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Chemically catalyzed oxidative cleavage of unsaturated fatty acids and their derivatives into valuable products for industrial applications: a review and perspective

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Oils and fats of vegetable and animal origin have recently attracted growing interest as renewable raw materials in oleochemical industries. This attention arises from not only environmental reasons, but also economic ones. Unsaturated fatty acids (UFAs), as the constituent of lipids, can be oxidized to produce mono- and dicarboxylic acids which are valuable materials in different industries. This oxidation process is called oxidative cleavage, since during the reaction carbon–carbon double bond(s) get cleaved. Although the oxidative cleavage of UFAs has now been developed using ozonolysis, hazardous problems associated with the use of ozone still represent controversial challenges. Replacing ozone with a more benign oxidant requires the use of an active catalyst. Several different combinations of transition metals like Os, Co, Mo, Cr, Au, Mn, Fe, Ru, and W have been investigated for this purpose, with a great deal of emphasis on the latter two, particularly tungsten. In this paper, we have tried to review all of the recent works regarding the use of different catalyst/oxidant systems in the oxidative cleavage of UFAs and their derivatives. Herein, we divided the reported catalytic systems into three classes: homogenous, heterogeneous, and semi-heterogeneous (nanoparticle (NP)-based) catalysts. Important features such as catalytic activity and recoverability, with specific respect to the viewpoint of commercialization, are discussed in a critical fashion for each class to be able to reasonably plan future works. The unique and interesting properties of NPs lead them to be proposed as the frontier of homogeneous and heterogeneous catalysts that can exploit the best features of both simultaneously. These properties, along with recent breakthroughs which would interestingly increase the performance of NP-based catalysts in the biphasic oxidative cleavage reaction of UFAs, are also reviewed.

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1. Introduction: applications of oils and fats as renewable raw materials

Being potentially faced with the warning "sorry, out of gas" in the near future is one of the most concerning challenges around the world. During the last few decades, fossil feedstock, derived from oil and gas, has been the most important raw material for the chemical industry, accounting for more than 90%. Even with this enormous amount, the chemical industries occupy third position in terms of the greatest users of oil and gas feedstocks, after energy generation and transportation.[1] Understandably, the shortage in petroleum reservoirs in the near future is a worldwide crisis which can be confirmed by Fig. 1,[2] which shows the oil and gas production profiles in the past and future for the whole earth. As can be

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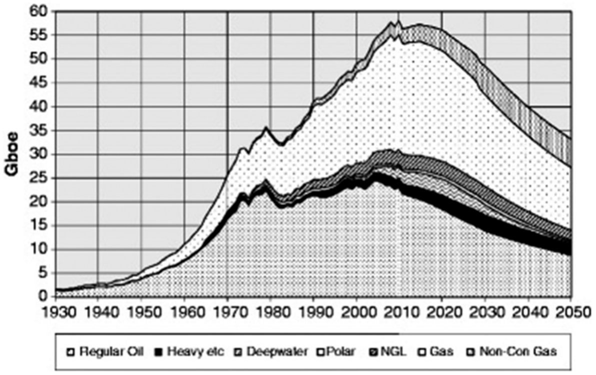

Fig. 1 Production profiles of oil and gas, 2010 base case (Gboe: gigabarrels of oil equivalent),[2] reprinted with permission from Springer.

seen, starting from 2010, a downward trend is obvious in the levels of oil and gas production.

In addition, global concern over environmental pollution associated with petroleum materials has propelled the attention of researchers towards renewable raw materials. Among the feedstocks from renewable resources, oils and fats of vegetable and animal origin could become major players in the chemical industry in the near future, due to not only economic reasons, but also environmental ones.[3,4] Oils and fats have chemical structures giving them the potential for industrial development in the field of feedstock materials.[5] 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 modification. Moreover, they are abundant in nature, biodegradable, and have nontoxic properties that make them promising candidates for the replacement of petrochemical materials.

Oils and fats differ in the state of material; oils are often liquid at ambient temperature, but fats are solid. They are derived from vegetables (*e.g.* palm, soybean, rapeseed (canola), sunflower seed (the so-called four major vegetable oils), palm kernel, coconut and olive) or animals (*e.g.* butter, lard, tallow, and fish oil). There is no widely-accepted definition for lipid, but the one which is presented by the AOCS† would be the best:[6] "Lipids are fatty acids and their derivatives, and substances related biosynthetically or functionally to these compounds."

Nowadays, the extraction of oils and fats from bio-based materials is being rapidly globalized. Oilseeds are obtained all over the world, under all sorts of climates, in both northern and southern hemispheres and from a variety of plants. In the most recent 30 years, the production of oilseeds has dramatically increased. From 1985 (190 million tons) to 2011 (more than 453 million tons), 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) was observed over a period of 26 years. This makes more sense when compared with "grains" (wheat, coarse grains and rice), which showed only a 34% increase in production across 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 per hectare in 1985 to 1.74 tons per hectare in 2011.[7]

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

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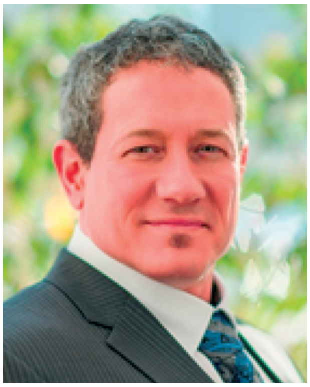
† American Oil Chemists' Society.



François Béland

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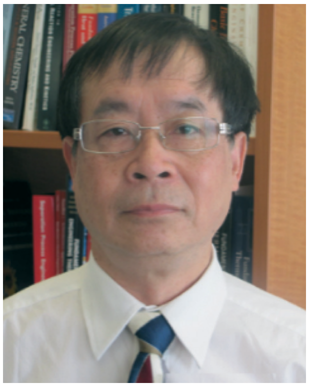

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used as the basis of the oleochemical industry, as well as a very small proportion for animal feeds. Interestingly, significant growth in the proportion of non-food uses is obvious in the data presented in Table 1.[8] The table shows the distribution 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. Going from 1999 to 2012, the non-food portion has increased from 10.5 to 23.9%. This increase is particularly remarkable from 2003/04 onwards.

According to the above-mentioned data, it can be concluded that significant growth in the production of oils and fats in recent years is clear all around the world. One reason is the human food use of oils and fats and the growing population of the world. The data in Table 1, however, confirms the increasing rate of non-food use of oils and fats in the world, particularly during the last decade.

