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Catalytic oxidative cleavage of unsaturated fatty acids and their derivatives into valuable products for industrial applications

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Oils and fats of vegetable and animal origin have recently attracted a growing interest as renewable raw materials in oleochemical industries. This attention arises from not only the 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 applicably valuable materials in different industries. This oxidation process is so-called oxidative cleavage, since during the reaction carbon-carbon double bond(s) get cleaved. Although oxidative cleavage of UFAs has been now developed using ozonolysis, hazardous problems associated with use of ozone is still a controversial challenge. Replacing ozone with a more benign oxidant requires using an active catalyst. Different combinations of several transition metals like Os, Co, Mo, Cr, Au, Mn, Fe, Ru, and W have been investigated for this purpose, with much emphasis on the latter two, particularly tungsten. In this paper, we have tried to review all of the recent works regarding 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 semiheterogeneous (nanoparticle (NP)-based) catalysts. Important features such as catalytic activity and recoverability with specific respect to commercializing viewpoint are discussed in a critical fashion for each class to be able to reasonably plan future works. The unique and interesting properties of NPs propose them as the frontier of homogeneous and heterogeneous catalysts that can exploit the best features of the both simultaneously. These properties along with the recent breakthroughs which would interestingly increase the performance of NP-based catalysts in the biphasic oxidative cleavage reaction of UFAs, are also reviewed.

1.Introduction: applications of 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 [1]. Understandably, the shortage in the petroleum reservoirs in the near future is a worldwide crisis which can be confirmed by Figure 1. It shows the oil and gas production profiles in the past and future for the whole earth which was published in an ASPO[†] Newsletter in 2009 [2]. As it can be seen, starting from 2010, a downward trend is obvious in the oil and gas production.

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 [3, 4]. Oils and fats have chemical structures giving them a potential for the 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 modifications. Moreover, they are abundant in nature, biodegradable, and have nontoxic properties that make them promising candidate for replacing 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 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[‡] would be the best [6]: "Lipids are fatty acids and their derivatives, and substances related biosynthetically or functionally to these compounds."

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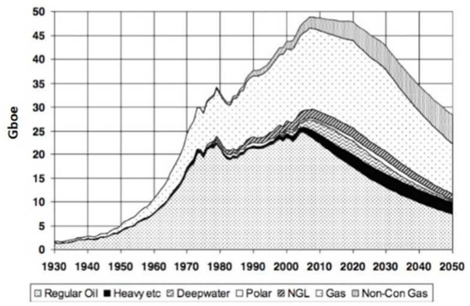


Figure 1 Production profiles of oil and gas based on 2008 (Gboe: gigabarrels of oil equivalent) [2].

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. 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 [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 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 1 [8]. 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. 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 1, however, confirms the increasing rate of non-food use of oils and fats in the world, in particular during the last decade.

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 [9]. The lipids are made from triglyceride, which, in turn, consists of glycerine and three fatty acids (Figure 2) [10]. The triglycerides which form animal fats, typically have more saturated fatty acids while those constitute vegetable oils, have more unsaturated fatty acids [11].

Table 1 Food and non-food consumptions (million tons and %) of nine major vegetable oils between 1999/00 and 2011/12 [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

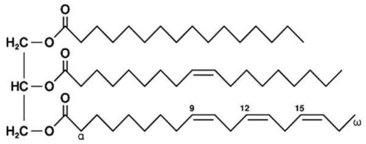


Figure 2 Typical example of a lipid structure with glycerol and three fatty acids (palmitic acid, oleic acid, and alpha-linolenic acid, from top to bottom) [10].

Decomposition of the 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 that is scarcely less than that of petrochemicals [9, 13]. Polymer is one of the most important industries which can exploit lipids and convert them into valuable products. Although oils and fats have been used in polymer for many years, their applications are currently undergoing rapid development to extend 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 polymer (dicarboxylic acids for polyesters or polyamides) [14]. Long-chain dicarboxylic acids can be used for the latter application. In general, dicarboxylic acids, HOOC(CH2)nCOOH (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

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

	Product/use	**Source**
Polymer materials		
- Polymerized soybean oil, castor oil	Drying oil	Soybean oil, castor oil
- Polymerized linseed oil	linoleum	Linseed oil
Polymer additives		
- Epoxides	Stabilizers, plasticizers	Soybean oil
- Soaps (Ba/Cd, Ca/Zn)	Stabilizers	Stearic acid
- Fatty acid esters or amides, waxes	lubricants	Rapeseed oil
Building blocks for polymers		
- Dicarboxylic acids	Polyamides, polyesters, alkyd resins	Tall oil, soybean oil, castor oil
- Ether/ester polyols	Polyurethanes	Sunflower oil, linseed oil Oleic acid

density, and more 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].

