

Ruthenium-Polydopamine-Supported Carbon Catalysts for the Oxidative Cleavage of Unsaturated Fatty Acids from Ecuadorian Palm Oil

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*A mi mamá, mi papá y mi hermano quienes me han enseñado los valores
fundamentales que me definen como persona y quienes han estado
conmigo en los momentos buenos y malos de mi vida.*

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Abstract

Oxidative cleavage involves the rupture of carbon-carbon double bonds in alkenes for the production of carbonyl compounds of high added value. Most of the works related to this matter are focused on small and aromatic alkenes, but only few of them address unsaturated fatty acids (UFAs). Yet UFAs can be cleaved into dicarboxylic acids, eventually with an odd number of carbon atoms rare in nature and highly demanded for polymer and pharmaceutical applications. This is typically the case of azelaic acid accessible by oxidative cleavage of oleic and linoleic acids, making these reactions particularly interesting. To date, the oxidative cleavage of UFAs is mainly performed by ozonolysis which is high energy demanding process with several risks associated to ozone handling. The other alternative is related to the use of transition metal catalysts in homogenous phase which are quite active in terms of conversion and yield, but they are pollutant and cannot be recovered. On the other hand, current heterogeneous catalysts display poor activity due to the poor contact amid the UFA and the active phase.

To solve this issue, we propose new heterogeneous catalysts formed by oxidized carbon black (CBO) and calcined carbon submicrometric particles (CCN) functionalized with polydopamine (PDA). The latter is a polymer with amine and catechol groups which act as tweezers for the complexation of metal cations. These functionalized carbon supports were impregnated with Ru which is a transition metal quite active in the oxidative cleavage reaction. All catalytic tests were carried out with oleic acid in a biphasic solution formed by $\text{H}_2\text{O}/\text{MeCN}/\text{AcOEt}$ (4/2/1) at room temperature with NaIO_4 as oxidizing agent. These catalysts completed the transformation of oleic acid into pelargonic and azelaic acids after 7 h of agitation. Moreover, they remained active even after 5 consecutive catalytic tests demonstrating their stability. Further characterization showed that the solid catalysts released Ru ions in the liquid phase which were oxidized by NaIO_4 into $\text{Ru}^{\text{VIII}}\text{O}_4$. The latter reacted with oleic acid via a pericyclic [3+2] reaction yielding a perruthenate ester which in turn was hydrolyzed producing 9,10 dihydroxystearic acid (diol) and $\text{H}_2\text{Ru}^{\text{VI}}\text{O}_4$. The diol is cleaved by NaIO_4 into nonanal and 9-oxononanoic acid which are over oxidized into pelargonic and azelaic acids.

The addition of N-Methylmorpholine N-oxide (NMO), a greener oxidant, reduced the reaction time to 5 h without sacrificing the yields of the desired oxidative cleavage products. Finally, the catalysts were assessed in the oxidative cleavage of UFAs from a real natural blend such as palm oil. This vegetable oil was submitted to hydrolysis (to break triglycerides) and esterification (to transform all fatty acids into methyl esters) prior catalytic tests. Conversions and yields attained were similar to those obtained with pure oleic acid demonstrating that the rest of the components from palm oil do not interfere with the normal ongoing of the reaction. Therefore, these new catalysts open a novel route for the production of high value-added

products with medical applications (i.e. azelaic acid) from a cheap feedstock as palm oil.

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List of Abbreviations

Carbon supports

AC	Activated carbon
ACO	Oxidized activated carbon
CB	Carbon black
CBO	Oxidized carbon black
CN	Carbon particles
CCN	Calcined carbon particles
CNT	Carbon nanotubes

Chemicals

NMO	N-Methylmorpholine N-oxide
MeCN	Acetonitrile
AcOEt	Ethyl acetate
bpy	2,2'-bipyridine
NHS	N-hydroxysuccinimide
EDC	1-ethyl-3-(3-dimethylaminopropyl) carbodiimide
DA	Dopamine hydrochloride
TRIS	Tris(hydroxymethyl)aminomethane

Characterization techniques

BET	Brunauer-Emmer-Teller
BJH	Barrett, Joyner and Halenda
DB	Dubin-Radushkevich
HK	Horvath-Kawazoe
PSD	Pore size distribution
SEM	Scanning electron microscopy
XPS	X-ray photoelectron spectroscopy
TEM	Transmission electron microscopy
FTIR	Fourier-transform infrared spectroscopy
TGA	Thermogravimetric analysis
DSC	Differential scanning calorimetry
AFM	Atomic force microscopy
NMR	Nuclear magnetic resonance spectroscopy
EPR	Electronic paramagnetic resonance spectroscopy
ICP-AES	Inductively coupled plasma - atomic emission spectrometry
GC	Gas chromatography
FID	Flame ionization detector

Oxidative cleavage

FA	Fatty acid
SFA	Saturated fatty acid

UFA	Unsaturated fatty acid
OA	Oleic acid
PA	Palargonic acid
AA	Azelaic acid
FAME	Fatty acid methyl ester
IS	Internal standard
NA	Nonanal
Oxo	9-oxononanoic acid
MO	Methyl oleate
ML	Methyl linoleate
MA	Monomethyl azelate
NH ₂ -bpy	4,4'-diamino-2,2'-bipyridine
PDA	Polydopamine

