 2000), while remarkably very few industrial reactions (less than 10% in 2000) are involved in the hydrocarbon chain in oleochemical industries [9,7]. However, because of wider range of obtainable products from the latter, progress in such reactions is highly-demanded [7]. At present, converting natural oils into nonedible products is limited, mainly because of economic reasons; the production costs of oleochemical processes cannot compete effectively with mature petrochemical industries [37]. To address this problem and improve the economic aspects, optimization of reaction conditions and, also, employing efficient catalysts are called for. Oxidation of UFAs is one of the reactions that targets C-C double bond(s) which will be explained in the following section. Other reactions of fatty acids such as hydrogenation or hardening, metathesis, C-H bond activation, hydroxylation, pericyclic, radical additions, and Lewis acid induced cationic addition have been nicely and widely reviewed in the literature [7,29,6].

2.2.2.1 Oxidation

From the industrial point of view, oxidation of UFAs possesses a great importance, since it has shown considerable potentials in the production of invaluable materials. Dicarboxylic acids, as mentioned earlier, are a striking example of such products, on which, this research focuses. Herein, two main oxidation pathways of UFAs are discussed.

2.2.2.1.1 Epoxidation

The carbon-carbon double bonds in oils and fats of vegetable and animals can be functionalized via epoxidation and, consequently, produce epoxidized oils and fats which contain epoxide groups or oxirane rings [38]. The term epoxide can be defined as a cyclic ether which has three ring atoms (Figure 2.12) and the general process for the synthesis of the epoxide groups is known as epoxidation reaction. Epoxides can be prepared from hydroperoxides, hydrogen peroxide, or molecular oxygen in the presence of different catalysts [39].

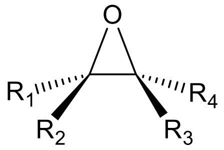
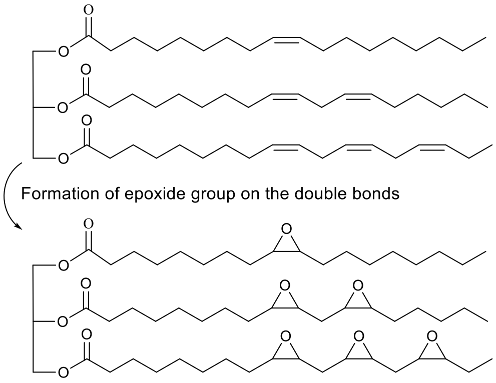


Figure 2.12. A generic epoxide.

Several methods have been reported for epoxidation of unsaturated fatty compounds such as *in situ* performic acid procedure, epoxidation with aldehydes and molecular oxygen, dioxiranes, H_2O_2/tungsten heteropolyacids, H_2O_2/methyl trioxorhenium, and enzymatic epoxidation [6,7,17]. Scheme 2.1 shows a typical epoxidation of a lipid including oleic acid, linoleic acid and α linolenic acid and formation of epoxide groups on the C-C double bonds.

Although, the epoxidized oils and fats have their own valuable applications such as plastic additives [40,41], plasticizers [40], flame retardants [7], heat stabilizers [7], antioxidants and light stabilizers [7], lubricants, cosmetics and biochemical applications [42,43] (which are summarized in Figure 2.13) , obtaining dicarboxylic acids via epoxidation requires a further reaction of ring opening of epoxides which, in turn, often needs different catalysts. Therefore, epoxidation does not seem to be reasonable method to produce dicarboxylic acids.



Scheme 2.1. Epoxidation of a lipid [7].

2.2.2.1.2 Oxidative cleavage

The term "oxidative cleavage" in olefins generally means breaking carbon-carbon bonds and forming carbon-oxygen double bonds (see Scheme 2.2). Sometimes, carbon-hydrogen bonds get cleaved in addition to carbon-carbon bonds. Therefore, a variety of products such as alcohols, aldehydes or ketones, and carboxylic acids can be obtained depending on the type of bond being oxidized and the reaction conditions [44].

Oxidative cleavage of olefins in large-scale typically occurs by ozonolysis with high yield. Ozone, O_3, is an allotrope of oxygen that can be added rapidly to the carbon-carbon double bonds, and transform alkenes into aldehydes or carboxylic acids without the use of a metal as catalyst [44]. Currently, azelaic acid (C9, dicarboxylic acid) as a very industrially important chemical is produced in large-scale via ozonolysis of oleic acid (Equation 2.1). Pelargonic acid (C9, monocarboxylic acid) is obtained as a co-product but also a valuable chemical [1]. These types of saturated acids that have short and odd hydrocarbon chains are rare in natural resources [2]. On the other hand, they are very attractive initial materials for the development of numerous bio-based products [3,4]. For instance, azelaic acid converts into different esters for the preparation of polymers (Nylon 6:9), plasticizers, adhesives, solvents, biodegradable lubricants, corrosion inhibitors, and anti-acneic agent for cosmetics [2,3]. Pelargonic acid is an intermediate in the production of lubricants, plasticizers, perfumes, herbicides, fungicides, resins [3,5].

$$H_3C(CH_2)_7CH{=}CH(CH_2)_7COOH + 4O \rightarrow H_3C(CH_2)_7COOH + HOOC(CH_2)_7COOH \quad (2.1)$$

These two valuable products are obtained only in the case of over-oxidation, whereas partial oxidative cleavage of oleic acid produces aldehyde nonanal and 9-oxononanoic acid [45] (Scheme 2.3). Presence of strong oxidants such as ozone favors over-oxidation.

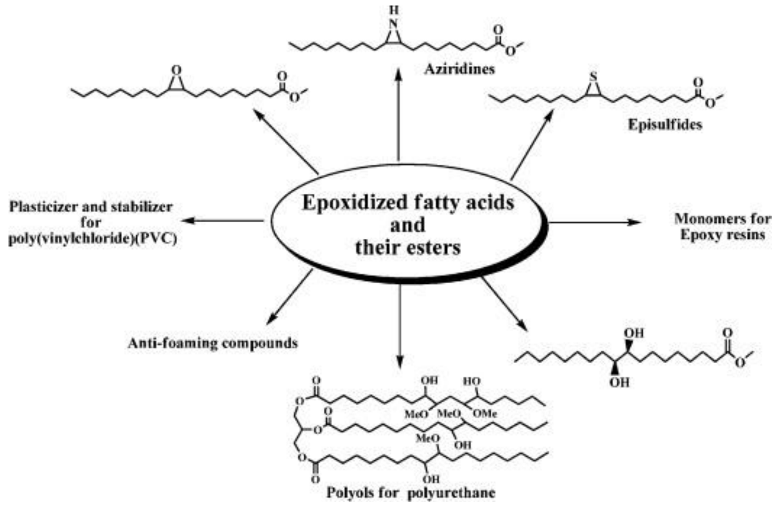
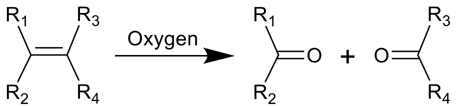
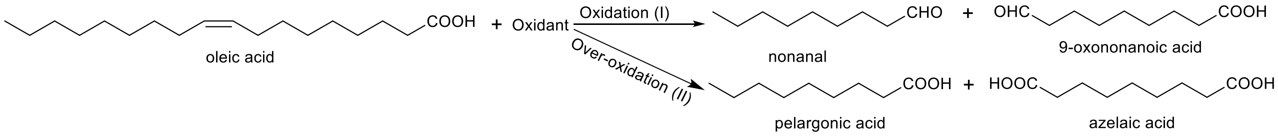


Figure 2.13. Applications of epoxidized fatty acids and their derivatives [42].



Scheme 2.2. A general oxidative cleavage process.

Although the ozonolysis of oleic acid has shown high conversion and selectivity [1-3,46,25], hazardous problems associated with the use of ozone have always been a challenge [8]. That is why the commercial applications of ozonolysis processes are still restricted. Handling of ozone has always various safety risks such as explosion and toxicity of ozone. Moreover, enormous energy demand of ozonolysis process and high-technology equipment required make the capital cost of process high [47,46]. Therefore, a new alternative method with safer and economically more viable process to produce dicarboxylic acids from oxidation of UFAs is of great interest to the industry. The dangerous ozone should be replaced by a safe and green oxidant. This makes it necessary to employ a highly efficient catalyst in the oxidative cleavage process. Therefore, in the following sections different types of oxidants and catalysts reported in the literature for oxidative cleavage of UFAs are reviewed.



Scheme 2.3. Oxidation of oleic acid into aldehydes (I) and over-oxidation into carboxylic acids (II).

2.3 Different catalyst-oxidant systems for oxidative cleavage of unsaturated fatty acids

Transition metal-based catalytic systems are considered to be most suitable for the oxidative cleavage of olefins. Their high catalytic activities make it possible to use more benign oxidants. Osmium, ruthenium, and tungsten are three metals that have attracted the most attentions for oxidation of unsaturated hydrocarbons. In the case of UFAs, on which tiny portion of oxidative cleavage-based research works have focused, the emphasis has been placed on the latter two, particularly tungsten. Additionally, iron, molybdenum, cobalt, chromium, manganese and gold are other metals that have been less investigated. Pure metals, simple metal salts, metal oxides and different metal complexes are different forms of metals that have been employed as catalysts. One noticeable point is that the common side reactions such as epoxidations, dihydroxylation or allylic oxidations should be prevented or minimized, which strongly depends on the nature of the transition metal used as catalyst.

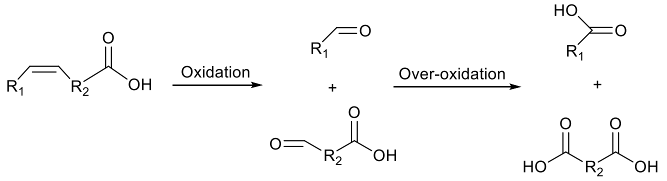
Oxidants are the source of oxygen during the oxidation reaction. Several oxidants have been reported in the literature to oxidize unsaturated fatty acids. Depending on the oxidizing power some oxidants need the aid of catalyst to act as co-oxidant, and some do not need. The strong oxidants such as sodium periodate, sodium hypochlorite, potassium permanganate, potassium peroxomonosulfate (oxone), peracetic acid, nitric acid and tert-butyl hydroperoxide (TBHP) can usually oxidize substrates without the need for an active catalyst [2,46,48,39]. But, the problem is that most of these oxidants are not eco-friendly, and the desired products are obtained in low yields due to the waste generation. Using the relatively moderate oxidants such as molecular oxygen and hydrogen peroxide could overcome this problem, because they produce no waste. However, in order to have acceptable reaction conversion and selectivity in such systems it is necessary to employ a highly efficient catalytic system [2,3].

In this section, we have tried to review all of the recent works which exploited different catalyst/oxidant systems in the oxidative cleavage of, only, UFAs and their derivatives. With specific respect to commercializing viewpoint arising from the global demand for developing a greener alternative for the conventional oxidative cleavage methods, we will compare the results of previous works in three groups: homogeneous, heterogeneous and semiheterogeneous (NP-based) catalysts. This classification associated with the critical discussions presented on the important features such as catalytic activity and recoverability would be helpful for future works planning. In addition, investigation of recent breakthroughs of NP-based catalysts that can increase their performance specially in the oxidative cleavage of UFAs, would present an outlook in the development of advanced catalysts for such reactions.

2.3.1 Mechanisms of the reaction

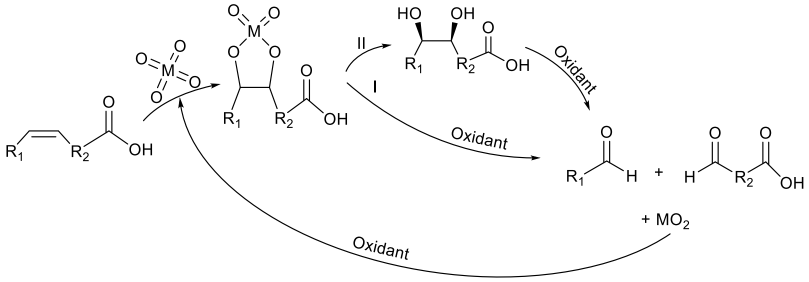
To reach a comprehensive interpretation, firstly it is important to investigate different proposed mechanisms for the oxidative cleavage reactions. In general, oxidative cleavage of C-C double bonds in the fatty molecules involves scission of the double bonds followed by incorporation of oxygen atoms into the two produced sections (see Scheme 2.4). Aldehydes and ketones are often the initial products whereas over-oxidation yields in the production of carboxylic acids [46].

Several mechanisms have been proposed for the oxidative cleavage of alkenes and cyclic olefins. For UFAs, however, the mechanism seems to be more complicated. The main reason would be the presence of carboxylic group which may results in side reactions. In addition, oxidative cleavage of cyclic olefins and alkenes is typically easier than fatty acids due to the role of the ring strain instability. This intermediate state can promote the oxidation reaction, while it is not highly effective in the case of fatty acids. Moreover, formation of radical intermediates in the oxidative cleavage of UFAs is very difficult, unlike the cyclic olefins. Herein, we presented the modified versions of two of proposed mechanisms for general olefins that are applicable to UFAs. Further works to propose a mechanism that carefully considers the mentioned difficulties, however, should be encouraged.



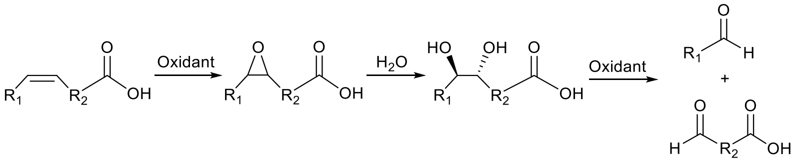
Scheme 2.4. Oxidative double bond cleavage of UFAs to aldehydes, ketones, and carboxylic acids [45].

The first mechanism, which is shown in Scheme 2.5, describes a catalytic system based on transition metals tetroxide such as RuO_4 and OsO_4 [45,49]. These oxides can be formed during the reaction also, and in the presence of oxidants, when their corresponding metal salts are used as catalysts [50,51]. In terms of selectivity, RuO_4 indicates better performance compared to OsO_4, because the reaction mechanism for RuO_4 does not involve dihydroxylated intermediates (Scheme 2.5 mechanism I) and immediately after the formation of metal diester as the main intermediate, the aldehydes will be formed, while OsO_4 tends to form diols after formation of the metal diester (Scheme 5 mechanism II) rather than aldehydes. The main advantage of osmium in comparison with ruthenium is the lower required metal loadings at the same conditions [45]. However, the toxic properties of osmium are stronger than ruthenium.



Scheme 2.5. First mechanism of oxidative cleavage of UFAs [45,49].

The second mechanism is based on the formation of epoxide groups following by the hydrolysis to diols and final oxidation to obtain aldehydes or carboxylic acids. This mechanism, which is schematically shown in Scheme 2.6, is mainly ascribed to the presence of tungsten compounds as catalyst [45].