In order to use oils and fats in advanced chemical industries, it is necessary to split them into so-called oleochemical base materials.[9] The lipids are made from triglyceride, which, in turn, consists of glycerine and three fatty acids (Fig. 2).[10] The triglycerides which form animal fats typically have more saturated fatty acids, while those that constitute vegetable oils have more unsaturated fatty acids.[11]

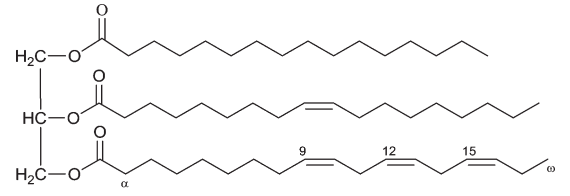


Fig. 2 Typical example of a lipid structure with glycerol and three fatty acids (palmitic acid, oleic acid, and alpha-linolenic acid, from top to bottom).[10]

Decomposition of triglycerides results in the release of fatty acids.[12] Apart from fatty acids (*ca.* 52%), oleochemical base materials mainly include fatty acid methyl esters (*ca.* 11%), fatty amines (*ca.* 9%), and fatty alcohols (*ca.* 25%).[13] They have shown a variety of chemical applications, scarcely less than petrochemicals have.[9,13] The polymer industry is one of the most important industries that can exploit lipids and convert them into valuable products. Although oils and fats have been used in polymers for many years, their applications are currently undergoing rapid development to extend the scope of the specialty and commodity products. These applications, either in the form of triglycerides or oleochemical base materials, are categorized in three groups in Table 2, including polymer materials (linseed oil and soybean oil as semi-drying oils), polymer additives (epoxidized soybean oil as plasticizer), and building blocks for polymers (dicarboxylic acids for polyesters or polyamides).[14] Long-chain dicarboxylic acids can be used for the latter application. In general, dicarboxylic acids, $HOOC(CH_2)nCOOH$ (where *n* represents the number of methylene groups and their derivatives), are industrially important chemicals due to their potential in the production of various intermediates.[15] 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 greater hydrophobicity than nylon-11 and nylon-12).[16] Furthermore, the esters of dicarboxylic acids are used as lubricants and hydraulic fluids over a wide temperature range,[15] as well as plasticizers for polyvinyl chloride.[15,17]

Table 1 Food and non-food consumption (million tons and %) of nine major vegetable oils between 1999/00 and 2011/12 (ref. 8)

	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

Dicarboxylic acids are produced from petrochemical feedstock (*e.g.*, production of adipic acid from the multistage butadiene oxidation[18]). The ring-opening oxidation of cyclic compounds is another route to produce these chemicals.[19] Biotechnological techniques have been also developed for this purpose[20] which are not the subject of this paper. Until recently, the production of only two of these dicarboxylic acids from oleochemical base materials have been commercialized, including sebacic acid, which is obtained by the alkaline cleavage of castor oil[19] and azelaic acid, which is produced from the oxidation of oleic acid through ozonolysis.[21] 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.[14,22]

In this review, we focus on the production of mono- and dicarboxylic acids through the oxidation of oil and fat components. In what follows, the basic concepts and seminal studies of UFAs and their reactions, which have been widely reviewed,[3,10,13,14] with an emphasis on oxidation will be shortly summarized in order to approach the main topic (section 2). Then, recent progresses made in the optimization of the catalytic oxidative cleavage of UFAs and their derivatives will be discussed in section 3. Although this subject has been briefly covered as a subsection in some more general review papers,[3,10,23,24] reviews which focus individually on the chemically catalyzed oxidative cleavage of UFAs are very rare. Spannring *et al.* recently reviewed the use of transition metals as catalysts in the oxidative cleavage of alkenes and UFAs.[25] Their presented classification for the catalysts provides a good opportunity for the readership to compare the oxidizing

Table 2 Examples of applications of oils and fats in the polymer industry[14]

Raw materials (oleochemical base or triglycerides)	Product	Application	Category
Castor and soybean oils	Polymerized castor and soybean oils	Drying oils	Polymer materials
Linseed oil	Polymerized linseed oil	Linoleum	
Soybean oil	Epoxides	Stabilizers and plasticizers	Polymer additives
Rapeseed oil	Fatty acid esters and amides	Lubricants	
Stearic acid	Soaps	Stabilizers	
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

power of first-, second-, and third-row transition metals in different forms, such as metal salts and metal complexes. In this paper, 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 the viewpoint of commercialization, arising from the global demand for the development of greener alternatives to the conventional oxidative cleavage methods, we will compare the results of previous work in three groups: homogeneous, heterogeneous and semi-heterogeneous (NP-based) catalysts. This classification, which has not been reported before, associated with the critical discussions presented on important features such as catalytic activity and recoverability would be helpful for the planning of future works. In addition, the investigation of recent breakthroughs of NP-based catalysts that can increase their performance especially in the oxidative cleavage of UFAs (section 3.4.1) would present an outlook in the development of advanced catalysts for such reactions.

2. Fatty acids and their reactions

2.1. Fatty acids: a primer

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

In the most generic classification, fatty acids are divided into saturated (without a carbon–carbon double bond) and unsaturated (with carbon–carbon double bond(s)) types. UFAs can, in turn, be categorized as mono-unsaturated (with one double bond) or poly-unsaturated (with more than one double bond). The two carbon atoms just near the double bond can occur in *cis* or *trans* configurations. However, most naturally occurring UFAs have the *cis* configuration.[26]

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).[6] Table 3 shows the common fatty acids extracted from animal and plant origins with their structures and different nomenclature systems.[6,27]

The most abundant mono-UFA in nature is oleic acid (C_{18})[28] which exists in various vegetable and animal oils and fats. Its systematic name is *cis*-9-octadecenoic acid with the 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 $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$).[29] 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,[30] giving rise to its name "oleic", which means "derived 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.[31–33] In addition, they are present abundantly in many animal fats, such as chicken and turkey fat and lard.[34] Oleic acid has numerous applications, such as being a component of human diet (in triglyceride form), a major component of soaps (in sodium salt form), in pharmaceuticals,[29] and in one of the most industrially important applications, the production of carboxylic acids *via* ozonolysis.[21]

The C_{18} poly-UFA like linoleic acid (shorthand form 18:2 (n − 6)) and α-linolenic acid (shorthand form 18:3 (n − 3)) are also available in most plant lipids, including many of the commercially important vegetable oils. The structures of C_{18} UFAs are shown in Fig. 3.