Dicarboxylic acids are produced from petrochemical feedstock (e.g., production of adipic acid from the multistage butadiene oxidation [18]). Also, ring-opening oxidation of cyclic compounds is another route to produce these chemicals [19]. Biotechnology techniques have been also developed for this purpose [20] which are not of the subject of this paper. 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 [19] and azelaic acid which is produced from 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].

Our interest in this review is focused on the production of mono- and dicarboxylic acids through oxidation of oils and fats components. In what follows, the basic concepts and seminal studies of UFAs and their reactions, focusing on oxidation, will be briefly summarized. Then, the recent progresses made in the optimization of catalytic oxidative cleavage of UFAs will be discussed.

2.Fatty acids and their reactions

2.1. Fatty acids: a primer

As mentioned earlier, the 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: hydrophilic carboxyl group and hydrophobic alkane chain.

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 [23].

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) [6]. Table 3 shows the common fatty acids extracted from animal and plant origins with their structures and different nomenclature systems [6, 24].

The most abundant mono-UFA in nature is oleic acid (C_{18}) [25] 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 $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$) [26]. 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 [27]. 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 [28-30]. In addition, they are abundantly present in many animal fats such as chicken and turkey fat and lard [31]. Oleic acid has numerous applications such as a component of human diet (in triglyceride form), major component of soaps (in sodium salt form), in pharmaceuticals [26], and as one of the most industrially important applications, production of carboxylic acids via ozonolysis [21].

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

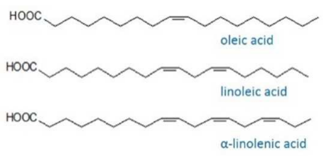


Figure 3 Different C_{18} mono and poly-UFAs.

Table 3 Common fatty acids of animal and plant origins; structures and nomenclature systems [6, 24].

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)

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 [10].

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 [10, 14]. However, because of wider range of obtainable products from the latter, progress in such reactions is highly-demanded [10]. 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 [32]. To address this problem and improve the economic aspects, optimization of reaction conditions and, also, employing efficient catalysts should be considered. 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 widely reviewed in the literature [10, 13, 25].

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 paper focuses. Herein, two different oxidation pathways of UFAs are discussed.

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 [33]. The term epoxide can be defined as a cyclic ether which has three ring atoms (Figure 4) 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 [34].

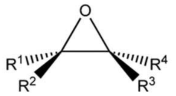
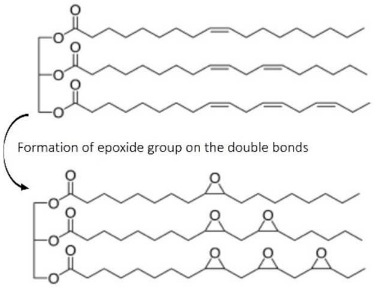


Figure 4 A generic epoxide.

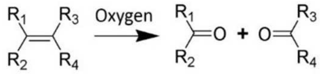
Several methods have been reported for epoxidation of unsaturated fatty compounds such as *in situ* performic acid procedure, epoxidation with aldehydes and molecular oxygen, dioxiranes, H_2O_2/tungsten heteropolyacids, H_2O_2/methyl trioxorhenium, and enzymatic epoxidation [9, 10, 13]. Scheme 1 shows 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 [35, 36], plasticizers [35], flame retardants [10], heat stabilizers [10], antioxidants and light stabilizers [10], lubricants, cosmetics and biochemical applications [37, 38], 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 reasonable method to produce dicarboxylic acids.



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 [39].



Scheme 2 A general oxidative cleavage process.

Oxidative cleavage of olefin typically occurs by ozonolysis. 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 [39]. Currently, azelaic acid (C9, dicarboxylic acid) as a very industrially important chemical is produced in large-scale via ozonolysis of oleic acid (Equation 1). Pelargonic acid (C9, monocarboxylic acid) is obtained as a co-product but also a valuable chemical [19]. These type of saturated acids that have short and odd hydrocarbon chains are rare in natural resources [40]. On the other hand, they are very attractive initial materials for the development of numerous bio-based products [41, 42]. 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 [40, 41]. Pelargonic acid is an intermediate in the production of lubricants, plasticizers, perfumes, herbicides, fungicides, resins [41, 43].