Scheme 2.6. Second mechanism of oxidative cleavage of UFAs [45].

2.3.2 Homogeneous catalysts

Homogeneous catalytic systems are believed to effectively increase the conversion in oils and fats reactions which are conducted mainly in liquid phase. The high performance of such catalysts owes to the formation of uniform mixture with the reactants resulting in minimum mass transfer limitations and high reaction rates.

In oxidative cleavage reactions of fatty acids, different coordination of metals such as simple metal salts, metal-oxo or peroxo complexes, and other metal complexes have been used as homogeneous catalyst. It is worth pointing out studies in this field, in order to find an alternative for ozonolysis process, are currently passing through lab-scale requirements such as better understanding of the reaction mechanism and, thus, have been less focused on industrialization aspects. In fact, that is why the use of homogeneous catalysts has been generally preferred in the literature. While heterogeneous catalysts are of interest to industry for their ease of recovery, homogeneous catalysts show more advantages for research-scale works such as lower mass transfer limitations which results in higher conversion. Therefore, the number of researches focused on homogenous system is much higher than heterogeneous one. Table 2.5 summarized the details of reported homogeneous catalytic systems for the oxidative cleavage of UFAs and their derivatives.

2.3.2.1 Osmium

Osmium is one of the first metals which have been investigated in catalytic oxidative cleavage of olefins [52]. The catalytic application of Os is usually accompanied with using NaIO4 or KHSO5 as secondary oxidants (Table 2.5, entry 1) [53]. Sodium periodate and oxone can form Os tetroxide from its precursor, in addition to their role in oxidizing the diol intermediates to aldehydes. Although catalytic systems based on Os require less loading of catalyst, its applications have been restricted due to the significant toxic properties of Os.

2.3.2.2 Cobalt

Diol oxidation can also be done with the cobalt polyoxometallate (POM) as shown by Santacesaria (Table 2.5, entry 2) [54]. Using cobalt acetate, they reported a POM based on the mixture of cobalt and tungsten. As soon as hydrogen peroxide is added to the system, the POM catalyst can be formed in situ which is introduced to be H6CoW12O40. However, the production yield of azelaic acid from oleic acid using this catalytic system is not high enough (52.5%).

2.3.2.3 Molybdenum

Turnwald reported the complex formed on the basis of molybdenum to convert oleic acid into pelargonic and azelaic acid with excess hydrogen peroxide (Table 4, entry 3) [3]. Using 2,6-dipicolinate as ligand, the active oxo-peroxo complex [MoO(O_2)(2,6-dipicolinate)](H_2O) could be formed as the catalyst which resulted in 82% yield of azelaic acid after 5 h at 90 ºC, albeit the large amount of H_2O_2, which should be employed, make such systems unreasonable for large-scale applications.

Table 2.5. Different homogeneous catalytic systems reported for the oxidative cleavage of UFAs and their derivatives.

Metal	Entry	Reactants	Main products	Catalyst/oxidant system	Reaction conditions [1]	System's efficiency (Yield) [2,3]	Reference
Os	1	Methyl oleate	Pelargonic acid Monomethyl azelate	OsO_4/oxone in DMF	3 h, RT	PA: 93%	[53]
Co	2	Oleic acid	Pelargonic acid Azelaic acid	A cobalt-based POM: $H_6CoW_{12}O_{40}$/ H_2O_2-O_2	4.5 h, 70 ºC	AA: 52.5%	[54]
Mo	3	Oleic acid	Pelargonic acid Azelaic acid	A molybdenum-based POM: $[MoO(O_2)(2,6\text{-dipicolinate})](H_2O)/H_2O_2$	5 h, 90 ºC	AA: 82%	[3]
Fe	4	Oleic acid Methyl oleate Elaidic acid Erucic acid Methyl erucate	Nonanal	An Iron-based complex/H_2O_2 and $NaIO_4$	24 h, RT	NL from OA: 90% NL from MO: 96% NL from ElA: 69% NL from ErA: 73% NL from ME 70%	[55]
	5	Oleic acid Methyl oleate	Nonanal Pelargonic acid Azelaic acid	An Iron-based complex/H_2O_2 and $NaIO_4$	48 h, RT	PA from OA: 85% NL from OA: 5% PA from MO: 82% NL from MO: 9%	[56]
Ru	6	Oleic acid	Pelargonic acid Azelaic acid	$RuCl_3/NaIO_4$	0.75 h, RT Ultrasonic radiation	AA: 81% PA: 96%	[57]
	7	Oleic acid	Pelargonic acid Azelaic acid	$RuCl_3/NaIO_4$	8 h, RT Using ultrasonic radiation Organic solvent-free	AA: 62% PA: 98%	[58]
	8	Oleic acid Methyl oleate	Pelargonic acid Azelaic acid	A ruthenium-based POM: $[Ru(2,6\text{-dipicolinate})_2]/H_2O_2$	24 h, 80 ºC	PA from OA: 59% PA from MO: 81%	[59,60]

Table 2.5. Different homogeneous catalytic systems reported for the oxidative cleavage of UFAs and their derivatives, continued.

Metal	Entry	Reactants	Main products	Catalyst/oxidant system	Reaction conditions [1]	System's efficiency (Yield) [2,3]	Reference
W	9	Oleic acid	Pelargonic acid Azelaic acid	H_2WO_4 and $Co(acac)_3$ /H_2O_2 and NHPI in O_2	5 h, 70-75 ºC	AA: 15% PA: 15%	[61]
	10	Methyl oleate	Pelargonic acid Methyl azelate	H_2WO_4 and $Co(acac)_3$ /H_2O_2 and NHPI in O_2	5 h, 70-75 ºC	MA: 19% PA: 20%	[61]
	11	Methyl erucate	Pelargonic acid Methyl brassylate	H_2WO_4 and $Co(acac)_3$ /H_2O_2 and NHPI in O_2	5 h, 70-75 ºC	MB: 41% PA: 54%	[61]
	12	Oleic acid	Pelargonic acid Azelaic acid	PCWP/H_2O_2	5 h, 90 ºC Organic solvent-free	AA: 57%	[3]
	13	Oleic acid	Pelargonic acid Azelaic acid	A peroxo-tungsten complex with Cs^+ as PTA/H_2O_2	10 h, 90 ºC Organic solvent-free	AA: 28%	[3]
	14	Oleic acid	Pelargonic acid Azelaic acid	PCWP/H_2O_2	4 h, 80 ºC	AA: 86% PA: 82%	[62]
	15	Methyl oleate	Pelargonic acid Methyl azelate	A peroxo-tungsten complex with Aliquat® 336 as PTA/H_2O_2	4 h, 85 ºC Organic solvent-free	MA: 83% PA: 84%	[63]
	16	Methyl ricinoleate	Methyl azelate Hydroxynonanoic acid	A peroxo-tungsten complex with Aliquat® 336 as PTA/H_2O_2	4 h, 85 ºC Organic solvent-free	MA: 85% PA 84%	[63]
	17	Oleic acid	Pelargonic acid Azelaic acid	A peroxo-tungsten complex with Aliquat® 336 as PTA/H_2O_2	5 h, 80 ºC	AA: 79% PA: 82%	[64]
	18	Oleic acid	Pelargonic acid Azelaic acid	PCWP/H_2O_2	5 h, 85 ºC Organic solvent-free	AA: 81% PA: 86%	[2]
	19	Methyl oleate	Nonanal	A peroxo-tungsten complex with Alk-PEI as PTA/H_2O_2	24 h, 70 ºC Organic solvent-free	NL: 97%	[65]

1. RT: room temperature
2. The best result of each work is presented in the table.
3. PA: pelargonic acid, AA: azelaic acid, NL: nonanal, OA: oleic acid, MO: methyl oleate, ElA: Elaidic acid, ErA: Erucic acid, ME: methyl erucate, MA: methyl azelate, and MB: methyl brassylate.

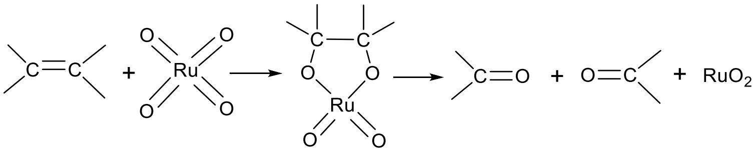
2.3.2.4 Iron

Although the first-row transition metals have the advantages of being cheaper and more environmentally friendly, their use in catalytic oxidative cleavage of UFAs has been limited due to their generally lower oxidizing potential compared to second- and third-row transition metals. It seems that the catalytic systems based on only first-row transition metals like iron have less ability to over-oxidize UFAs and produce dicarboxylic acids.

Spannring *et al.* have introduced a catalytic system based on the first-row transition metal for the oxidation of UFAs (Table 2.5, entries 4 and 5) [55,56]. They used Fe-based coordination metal complexes to produce aldehydes (entry 4) and carboxylic acids (entry 5). For the first case (aldehyde), the iron complex [Fe(OTf)$_2$(mix-BPBP)] has been used as catalyst and hydrogen peroxide and sodium periodate as oxidant in acetonitrile, where OTf is trifluoromethane sulfonate anion and mix-BPBP is the mixture of R,S-, R,R- and S,S isomers of N,N′-bis(2-picolyl)-2,2′-bipyrrolidine). After epoxidation, water was added followed by acidification with H_2SO_4 and subsequent pH neutralization using $NaHCO_3$ to perform the epoxide hydrolysis and diol cleavage (second mechanism, Scheme 2.6). Adding acetic acid to increase the conversion, they succeeded to produce nonanal with the yields of 96 and 90% from methyl oleate and oleic acid, respectively. The total time of reaction was 24 hours at ambient temperature. However, longer reaction time (48 h) is needed to produce carboxylic acids using Fe-based complexes (see Table 2.5, entry 5). The complex used for this purpose was [Fe(OTf)$_2$(6-Me-PyTACN)] where 6-Me-PyTACN is 1-[(6-methyl-2-pyridyl)methyl]-4,7-dimethyl-1,4,7-triazacyclononane. Here, the mechanism includes the direct *cis*-dihydroxylation of the double bond, oxidative cleavage and subsequent over-oxidation to the carboxylic acids. Applying several one-pot procedures with different combinations of oxidants and additives resulted in different substrate conversions and product distributions. The best obtained yields, which are presented in Table 2.5, are 82 and 85% for pelargonic acid from methyl oleate and oleic acid, respectively. Nevertheless, the low oxidizing power of iron, which leads to the longer reaction time, is still the main disadvantage of such catalytic systems.

2.3.2.5 Ruthenium

Ruthenium is one of the oldest transition metals which have been employed in the oxidative cleavage of C-C double bonds [66,50,51]. Its tetroxide is an interesting metal oxide, because the stoichiometric oxidation of double bonds by RuO_4 is fast and very selective. This arises from the fact that the reaction mechanism does not involve epoxide or hydroxylated intermediates. This mechanism is shown in Scheme 2.7, (mechanism I in Scheme 2.5) and involves the formation of a cyclic perruthenate ester [67]. RuO_4 can also be used as catalyst when $RuCl_3$ is employed with a secondary oxidant like $NaIO_4$, NaClO, *t*-BuOOH or RCOOOH. These oxidants can perform the re-oxidization of RuO_2 to RuO_4. By contrast to the common metal oxides like MnO_2, ruthenium oxide is soluble in solvents such as CCl_4 or MeCN and this property, is crucial in its catalytic applications [68].



Scheme 2.7. Oxidative cleavage of C-C double bonds by RuO4 (formation of cyclic perruthenate ester) [67].

Optimization of the methods presented by Zimmermann *et al.* [69] for the oxidative cleavage of oleic acid using $RuCl_3$ as catalyst and $NaIO_4$ as oxidant, resulted in the production of azelaic and pelargonic acid with 81 and 96% yield, respectively, in the mixture of acetonitrile and water (Table 2.5, entry 6) [57]. Using the surfactant Aliquat® 336 (methyltrioctylammonium chloride) and ultrasonification in the system significantly increased the reaction rate and made these yields possible in only 45 minutes at ambient temperature. Further improvement including the elimination of organic solvent by means of 20 kHz ultrasonic irradiation and increasing the reaction time was obtained by Rup *et al.* (Table 2.5, entry 7) [58].

Recently, Behr and his co-workers tried to eliminate the secondary oxidant $NaIO_4$ using Ru-based metal complexes (Table 2.5, entry 8) [59,60]. They demonstrated that the presence of excess amount of a ligand and *in situ* formation of the complex, make the oxidative cleavage possible only with hydrogen peroxide. The procedure includes the use of $Ru(acac)_3$ as a precursor and 2,6-dipicolinic acid as a ligand in the mixture of tert-butyl alcohol and water and reaction at 80 ^{0}C for 24 h. However, the yield of production of pelargonic acid with this system (59 and 81% from oleic acid and methyl oleate, respectively) are lower than those systems based on Ru salt and $NaIO_4$. This is mainly because of the higher number of side reactions in this case.

Ruthenium is one of the rare transition metals, and its precursors are very expensive. Its toxic property, although less than Os, is another problem. Considering scale up aspects, therefore, an alternative transition metal is desirable for catalytic oxidation of olefins.

2.3.2.6 Tungsten

Since the mechanism of W-based catalytic oxidative cleavage of olefins (Scheme 2.6) includes formation of epoxides and hydroxylated intermediates, performing the reaction in one step and minimization of by-products are very important. Oakley *et al.* reported using tungsten oxide (in hydrated form is tungstic acid, H_2WO_4) as catalyst for the oxidative cleavage of oleic acid, methyl oleate and methyl erucate (Table 2.5, entries 9, 10 and 11) [61]. The catalytic system includes using Co(acac)$_3$, and N-hydroxyphthalimide (NHPI) in O_2 and H_2O_2 as oxidant in order to over-oxidize the intermediates diols into carboxylic acids. This system provides one-pot reaction and use of a limited amount of H_2O_2, but the production yields are very low (see Table 2.5).

Many efforts have been done to eliminate the secondary oxidants in the oxidative cleavage of olefins during the last decades. For this purpose, tungsten-containing catalysts are ideal, because they have a unique ability in combination with hydrogen peroxide that makes elimination of the secondary oxidants possible. That is the main reason for the much more frequent applications of tungsten as catalyst in the oxidation of UFAs in recent years. Moreover, W is cheaper and less toxic compared to Ru and Os.