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 the aliphatic chain, the 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 the formation of a variety of products, even more than for petrochemistry products.[10]

The reactive sites in the structure of a fatty acid can be categorized into 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.[10,14] However, because of the wider range of obtainable products from the latter, progress in such reactions is highly demanded.[10] At present, converting natural oils into

Table 3 Common fatty acids of animal and plant origins; structures and nomenclature systems[6,27]

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
Mono-unsaturated 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 ($n - 9$)
Poly-unsaturated 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 ($n - 3$)

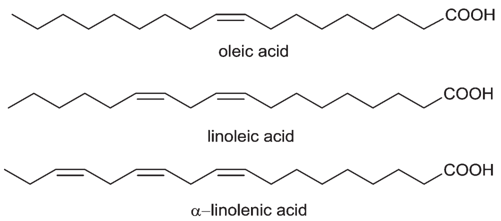


Fig. 3 Different C_{18} mono and poly-UFAs.

non-edible products is limited, mainly because of economic reasons; the production costs of oleochemical processes cannot compete effectively with mature petrochemical industries.[35] To address this problem and improve the economic aspects, the optimization of reaction conditions and the employment of efficient catalysts should be considered. The oxidation of UFAs is one of the reactions that targets the 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 widely reviewed in the literature.[10,13,28]

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

2.2.1.1. Epoxidation. Carbon–carbon double bonds in oils and fats of vegetables and animals can be functionalized *via* epoxidation, consequently producing epoxidized oils and fats which contain epoxide groups or oxirane rings.[36] The term epoxide can be defined as a cyclic ether which has three ring atoms (Fig. 4) and the general process for the synthesis of the epoxide group is known as an epoxidation reaction. Epoxides can be prepared from hydroperoxides, hydrogen peroxide, or molecular oxygen in the presence of different catalysts.[23]

Several methods have been reported for the epoxidation of unsaturated fatty compounds such as an *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.[9,10,13] Scheme 1 shows the typical epoxidation of a lipid including oleic acid, linoleic acid and α-linolenic acid and the formation of epoxide groups on the C–C double bonds.

Although the epoxidized oils and fats have their own valuable applications, such as acting as plastic additives,[37,38] plasticizers,[37] flame retardants,[10] heat stabilizers,[10] antioxidants and light stabilizers,[10] lubricants, cosmetics and in biochemical applications,[39,40] obtaining dicarboxylic acids *via* epoxidation requires a further ring opening reaction of the epoxides which, in turn, often needs different catalysts. Therefore, epoxidation does not seem a reasonable method to produce dicarboxylic acids.

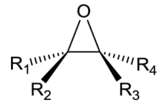
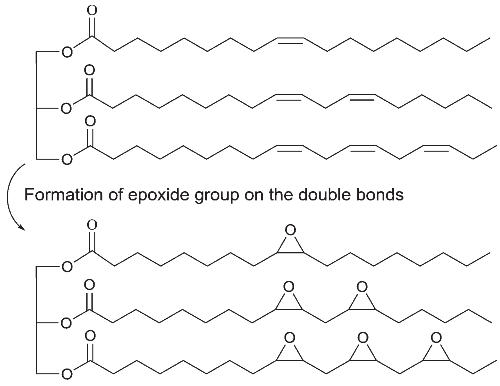


Fig. 4 A generic epoxide.



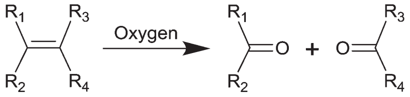
Scheme 1 Epoxidation of a lipid.[10]

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). 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.[41]

Oxidative cleavage of olefins typically occurs by ozonolysis. Ozone, O_3, is an allotrope of oxygen that can be added rapidly to carbon–carbon double bonds, transforming alkenes into aldehydes or carboxylic acids without the use of a metal as catalyst.[41] Currently, azelaic acid (C9, dicarboxylic acid), a very industrially important chemical, is produced on a large scale *via* the ozonolysis of oleic acid (eqn (1)). Pelargonic acid (C9, monocarboxylic acid) is obtained as a co-product, but is also a valuable chemical.[19] These type of saturated acids that have short and odd hydrocarbon chains are rare in natural resources.[42] On the other hand, they are very attractive initial materials for the development of numerous bio-based products.[43,44] 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.[42,43] Pelargonic acid is an intermediate in the production of lubricants, plasticizers, perfumes, herbicides, fungicides, resins.[43,45]

$$H_3C(CH_2)CH{=}CH(CH_2)_7COOH + 4[O] \rightarrow H_3C(CH_2)_7COOH + HOOC(CH_2)_7COOH \quad (1)$$

These two valuable products are obtained only in the case of over-oxidation, whereas the partial oxidative cleavage of oleic



Scheme 2 A general oxidative cleavage process.

acid produces the aldehyde nonanal and 9-oxononanoic acid[25] (Scheme 3). The presence of strong oxidants such as ozone favors over-oxidation.

Although the ozonolysis of oleic acid has shown high conversion and selectivity,[19,21,42,43,46] hazardous problems associated with the use of ozone have always presented a challenge,[3] which is why the commercial applications of ozonolysis processes are still restricted. The handling of ozone always has various safety risks such as explosion and toxicity. Moreover, the enormous energy demand of the ozonolysis process and the high-technology equipment required make the capital cost of the process high.[46,47] Therefore, a new alternative method with a safer and more economically viable process for the production of dicarboxylic acids from the oxidation of UFAs is of great interest to industry. The dangerous ozone should be replaced by a safe and green oxidant. In general, oxidants are the source of oxygen during oxidation reactions. Depending on their oxidizing power, some oxidants need the aid of a catalyst to act as a co-oxidant, and some do not. 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.[23,42,46,48] However, the problem is that most of these oxidants are not eco-friendly, and the desired products are obtained in low yields due to waste generation. Using 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 conversions and selectivities in such systems, it is necessary to employ a highly efficient catalytic system.[42,43]

3. Transition metal-based catalytic 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 attention for the oxidation of unsaturated hydrocarbons. In the case of UFAs, on which a 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 frequently investigated. Pure metals, simple metal salts, metal oxides and different metal complexes are different forms of the metals that have been employed as catalysts. One noticeable point is that 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 the catalyst.