$H_3C(CH_2)_7CH{=}CH(CH_2)_7COOH + 4O \rightarrow H_3C(CH_2)_7COOH + HOOC(CH_2)_7COOH \quad (1)$

These two valuable products are obtained only in the case of over-oxidation, whereas partial oxidative cleavage of oleic acid produces aldehyde nonanal and 9-oxononanoic acid [44] (Scheme 3). Presence of strong oxidants such as ozone favors over-oxidation.

Although the ozonolysis of oleic acid has shown high conversion and selectivity [19, 21, 40, 41, 45], hazardous problems associated with the use of ozone have always been a challenge [3]. 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 [45, 46]. Therefore, a new alternative method with safer and economically more viable process for the production of dicarboxylic acids from oxidation of UFAs is of great interest to the industrials. The dangerous ozone should be replaced by a safe and green oxidant. In general, oxidants are the source of oxygen during the oxidation reaction. 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 [34, 40, 45, 47]. 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 [40, 41].

3. Transition metal-based catalytic oxidative cleavage of unsaturated fatty acids

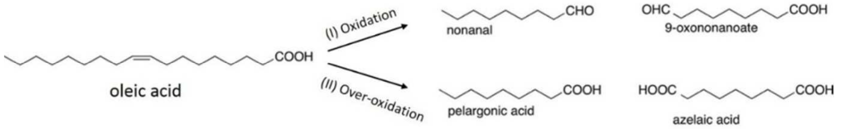
Transition metal-based catalytic systems are considered to be most suitable for the oxidative cleavage of olefins. Their high catalytic activities make it possible to use more benign oxidants. Osmium, ruthenium, and tungsten are three metals that have attracted the most attentions for oxidation of unsaturated 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 catalyst. 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.

We have tried to review all of the recent works regarding use of different catalyst/oxidant systems in the oxidative cleavage of UFAs and their derivatives. In this section, after introducing the proposed reaction mechanisms, results of previous works will be discussed in three groups: homogeneous, heterogeneous and semiheterogeneous (NP-based) catalysts. It should be noted that bio-based catalysts are not discussed in this paper. Although more general topics like applications and reactions of oils and fats have been widely investigated [3, 10, 13, 14], the oxidative cleavage of alkenes and UFAs have poorly been reviewed, in particular the latter [34, 44, 48].

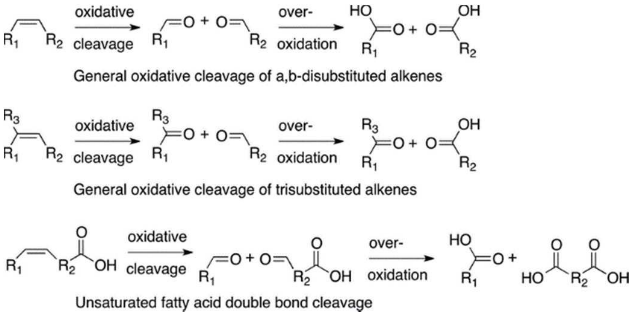
3.1. Mechanisms of the reaction

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 following by incorporation of oxygen atoms into two produced sections (see Scheme 4). Aldehydes and ketones are often the initial products whereas over-oxidation yields in the production of carboxylic acids [45].

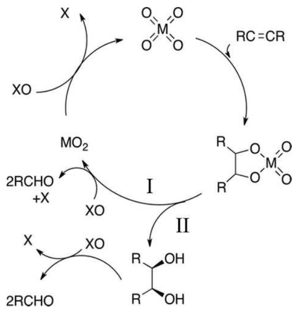
Three mechanisms have been reported in the literature for catalytic oxidative cleavage of olefin. The first mechanism, which is shown in Scheme 5, describes a catalytic system based on transition metals tetroxide such as RuO4 and OsO4 [44, 49]. These oxides can be formed during the reaction also, and in the presence of oxidants, when their corresponding metal salts are used as catalysts [50, 51]. In terms of selectivity, RuO4 indicates better performance compared to OsO4, because the reaction mechanism for RuO4 does not involve dihydroxylated intermediates (Scheme 5 mechanism I) and immediately after the formation of metal diester as the main intermediate, the aldehydes will be formed, while OsO4 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 [44]. However, the toxic properties of osmium are stronger than ruthenium.



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

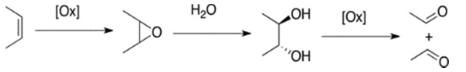


Scheme 4 Oxidative double bond cleavage of alkenes and UFAs to aldehydes, ketones, and carboxylic acids [44].