Recently, catalytic systems that involve W-based POM have been significantly investigated. Such systems mainly include a phase transfer agent (PTA) (usually a quaternary ammonium salt) to increase the solubility of substrates in the biphasic reaction, often tungstophosphoric acid (TPA, $H_3PW_{12}O_{40}$) as the W precursor and hydrogen peroxide solution. The *in situ* protocol upon the addition of H_2O_2 leads to the formation of peroxo-tungsten complex $Q_3\{PO_4[WO(O_2)_2]_4\}$, where Q is the cationic part of the quaternary ammonium salt. Several salts have been used for this purpose such as cetylpyridinium chloride (CPC), methyltrioctylammonium chloride (Aliquat® 336), tetrabutylammonium chloride and tetraoctylammonium chloride. The most common one is CPC which causes the complex peroxo-tris (cetylpyridinium)12-tungstophosphate (PCWP) to be formed with the chemical formula $\{C_5H_5N\text{-}C_{16}H_{33}\}_3\{PO_4[WO(O_2)_2]_4\}$).

Turnwald *et al.* reported one step solvent-free oxidative cleavage of oleic acid to produce azelaic and pelargonic acids using PCWP (Table 2.5, entry 12) [3]. After 5 h reaction at 90 ºC, the yield of azelaic acid was 57%. Increasing the reaction time to 10 h led to higher yield (64%), but the catalyst was decomposed. The substitution of counter-ion cetylpyridinium with Cs^+ (the complex tris (caesium) tungstophosphate), increased the thermal stability of the complex, but the obtained yield was lower even in longer time (28%) (Table 2.5, entry 13).

With the same catalytic system and only altering the amounts of initial reactants, Pai *et al.* reported a higher yield (86% for azelaic acid) in even shorter time (4 h) and lower temperature (80 ºC) (Table 2.5, entry 14) [62]. Changing the phase transfer agent, Khlebnikova *et al.* employed another catalytic peroxo-tungsten complex system to perform the oxidative cleavage on methyl esters of fatty acids (Table 2.5, entries 15 and 16) [63]. Using Aliquat® 336 instead of CPC, they succeeded to synthesize the complex methyltrioctylammonium tetra (diperoxotungsto) phosphate. In comparison with entry 14, it is interesting to say that at the same reaction time and, almost, temperature, the obtained yields were also the same, however the catalyst loadings used for the oxidation of fatty acids (entry 14) are higher than those used for the oxidation of their corresponding methyl esters (entry 15).

Antonelli *et al.* tried to apply the same complex system as entry 15 and 16 for the oxidative cleavage of oleic acid into pelargonic acid and azelaic acid (Table 2.5, entry 17) [64]. Performing the reaction at 80 ºC for 5 h resulted in the production of azelaic acid with the 79% yield which is slightly lower than what was obtained using CPC (entry 14).

In order to obtain a more precise comparison between the performances of different phase transfer agents in the oxidation of UFAs, Godard *et al.* employed four PTA including CPC, Aliquat® 336, tetra butyl and tetra octyl ammonium chloride in a same oxidative cleavage of oleic acid (Table 2.5, entry 18) [2]. CPC and subsequent catalytic complex system PCWP were found to give the best results and further optimizations of the reaction conditions led to the production of azelaic and pelargonic acid with 81 and 86% yields, respectively, in organic solvent-free system and in 5 h at 85 ºC.

A new type of phase transfer agent is introduced in the work that was done by Haimov *et al.* (Table 2.5, entry 19) [65]. The alkylated form of polyethyleneimine (Alk-PEI) was used in the production of aldehydes from methyl oleate. The system showed high selectivity for nonanal (97% yield) with the reaction temperature of 70 ºC and relatively long reaction time (24 h) in the absence of organic solvent.

The majority of homogeneous catalytic systems reported here have conversions of more than 90%. Nevertheless, their applications in industry are restricted as a result of problems such as lack of recycling ability, metal contamination, poor control of selectivity, and disposal of potentially toxic wastes. Since employing insoluble heterogeneous catalytic systems is an efficient strategy in order to achieve the isolation and separation of catalysts, developing solid catalysts would be favorable to solve these problems.

2.3.3 Heterogeneous catalysts

Employing solid catalysts in liquid phase reactions has been always proposed as a promising way in large-scale production of chemicals. The most important feature of heterogeneous catalysts is their recycling ability, owing to the ease of recovery, which makes them able to be commercialized. In spite of many positive aspects, application of heterogeneous catalysts in oils and fats reactions has been restricted, mainly because of poor reactant/catalyst contact which, in turn, arises from pore diffusion limitations or low active site availability. This would be a main reason that heterogeneous catalytic systems for the oxidative cleavage of UFAs have been remarkably less documented. The results of these systems are summarized in Table 2.6.

Noureddini *et al.* investigated the liquid-phase catalytic oxidation of oleic acid with hydrogen peroxide in the presence of different metals or metal oxides, supported and unsupported (Table 2.6, entries 1 and 2) [48]. They reported the production of azelaic and pelargonic acids as the major products and some by-products mainly including C_5-C_8 carboxylic acids. Using metals including tungsten, tantalum, molybdenum, zirconium and niobium in the form of a wire, and tungsten oxide and tantalum oxide as catalyst showed that transition metals in their pure form could not be efficient catalysts, in particular for large-scale applications. It is believed that the metal oxide is responsible for catalyzing the oxidation of UFAs. Therefore, in the case of using pure metals, firstly they have to be oxidized to metal oxides and then, catalyze the reaction. This multi-step process reaction requires larger amounts of oxidant. Supported tungsten oxide showed the highest conversion at reaction temperature of 130 ºC. About 79% of the initial oleic acid was converted after 1 h, 96% in 2 h and 98% after 3 h and longer. One interesting point mentioned in this work is that during the reaction, the concentrations of the main products, azelaic and pelargonic acid, showed an increasing trend until reaching a maximum and then started to decrease. This arises from the degradation of azelaic and pelargonic acids in the prolonged heating process. The time at which maximal concentration of desired product was obtained depended on the type of catalyst used. For supported tungsten oxide, maximal azelaic acid concentration was reached in 1 h or less. Therefore, optimization of the reaction residence time to obtain the highest yield (and acceptable conversion) seems critical, in particular for scale up of the reaction. Another interesting point in this work is the effect of the support. Initially higher pore diffusion resistance of the porous support led to a lower catalytic activity of supported tungsten oxide in comparison with the unsupported form, only in the early stages of the reaction. After about 20 min, however, a significant increase in catalytic activity of the supported catalyst was obtained while the activity of the unsupported catalyst stayed constant throughout the whole 1 h of the reaction. The selectivity of azelaic and pelargonic acids in the case of the supported catalyst (32 and 36%, respectively) were slightly higher compared to unsupported catalyst (30 and 29%, respectively). Finally, it is clear that the conversions, in both cases of supported and unsupported catalysts, are not as high as what was obtained in homogeneous catalytic oxidation of oleic acid.

Porous solids have been widely employed in a variety of reactions to improve the performance of heterogeneous catalytic systems. In a classification presented by IUPAC[‡], there are three types of porous solids: (i) microporous materials (e.g., zeolites) with pore diameter less than 2 nm, (ii) mesoporous materials with pore diameter between 2 and 50 nm and (iii) macroporous materials with the pore diameter larger than 50 nm [70]. Microporous zeolites, which generally have very high surface area and crystalline structure with uniform micropore size, are widely used as heterogeneous catalysts in the refining and petrochemical industry. However, these materials are not useful for the oils and fats reactions because of the relatively large molecular size of oleochemicals. For example, employing zeolites (pore size less than 1.5 nm [71]) as catalysts in oxidative cleavage of oleic acid (molecular size about 2 nm [72]) does not seem favorable due to the lower dimensionality of the interaction between the components and the catalyst surface. On the other hand, catalytic activity of macroporous materials is poor as the result of their relatively low surface area. Efforts to increase the pore size of catalytic materials while maintaining high surface area led to the discovery of mesoporous materials in 1992 by Mobil Research and Development Corporation [73]. This type of porous materials has shown potential applications as either catalyst or support for liquid-phase reactions of oils and fats [37]. A comprehensive review on the catalytic applications of mesostructured materials has been presented in our previous work [74].

Using mesoporous molecular sieves (Cr-MCM-41, Mn-MCM-41, Co-MCM-41) and microporous zeolites (Cr-APO-5, Co-MFI, Mn-MFI) as supports, Dapurkar *et al.* employed chromium, manganese and cobalt as active sites to oxidize oleic acid into azelaic and pelargonic acids in supercritical carbon dioxide ($scCO_2$) media with molecular oxygen (Table 2.6, entry 3) [75]. The reaction was performed at 80 ºC for 8 h. Mesoporous MCM-41 containing chromium converted more than 95% of initial oleic acid with almost the same products yields (32.4% for azelaic acid, and 32.2% for pelargonic acid) as the previous work. Their results confirm the advantages of mesoporous catalysts in comparison with microporous catalysts in the reactions of fats and oils. However, the disadvantage of this catalytic system is an insufficient selectivity for azelaic and pelargonic acids, due to the production of C_6–C_{10} di- and monocarboxylic acids as by-product.

While reusability of heterogeneous catalysts would make them cost effective for large-scale applications, their lower conversion, yield or selectivity in the oxidative cleavage of UFAs compared to homogeneous ones is a big obstacle to commercialization. Tackling this obstacle requires some improvements in the structure of solid catalysts. An advanced heterogeneous catalytic system should be developed that includes the advantages of homogeneous catalysts on one hand, and the recycling ability on the other hand. NP-based catalysts seem to be most suitable for this purpose, since it has been shown that they can act like a homogeneous catalyst in the reaction medium insofar as sometimes discriminating NPs and homogenous catalysts requires different techniques such as NMR, DFT, electron microscopy imaging, dynamic light scattering (DLS), X-ray photoelectron microscopy (XPS), magnetometry, and multiphasic analysis [76]. Hopefully, it can be said that homogenization of heterogeneous catalyst in order to combine the best properties of both homogeneous and heterogeneous catalysts would be possible by employing NP-based catalysts.

2.3.4 Nanoparticle-based catalysts

Owing to the natural high surface-to-volume ratio and quantum size effects, NPs demonstrate unique properties which make them prominent compared to larger particles or bulk materials for catalytic applications [77-85]. This can be confirmed by the fact that NP-based catalysts have, generally, exhibited higher catalytic activity compared to conventional catalysts in different types of reactions. For example, Carrettin *et al.* showed that nanocrystalline CeO_2-supported Au catalysts are 2 orders of magnitude more active than conventional Au/CeO_2 catalysts for the CO oxidation [86]. In spite of this, curiously only few research works have employed NPs as catalyst in the oxidative cleavage of UFAs (Table 2.7). Ho *et al.* reported using ruthenium NPs supported on hydroxyapatite in the oxidative cleavage of alkenes and unsaturated fatty compounds with sodium periodate as oxidant (Table 2.7, entry 1) [87]. Their results showed that applying this catalytic system for UFAs, however, is not favorable. While full conversion was obtained for alkenes oxidation in the reaction time of 2-7 h, only 16% of methyl oleate was converted to aldehyde with this system even after 12 h, albeit at good yields (84% for nonanal and 79% for methyl 9-oxononanoate).

Recently, vicinal dihydroxy derivatives of oleic acid, methyl oleate, and erucic acid were converted by oxidative cleavage to the respective di- and monocarboxylic acids in the presence of supported gold catalyst and molecular oxygen as oxidant by Kulik *et al.* (Table 2.7, entry 2) [1]. Deposition of Au NPs on different supports (Al_2O_3, CeO_2, TiO_2, and ZrO_2) was investigated. The obtained results showed that the highest catalytic activity belonged to Au/Al_2O_3 catalyst with highly dispersed gold particles which could convert more than 80% of 9,10-dihydroxystearic acid in 260 min at 80 ^oC yielding 86% azelaic acid and 99% pelargonic. The main drawback of this system is the significant decrease in the catalytic activity after the catalyst recovery. After two recycling experiments using the Au/Al_2O_3 catalyst, considerable decrements were observed in the catalyst activity; conversion decreased from 94% to 77%, and production yields of azelaic and pelargonic acids decreased by 30%, approximately. Since Au is an expensive metal, this weak recovery potential prevents commercializing of the gold-based heterogeneous catalytic systems.

Table 2.6. Different heterogeneous catalytic systems reported for the oxidative cleavage of UFAs and their derivatives.

Metal	Entry	Reactants	Main products	Catalyst/oxidant system	Reaction conditions [1]	System's efficiency [2, 3]	Reference
W	1	Oleic acid	Azelaic acid Pelargonic acid	Tungsten oxide supported on silica/ H_2O_2	1 h, 130 ºC	Conversion: 79% Selectivity (AA): 32% Selectivity (PA): 36%	[48]
	2	Oleic acid	Azelaic acid Pelargonic acid	Tungsten oxide (unsupported)/ H_2O_2	1 h, 130 ºC	Conversion: 56% Selectivity (AA): 30% Selectivity (PA): 29%	[48]
Cr	3	Oleic acid	Azelaic acid Pelargonic acid	Chromium supported on MCM-41/ O_2	8 h, 80 ºC	Conversion > 95% Yield (AA): 32.4% Yield (PA): 32.2%	[75]

1. RT: room temperature
2. The best result of each work is presented in the table.
3. AA: azelaic acid and PA: pelargonic acid.

Table 2.7. Different semiheterogeneous (nanoparticle-based) catalytic systems reported for the oxidative cleavage of UFAs and their derivatives.

1. RT: room temperature

Metal	Entry	Reactants	Main products	Catalyst/oxidant system	Reaction conditions [1]	System's efficiency [2, 3]	Reference
Ru	1	Methyl oleate	Nonanal methyl 9-oxononanoate	Ruthenium nanoparticles supported on hydroxyapatite/ $NaIO_4$	12 h, RT	Conversion: 16% Yield (NL): 84% Yield (M9-ON): 79%	[87]
Au	2	9,10-dihydroxystearic acid	Azelaic acid Pelargonic acid	Gold nanoparticles supported on alumina/ O_2	4.33 h, 80 ºC	Conversion > 80% Yield (AA): 86% Yield (PA): 99%	[1]

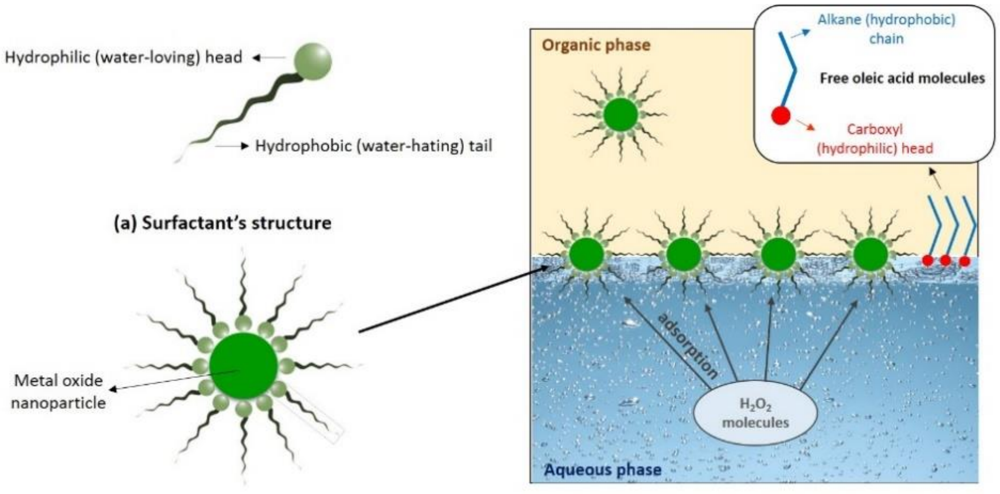
2. The best result of each work is presented in the table.
3. NL: nonanal, M9-ON: methyl 9-oxononanoate, AA: azelaic acid, and PA: pelargonic acid.