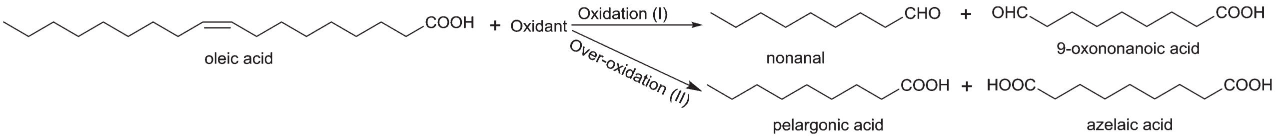
3.1. Mechanisms of the reaction

To reach a comprehensive interpretation, it is firstly important to investigate different proposed mechanisms for the oxidative cleavage reactions. In general, the oxidative cleavage of C–C double bonds in fatty molecules involves the scission of the double bonds, followed by the incorporation of oxygen atoms into the two produced sections (see Scheme 4). Aldehydes and ketones are often the initial products, whereas over-oxidation yields the production of carboxylic acids.[46]

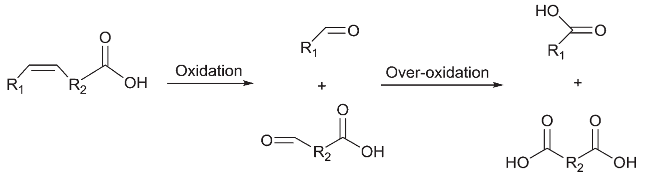
Several mechanisms have been proposed for the oxidative cleavage of alkenes and cyclic olefins. For UFAs, however, the mechanism seems to be more complicated. The main reason is the presence of the carboxylic group which may result in side reactions. In addition, the oxidative cleavage of cyclic olefins 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, the formation of radical intermediates in the oxidative cleavage of UFAs is very difficult, unlike the cyclic olefins. Herein, we presented modified versions of two of the proposed mechanisms for general olefins that are applicable to UFAs. Further work to propose a mechanism that carefully considers the mentioned difficulties, however, should be encouraged.

The first mechanism, which is shown in Scheme 5, describes a catalytic system based on transition metal tetroxides such as RuO_4 and OsO_4.[25,49] These oxides can be formed during the reaction 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 5 mechanism I), and immediately after the formation of the metal diester as the main intermediate, aldehydes will be formed, while OsO_4 tends to form diols after the formation of the metal diester (Scheme 5 mechanism II), rather than aldehydes. The main advantage of osmium in comparison with ruthenium is the lower metal loading required under the same conditions.[25] However, the toxic properties of osmium are stronger than ruthenium.

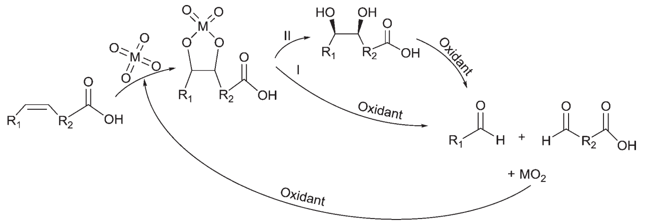
The second mechanism is based on the formation of an epoxide group, followed by hydrolysis to diols, and finally



Scheme 3 Oxidation of oleic acid into aldehydes (I) and over-oxidation into carboxylic acids (II).



Scheme 4 Oxidative double bond cleavage of UFAs to aldehydes, ketones, and carboxylic acids.[25]



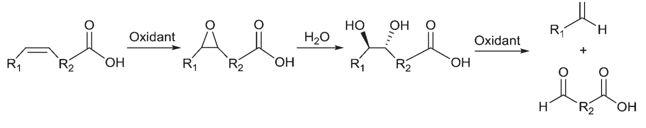
Scheme 5 First mechanism of oxidative cleavage of UFAs.[25,49]

oxidation, to obtain aldehydes or carboxylic acids. This mechanism, which is schematically shown in Scheme 6, is mainly ascribed to the presence of tungsten compounds as catalysts.[25]

3.2. Homogeneous catalysts

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

In the oxidative cleavage reactions of fatty acids, different coordinations of metals, such as simple metal salts, metal–oxo or peroxo complexes, and other metal complexes, have been used as homogeneous catalysts. It is worth pointing out that studies in this field, in order to find an alternative to the ozonolysis process, are currently passing lab-scale requirements such as gaining a better understanding of the reaction mechanism and, thus, have focused less on industrialization aspects. In fact, this 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 greater advantages for research-scale works, such as the lower mass transfer limitations which results in higher conversion. Therefore, the amount of research focused on homogenous systems is much higher than for heterogeneous systems. Table 4 summarizes the details of reported homogeneous catalytic systems for the oxidative cleavage of UFAs and their derivatives.



Scheme 6 Second mechanism of oxidative cleavage of UFAs.[25]

3.2.1. **Osmium.** Osmium was one of the first metals investigated in the catalytic oxidative cleavage of olefins.[52] The catalytic application of Os is usually accompanied with the use of $NaIO_4$ or $KHSO_5$ as secondary oxidants (Table 4, 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 the catalyst, its applications have been restricted due to the significant toxic properties of Os.

3.2.2. **Cobalt.** Diol oxidation can also be carried out with the cobalt polyoxometalate (POM) as shown by Santacesaria (Table 4, entry 2).[54] Using cobalt acetate, they reported a POM based on a 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 $H_6CoW_{12}O_{40}$. However, the production yield of azelaic acid from oleic acid using this catalytic system is not high enough (52.5%).

3.2.3. **Molybdenum.** Turnwald reported a complex formed on the basis of molybdenum to convert oleic acid into pelargonic and azelaic acid with excess hydrogen peroxide (Table 4, entry 3).[43] Using 2,6-dipicolinate as a ligand, the active oxo–peroxo complex $[MoO(O_2)(2,6\text{-dipicolinate})](H_2O)$ could be formed as a catalyst, which resulted in an 82% yield of azelaic acid after 5 h at 90 °C. However, the large amount of H_2O_2 which should be employed, makes such systems unreasonable for large-scale applications.

3.2.4. **Iron.** Although the first-row transition metals have the advantages of being cheaper and more environmentally friendly, their use in the 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 catalytic systems based on only first-row transition metals like iron have a lesser ability to over-oxidize UFAs and produce dicarboxylic acids.