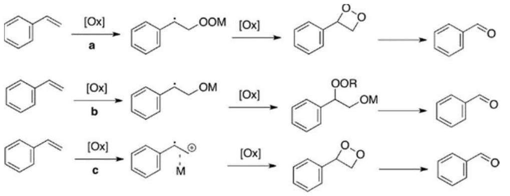
Scheme 5 First mechanism of oxidative cleavage of olefins (OX: oxidant) [44, 49].

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 6, is mainly ascribed to the presence of tungsten compounds as catalyst [44].



Scheme 6 Second mechanism of oxidative cleavage of olefins (OX: oxidant) [44].

The last mechanism which is developed for styrene derivatives includes the formation of benzyl radical after attack of the metal oxides to the reactant molecule. This mechanism, Scheme 7, has different sub-mechanisms depending on the type of metal oxides [44]. However, because cyclic olefins are not of the subjects of this research, more detailed discussion is beyond the scope of this paper.



Scheme 7 Third mechanism of oxidative cleavage of olefins (OX: oxidant) [44].

The mentioned mechanisms were proposed for all the unsaturated hydrocarbons which have C-C double bond(s). For UFAs, however, the mechanism of catalytic oxidative cleavage 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 (third mechanism, Scheme 7). Further work to propose a mechanism that considers these difficulties, therefore, should be encouraged.

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 the lab scale requirements such as better understanding of the reaction mechanism and, thus, have less focused on industrialization aspects. In fact, that is why use of homogeneous catalysts has been generally preferred in the literature. While heterogeneous catalysts are of the 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 4 summarized the details of reported homogeneous catalytic systems for the oxidative cleavage of UFAs and their derivatives.

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 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 catalyst, its applications have been restricted due to the significant toxic properties of Os.

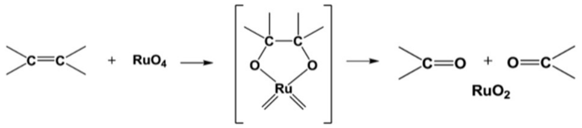
3.2.2. Cobalt. Diol oxidation can also be done with the cobalt polyoxometallate (POM) as shown by Santacesaria (Table 4, entry 2) [54]. Using cobalt acetate, they reported a POM based on the mixture of cobalt and tungsten. As soon as hydrogen peroxide is added to the system, the POM catalyst can be formed in situ which is introduced to be H6CoW12O40. However, the production yield of azelaic acid from oleic acid using this catalytic system is not enough high (52.5%).

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) [41]. Using 2,6-dipicolinate as ligand, the active oxo-peroxo complex $[MoO(O_2)(2,6\text{-dipicolinate})](H_2O)$ could be formed as the catalyst which resulted in 82% yield of azelaic acid after 5 h at 90 °C, albeit the large amount of H_2O_2, which should be employed, make 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 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 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 $[Fe(OTf)_2(\text{mix-BPBP})]$ 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 epoxidation hydrolysis and diol cleavage (second mechanism, Scheme 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 4, entry 5). The complex used for this purpose was $[Fe(OTf)_2(\text{6-Me-PyTACN})]$ 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 the different substrate conversion and product distribution. The best obtained yields, which are presented in Table 4, 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.

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 [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 epoxide or hydroxylated intermediates. This mechanism is shown in Scheme 8, (mechanism I in Scheme 5) and involves the formation of a cyclic perruthenate ester [58]. 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 [59].



Scheme 8 Oxidative cleavage of C-C double bonds by RuO_4 including the formation of cyclic perruthenate ester [58].

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 with 81 and 96% yield, respectively, in the 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 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 °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 is less than Os, is another problem. Considering scale up aspects, therefore, an alternative transition metal is desirable for catalytic oxidation of olefins.

3.2.6. Tungsten. Since the mechanism of W-based catalytic oxidative cleavage of olefins (Scheme 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 4, entries 9, 10 and 11) [65]. 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 the limited amount of H_2O_2, but the production yields are very low (see Table 4).

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 much more 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 cause 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 4, entry 12) [41]. After 5 h reaction at 90 °C, 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 4, 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 °C) (Table 4, entry 14) [66]. 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 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 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 4, entry 17) [68]. Performing the reaction at 80 °C 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 4, entry 18) [40]. 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 °C.

A new type of phase transfer agent is 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 the reaction temperature of 70 °C and relatively long reaction time (24 h) in the absence of organic solvent.