Exploiting the interesting and unique properties of NP-based catalysts in the oxidative cleavage of UFAs has sparsely investigated in the literature. The two mentioned papers above, which are the only works done in this field to our knowledge, seem curiously insufficient. On the other hand, thanks to the explosive development of nanomaterials science, new breakthroughs in nanocatalysis are appearing at a fast rate, which have been reviewed in our recent feature article [88]. Further works, therefore, seem to be required to push the use of NP-based catalysts to the oxidative cleavage of UFAs. For this purpose, the interesting features of NPs which would enhance their efficiency in the oxidative cleavage of UFAs will be discussed in the following section.

2.3.4.1 Performance enhancement of NP-based catalysts in oxidative cleavage of UFAs

One strategy to increase the catalytic performance of NPs in some reaction media is capping their surfaces with a surfactant. This increase, however, depends on several parameters such as surface properties of NPs, the type and amount of surfactant, and the involving phases in the reaction and their miscibility. Using surfactant, not only size and shape of NPs can be controlled during the synthesis [89] but this could also result in a better dispersion of NPs in the liquid medium of oils and fats reactions due to the fact that surfactants can oppose van der Waals forces. In this way, the aggregation of particles will be prevented and, consequently, catalytic activity of the catalyst will not decrease during the reaction [90]. The role of surfactant becomes more crucial, if we consider a typical oxidative cleavage reaction of UFAs which uses hydrogen peroxide as the most common benign oxidant. Presence of aqueous H_2O_2, on one hand and organic reactants, on the other hand provides a biphasic reaction with immiscible phases. In this circumstance, the presence of a well-chosen surfactant on the surface of NPs can increase their dispersion.

To illustrate the role of surfactant better, Scheme 2.8 shows the performance of surfactant-capped nanoparticles (SCNPs) as catalyst in the oxidative cleavage of oleic acid, as an example for UFAs, with hydrogen peroxide. The surfactant capped on the surface of metal oxide NPs can be oleylamine, oleic acid or other similar chemicals. Having both hydrophilic head and hydrophobic chain, surfactants reinforce the stability of emulsion in the biphasic reaction which consists of aqueous phase and organic phase. It should be noted that free molecules of the reactant, oleic acid, also would contribute to the emulsion stability, because they can be laid at the interface due to their hydrophilic and hydrophobic parts. Since the reaction takes place mostly at the interface, high concentration of the catalyst particles at the interface is preferred which would be possible by using SCNPs. This arises from two counter effects; while hydrophilic surface of transition metals oxides immerses them into the aqueous phase, hydrophobic chain of surfactant drags SCNPs toward the organic phase. The presence of SCNPs at the interface will make adsorption of H_2O_2 molecules from aqueous phase easier. Consequently, a kind of peroxo-metal complex will be formed at the surface of NPs. On the other hand, the hydrophobic chain of the surfactant attracts the oleic acid molecules, as the main reactant, from organic phase, and then the reaction will occur on the surface of SCNPs. The peroxo-metal complex, as discussed in homogeneous catalysts, is believed to be able to efficiently oxidize the olefins. Due to the presence of SCNPs at the interface, as soon as consumption of molecules of H_2O_2 and formation of a peroxo species on the NPs surface, another molecule of hydrogen peroxide will be adsorbed on the surface and this process will be continuously repeated. In fact, the role of phase transfer agent (PTA) in the homogenous systems, to which the high reaction efficiency was attributed, can be played by the surfactant in heterogeneous systems.



(b) Surfactant-capped nanoparticle: molecules of surfactant attach to the surface of metal oxide nanoparticles from hydrophilic head.

(c) Performance in the reaction (under high stirring): H_2O_2 molecules are adsorbed on the surface of nanoparticles which are accumulated at the interface.

Scheme 2.8. Schematic illustration for SCNPs as efficient nanocatalyst. (a) Surfactant molecule, (b) hydrophobic SCNPs surface and (c) Performance in the biphasic oxidative cleavage of oleic acid using H2O2 as oxidant. Presence of surfactant (i) contribute to the stability of emulsion, (ii) prevents aggregation of the NPs, and (iii) make the recovery of catalysts easier [91].

Capping the NPs of an active metal oxide with an appropriate surfactant, a catalytic system may be developed that has the best properties of both homogeneous and heterogeneous systems. Moreover, considering the significant effects of SCNPs, it is highly likely that the reaction solvent can be eliminated, like what happened in the case of using homogeneous catalysts. Even, a decrease in the amount of solvent would be a great milestone in the oxidative cleavage reactions of UFAs, which will result in fewer by-products, easier separation of the products and lower operating cost.

The presence of a surfactant on the surface of metal oxide NPs provides another substantial advantage in terms of economic aspects. SCNPs can be easily separated from the mixture after the reaction and reused via the method which was developed in our previous work [89]. Based on the hydrophobic or hydrophilic properties of the surface of NPs, changing the solvent from nonpolar, e.g. toluene, to polar, e.g. ethanol or vice versa will results in the precipitation of the SCNPs. This method is shown in Figure 2.14. ZrO_2, TiO_2, Au and Cu particles capped by oleic acid are highly dispersed in toluene and make a clear solution (Figure 5a), while they will be precipitated in ethanol (Figure 2.14 b).

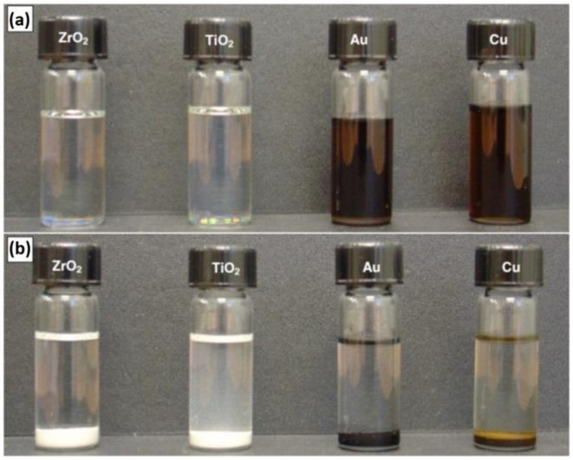


Figure 2.14. (a) Oleic acid-capped NPs of some metals/metal oxides dispersed in toluene (clear/transparent solutions) and (b) those NPs precipitated with excess ethanol [89].

Other approaches to address the recyclability of NP-based catalysts, as the main bottleneck for their industrial application, are currently undergoing rapid development. The efforts done in this field have been well documented in several review papers [92-98]. A facile, highly efficient, economical and environmentally benign method that attracted lots of attention is magnetic separation. The main issue, however, is that magnetic separation is only applicable to the materials which have intrinsically magnetic parts. Nevertheless, the high efficiency of magnetic separation compared to filtration and centrifugation [99-101] has led to developing different strategies for the preparation of either magnetic nanocatalysts or non-magnetic catalysts immobilized onto magnetic nanomaterials, which have been separately investigated in the recent review papers of Hudson et al. [102] and Rossi *et al.* [103], respectively. A thorough review of the applications of magnetically recyclable nanocatalysts has been presented in the recent and precious review paper of Wang and Astruc [104]. Given the wide range of reactions such as oxidation of alcohols, epoxidation of alkenes, hydrogenation of unsaturated compounds, C-C coupling, reduction of nitroaromatics, arylation and alkylation, extension of the scope of magnetically recyclable nanocatalysts for oxidative cleavage of UFAs seems to be of great interest.

2.4 Heterogeneous tungsten-based polyoxometalate catalysts

2.4.1 Tungsten: a fascinating metal for catalysis

At the end of 18th century and dawn of tungsten chemistry, when the charming yellow color of tungsten oxide fascinated the chemists to propose its use as 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” [105], probably they did not think that this pretty color material would find wide applications 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 indispensable to our lives. Besides its application in hydrogen reduction to manufacture elemental tungsten for industries such as electronic and electrical, alloy and steel, jewellery, biology, sport and leisure equipment, etc., tungsten oxide is used for many purposes in everyday life such as production of smart windows, fireproofing fabrics, gas sensors, semiconductors and efficient catalysts and photocatalysts [106].

The major modern days use of tungsten oxides is nevertheless in the area of catalysis. Oil industry is the most striking consumer of tungsten catalysts for treating of crude oils since the 1930’s [107]. Basic reactions such as hydrotreating (hydrodesulphurization, hydrodenitrogenation, and hydrodearomatisation), de-NO_x, and reforming are of the most important reactions catalyzed by tungsten compounds in chemical industry [108,109]. 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 less price and toxic properties compared to its alternatives from second and third rows of transition metals for organic reactions (chiefly osmium and ruthenium) [45]. Second, tungsten oxides and sulfides exhibit very strong Brönsted acid sites, to which catalytic activities of transition metals in many reactions are attributed [110-112], either as a bulk oxide or when supported [113-118]. Compared to other metal oxides, tungsten oxide has shown relatively low point of zero charges (PZCs) in the literature [119], 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. Numerous oxidation states of tungsten from -2 to +6 [120,121] have led to several tungsten oxides WO_x (x mainly between 2-3) including WO_3 (yellowish), $WO_{2.9}$ or $W_{20}O_{58}$ (bluish), $WO_{2.72}$ or $W_{18}O_{49}$ (violet), and WO_2 (brownish), as can be seen in Figure 2.15 [105]. The most common state is tungsten trioxide, which in turn, includes hydrated ($WO_3.nH_2O$) and anhydrous (WO_3) form. It has even been shown that the number of water molecules in the structure affects the catalytic activity, particularly in oxidation reactions [122]. Furthermore, WO_3 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.

Applications of the tungsten containing materials in heterogenous catalytic oxidation reactions have been nicely and recently reviewed [123]. However, this review does not cover polyoxotungstates, which are another type of tungsten oxide-based catalysts increasingly attracting interest nowadays. In what follows, we will discuss about this type.

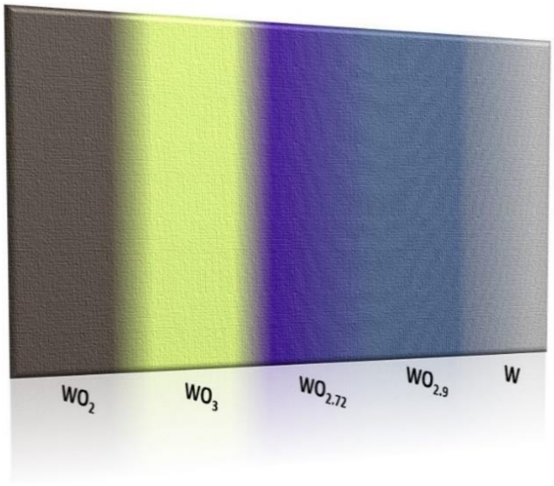


Figure 2.15. Amazingly colorful world of the tungsten oxides: yellow WO3, blue WO2.9, violet WO2.72, brown WO2, and gray W metal [105].

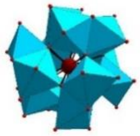
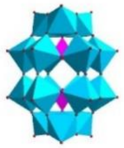
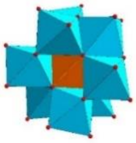
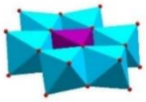
2.4.2 Fundamentals of polyoxometalate catalysis

Polyoxometalates or their more descriptive synonym heteropoly oxoanions are polymeric oxoanions formed by condensation of more than two different oxoanions, which can give hetero poly acids. In contrast, isopolyanions are composed of one kind of oxoanions, which their acid forms are called isopoly acids. In fact, although the words POM and HPA (heteropoly acid) 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, majority of the literature cites Berzelius, who reported the preparation of ammonium 12-molybdophosphate in 1826, as the pioneer of heteropoly compounds 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. [124,125]), and hence would be redundant here. Over the years, with the better understanding of POMs chemistry, various structures were discovered, which are summarized in Table 2.8. Further information on details of POMs structures are available in numerous papers and books (e.g. [126,127,124,128]).

Although some POMs with Dawson, Anderson, Allman-Waugh, and, less known, Preyssler structures have been also examined as catalyst, most of the heteropoly oxometallate catalysts are of Keggin structure, which has been reported for the first time in 1934 by Keggin [129], most likely because of higher thermal stability and ease of synthesis of this structure compared to others [130]. The Keggin cluster of POMs has the general formula $H_nXM_{12}O_{40}$, 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), and M is the addenda atom (mainly W, Mo, and V).

Table 2.8. Different structures of polyoxometalates.

Name	General formula [1]	X (typical examples)	Structure
Keggin	$XM_{12}O_{40}^{n-}$	P^{5+}, As^{5+}, Si^{4+}, Ge^{4+}	
Dexter-Silverton	$XM_{12}O_{42}^{n-}$	Ce^{4+}, Th^{4+}	
Dawson	$X_2M_{18}O_{62}^{n-}$	P^{5+}, As^{5+}	
Allman-Waugh	$XM_9O_{32}^{n-}$	Mn^{4+}, Ni^{4+}	
Anderson (type A)	$XM_6O_{24}^{n-}$	Te^{6+}, I^{7+}	

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

Heteropoly compounds are progressively attracting interest in catalysis science particularly in the last decade. Widely tunable physical and chemical properties of POMs at molecular level have been the subject of extensive research in recent years giving them promise for applications in various fields such as medicine, material science, photochromism, electrochemistry, magnetism as well as catalysis. Their strong acidity has tempted the researchers to examine their efficiency in the 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 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 [131].

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 molecular or atomic level by removing one or more constituent transition metal atoms giving the parent POM a defected structure, so-called lacunary structure, and then, incorporation of 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 [132]) have been reported up to now in two forms of heterogeneous solid catalysts and homogeneous solution catalysts, which have been widely reviewed for general [133,125,134-136] or specific [137-140] 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) [127,128].