Spannring *et al.* introduced a catalytic system based on first-row transition metals for the oxidation of UFAs (Table 4, 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 $[Fe(OTf)_2(\text{mix-BPBP})]$ was used as the catalyst and hydrogen peroxide and sodium periodate used as oxidants in acetonitrile, where OTf is the trifluoromethane sulfonate anion and mix-BPBP is a mixture of the *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 epoxidation hydrolysis and diol cleavage (second mechanism, Scheme 6). Adding acetic acid to increase the conversion, they succeeded in producing nonanal in yields of 96 and 90% from methyl oleate and oleic acid, respectively. The total time of the reaction was 24 hours at ambient temperature. However, a longer reaction time (48 h) was needed to produce carboxylic acids using Fe-based complexes (see Table 4, entry 5). The complex used for this purpose was $[Fe(OTf)_2(6\text{-Me-PyTACN})]$ where

Table 4 Different homogeneous catalytic systems reported for the oxidative cleavage of UFAs and their derivatives

Metal	Entry	Reactants	Main products	Catalyst/oxidant system	Reaction conditions[a]	System efficiency[b,c] (yield)	Ref.
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 °C	AA: 52.5%	54
Mo	3	Oleic acid	Pelargonic acid Azelaic acid	A molybdenum-based POM: [MoO(O_2)(2,6-dipicolinate)](H_2O)/H_2O_2	5 h, 90 °C	AA: 82%	43
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%	61
	7	Oleic acid	Pelargonic acid Azelaic acid	$RuCl_3/NaIO_4$	8 h, RT Using ultrasonic radiation Organic solvent-free	AA: 62% PA: 98%	62
	8	Oleic acid Methyl oleate	Pelargonic acid Azelaic acid	A ruthenium-based POM: [Ru(2,6-dipicolinate)$_2$]/H_2O_2	24 h, 80 °C	PA from OA: 59% PA from MO: 81%	63, 64
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 °C	AA: 15% PA: 15%	65
	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 °C	MA: 19% PA: 20%	65
	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 °C	MB: 41% PA: 54%	65
	12	Oleic acid	Pelargonic acid Azelaic acid	PCWP/H_2O_2	5 h, 90 °C Organic solvent-free	AA: 57%	43
	13	Oleic acid	Pelargonic acid Azelaic acid	A peroxo–tungsten complex with Cs^+ as PTA/H_2O_2	10 h, 90 °C Organic solvent-free	AA: 28%	43
	14	Oleic acid	Pelargonic acid Azelaic acid	PCWP/H_2O_2	4 h, 80 °C	AA: 86% PA: 82%	66
	15	Methyl oleate	Pelargonic acid Methyl azelate	A peroxo–tungsten complex with Aliquat® 336 as PTA/H_2O_2	4 h, 85 °C Organic solvent-free	MA: 83% PA: 84%	67
	16	Methyl ricinoleate	Methyl azelate Hydroxynonanoic acid	A peroxo–tungsten complex with Aliquat® 336 as PTA/H_2O_2	4 h, 85 °C Organic solvent-free	MA: 85% PA 84%	67
	17	Oleic acid	Pelargonic acid Azelaic acid	A peroxo–tungsten complex with Aliquat® 336 as PTA/H_2O_2	5 h, 80 °C	AA: 79% PA: 82%	68
	18	Oleic acid	Pelargonic acid Azelaic acid	PCWP/H_2O_2	5 h, 85 °C Organic solvent-free	AA: 81% PA: 86%	42
	19	Methyl oleate	Nonanal	A peroxo–tungsten complex with Alk-PEI as PTA/H_2O_2	24 h, 70 °C Organic solvent-free	NL: 97%	69

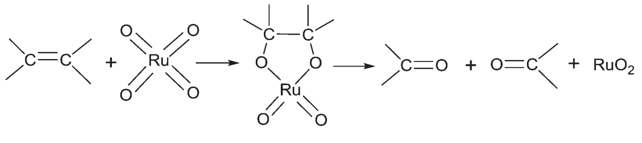
[a] RT: room temperature. [b] The best result of each work is presented in the table. [c] PA: pelargonic acid, AA: azelaic acid, NL: nonanal, OA: oleic acid, MO: methyl oleate, ElA: elaidic acid, ErA: erucic acid, ME: methyl erucate, MA: methyl azelate, and MB: methyl brassylate.

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 4, were 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.

3.2.5. Ruthenium. Ruthenium is one of the oldest transition metals employed in the oxidative cleavage of C–C double bonds.[50,51,57] 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 epoxides or hydroxylated intermediates. This mechanism is shown in Scheme 7, (mechanism I in Scheme 5) and involves the formation of a cyclic perruthenate ester.[58] RuO_4 can also be used as a 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. In contrast to 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.[59]

Optimization of the methods presented by Zimmermann *et al.*[60] 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 in 81 and 96% yields, respectively, in a mixture of acetonitrile and water (Table 4, entry 6).[61] 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 4, entry 7).[62]

Recently, Behr and his co-workers tried to eliminate the secondary oxidant $NaIO_4$ using Ru-based metal complexes (Table 4, entry 8).[63,64] They demonstrated that the presence of an excess amount of a ligand and the *in situ* formation of the complex makes the oxidative cleavage possible with only hydrogen peroxide. The procedure includes the use of $Ru(acac)_3$ as a precursor and 2,6-dipicolinic acid as a ligand in a mixture of *tert*-butyl alcohol and water, and reaction was carried out at 80 °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 salts and $NaIO_4$. This is mainly because of the higher number of side reactions in this case.



Scheme 7 Oxidative cleavage of C–C double bonds by RuO_4, including the formation of a cyclic perruthenate ester.[58]

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

3.2.6. Tungsten. Since the mechanism of W-based catalytic oxidative cleavage of olefins (Scheme 6) includes the formation of epoxides and hydroxylated intermediates, performing the reaction in one step and minimizing the formation of byproducts are very important aspects. Oakley *et al.* reported using tungsten oxide (in hydrated form, tungstic acid, H_2WO_4) as a catalyst for the oxidative cleavage of oleic acid, methyl oleate and methyl erucate (Table 4, entries 9, 10 and 11).[65] The catalytic system includes the use of $Co(acac)_3$, and *N*-hydroxyphthalimide (NHPI) in O_2 and H_2O_2 as oxidants in order to over-oxidize the intermediate diols into carboxylic acids. This system provides a one-pot reaction and uses a limited amount of H_2O_2, but the production yields are very low (see Table 4).