The majority of homogeneous catalytic systems reported here have the conversions of more than 90%. Nevertheless, their applications in industry are restricted as a result of the 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.

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 commercialize. 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 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 the cases of supported and unsupported (Table 5, entries 1 and 2) [47]. They reported the production of azelaic and pelargonic acid 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 catalysing the oxidation of UFAs. Therefore, in the case of using

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 ^{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 °C	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 °C	AA: 82%	[41]
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: $[Ru(2,6\text{-dipicolinate})_2]/H_2O_2$	24 h, 80 °C	PA from OA: 59% PA from MO: 81%	[63, 64]

Table 4 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 °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%	41
	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%	41
	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%	40
	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

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.

pure metals, firstly they have to oxidize 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 concentration of main products, azelaic and pelargonic acid, showed an increasing trend until reach 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 effect of support. Initially higher pore diffusion resistance of the porous support led to the lower catalytic activity of supported tungsten oxide in comparison with 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 acid 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 supported and unsupported catalysts, are not as high as what was obtained in 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 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 controversial subject, it is believed that the acid sites in the structure of tungsten oxide are strongly dependent on the synthesis procedure, such as tungsten precursor, the loading amount of the oxide, and the 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 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 [84]. 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 [85]) as catalyst in oxidative cleavage of oleic acid (molecular size about 2 nm [86]) 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 [87]. This type of porous materials has shown the potential applications as either catalyst or support for liquid-phase reactions of oils and fats [32]. 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 support, 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 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, disadvantage of this catalytic system is 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 commercializing them. 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 seems 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 [90]. 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.

3.4. Nanoparticle-based catalysts

Nanostructured materials have shown great achievements in different practical applications, in particular catalysis. Breaking up the common solid catalysts into the ultra-small particles would make higher contact between the catalyst and reactants, as well as better homogeneity in the liquid-phase reactions and therefore, increase the rate of reactions. 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 [91-99]. Several synthetic methods have been developed by many research groups, as well as our group, to produce uniform-sized NPs of metals/metal oxides with the abilities to control particles sizes and shapes [97-108]. Dispersion of such NPs on oxide supports is an efficient strategy to increase their stability in the reaction medium [109]. The self-assembly of monodisperse NPs into a well-defined three-dimensional nanostructure has attracted a growing interest [110-112]. Mesoporous metal/oxide NPs, particularly, could provide catalytic performance over conventional catalysts [104]. In our recent feature article, the enhancement of catalytic activity of nanomaterials with tailoring the assembly, interfaces, and porosity of diverse inorganic nanostructures has been reviewed [113].

Generally, NP-based catalysts exhibit 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 [114]. In spite of this, curiously only 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) [115]. 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 6, entry 2) [19]. 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 is 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 °C 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. During 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.

Thanks to the explosive development of nanomaterials science, new breakthroughs in the fields of synthesis and recovery of nanocatalysts are appearing at a fast rate. In the following sections, we briefly summarize the recent progresses which would be effective in the performance enhancement of NP-based catalysts for oxidative cleavage reaction of UFAs.

3.4.1.Surfactant-capped nanoparticles. One strategy to increase the catalytic performance of NPs in some reaction mediums 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 present phases in the reaction and their miscibility. In the liquid medium of oils and fats reactions, using a proper surfactant could result in better dispersion 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 [116]. 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 H2O2, on one hand and organic reactants, on the other hand provides a biphasic reaction with immiscible phases. In this circumstance, presence of a well-chosen surfactant on the surface of NPs can increase their dispersion.

To illustrate the role of surfactant better, Scheme 9 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 lied at the interface due to possessing 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 immerse them into the aqueous phase, hydrophobic chain of surfactant drags SCNPs toward the organic phase. 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, 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 in 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,