2.4.3 Polyoxotungstates

Among all the mentioned transition metals, a great deal of attention has been paid to tungsten, since its heteropoly compounds have shown considerable superiorities, especially in heterogeneous form in terms of acidity, thermal stability, and hydrophobicity, in comparison with the other metals [126,131] [130]. 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. Equation 2.2 indicates the formation of phosphotungstate, the most common POM, from tungstate and phosphate under controlled temperature and pH:

$$12WO_4^{2-} + HPO_4^{2-} + 23H^+ \rightarrow (PW_{12}O_{40})^{3-} + 12H_2O \qquad (2.2)$$

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 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 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 [141-143]. Moreover, compared to the other solid acids, heterogenous HPTAs have shown excellent water-tolerant properties [131], which hold a promise for their application in the 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, relatively low thermal stability of HTPAs leading to difficult catalyst regeneration process, which had influenced their application to some extent, has been overcame by offering some approaches such as developing novel HTPAs enjoying 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 [144].

So far, solidification of HPTAs have 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. 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). In what follows, we have tried to review all of the recent works on heterogeneous POM-based catalysts made of W as central atom. Herein, different solid POT catalysts are classified based on the heterogenization strategy, which will be investigated in sections 2.4.3.1-6, along with their applications in liquid phase organic reactions. The target reactions, although include a variety of liquid organic reactions, can be conveniently categorized into two general groups, acid catalysis and oxidation reactions. In order to enable a better comparison and outlook, the reported works in the literature have been tabulated in the following sections (Tables 2.9-2.16).

2.4.3.1 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 synthesis of microporous POT catalysts using salts of heteropoly compounds with different monovalent cations [145]. To date, cations such as Cs^+, Na^+, K^+, NH_4^+, Ag^+, Sn^{2+}, Zn^{2+}, Bi^{3+}, Mn^{2+}, Co^{2+}, and Cu^{2+} have successfully substituted protons of the homogeneous POTs to heterogenize them. They are listed in Tables 2.9, 2.10, and 2.11. 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 2.9). Tables 2.10 and 2.11 list the works in this field, including applications in acid catalysis and oxidation reactions, respectively.

Extensive researches have focused particularly on caesium cation, most likely because of its unique effects not only on the solubility but also on surface area, pore structure and surface acidity of the resultant POT [131]. 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 [131,146-148]; water soluble PTA was converted to a water-tolerant acid catalyst ($Cs_xH_{3-x}PW_{12}O_{40}$), the hydrophobicity of which is even higher than silica-alumina and some zeolites [131] and, interestingly, its catalytic features could be well tuned via varying the amount of Cs^+ cations. Changing the pore structure from ultramicropores (pore width 0.43 to 0.50 nm) in $Cs_{2.1}H_{0.9}PW_{12}O_{40}$ to mespopores in $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ enables shape-selective catalysis properties. More importantly, upon incorporation of Cs^+ in PTA, the surface area slightly decreased from 6 m^2/g at x=0 to 1 m^2/g at x=2, but further increasing the Cs^+ content to x=3 surprisingly increased the surface area to 156 m^2/g [147]. Figure 2.16 shows the surface area as well as surface concentration of acid sites of $Cs_xH_{3-x}PW_{12}O_{40}$ as a function of Cs^+ content [131,148].

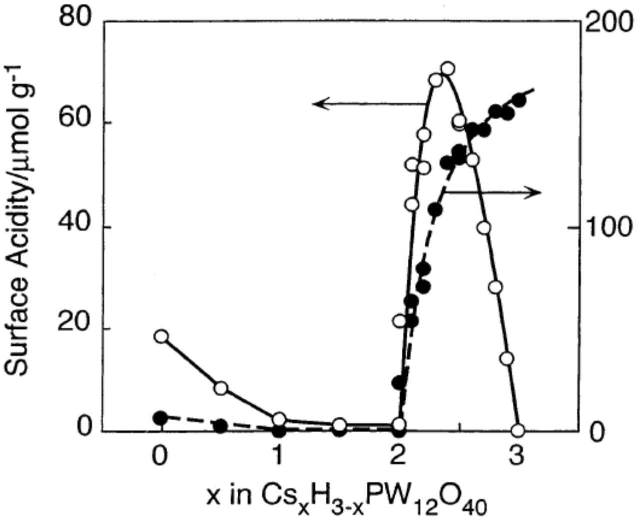


Figure 2.16. Surface area and acidity of CsxH3-xPW12O40 as a function of Cs+ content [131,148].

As Figure 2.16 shows, the surface acidity (number of protons on the surface), which was determined by IR spectroscopic 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 $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (abbreviated as Cs2.5), measured by microcalorimetry of NH_3 adsorption and TPD of NH_3, compared to the common solid acid catalysts (e.g. H-ZSM-5 and SiO_2-Al_2O_3) [149,147] have 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 2.10). Cs3, in spite of its weaker acidity compared to the more known Cs2.5, has been also investigated as support for Ru nanoparticles in conversion of cellobiose and cellulose into sorbitol in aqueous medium [150].

Silicotungstic acid is another POT that has been heterogenized by substitution of Cs^+ cations [151-153]. For example, Pesaresi et al. have reported the synthesis of $Cs_xH_{4-x}SiW_{12}O_{40}$ and its application for C_4 and C_8 triglyceride transesterification and palmitic acid esterification with methanol [153]. 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.

Table 2.9. Inorganic cations substituted POTs for general catalytic purposes.

Entry	Counter-cation	IC-substituted POT [1]	Remarks	Ref.
1	Cs^+	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	- Meso- and microporous structure of the POT have been examined. - Presence of very strong acidic sites on the POT has been indicated.	[147]
2		$Cs_3PW_{12}O_{40}$	- Self-organization of the POT nanocrystallites has been successfully controlled by the changes in the synthetic temperatures and countercations (Cs^+, Ag^+, and NH_4^+). - Formation and growth mechanism of the POT particles have been investigated.	[154]
3	NH_4^+	$(NH_4)_3PW_{12}O_{40}$	- "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 has afforded nanospaces in the crystals. - Changing the synthesis temperature, the POTs with high surface areas, ranging from 65 to 116 m2/g, have been prepared.	[155,156]
4		$(NH_4)_3PW_{12}O_{40}$	- Self-organization of the POT nanocrystallites has been successfully controlled by the changes in the synthetic temperature and countercation (Cs^+, Ag^+, and NH_4^+). - Formation and growth mechanism of the POT particles have been investigated.	[154]
5	Ag^+	$Ag_3PW_{12}O_{40}$	- Self-organization of the POT nanocrystallites has been successfully controlled by the changes in the synthetic temperature and countercation (Cs^+, Ag^+, and NH_4^+). - Formation and growth mechanism of the POT particles have been investigated.	[154]

1. IC: inorganic cation

Table 2.10. Inorganic cations substituted POTs for acid catalysis reactions.

Entry	Counter-cation	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 solid superacid in liquid organic reaction.	[148]
2		$Cs_xH_{4-x}SiW_{12}O_{40}$	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 Cs^+ content has been investigated.	[153]
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.	[157]
4		$Cs_xH_{3-x}PW_{12}O_{40}$ (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.	[158]
5		$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	cycloaddition of crotonaldehyde to monoterpenic alkenes	- - Catalytic activity of the POT has been compared with silica-supported HTPA ($H_3PW_{12}O_{40}$).	[159]
6		$Cs_3PW_{12}O_{40}$	Conversions of cellobiose and cellulose into sorbitol in water	- Ru nanoparticles have been supported on the POT, which despite of not having strong acidity, was efficient catalyst.	[150]
7		$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	Glycerol acetalization with formaldehyde	- 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.	[160]
8		$Cs_2HPW_{12}O_{40}$ $Cs_3HSiW_{12}O_{40}$	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.	[151]
9		$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	Synthesis of xanthenedione derivatives from aldehydes	- CS2.5 has been employed for the first time for 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.	[161]
10		$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	Thioacetalization and transthioacetalization reactions	- The POT was an effective catalyst with high selectivity.	[162]
11		$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ $Cs_{3.5}H_{0.5}SiW_{12}O_{40}$	Production of methyl *tert*-butyl ether (MTBE) from methanol and *tert*-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.	[152]
12	Ag^+	$Ag_xH_{4-x}SiW_{12}O_{40}$ x= 0, 1, 2, 3, and 4	Transformation of alkynyloxiranes to furan	- Ag content to reach good catalytic efficiency was optimized.	[163]

13		$Ag_3PW_{12}O_{40}$	Conversion of fructose and glucose into 5-hydroxymethylfurfural	- The POT was tolerant to high concentration feedstock, and showed environmentally benign properties with double acidity.	[164]
14		$Ag_3PW_{12}O_{40}$	Intermolecular hydroamination of olefins	- Compared to the parent HPTA, the synthesized POT exhibited lower catalytic efficiency.	[165]
15	Na^+	$H_{14}[NaP_5W_{29}MoO_{110}]$	Different functional groups protective reactions such as tetrahydropyranylation of phenol and alcohols, acetylation of alcohols, phenols, amines and thiols with Ac_2O, 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.	[166]
16		$Na_8H[PW_9O_{34}]$	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.	[167]
17	K^+	$K_{2.2}H_{0.8}PW_{12}O_{40}$	Esterification of 2-keto-L-gulonic acid	- The POT showed good catalytic activity (slightly lower than that of homogeneous HPTA).	[168]
18		$K_xH_{3-x}PW_{12}O_{40}$ (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 x=2.	[169]
19	NH_4^+	$(NH_4)_3PW_{12}O_{40}$	Intermolecular hydroamination of olefins	- Compared to PTA, the POT exhibited lower catalytic efficiency.	[165]
20		$(NH_4)_2HPW_{12}O_{40}$	Thioacetalization and transthioacetalization reactions	- The POT was an effective catalyst with high selectivity.	[162]
21	Sn^{2+}	$Sn_x[H_3PW_{12}O_{40}]$ (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	[170]
22	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.	[171]
23	Bi^{3+}	$BiPW_{12}O_{40}$	Esterification of oleic acid with *n*-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.	[172]

Table 2.11. Inorganic cations substituted POTs for oxidation reactions.

Entry	Counter-cation	IC-substituted POT	Reaction	Remarks	Ref.
1	K^+	$K_6[PW_9V_3O_{40}]$	Ammoximation of different ketones and aldehydes	- The V-substituted POT has been proved to be heterogeneous in isopropanol and recyclable.	[173]
2	Mn2+ Co2+ Cu2+	$\{[M_2(H_2O)_6][Mn_4(H_2O)_{16}][WZn(Mn(H_2O))_2(ZnW_9O_{34})_2]\}\cdot 10H_2O$ (M = Co^{II} and Cu^{II})	Oxidative aromatization of Hantzsch 1,4-dihydropyridines	- The POT-based solid was prepared by using $\{Mn_2Zn_3W_{19}\}$ 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.	[174]

Substitution of some other inorganic cations including Na^+, K^+, NH_4^+, Ag^+, Sn^{2+}, Zn^{2+}, Bi^{3+}, Mn^{2+}, Co^{2+}, and Cu^{2+} into the POTs structures in order to heterogenize them have been also documented, but not as much as cesium (please see Tables 2.10 and 2.11). As these Tables show, this class of solidified POT catalysts are more interesting for acid catalysis reactions compared to oxidation reactions, most probably because of their high and tunable acidity.

2.4.3.2 Organo-solidified POTs

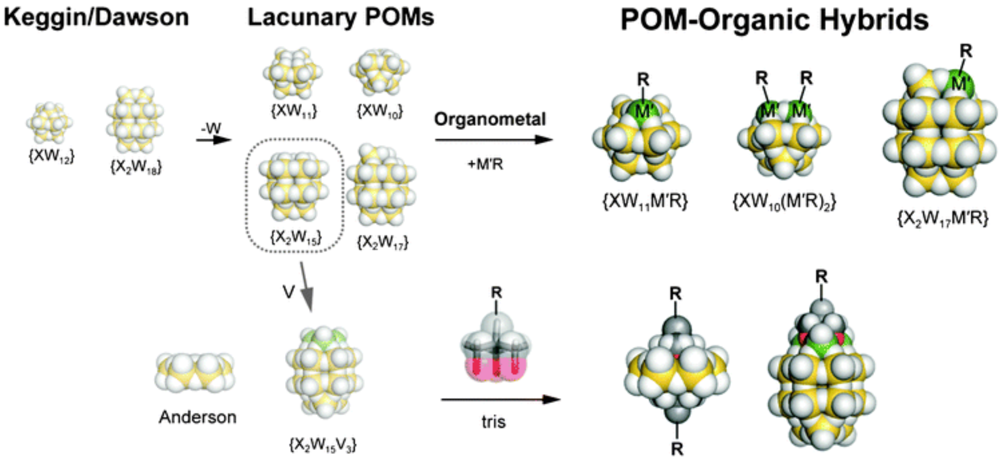
Parallel to the intrinsically interesting properties of POMs, succinctly summarized in section 2.4.2, their potential for functionalization via organic compounds is a tremendous impetus that has pushed working and research on POMs in the last ten years. Such functionalization has been found compulsory 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 [175]. This gives an additional firm rise to push the essentially attractive area of organic-inorganic hybrid materials to be applied in POMs preparation.

In the field of catalysis, employing hybrid organic-inorganic polyoxometallate-based catalysts is currently a hot topic being enthusiastically and rapidly explored, not only for heterogenization purposes, but also for their versatilities 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 POTs structures are increasing catalyst hydrophobicity, and thus, preventing (i) aggregation of catalyst particles, and (ii) poisoning of acid sites by H_2O in water-involving reactions. On the other hand, functionalization and even post-functionalization of POTs with organic moieties are currently performed under either hydrothermal condition benefiting from a simple, often one-pot, procedure or mild synthetic conditions complying with the principles of "Chimie Douce" [176-178]. Given the aforementioned positive features and comparatively huge number of recent publications in this domain, incorporation of organic groups into the structure of POMs has been the sole subject of several recent review papers [177,179-183,175,184-186].

Different techniques developed for design and synthesis of organic-inorganic hybrid POM compounds have been widely investigated. Abridgedly, 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 POTs 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 [187-189], most probably due to its comparatively convenient fabrication, 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 counter cations feasible. As mentioned before, 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 to electrostatically interact with positively charged solutes, resulting in facile incorporation of inorganic and organic cations into the structures of POTs. Organic cations in ionic liquids have attracted a large attention to act as counter-cation pairing with POT anions since 2004 [190,191]. 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) [192,186]. Many works have then been done on the preparation of catalytically active solid POT-organic hybrids out of ionic liquids. Hydrogen bonding in fabrication of POM-organic hybrids based on non-covalent interactions has been also reported, like what was obtained in linking proteins to POMs [193,194], 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 iono-covalent bonds. These hybrids are usually formed either by substitution of an oxo group of the POMs by an organic ligand or approaching electrophilic organic components to 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 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 lacunary structure. Then, organic moieties can be grafted to the organometallic compounds of lacunary POT clusters (Scheme 2.9). Different strategies for the second step have been employed based on functionalization and/or post-functionalization of POTs (Figure 2.17), which have been nicely investigated and compared in a critical review paper presented by Proust et al. [175].



Scheme 2.9. Schematic view of preparation of covalent POT-organic hybrids [186].