Many efforts have been made to eliminate the secondary oxidants in the oxidative cleavage of olefins during the last few 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 greater number of applications of tungsten compounds as catalysts in the oxidation of UFAs in recent years. Moreover, W is cheaper and less toxic when compared to Ru and Os.

Recently, catalytic systems that involve W-based POMs have been investigated significantly. Such systems mainly include a phase transfer agent (PTA) (usually a quaternary ammonium salt) to increase the solubility of the 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 a 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 $\{C_5H_5N{-}C_{16}H_{33}\}_3\{PO_4[WO(O_2)_2]_4\}$.

Turnwald *et al.* reported the one step solvent-free oxidative cleavage of oleic acid to produce azelaic and pelargonic acids using PCWP (Table 4, entry 12).[43] After a 5 h reaction at 90 °C, the yield of azelaic acid was 57%. Increasing the reaction time to 10 h led to a higher yield (64%), but the catalyst was decomposed. The substitution of the counter-ion cetylpyridinium with Cs^+ (the complex tris (caesium) tungstophosphate) increased the thermal stability of the complex, but the obtained yield was lower, even after a longer reaction time (28%) (Table 4, entry 13).

With the same catalytic system, and only altering the amounts of the initial reactants, Pai *et al.* reported a higher yield (86% for azelaic acid) in an even shorter time (4 h) and lower temperature (80 °C) (Table 4, entry 14).[66] Changing the phase transfer agent, Khlebnikova *et al.* employed another catalytic peroxo–tungsten complex system to perform oxidative cleavage on the methyl esters of fatty acids (Table 4, entries 15 and 16).[67] 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 see 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 4, entry 17).[68] Performing the reaction at 80 °C for 5 h resulted in the production of azelaic acid with a 79% yield, which was slightly lower than that obtained using CPC (entry 14).

In order to obtain a more precise comparison between the performances of the different phase transfer agents in the oxidation of UFAs, Godard *et al.* employed four PTAs including CPC, Aliquat® 336, tetra butyl and tetra octyl ammonium chloride in the same oxidative cleavage of oleic acid (Table 4, entry 18).[42] CPC and the subsequent catalytic complex system PCWP were found to give the best results, and further optimization of the reaction conditions led to the production of azelaic and pelargonic acid in 81 and 86% yields, respectively, in an organic solvent-free system and in 5 h at 85 °C.

A new type of phase transfer agent was introduced in the work that was done by Haimov *et al.* (Table 4, entry 19).[69] 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 a reaction temperature of 70 °C and a 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 a lack of recycling ability, metal contamination, poor control of selectivity, and the 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 is favorable in terms of solving these problems.

3.3. Heterogeneous catalysts

Employing solid catalysts in liquid phase reactions has been always proposed as a promising method in the large-scale production of chemicals. The most important feature of heterogeneous catalysts is their ability to be recycled, owing to the ease of their recovery, which makes them able to be commercialized. In spite of many positive aspects, the application of heterogeneous catalysts in reactions with oils and fats has been restricted, mainly because of the poor reactant/catalyst contact which, in turn, arises from pore diffusion limitations or low active site availability. This is a major reason why heterogeneous catalytic systems for the oxidative cleavage of UFAs have been remarkably less documented. The results of these systems are summarized in Table 5.

Noureddini *et al.* investigated the liquid-phase catalytic oxidation of oleic acid with hydrogen peroxide in the presence of different metals or metal oxides in supported and unsupported cases (Table 5, entries 1 and 2).[48] They reported the production of azelaic and pelargonic acid as the major products and some by-products, including mainly 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 application. It is believed that the metal oxide is responsible for catalysing the oxidation of UFAs. Therefore, in the case of using pure metals, they firstly have to be oxidized to metal oxides to then catalyze the reaction. This multi-step process reaction requires larger amounts of oxidant. Supported tungsten oxide showed the highest conversion at a reaction temperature of 130 °C. About 79% of the initial oleic acid was converted after 1 h, 96% after 2 h, and 98% after 3 h and longer. One interesting point mentioned in this work is that during the reaction, the concentration of the main products, azelaic and pelargonic acid, showed an increasing trend until a maximum was reached, and the concentration then started to decrease. This arises from the degradation of azelaic and pelargonic acids in the prolonged heating process. The time at which the maximal concentration of desired product was obtained depended on the type of catalyst used. For supported tungsten oxide, the 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 the scale up of the reaction. Another interesting point in this work is the effect of the support. Initially, the higher pore diffusion resistance of the porous support led to a lower catalytic activity of the supported tungsten oxide in comparison with the unsupported form, but only in the early stages of the reaction. After about 20 min, a significant increase in the catalytic activity of the supported catalyst was obtained while the activity of the unsupported catalyst stayed constant throughout the 1 h reaction. The selectivities of azelaic and pelargonic acid in the case of the supported catalyst (32 and 36%, respectively) were slightly higher compared to the unsupported catalyst (30 and 29%, respectively). Finally, it is clear that the conversions, in both cases of the supported and unsupported catalysts, are not as high as what was obtained in the homogeneous catalytic oxidation of oleic acid.

In general, the catalytic activities of transition metals are attributed to the formation of strong Brönsted acid sites.[70–72] It has been mentioned in the literature that tungsten oxide

Table 5 Different heterogeneous catalytic systems reported for the oxidative cleavage of UFAs and their derivatives

Metal	Entry	Reactants	Main products	Catalyst/oxidant system	Reaction conditions[a]	System efficiency[b,c]	Ref.
W	1	Oleic acid	Azelaic acid Pelargonic acid	Tungsten oxide supported on silica/H_2O_2	1 h, 130 °C	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 °C	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 °C	Conversion >95% Yield (AA): 32.4% Yield (PA): 32.2%	89

[a] RT: room temperature. [b] The best result of each work is presented in the table. [c] AA: azelaic acid and PA: pelargonic acid.

has very strong Brönsted acid sites either as a bulk oxide or when supported.[73–78] Although the nature of active sites and their modifications are currently a controversial subject, it is believed that the acid sites in the structure of tungsten oxide are strongly dependent on the synthetic procedure, such as the tungsten precursor, the loading amount of the oxide, and thermal treatment.[79,80] Interestingly, tungsten oxide (WO_x) has a large number of stable oxidation states which enable a variety of properties and morphologies for catalytic applications in many chemical reactions.[81,82] WO_x mainly includes WO_3 (yellowish), $WO_{2.9}$ (bluish), $WO_{2.72}$ (violet), and WO_2 (brownish).[83]