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

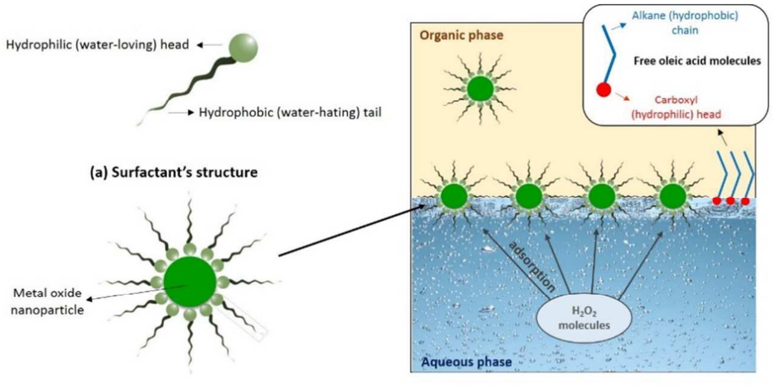
Metal	Entry	Reactants	Main products	Catalyst/oxidant system	Reaction conditions [1]	System's efficiency [2, 3]	Reference
W	1	Oleic acid	Azelaic acid Pelargonic acid	Tungsten oxide supported on silica/ H_2O_2	1 h, 130 °C	Conversion: 79% Selectivity (AA): 32% Selectivity (PA): 36%	47
	2	Oleic acid	Azelaic acid Pelargonic acid	Tungsten oxide (unsupported)/ H_2O_2	1 h, 130 °C	Conversion: 56% Selectivity (AA): 30% Selectivity (PA): 29%	47
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

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 6 Different semiheterogeneous (nanoparticle-based) 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
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%	115
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

1. RT: room temperature
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.



(a) Surfactant's structure

(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 9 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 H_2O_2 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.

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.

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 was 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 results in fewer by-products, easier separation of the products and lower operating cost. It is worth pointing out that our previous works demonstrated that using surfactant in the synthesis procedure, size and shape of the produced NPs can be controlled [104] which, in turn, would affect their catalytic performances.

3.4.2. Recovery of nanoparticles. The common solid catalysts can be efficiently separated from the reaction mixture and recovered using conventional methods such as filtration and centrifugation. These methods, however, are not convenient or enough efficient for the nanocatalysts due to the ultra-small size of the particles. In fact, separation of NPs from a complex heterogeneous system has been remained one of the major obstacles in the application of nanocatalysts. Many efforts have been done recently to circumvent this obstacle. Herein we review two interesting methods for separation of NP-based catalysts.

3.4.2.1. Magnetic separation. This method has attracted lots of attentions as a facile, highly efficient, economical and environmentally benign method for catalyst separation. Although it has long time history in the mining and food industries [117], magnetically recyclable nanocatalysts are currently undergoing rapid development. The main issue, however, is that magnetic separation is only applicable to the materials which have some intrinsically magnetic parts. Nevertheless, the high efficiency of magnetic separation compared to filtration and centrifugation [118-120] leads to developing different strategies for the preparation of either magnetic catalysts or non-magnetic catalysts immobilized onto magnetic supports, which have been separately investigated in two recent review papers. Hudson *et al.* reviewed the synthesis and applications of bare magnetic nanoparticles (MNPs) that may serve the dual role of a catalyst and a magnetically recoverable entity, focusing on iron containing compounds [121]. On the other hand, in the review paper of Rossi *et al.* emphasis has been placed on the common synthetic approaches to attach or immobilize non-magnetic catalytic active phases such as metal complexes, metal or oxide NPs, enzymes, or organocatalysts onto magnetic nanomaterials [117].

It is evident that separation by means of applying an external magnetic field requires at least one magnetic metal which can be iron [122, 123], cobalt [124] or nickel [125, 126]. Magnetic core is generally made of oxides (e.g. iron oxide) or reduced species. Figure 5 shows different strategies for the design of catalytic MNPs [121]. Incorporating another catalytically active metal is readily possible using decorated [127, 128] or core shell structures [129, 130] to expand their applications. Thanks to the rapid progress of catalytic MNPs, they have been employed in a wide range of reactions such as C-C coupling, alkyne-azide cycloaddition, hydrogenation of unsaturated compounds, reduction of nitroaromatics, oxidation, arylation, alkylation, epoxidation of alkenes, multicomponent "one-pot" synthesis, and Fenton-like reaction during the past 3 years. These applications along with the magnetically recyclable organocatalysts, biocatalysts, and photocatalysts have been thoroughly investigated in a precious review paper presented by Wang and Astruc [131].

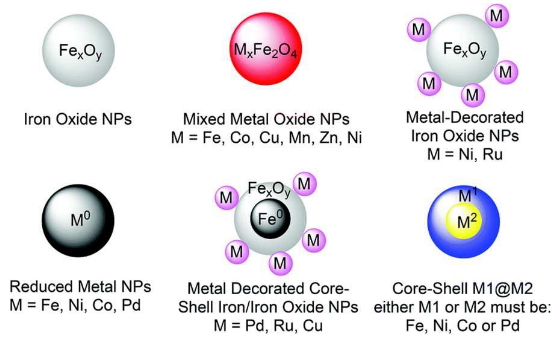


Figure 5 Different strategies for the design of catalytic MNPs [121].