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 [179,183,184]; 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 [183], while the other two references addressed heterogeneous catalysis by organic-inorganic hybrids POMs [179,184]. 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 section 2.4.1, and heterogeneous organo-modified POMs, simultaneously, which could be advantageous to be employed in several organic liquid reactions. Tables 2.12 and 2.13 summarize the organo-modified POT catalysts with their applications in acid catalysis and oxidation reactions, respectively.

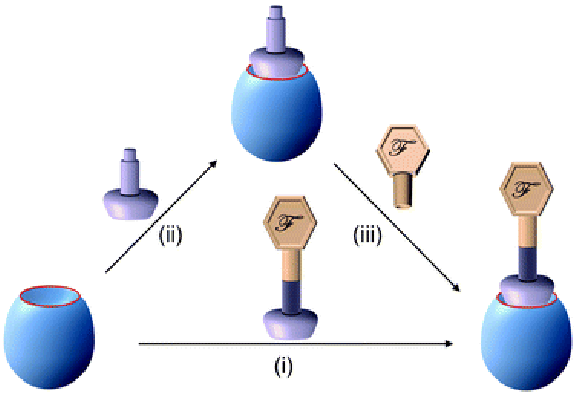
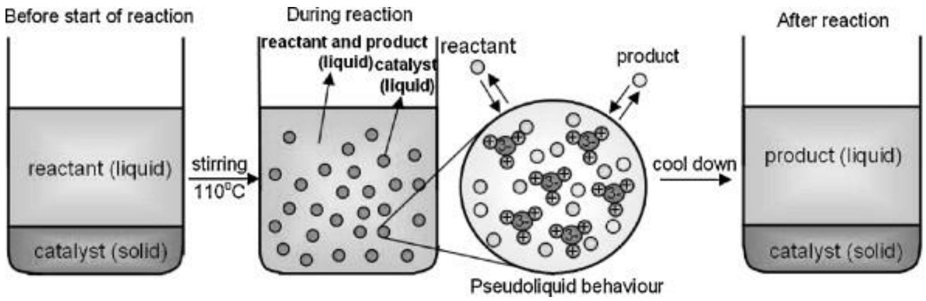


Figure 2.17. Different strategies for preparation of covalent POT- organic hybrids. Path (i): direct functionalization, paths (ii, iii): post-functionalization. The lacunary POM is represented in blue, while the anchoring tether is lilac and the added functional moiety (F) is beige [175].

One of the most common and unique advantages of organo-solidified POTs is their improved compatibilities 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 reaction. Intriguingly, the organic-POT hybrid catalyst is capable to change its heterogeneous behavior during liquid-phase organic reactions; in the beginning of reaction, it is obviously a solid catalyst in the reaction mixture, which would then turn into pseudo-homogeneous system during the reaction, often upon heating. Afterwards, the reaction mixture keeps a pseudo-liquid phase until the end of reaction, when the catalyst starts to precipitate, often upon cooling down to room temperature (Scheme 2.10). 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 $[C_{12}]_3PW_{12}O_{40}$ in the presence of water and an aromatic solvent (Figure 2.18). Combining the advantages of biphasic catalysis and heterogeneous catalysis in such catalytic emulsions made separation of the products easy and prevented catalyst leaching [195]. Mizuno et al. have reported preparation of a size-selective catalyst via organo-modification of the POT silicodecatungstate 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 (Figure 2.19) [196].



Scheme 2.10. Schematic diagram of a typical organic liquid-phase reaction over organic-POT hybrids with self-separation performance.

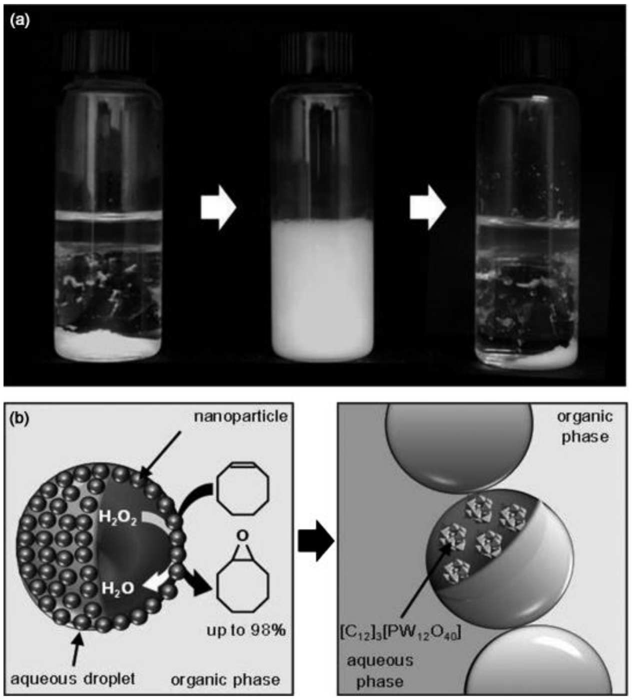


Figure 2.18. a) Macroscopic views of the water/toluene/[C12]3[PW12O40] system before emulsification, during the reaction, and after centrifugation (from left to right). b) Schematic representation of the catalytic epoxidation of olefins inside this emulsion [195].

Table 2.12. 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	[197]
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.	[198]
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.	[199]
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.	[200, 201]
5	Ionic liquid	$[TPSPP]_3PW_{12}O_{40}$	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 ionic intermediates.	[202]
6	Ionic liquid	$[MIM\text{-}PSH]_xH_{3-x}PW_{12}O_{40}$ x: 1 to 3	Esterification of palmitic acid	- Superior catalytic efficiency of the POT arose from better super-acidity and lower molecular transport resistance of catalyst.	[203]
7	Ionic liquid	$[NMP]_3PW_{12}O_{40}$	Prins cyclization of styrene with form alin	- Excellent catalytic performance of the POT was because of 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.	[204]
8	Ionic liquid	$[MIMPS]_3PW_{12}O_{40}$	Beckmann rearrangements of ketoximes	- Using $ZnCl_2$ as cocatalyst, the POT was highly efficient and recoverable.	[205]
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.	[206]

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 homogeneous catalyst during the reaction which upon cooling down at the end of reaction, became solid enabling self-separation performance.	[207]
11	Ionic liquid	$[MIMBS]_3PW_{12}O_{40}$	Conversion of furfuryl alcohol into alkyl levulinates	- The POT was highly efficient and recoverable.	[208]
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.	[209]
13	Ionic liquid	$[PySaIm]_3PW_{12}O_{40}$	Knoevenagel condensation	- The acid–base bifunctional POT provided a controlled nearby position for the acid–base dual sites.	[210]
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 catalytic process, which, after reaction, was broken by addition of a weakly polar organic solvent to facilitate separation of the POT.	[211]
15	Organozirconium complexes	$[(n\text{-}C_4H_9)_4N]_6[\alpha\text{-}PW_{11}Al(OH)O_{39}ZrCp_2]_2$ $[(n\text{-}C_4H_9)_4N]_6[\alpha\text{-}SiW_{11}Al(OH)_2O_{38}ZrCp_2]_2\cdot 2H_2O$ $(Cp = \eta^5\text{-}C_5H_5^-)$	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.	[212]
16	Cationic Al(III)-Schiff base complex (Al(III)–salphen)	$[Al(salphen)(H_2O)_2]_3[\alpha\text{-}PW_{12}O_{40}]\cdot mC_8H_{10}\cdot nCH_3COCH_3$	Pinacol rearrangement	- The organo-modified POT exhibited higher activity than its parent components, arising form synergetic effect of Al(III)-salphen and POT in a porous framework.	[213]

TPSPP: triphenyl(3-sulfopropyl)phosphonium
MIM-PS: zwitterion 3-(1-methylimidazolium-3-yl) propane-1-sulfonate
NMP: *N*-methyl-2-pyrrolidonium
$DPySO_3$: *N,N′*-di(3-sulfopropyl) 4,4′-dipyridinium
MIMBS: methylimidazolebutylsulfate
PySalm: 1-(2-salicylaldimine)pyridinium
Salphen = *N*,*N*‘-phenylenebis(salicylideneimine)

Table 2.13. Organo-solidified POTs for oxidation reactions.

Entry	Organic source	POT-organic hybrid	Reaction	Remarks	Ref.
1	Quaternary ammonium surfactant: tetra-*n*-butylammonium	$[(n\text{-}C_4H_9)_4N]_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$. H_2O	Size-selective oxidation of various organic substrates, including olefins, sulfides, and silanes with H_2O_2	- The nonporous POT has been synthesized via 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.	[196]
2	Quaternary ammonium surfactant: tetra methylammonium Tetra-n-propylammonium tetra-*n*-butylammonium tetra-*n*-pentylammonium	$[(CH_3)_4N]_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$ $[(n\text{-}C_3H_7)_4N]_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$ $[(n\text{-}C_4H_9)_4N]_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$ $[(n\text{-}C_5H_{11})_4N]_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$	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 is important for the design and synthesis of highly active POT.	[214]
3	Quaternary ammonium surfactants with varying alkyl chain length: DDA, TDA, HAD, and ODA	$(DDA)_3PW_{12}O_{40}$ $(TDA)_3PW_{12}O_{40}$ $(HDA)_3PW_{12}O_{40}$ $(ODA)_3PW_{12}O_{40}$	Oxidative desulphurization of dibenzothiophene with H_2O_2	- The mesostructured POT was highly efficient due to 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 products sulfones.	[215]
4	Quaternary ammonium surfactant: CTAB	$[C_{16}H_{33}(CH_3)_3N]_4H_2SiV_2W_{10}O_{40}$	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 $H_2SiV_2W_{10}O_{40}^{4-}$.	[216]
5	Quaternary ammonium surfactants with varying alkyl chain length: DA, DDA, and TDA	$[C_n]_3PW_{12}O_{40}$ n= 10, 12, 14	Epoxidation of olefins with H_2O_2	- The $(DDA)_3PW_{12}O_{40}$ POT formed a Pickering emulsion in the presence of water and an aromatic solvent, which is particularly efficient for the epoxidation of olefins.	[195]
6	Quaternary ammonium surfactants with varying alkyl chain length: DDA, TSA, and DODA	$(DDA)_9LaW_{10}O_{36}$ $(TSA)_9LaW_{10}O_{36}$ $(DODA)_9LaW_{10}O_{36}$	Oxidative desulphurization of dibenzothiophene with H_2O_2	- Alkyl chains on surface of the amphiphilic POT adsorbed weakly polar sulfide by hydrophobic-hydrophobic interactions, where they were oxidized to sulfones by active POT species.	[217]
7	Ionic liquid	$[PSPy]_3PW_{12}O_{40}$	Oxidative desulphurization of dibenzothiophene (DBT), 4,6-dimethyldibenzothiophene (4,6-DMDBT), and benzothiophene (BT) with H_2O_2	- Catalytic oxidation activity of the sulfur-containing compounds occurred in the following order: DBT > 4,6-DMDBT > BT	[218]
8	Ionic liquid	$[BuPyPS]_3PW_{12}O_{40}$ $[PhPyPS]_3PW_{12}O_{40}$ $[BzPyPS]_3PW_{12}O_{40}$	Oxidation of thioethers and thiophenes and desulfurization of model fuels	- 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.	[219]
9	Ionic liquid	$[HDIm]_2[\{W{=}O(O_2)_2\}_2(\mu\text{–}O)]$ $[HHIm]_2[\{W{=}O(O_2)_2\}_2(\mu\text{–}O)]$	Epoxidation of olefins	- Efficient reaction-induced phase-separation POT has been developed in this work. The reaction system	[220]

				switched from tri-phase to emulsion and then to biphase and finally to all the POT self-precipitating at the end of the reaction.	
10	Ionic liquid	PEG chain-functionalized *N*-dodecylimidazolium POT	Epoxidation of olefins with H_2O_2	- The highly efficient POT was also self-separation catalyst.	[221]
11	Ionic liquid	[PEG-300-C_{12}MIM] [$\{W{=}O(O_2)_2\}_2(\mu\text{–}O)$] [PEG-800-$C_{12}$MIM] [$\{W{=}O(O_2)_2\}_2(\mu\text{–}O)$]	Epoxidation of olefins with H_2O_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.	[222]
12	Ionic liquid	MimAM(H)-PW	Epoxidation of alkenes with H_2O_2	- The POT exhibited advantages of convenient recovery, steady reuse, simple preparation, and flexible composition.	[223]
13	Ionic liquid	DPyAM(H)-PW	Oxidation of benzyl alcohol with H_2O_2	- The POT gave high conversion and selectivity in the heterogeneous solvent-free catalytic system.	[224]
14	Ionic liquid	$[Dmim]_{1.5}PW$	Oxidation of alcohols with H_2O_2	- The POT was an efficient solid catalyst with easy recovery, and good reusability.	[225]
15	Ionic liquid	$[C_4mim]_3PW_{12}O_{40}$ $[C_4mim]_4SiW_{12}O_{40}$	Oxidation of sulfides with H_2O_2	- Excellent performance of the POT was attributed to its promoted redox property arising from neighboring functionalized ionic liquid-cations.	[226]
16	Ionic liquid	$[TMGDH]_{2.3}H_{0.7}PW$ $[TMGDH]_3PW$ $[TMGOH]_{2.2}H_{0.8}PW$ $[TMG]_3PW$	Epoxidation of *cis*-cyclooctene with H_2O_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.	[227]
17	Ionic liquid	$[TMGHA]_{2.4}H_{0.6}PW$	Oxidation of benzyl alcohol with H_2O_2	- High activity of the POT was ascribed to its mesoporosity and dual wettability for water and alcohols.	[228]
18	Amine: hexamethylenetetramine	$[C_6H_{13}N_4]_2[HPW_{12}O_{40}]\cdot 2H_2O$	Oxidative desulfurization of sulfur-containing model fuel with H_2O_2	- The Hybrid POT was highly active and recoverable.	[229]
19	Tripodal organic triammonium cation: BTE	BTE-$PW_{11}O_{39}$	Epoxidation of olefins with H_2O_2	- The hybrid POT catalyzed olefins epoxidation efficiently.	[230]
20	Quaternary ammonium surfactant: DA	$DA_{11}[La(PW_{11}O_{39})_2]$	Oxidation of alkenes, alkenols, sulfides, silane and alcohol with H_2O_2	- The catalyst played a dual trapping role for both substrate and oxidant.	[231]
21	C_{12}mim CTA TBA	$[C_{12}mim]_5PTiW_{11}O_{40}$ $[CTA]_5PTiW_{11}O_{40}$ $[TBA]_5PTiW_{11}O_{40}$	Epoxidation of olefins with H_2O_2	- Organic countercations greatly affected catalytic activity.	[232]