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 diameters of less than 2 nm, (ii) mesoporous materials with pore diameters between 2 and 50 nm and (iii) macroporous materials with pore diameters larger than 50 nm.[84] Microporous zeolites, which generally have a 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 reactions with oils and fats because of the relatively large molecular size of oleochemicals. For example, employing zeolites (with pore size less than 1.5 nm (ref. 85)) as a catalyst in the oxidative cleavage of oleic acid (molecular size of about 2 nm (ref. 86)) does not seem favorable due to the lower dimensionality of the interaction between the components and the catalyst surface. On the other hand, the catalytic activity of macroporous materials is poor as a 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.[87] This type of porous material has shown potential applications as either catalysts or supports in liquid-phase reactions of oils and fats.[35] A comprehensive review on the catalytic applications of mesostructured materials has been presented in our previous work.[88]

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 5, entry 3).[89] The reaction was performed at 80 °C for 8 h. Mesoporous MCM-41, containing chromium, converted more than 95% of the initial oleic acid with almost the same product yields (32.4% for azelaic acid, and 32.2% for pelargonic acid) as 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 the insufficient selectivity towards azelaic and pelargonic acids, due to the production of C_6–C_{10} di- and monocarboxylic acids as by-products.

While the 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 catalysts is a big obstacle towards their commercialization. Tackling this obstacle requires some improvements in the structures of solid catalysts. An advanced heterogeneous catalytic system should be developed that includes on one hand the advantages of homogeneous catalysts, and on the other hand, the recycling ability of heterogeneous catalysts. NP-based catalysts seem to be most suitable for this purpose, since it has been shown that they can act like homogeneous catalysts in the reaction medium, insofar as that sometimes, discriminating between 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.[90] Hopefully, it can be said that the homogenization of heterogeneous catalysts in order to combine the best properties of both homogeneous and heterogeneous catalysts could be possible by employing NP-based catalysts.

3.4. Nanoparticle-based catalysts

Owing to their naturally high surface-to-volume ratio and quantum size effects, NPs demonstrate unique properties

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‡ International Union of Pure and Applied Chemistry.

which make them prominent compared to larger particles or bulk materials for catalytic applications.[91–99] This can be confirmed by the fact that NP-based catalysts have, generally, exhibited higher catalytic activities 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 CO oxidation.[100] In spite of this, curiously, only a few research works have employed NPs as catalyst in the oxidative cleavage of UFAs (Table 6). 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 6, entry 1).[101] Their results showed that applying this catalytic system for UFAs, however, was not favorable. While full conversion was obtained for alkene 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 a supported gold catalyst and molecular oxygen as oxidant by Kulik *et al.* (Table 6, entry 2).[19] The 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 the 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 °C, yielding 86% azelaic acid and 99% pelargonic acid. The main drawback of this system was the significant decrease in the catalytic activity after catalyst recovery. During two recycling experiments using the Au/Al_2O_3 catalyst, considerable decrements were observed in the catalyst activity; the conversion decreased from 94% to 77%, and production yields of azelaic and pelargonic acids decreased by approximately 30%. Since Au is an expensive metal, this weak recovery potential prevents commercialization of gold-based heterogeneous catalytic systems.

Exploitation of the interesting and unique properties of NP-based catalysts in the oxidative cleavage of UFAs has been sparsely investigated in the literature. The two above-mentioned papers, which are the only works done in this field, to our knowledge, seems curiously insufficient. On the other hand, thanks to the explosive development of nanomaterials science, new breakthroughs in nanocatalysis are appearing at a fast rate, some of which have been reviewed in our recent feature article.[102] Further work, therefore, seems to be required in order to push the use of NP-based catalysts towards 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.

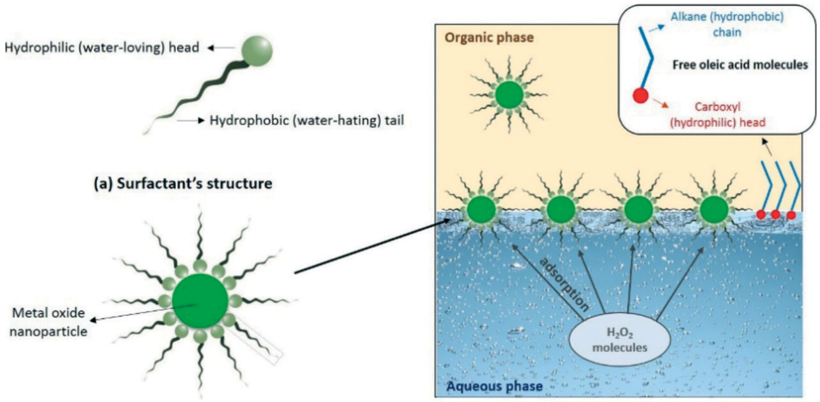
3.4.1. Performance enhancement of NP-based catalysts in oxidative cleavage of UFAs: outlook. One strategy to increase the catalytic performance of NPs in some reaction mediums is by capping their surfaces with a surfactant. This increase, however, depends on several parameters such as the surface properties of NPs, the type and amount of surfactant, and the phases present in the reaction and their miscibility. Using a surfactant, not only can the size and shape of NPs be controlled during the synthesis,[103] but a better dispersion of NPs in the liquid medium of oils and fats reactions could also result, due to the fact that surfactants can oppose van der Waals forces. In this way, the aggregation of particles will be prevented and, consequently, the catalytic activity of the catalyst will not decrease during the reaction.[104] 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. The 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 the NPs can increase their dispersion.

To better illustrate the role of the surfactant, Scheme 8 shows the performance of surfactant-capped nanoparticles (SCNPs) as catalysts in the oxidative cleavage of oleic acid, as an example for UFAs, with hydrogen peroxide. The surfactant capped on the surface of the metal oxide NPs can be oleylamine, oleic acid or other similar chemicals. Having both a hydrophilic head and a hydrophobic chain,

Table 6 Different semi-heterogeneous (nanoparticle-based) catalytic systems reported for the oxidative cleavage of UFAs and their derivatives

Metal	Entry	Reactants	Main products	Catalyst/oxidant system	Reaction conditions[a]	System efficiency[b,c]	Ref.
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%	101
Au	2	9,10-Dihydroxystearic acid	Azelaic acid Pelargonic acid	Gold nanoparticles supported on alumina/O_2	4.33 h, 80 °C	Conversion >80% Yield (AA): 86% Yield (PA): 99%	19

[a] RT: room temperature. [b] The best result of each work is presented in the table. [c] NL: nonanal, M9-ON: methyl 9-oxononanoate, AA: azelaic acid, and PA: pelargonic acid.