For instance, magnetic separation was employed by Sun *et al.* to recover nanocatalysts [132] and mesoporous microspheres [133] with high efficiency. Immobilizing Pd (or Pt) NPs on the carbon protected magnetic cores, a nanocatalyst with well-defined core-shell nanostructures was synthesized in their work and designated as Fe_3O_4@C–Pd@mSiO_2 [132]. By applying a magnetic field, the catalyst was readily recovered (Figure 6) and reused in Suzuki-Miyaura cross-coupling reaction. Figure 7 shows the great recycling potential of this catalyst that could be reused for at least 6 cycles without considerable activity loss.

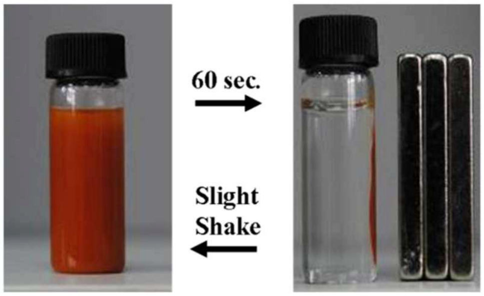


Figure 6 The magnetic separation process of the nanocatalyst Fe_3O_4@C-Pd@mSiO_2 achieved by a hand-held magnet [132].

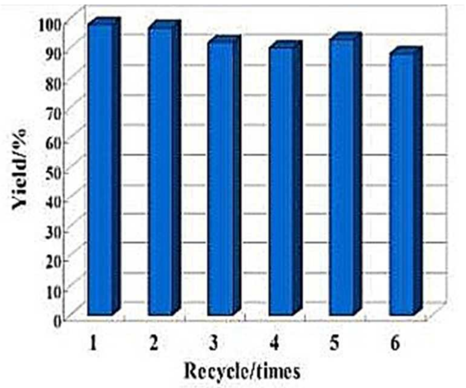


Figure 7 Reaction yield vs. number of reuse cycles for the nanocatalyst Fe3O4@C-Pd@mSiO2 in Suzuki-Miyaura cross-coupling reaction [132].

Considering the advantages of combination of MNPs and catalytic active phases in solving the problems of catalyst recovery in many reactions, extension of the scope of magnetically recyclable nanocatalysts for oxidative cleavage of oleic acid seems to be of great interest.

3.4.2.2. Surfactant-capped nanoparticles separation. Presence of surfactant on the surface of metal oxide NPs provides another facile recovery method which was developed by our research group [104]. 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 8. ZrO2, TiO2, Au and Cu particles capped by oleic acid are highly dispersed in toluene and make a clear solution (Figure 8a), while they will be precipitated in ethanol medium (Figure 8b).

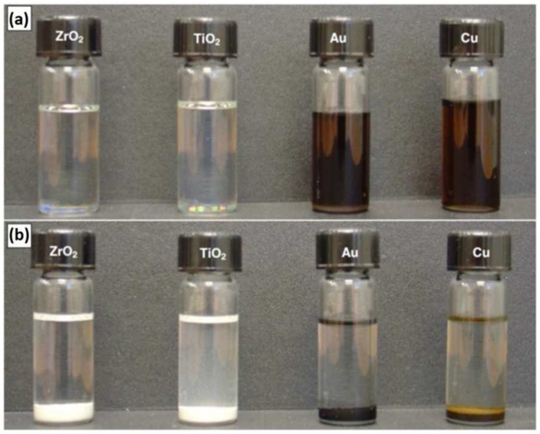


Figure 8 (a) Oleic acid-capped NPs of some metals/metal oxides dispersed in toluene (clear/transparent solutions) and (b) those NPs precipitated with excess ethanol [104].

4. Conclusion and perspective

One of the most important aspects of sustainable development in the field of chemistry is focused on using renewable materials as feedstock in industry. Among all the renewable raw materials, oils and fats of vegetable and animal origin have attracted lots of attention due to not only their special chemical structure, but also environmental reasons. They can make up a considerable proportion of consumption of petroleum materials. It makes more sense given the fact that oil and gas reservoirs are going to be depleted in near future. At present, although the main use of oils and fats is in food industries, a growing importance has been confirmed in oleochemical industries in the last decade. Polymer as an important industry, which needs petroleum feedstock, can exploit oils and fats as raw materials and converts them into the valuable products. One of these products is dicarboxylic acids which are currently produced from oxidation of UFAs via ozonolysis. The hazardous problems associated with use of ozone, however, has been always a controversial challenge. Replacing ozone with a more benign oxidant, like hydrogen peroxide, makes it necessary to employ an active catalyst in the reaction.