22	Tripodal polyammmonium cations	$[WZnZn_2(H_2O)_2][(ZnW_9O_{34})_2]\}^{12-}$	Epoxidation of allylic alcohols and oxidation of secondary alcohols with H_2O_2	- Mesoporosity of the synthesized catalyst enabled oxidation of many organic substrates irrespective of molecular shape, with efficiency similar to corresponding homogeneous catalyst. - The catalyst showed three-dimensional perforated coral-shaped amorphous materials with the organic cations surrounding the POT anions.	[233]
23	Coordination polymers	$[Cu^{II}_2(C_5H_5NCOO)_2(4\text{-}bpo)_2(H_2O)_2]SiW_{12}O_{40}\cdot H_2O$ (1) $[Cu^{I}_4(4\text{-}bpo)_6]SiW_{12}O_{40}\cdot 3H_2O$ (2) $[Cu^{I}_4(3\text{-}bpo)_4]SiW_{12}O_{40}\cdot 3H_2O$ (3)	Epoxidation of styrene with *tert*-butyl hydroperoxide	- Geometry and coordination mode of bpo ligands played important roles in the formation of the hybrid solidified POT.	[234]
24	Coordination polymers	$[\{Cu(en)_2\}_3\{TeW_6O_{24}\}]\cdot 6H_2O$	Epoxidation of cyclohexene and styrene by *tert*-butyl hydroperoxide	- One of the rare examples on 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.	[235]
25	Metalloporphyrins	$\{[Cd(DMF)_2Mn^{III}(DMF)_2TPyP](PW_{12}O_{40})\}\cdot 2DMF\cdot 5H_2O$	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.	[236]

(DA.Br) decyltrimethylammonium bromide, dodecyltrimethylammonium bromide (DDA.Br), tetradecyltrimethylammonium bromide (TDA.Br), hexadecyltrimethylammonium bromide (HDA.Br), and octadecyltrimethylammonium bromide (ODA.Br).
dodecyltrimethylammonium bromide (DDA·Br), trimethylstearylammonium bromide (TSA·Br), and dimethyldioctadecylammonium bromide (DODA·Br)
(DDA=dimethyldioctadecylammonium, 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)
C_4mim: 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
C_{12}mim: 1-dodecyl-3-methylimidazolium
CTA: cetyltrimethylammonium
TBA: tetrabutylammonium
n-bpo: (2,5-bis(n-pyridyl)-1,3,4-oxadiazole)
en: ethyline-diamine
DMF: *N*,*N*-dimethylformamide; TPyP: tetrapyridylporphyrin
DA: dodecyltrimethylammonium bromide

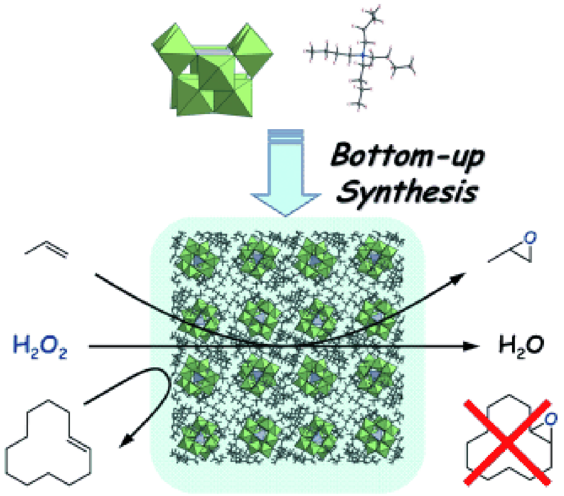


Figure 2.19. Size-selective oxidation of olefins over [(n-C4H9)4N]4[γ-SiW10O34(H2O)2].H2O synthesized via bottom-up approach [196].

2.4.3.3 POTs solidified via immobilization onto supports or into matrixes

The most conventional method to prepare heterogenous POT-based catalysts is deposition of POTs onto supports or into matrixes [237]. Depending on the nature of 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 immobilizer: graphite (HOPG) [238-240], carbon nanotubes (CNTs) [241-248], and metals surfaces such as Au [249,250]and Ag [251] have been employed as support for several applications like microscopy imaging, electrodes and electro-assisted catalysis and sensing.

Focusedly 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 causing eventually deactivation of the catalysts. To address this matter, efforts on covalently linking POTs to supports, which requires, often, advanced functionalization prior or during the immobilization, are rapidly underway todays. These efforts have chiefly focused on using polymeric and MOFs-made supports due to their capabilities to covalently encapsulate POTs arising from their organic frameworks. This is, most probably, the reason for much more reported works on these two supports to carry catalytically active POMs compared to the other types of supports, and consequently, for presenting exclusive review papers on POM-MOF [252] and POM-polymer [253,189] hybrids.

In general, thanks to 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 organic framework of the polymers. Employing transition metal oxides as support, strong host-guest interactions, as well as tunable chemical composition and active sites can be obtained. MNPs-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 [137] and Zhou et al. in 2014 [191]. Herein we try to cover all of the recent works dealing, exclusively, with tungsten-based POMs immobilized on supports and their catalytic applications. Tables 2.14 and 2.15 show the reported POT/support catalytic systems along with their applications in acid catalysis and oxidation reactions.

2.4.3.4 POTs heterogenized via combined strategies

Combining the three heterogenization strategies, discussed in sections 2.4.3.1-3, offers some additional advantages in the design 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 or the supports or both) can be employed prior to immobilization in order to either enhance the stability of the supported POTs or improve dispersion of the POT active sites into the support’s structure.

Table 2.14. POTs solidified with immobilization on supports for acid catalysis reactions.

Entry		Support	POT	Reaction	Remarks	Ref.
1	Silica	C_8-AP grafted SBA-15	$H_3PW_{12}O_{40}$	Hydrolysis of ester	- The supported POT was surrounded by hydrophobic alkyl groups in channels of mesoporous silica nanostructured, which afforded paths for the efficient approach of reactant molecules and water to the active sites.	[254]
2		AP grafted SBA-15	$H_3PW_{12}O_{40}$	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.	[255]
3		SiO_2	$H_3PW_{12}O_{40}$	Polymerization of β-pinene	- The supported POT had no poison to hydrogenation catalysts, as well as low corrosion to polymerization and hydrogenation equipment.	[256]
4		SiO_2	$H_3PW_{12}O_{40}$	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.	[257]
5		SiO_2	$H_3PW_{12}O_{40}$	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.	[258]
6		SiO_2	$H_3PW_{12}O_{40}$	Conversion of citronellal to menthol	- Adding Pd to the supported POT's structure, a bifunctional catalyst was developed that direct the reaction via acid-catalyzed cyclization followed by Pd-catalyzed hydrogenation.	[259]
7		SiO_2	$H_4SiW_{12}O_{40}$	Esterification of oleic acid with methanol	- The supported POT showed high catalytic activity close to that of unsupported one; however, leaching of active sites resulted in gradual deactivation of the catalyst.	[260]
8	Transition metal oxides	- Mesoporous ZrO_2 - Mesoporous ZrO_2- ethane-bridged organosilica	$H_3PW_{12}O_{40}$	Transesterification of Eruca Sativa Gars oil	- The ethane-containing supported POT exhibited higher catalytic activity due to combination of strong Brϕnsted acidity, 3D interconnected mesostructure, and enhanced hydrophobicity.	[261]

9		- Mesoporous ZrO_2 - Mesoporous ZrO_2-benzene/ethane-bridged organosilica	$H_3PW_{12}O_{40}$	Esterification of levulinic acid	- The alkyl-containing supported POT exhibited higher catalytic activity due to the combination of strong Brönsted acidity, well-defined ordered mesostructure, homogeneous dispersion of active sites, and enhanced surface hydrophobicity of the hybrid catalysts	[262,263]
10		Ta_2O_5	$H_3PW_{12}O_{40}$	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.	[264]
11		Hydrous ZrO_2	$H_3PW_{12}O_{40}$	Condensation of dimedones, urea, aryl aldehydes, enolizable ketones, and acetyl chlorides	- Structural integrity and good dispersion of the POT in the support were responsible for high catalytic efficiency.	[265]
12		ZrO_2	$H_3PW_{12}O_{40}$	Regioselective monobromination of aromatic substrates	- The supported POT exhibited excellent yields and efficient recovery.	[266]
13	MOFs	MIL-101 (Cr)	$H_3PW_{12}O_{40}$	Knoevenagel condensation of benzaldehyde, esterification of acetic acid, dehydration of methanol	- The supported POT was bi-functional porous solid with outstanding catalytic performance in base- and acid-catalyzed reactions, which was obtained by direct and one-pot encapsulation of POT into support.	[267]
14		MIL-101 (Cr)	$H_3PW_{12}O_{40}$	Dehydration of fructose and glucose to HMF	- Different loadings of POT were investigated resulting in highly active and recyclable solid acid catalyst.	[268]
15		MIL-101 (Cr)	Ru- $H_3PW_{12}O_{40}$	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 highest reaction efficiency.	[269]
16		MIL-101 (Cr)	$H_3PW_{12}O_{40}$	Baeyer condensation of benzaldehyde and 2-naphthol and epoxidation of caryophyllene by H_2O_2	- Under microwave-assisted heating reaction, the supported POT was highly active and exceptionally stable.	[270]
17		MIL-101 (Cr)	$H_3PW_{12}O_{40}$	Alcoholysis of styrene oxide	- Probing the acid sites using in situ FTIR showed generation of additional hydroxyl groups and Lewis acid sites, which were responsible for high efficiency of the supported POT in a short reaction time.	[271]
18	Polymers	Polymeric ionic liquid: Poly(VMPS)	$H_3PW_{12}O_{40}$	Esterification of alcohols	- Both polymeric framework and large heteropolyanion were responsible for solid nature of the catalyst. - Excellent catalytic activity came from acidic SO_3H functional groups in the hybrid catalyst.	[272]

19		Povidone (PVP)	$H_3PW_{12}O_{40}$	Azidation of alcohols	- Higher surface area of the PVP-POT (10.5 m^2 g^{-1}) compared to PTA was responsible for enhancing catalytic activity.	[273]
20		PDVC (Poly (*P*-divinylbenzene, 4-vinylbenzyl chloride))	$H_3PW_{12}O_{40}$	Acetylation of glycerol	- Ethylenediamine was used as soft linker between polymer and PTA. The POT showed hybrid characteristic of heterogeneous and homogeneous catalysts, resulting in superior activity compared to the literature.	[274]
21	Magnetic NPs	organo- functionalized SiO_2 (shell)-iron oxide (core)	$H_3PW_{12}O_{40}$	Friedel–Crafts reactions of indoles	- The first report on non-covalent immobilization of POT on MNPs.	[275]
22		organo- functionalized SiO_2 (shell)-iron oxide (core)	$H_3PW_{12}O_{40}$	Esterification of free fatty acid	- The first-time application of MNPs-supported POTs in esterification reactions.	[276]
23		poly(glycidyl methacrylate) (PGMA) (shell)-iron oxide (core)	$H_3PW_{12}O_{40}$	Esterification of free fatty acids and transesterification of triglycerides	- Good catalytic performance was ascribed to high acidity and nano-size of the catalyst. - Firm attachment of POT on MNPs via covalent binding, stable PGMA shell, and superparamagnetic properties of MNPs led to high stability and recyclability of the catalyst.	[277]
24		Diamine-functionalized silica-coated magnetite (Fe_3O_4)	$H_3PW_{12}O_{40}$	Synthesis of tetrahydrobenzo[b]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.	[278]
25	Zeolites	Zeolite imidazolate framework (ZIF-67)	$H_3PW_{12}O_{40}$	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.	[279]
26	Carbon materials	Activated carbon	$H_3PW_{12}O_{40}$	Polymerization of β-pinene	- The POT could interact strongly with surface oxygen-containing groups on the activated carbon, resulting in stable immobilization of POT, which led to a decrease in the specific surface area of the activated carbon.	[280]
27	Other supports	Mineral clay: Bentonite (BNT)	$H_3PW_{12}O_{40}$	Hydroxyalkylation of phenol	- Optimized amount of the POT 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 Brönsted and Lewis acid sites on BNT.	[281]

28	Clay: K10 and KSF montmorillonite	$H_3PW_{12}O_{40}$	Condensation of 1,2-phenylenediamines and ketones	- The supported POT was highly active, non-hygroscopic, non-corrosive, and efficiently recyclable.	[282]

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

Table 2.15. POTs solidified with immobilization on supports for oxidation reactions.

Entry		Support	POT	Reaction	Remarks	Ref.
1	Silica	Ionic liquid-modified SiO_2	$[\{W(=O)(O_2)_2(H_2O)\}_2(\mu\text{-}O)]^{2-}$	Epoxidation of olefins with H_2O_2	- Activity of the supported POT was comparable to homogeneous analogue, confirming successful heterogenization. - No leaching of active sites was obtained.	[283]
2		Ionic liquid-modified SBA-15	$H_3PW_{12}O_{40}$	Oxidation of alcohols with H_2O_2	- The supported POT exhibited high catalytic activity and selectivity and reusability without leaching in solvent-free catalytic reaction.	[284]
3		Ionic liquid-modified SBA-15	$H_3PW_{12}O_{40}$	Oxidation of alcohols with H_2O_2	- The supported POT prepared via 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.	[285]
4		Ionic liquid-modified SBA-15	$H_3PW_{12}O_{40}$	Oxidative desulfurization of fuels	- The hybrid POT possessed ordered mesopore 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 significant contribution to desulfurization activity.	[286]
5		Mesoporous SBA-16	$H_6P_2W_{18}O_{62}$	Epoxidation of olefins and oxidation of alcohols with H_2O_2	- Pore entrance size of the SBA-16 was modified by silylation reaction to enable trapping the POT.	[287]
6	transition metal oxides	Ordered mesoporous ZrO_2	$H_3PW_{12}O_{40}$ $H_4SiW_{12}O_{40}$	Oxidation of alkenes with H_2O_2	- The supported POT exhibited higher catalytic activity compared to its parents: ZrO2 and heteropoly acids.	[288]
7	MOFs	MIL-101	$[PW_4O_{24}]^{3-}$ $[PW_{12}O_{40}]^{3-}$	Oxidation of alkenes with H_2O_2	- The supported POTs demonstrated good activity comparable to that of homogeneous heteropoly acids. - In contrast to homogeneous systems, use of a higher H_2O_2/alkene molar ratio allowed increasing both alkene conversion and epoxide selectivity, arising from specific sorption properties of support.	[289]
8		MIL-101 (Cr)	$[PW_{11}O_{39}]^{7-}$ $[SiW_{11}O_{39}]^{8-}$	Oxidation of alkenes with H_2O_2	- The supported POTs were highly active, selective (comparable to homogeneous ones) and recyclable catalysts.	[290]