(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 8 Schematic illustration for SCNPs as efficient nanocatalysts. (a) Surfactant molecule, (b) hydrophobic SCNP surface and (c) performance in the biphasic oxidative cleavage of oleic acid using H_2O_2 as oxidant. The presence of the surfactant (i) contributes to the stability of the emulsion, (ii) prevents aggregation of the NPs, and (iii) makes the recovery of the catalysts easier.

surfactants reinforce the stability of an emulsion in a biphasic reaction consisting of an aqueous phase and an organic phase. It should be noted that free molecules of the reactant, oleic acid, would also contribute towards the emulsion stability, because they can be situated at the interface due to them possessing hydrophilic and hydrophobic parts. Since the reaction mostly takes place at the interface, a 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 the hydrophilic surface of the transition metal oxides immerses them in the aqueous phase, the hydrophobic chain of the surfactant drags the SCNPs towards the organic phase. The presence of SCNPs at the interface will make the adsorption of H_2O_2 molecules from the aqueous phase easier. Consequently, a kind of peroxo–metal complex will be formed at the surface of the NPs. On the other hand, the hydrophobic chain of the surfactant attracts the oleic acid molecules, as the main reactant, from the organic phase, and then the reaction will occur on the surface of the SCNPs. The peroxo–metal complex, as discussed in the section on homogeneous catalysts, is believed to be able to efficiently oxidize the olefins. Due to the presence of SCNPs in the interface, as soon as the consumption of molecules of H_2O_2 and the formation of a peroxo species on the NP surface occurs, another molecule of hydrogen peroxide will be adsorbed on the surface and this process will be continuously repeated. In fact, the role of the phase transfer agent (PTA) in homogenous systems, to which the high reaction efficiency is attributed, can be played by the surfactant in heterogeneous systems.

By 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 occurred 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, and would result in the formation of fewer by-products, easier separation of the products and a lower operating cost.

3.4.2. Recovery of nanoparticles. The presence of the surfactant on the surface of metal oxide NPs provides another substantial privilege 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.[103] Based on the hydrophobic or hydrophilic properties of the surface of the NPs, changing the solvent from nonpolar, *e.g.* toluene, to polar, *e.g.* ethanol or *vice versa* will result in the precipitation of the SCNPs. This method is shown in Fig. 5. ZrO_2, TiO_2, Au and Cu particles capped by oleic acid are highly dispersed in toluene and make a clear solution (Fig. 5a), while they will be precipitated in ethanol medium (Fig. 5b).

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 made in this field have been well documented in several review papers.[105–111] A facile, highly efficient, economical and environmentally benign method that has 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[112–114] has led to the development of 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.*[115] and Rossi *et al.*,[116] respectively. A thorough review of the applications of magnetically recyclable nanocatalysts has been

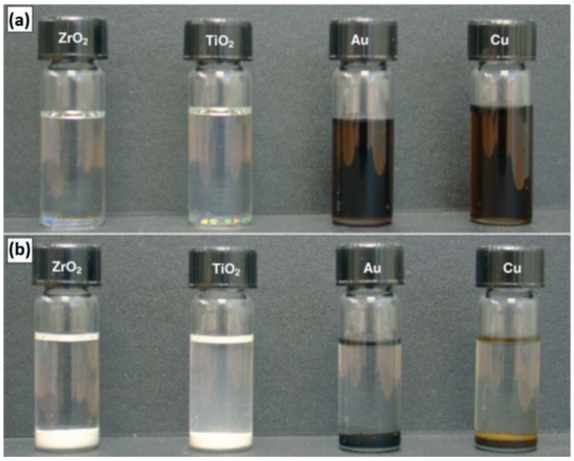


Fig. 5 (a) Oleic acid-capped NPs of some metals/metal oxides dispersed in toluene (clear/transparent solutions) and (b) those NPs precipitated with excess ethanol.[103]

presented in the recent and precious review paper of Wang and Astruc.[117] 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 the oxidative cleavage of UFAs seems to be of great interest.

4. Conclusion and perspective

As has been shown here, many efforts have been made in the context of the high demands for the development of sustainable and green chemistry in order to find an alternative to the hazardous ozonolysis of UFAs, which is the current 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 review indicates that several catalytic systems in three general classes of homogeneous, heterogeneous, and semi-heterogeneous (NP-based) catalysts 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 greater emphasis placed on Ru and particularly W.

Homogeneous catalysts, on which more research has been done, show excellent conversion and selectivity. However, their large-scale application has always been restricted due to the lack of catalyst recovery. Curiously, the use of heterogeneous catalysts with recycling ability has been scarcely reported, which could be ascribed to their lower conversion compared to homogeneous catalysts. This is mainly because of the low catalyst/reactant contact resulting from either low active site availability or pore diffusion limitations. Even mesostructured catalysts, which were previously recommended for reactions with oils and fats due to the higher dimensionality of the interaction between the components and the catalyst surface, could not significantly change the reaction conversion and selectivity. The available results for NP-based catalysts, although very rare, confirm that they could improve the performance of solid catalysts. Having insufficiently explored nanocatalysis in the oxidative cleavage of UFAs, further works in this field are called for. It even makes more sense given the fact that the surface properties of metal oxide NPs provide great promise in terms of their further modifications, which can increase their catalytic efficiency in the biphasic oxidative cleavage of UFAs. Interestingly, considering the high degree of dispersion of SCNPs, one can properly assume them to be proposed as the frontier of homogeneous and heterogeneous catalysts that can exploit the best features of both simultaneously.

Good dispersion of a catalyst in a solvent, despite increasing the catalytic activity, can be a double edged sword if it makes the separation of the catalyst from the product complicated. Owing to recent advances, however, the recovery of NP-based catalysts, particularly SCNPs, is possible *via* facile and highly efficient methods. Considering the fast pace of progress in catalysis, it is definitely only a matter of time before an environmentally benign process for the oxidative cleavage of UFAs in industry is achieved.

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