This review indicates that several catalytic systems in three general classes of homogeneous, heterogeneous, and semiheterogeneous (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 more emphasis on Ru and particularly W. Homogeneous catalyst, on which more researches have been done, showed excellent conversion and selectivity. However, their large-scale application have been always restricted due to the lack of catalyst recovery. Curiously, 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. Even mesostructured catalysts, which were previously recommended for oils and fats reactions 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 are very rare, confirm that they could improve the performance of solid catalysts. However, large-scale use of NP-based catalysts in oxidative cleavage of UFAs is a challenging goal yet. Thanks to the unique properties of metal oxides NPs, nanocatalysts are able to exploit the good features of homogeneous and heterogeneous catalysts. Surface properties of metals oxides NPs provide a great promise in their further modifications, which will make them favorable for using as catalyst in the biphasic oxidative cleavage of UFAs. Interestingly, considering high degree of dispersion of SCNPs, one can properly assumed them as the frontier of homogenous and heterogeneous catalysts that benefit from the best properties of the both. Moreover, owing to the recent progress, recovery of nanocatalysts can be efficiently done via magnetic separation. Further works is required to expand the scope of magnetically recyclable catalysts by incorporating the catalytically active metals for oxidative cleavage of UFAs, such as tungsten, into the magnetic core. In addition, presence of surfactant on the surface of NPs provide another facile and highly efficient recovery method. Given the fast pace of nanomaterials, progress, and perspectives it is most certainly only a matter of time before industrial application of nanocatalysts in oxidative cleavage of UFAs are realized.

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[‡] The American oil chemists' society

[§] International Union of Pure and Applied Chemistry

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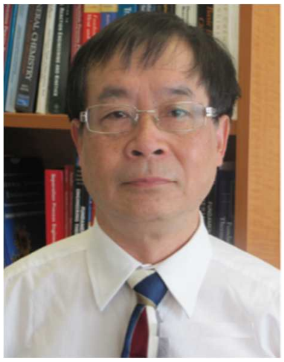

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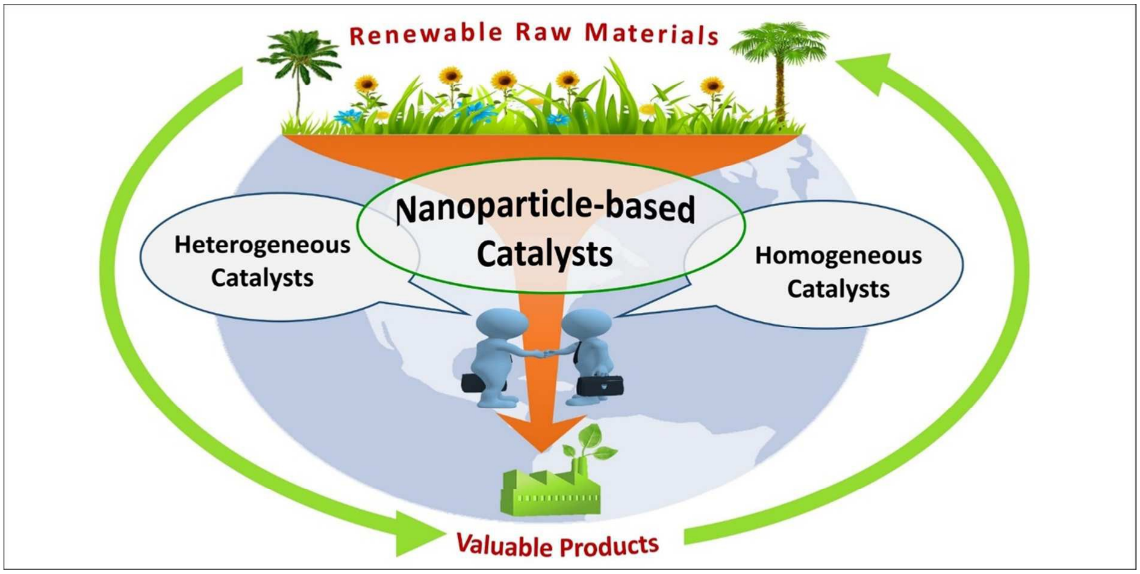

Recent catalytic systems reported for oxidative cleavage of UFAs have been investigated in three classes; homogeneous, heterogeneous, and semiheterogeneous catalysts.