9		rht-MOF-1	$H_3PW_{12}O_{40}$	Oxidation of alkylbenzene	- The Keggin POT could be immobilized into the *β*-cage of rht-MOF-1 by a solvothermal method with highly ordered and porous structure, resulting in good dispersion of POT in the reaction and enhancement of catalytic activity.	[291]
10		$Cu_3(BTC)_2$ MOF (HKUST-1)	$H_3PW_{12}O_{40}$ $H_4SiW_{12}O_{40}$	Oxidative desulfurization of model fuels	- The POT encapsulated in MOF showed selective oxidation of sulfides to corresponding sulfones or sulfoxides with efficient reusability.	[292]
11		Copper organic frameworks with pyrazine derivatives	$H_3PW_{12}O_{40}$ $H_4SiW_{12}O_{40}$	Epoxidation of alkenes with H_2O_2	- The heterogenized POT showed higher catalytic activity compared to the corresponding homogeneous POT.	[293]
12		Metal-organic coordination network (MOCN): (1) $Co(BBTZ)_{1.5}(HBBTZ)(H_2O)_2$ (2) $Co_{2.5}(BBTZ)_4(H_2O)_2$ (3) $Cu(BBTZ)_2$	$PW_{12}O_{40}$ $BW_{12}O_{40}$	Oxidative desulfurization of dibenzothiophene	- 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 molecular level exposing more active POT sites.	[294]
13		$[Cu(4,4'\text{-bipy})_2(H_2O)_2]_n^{2n+}$ (bipy = bipyridine)	$H_3PW_{12}O_{40}$ $H_4SiW_{12}O_{40}$	Oxidation of ethylbenzene	- Oxidation of the substrate occurred in the pore of the framework, and valence of the metal ion in the POTs significantly influenced catalytic activity of the 3D framework.	[295]
14		MIL-101 (Cr)	$[PW_{11}CoO_{39}]^{5-}$ $[PW_{11}TiO_{40}]^{5-}$	Oxidation of alkenes with molecular oxygen and H_2O_2	- The POTs were electrostatically attached to surfaces of the support, which showed good stability and no leaching under mild conditions (T< 50 °C).	[296]
15		MIL-101 (Cr)	$[Ln(PW_{11}O_{39})_2]^{11-}$ Ln = Eu^{3+} and Sm^{3+}	Oxidation of styrene with H_2O_2	- The supported POTs exhibited higher activity than that of homogeneous parent POTs, which was further increased by microwave-assisted oxidative reactions.	[297]
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.	[298]
17	Polymers	Ionic copolymer: AM-BM	$H_3PW_{12}O_{40}$	Epoxidation of alkenes with H_2O_2	- Peroxo–W active sites in the POT promoted by the amino groups in polymer matrix was responsible for catalyst's excellent performances. Stable structure of the catalyst came from cross-linked structure of the copolymer cations.	[299]
18		Ionic copolymer: DIM-CIM	$H_3PW_4O_{16}$	Epoxidation of alkenes with H_2O_2	- Amphiphilic structure of the supported POT acted as a “trapping agent” for both hydrophobic alkene substrates and hydrophilic H_2O_2, promoting catalytic activity.	[300]

19		Ionic copolymer: NDMAM-AVIM	$H_3PW_{12}O_{40}$	Oxidation of alcohols with H_2O_2	- Excellent performance of the supported POT comes from featured structure of polymeric framework giving the catalyst solid nature and stimuli-responsive behavior.	[301]
20		Ionic copolymer: AVIM-DVB and PDIM-DVB	$H_3PW_{12}O_{40}$	Oxidation of benzyl alcohol with H_2O_2	- High activity of the catalyst arose from amino functional groups and high BET surface area of polymeric framework.	[302]
21		Poly(ethylene oxide-pyridinium)	$H_3PW_{12}O_{40}$	Oxidation of alcohols with H_2O_2	- Using the supported POT, chemoselective oxidation of sterically hindered secondary alcohols in presence of primary alcohols was achieved.	[303]
22		Amphiphilic resins	$H_3PW_{12}O_{40}$	Epoxidation of unsaturated fatty esters with H_2O_2	- Catalytic properties of the supported POT varied with hydrophilic/lipophilic balance (carbon chain number, spacer arm between benzene cycle and imidazole group, N-substitution of imidazole ring).	[304]
23		Polymer-immobilised ionic liquid phase	$[PO_4\{WO(O_2)_2\}_4]^{3-}$	Epoxidation of allylic alcohols and alkenes with H_2O_2	- A new polymeric support with tuneable surface properties and microstructure has been prepared by ring-opening metathesis polymerisation.	[305]
24		Poly(divinylbenzene)	$[PO_4\{WO(O_2)_2\}_4]^{3-}$	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.	[306]
25		Poly(methyl methacrylate)	$[\{CH_2{=}CH(CH_2)_6Si\}_xO_ySiW_wO_z]^{4-}$ (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.	[307]
26		A modified porous resin	$(NBu_4)_6[\alpha_2\text{-}P_2W_{17}O_{61}(SiC_6H_4CH_2N_3)_2O]$	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.	[308]
27		Biopolymer: chitosan	$H_3PW_{12}O_{40}$	Degradation of chitosan with H_2O_2	- The POT was easy to separate from chitosan at the end of reaction, improving purity of the products.	[309]
28	Magnetic NPs	Ferromagnetic nanocrystals (iron oxide)	$(DODA)_3PW_{12}O_{40}$	Oxidation of sulfides to sulfones	- Nanospaces and increased surfactant alkyl chain density around the POT in the nanocones provided enhanced catalytic performance.	[310]

29		Poly(ionic liquid) coated iron oxide	$H_3PW_{12}O_{40}$	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 aqueous phase.	[311]
30	Alumina	Au/ Al_2O_3	$K_8[BW_{11}O_{39}H]\cdot nH_2O$	Epoxidation of cyclooctene with molecular oxygen	- Adding Au NPs and combining catalytic activities of the POT and gold, an efficient and recoverable catalyst was developed.	[312]
31	Other supports	layered double hydroxides (LDHs)	$[WZn_3(ZnW_9O_{34})_2]^{12-}$	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.	[313]
32		$Mg_3Al{-}NO_3$	$[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$	Oximation of aldehydes by H_2O_2	- Selectivity of oximation of various aldehydes was increased under mild conditions by using the supported POT.	[314]

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

For example, Villanneau et al. have reported successful covalent immobilization of the hybrid POT $[AsW_9O_{33}\{P(O)(CH_2CH_2CO_2H)\}_2]^{5-}$ 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 interactions-based supported POTs. They prepared anchored homogeneous catalysts retaining important mesoporosity, in which the POT would play the role of polydentate inorganic ligands for active centers [315]. Furthermore, such hybridization of polyoxometallates via an organic-inorganic association has been exploited to develop a heterogeneous catalyst with tunable functionality imparted through supramolecular assembly [316]. 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 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 (Figure 2.20) [317]. 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 nano-sized channels in the lattice of the produced complex, $K_3[Cr_3O(OOCH)_6(H_2O)_3]SiW_{12}O_{40}.12H_2O$, resulting in catalytically interesting properties [318]. Table 2.16 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.

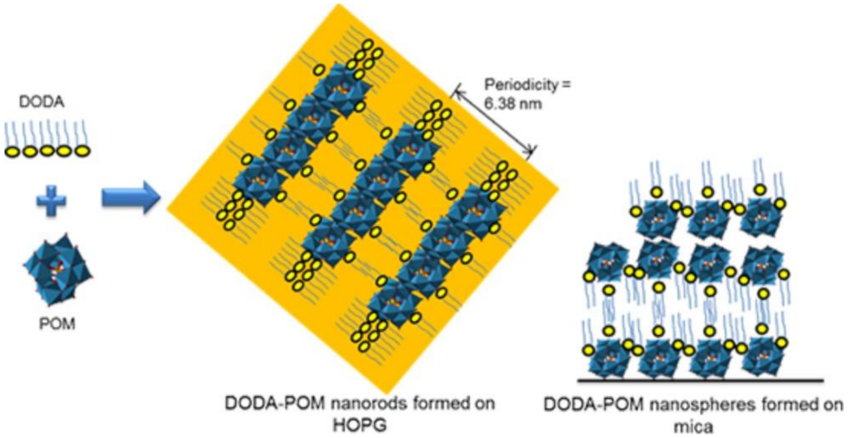


Figure 2.20. Controlling morphology and dispersion of supported POT heterogeneous catalysts via organo-modification of the POT [317].

Table 2.16. 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_2O_2	- Adding Fe to the POT's structure, the catalyst showed superior catalytic performance from acidic to neutral pH values.	[319]
2	$Na_7H_2LaW_{10}O_{36}\cdot 32\ H_2O$	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.	[320]
3	$(TBA)_7H_3[Co_4(H_2O)_2(PW_9O_{34})_2]$	-	Quaternary ammonium surfactant: TBA	MOF: MIL-101	Oxidation of olefins with H_2O_2	- Immobilization of this sandwich-type POT on MOF was reported for the first time, which showed high activity for oxidation of various hydrocarbons.	[321]
4	$[Cu_2(BTC)_{4/3}(H_2O)_2]_6[H_nXW_{12}O_{40}]\cdot(C_4H_{12}N)_2$ (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) highly stable crystalline framework, allowing for catalyst recycling.	[322]
5	$H_3[(Cu_4Cl)_3(BTC)_8]_2[PW_{12}O_{40}]\cdot(C_4H_{12}N)_6\cdot 3H_2O$	-	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.	[323]
6	$[Cu_3(C_9H_3O_6)_2]_4[\{(CH_3)_4N\}_4CuPW_{11}O_{39}H]$	-	Quaternary ammonium surfactant: TMA	MOF-199 (HKUST-1)	Aerobic oxidations	- 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.	[324]
7	$PYI\text{-}Ni_2H[BW_{12}O_{40}]$	Ni^{2+}	Asymmetric organocatalytic group: l- or d-pyrrolidin-2-ylimidazole (PYI),	Chiral MOF	Asymmetric dihydroxylation of aryl olefins with H_2O_2	- Hydrophilic/hydrophobic properties of channels of the enantiomorphs POT-MOF were modulated to adsorb oxidant and olefins, resulting in excellent stereoselectivity.	[325]
8	$[Cu_3(4,4'\text{-bpy})_3][HSiW_{12}O_{40}]\cdot(C_3H_4N_2)$ $[Cu(Phen)(4,4'\text{-bpy})(H2O)]_2[PW_{12}O_{40}]\cdot(4,4'\text{-bpy})$	-	Imidazole and bipyridine	MOF	Oxidation of alcohols with H_2O_2	- The synthesized POT exhibited higher activity compared to the corresponding Mo-based POMs.	[326]

9	$TBA_{4.2}H_{0.8}[PW_{11}Zn(H_2O)O_{39}]$		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.	[327]
10	$K_6P_2W_{18}O_{62}$ $K_{14}[NaP_5W_{30}O_{110}]$	K^+	-	Silica: MCM-48, SBA-3, SBA-15 and NH_3^+ functionalized SiO_2	Oxidation of thioethers with H_2O_2	- Preyssler complex was more active compared to its Dawson analog. Characteristics of the support also affect the catalytic activity.	[328]
11	$TBA_4HPW_{11}CoO_{39}$ $TBA_5PW_{11}CoO_{39}$	-	Quaternary ammonium surfactant: TBA	NH_2- 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 3rd cycle.	[329]
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.	[330]
13	$MoO_2(acac)$-$K_8[SiW_{11}O_{39}]$	K^+	Molybdenylacetylacetonate complex	-	Epoxidation of alkenes with *tert*-BuOOH	- Catalytic activity of $MoO_2(acac)_2$ was modified by incorporation of the POT via covalent bonding because of charge-transfer role of the resultant complex.	[331]
14	Pd(salen)-$K_8[SiW_{11}O_{39}]$	K^+	Palladium (salen)	-	Suzuki cross-coupling reactions	- 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.	[332]

DBT: dibenzothiophene
BT: benzothiophene
4,6-DMDBT: 4,6-dimethyldibenzothiophene
TBA: tetrabutylammonium
BTC: benzentricarboxylate
TMA: tetramethylammonium
Bpy: bipyridine
Phen = 1,10-phenanthroline
salen = *N*,*N′*-bis(salicylidene)ethylenediamine

2.5 Conclusion and perspective

As shown here, many efforts have been done in the context of the high demands for development of sustainable and green chemistry in order to find an alternative for hazardous ozonolysis of UFAs, which is currently the industrial method for the production of dicarboxylic acids from oils and fats. Replacing ozone with a more benign oxidant, like hydrogen peroxide, makes it necessary to employ an active catalyst in the reaction. To push this catalyst to its use in multikilogram-scale toward industrial production, the substantial feature of recyclability should, also, be considered. This chapter indicates that several catalytic systems in homogeneous and heterogeneous forms have been developed for oxidative cleavage of UFAs. Transition metals such as osmium, cobalt, molybdenum, chrome, gold, manganese, iron, ruthenium, and tungsten have been used as catalytic active sites, with considerably more emphasis on W.

Homogeneous catalysts, on which more researches have been done, showed excellent conversion and selectivity. However, their large-scale application has been always restricted due to the lack of catalyst recovery. Curiously, the use of heterogeneous catalysts with recycling ability has been scarcely reported, which would be ascribed to their lower conversion compared to homogeneous catalysts. This is mainly because of low catalyst/reactant contact from either low active site availability or pore diffusion limitations. The available results for NP-based catalysts, although they are very rare, confirm that they could show improved performances compared to solid catalysts. Insufficiently explore of nanocatalysts in oxidative cleavage of UFAs, called for further works in this field. It even makes more sense given the fact that surface properties of metals oxides NPs provide a great promise in their further modifications, which can increase their catalytic efficiency in the biphasic oxidative cleavage of UFAs. Interestingly, considering the high degree of dispersion of organo-functionalized NPs, one can properly assume that such catalysts are at the frontier of homogenous and heterogeneous catalysts as they possess the best aspects of the both, simultaneously. The good dispersion of a catalyst in a solvent, although it increases the catalytic activity, can be a double-edged sword if it makes the separation of catalyst from product complicated. Owing to the recent advances, however, recovery of NP-based catalysts is possible via facile and highly efficient methods.

Furthermore, the excellent inherent properties of polyoxotungstates (e.g. strong acidity, high thermal stability, and hydrophobicity) hold, nowadays, a promise for application in various organic reactions chiefly including oxidation and acid catalysis reactions. However, POTs are originally soluble in water and polar solvents, resulting in lack and/or difficulty of recovery. 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 versatilities 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 pseudo-homogeneous phase and/or stabilization of Pickering emulsion medium resulting in enhancement of catalyst efficiency, (ii) increasing catalyst hydrophobicity which results in prevention of catalyst particles aggregation and poisoning of acid sites by water, (iii) enabling self-separation of the catalyst at the end of reaction, and even (iv) preparation of size-selective catalysts to selectively allow desired molecules to ingress and egress.

Considering the fast pace of catalysis progress, it is definitely only a matter of time before an environmentally benign process for oxidative cleavage of UFAs in industry is achieved.