Catalytic performance

F _R	Response factor
K _{AA}	Partition coefficient
X	Conversion
Y _i	Yield
S _i	Selectivity

Miscellaneous

POM	Polyoxometalate
HAP	Hydroxyapatite
PZC	Point of zero charge
OTf	Trifluoromethane sulfonate
DMF	N, N-Dimethylformamide
TBHP	Tert-butylhydroperoxide
<i>t</i> BuOH	<i>tert</i> -butanol
NHPI	N-hydroxyphthalimide
CPC	Cetylpyridinium chloride
Aliquat® 336	Methyltriethylammonium chloride
PCWP	Peroxo-tris (cetylpyridinium)12-tungstophosphate
PDC	2,6-dipicolinic acid
DCM	Dichloromethane
CTAB	Cetyltrimethylammonium bromide

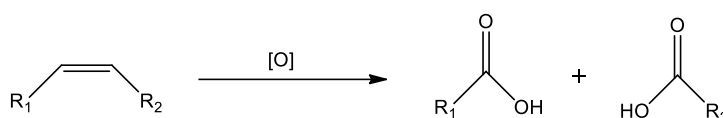
CONTEXT

In the last century, petrochemical industry has become the source of economic growth in various societies and countries [1,2]. Through high-tech refinery plants and efficient processes, it is possible to exploit non-renewable fossil fuels in order to obtain highly demanded products required for the development of our industries [3,4]. In fact, the chemical industry is the third largest consumer of raw materials that come from fossil fuels after energy generation and transportation [5]. Nevertheless, the production of chemicals from petrochemical sources has also become a global concern due to the shortage in petroleum reservoirs and pollution issues [6,7]. Carbon emissions related to petrochemical processes must be restrained to reduce global warming to less than 2 °C and so diminish world damage due to climate change [1,8]. Since many goods are currently obtained from the petrochemical industry (e.g. fuels, petrochemical feedstock, waxes, oils, asphalts, etc.), it is important to look for new renewable raw materials in order to produce the mentioned products through ecological and sustainable ways [9].

To meet the climate and economic requirements of 21st century, biomass has begun to be used for two main applications such as energy generation and chemical production [10]. As regards the former application, biomass can store energy in its chemical bonds which can be broken for electricity and heat generation (e.g. bagasse, palm shells, waste wood) [11,12]. On the other hand, biomass can also be transformed into liquid fuels (e.g. alkanes, alcohols) and chemicals (e.g. aromatics, olefins, acetone) which are normally produced in the petrochemical industry [13]. In fact, biomass is the only source of carbon which should be exploited in a sustainable manner. According to U.S. government, the amount of biomass to produce must scale-up to 1.2 billion tons per year in order to replace all products derived from petroleum by 2050 [12]. In addition, policies for the cultivation and distribution of biomass must be applied to have a sustainable development in the next decades [12,14].

Among the different types of biomass sources and their potential applications, oils and fats appear as a promising and sustainable alternative [15]. In the specific case of oleochemical industry, oils and fats have become an interesting source of chemical base materials for several industries (e.g. polymers, cosmetics, plasticizers, pharmaceuticals) [15,16]. These natural raw materials are characterized for their abundance and biodegradability [16]. Moreover, they do not contain toxic elements as in the case of petrochemical derivatives which make them friendly to the environment [15-17]. In addition, the molecules inside this renewable feedstock contain several functional groups which can be exploited for various applications in organic synthesis (e.g. glycerol production) [18]. Mainly, oils and fats are formed by triglycerides, which after a hydrolysis treatment can be transformed into free fatty acids and glycerol. As regards fatty acids (FAs), they possess two important functional groups: carboxylic acid and carbon-

carbon double bonds (unsaturation) throughout their long hydrocarbon chain. If FAs are derived from animal fats, they do not have unsaturations and they are known as saturated fatty acids (SFAs) [19,20]. On the other hand, vegetable oils generally present FAs with a high degree of unsaturation. The latter is quite interesting for scientists specifically in the field of polymers. Unsaturated fatty acids (UFAs) can be transformed into carboxylic and dicarboxylic acids through the scission of the carbon-carbon double bonds and a subsequent oxidation step as depicted in Scheme 1. The mentioned reaction is known as oxidative cleavage and it has been widely studied on small and aromatic alkenes [21,22].



Scheme 1. Oxidative cleavage of olefinic bonds [21,22]

Dicarboxylic acids are currently mainly produced from petrochemical raw materials. In this case, the conventional method consists in the oxidation of cyclohexene to hexanedioic acid (i.e. adipic acid) in a multistage air oxidation equipment [23]. Other possibility for dicarboxylic acids production is related to ring-opening of cyclic compounds plus an oxidation step [24]. These molecules are not found in nature and can be employed in the pharmaceutical chemistry or as polymer precursors for the synthesis of polyamides, nylon 1313 and polyesters [25,26].

On the other hand, the production of dicarboxylic acids from vegetable oils can be achieved through oxidative cleavage of UFAs. The most common way consists in the rupture of carbon-carbon double bonds of the long hydrocarbon chain via ozonolysis. In the literature, there are two examples that involve ozonolysis for dicarboxylic acids synthesis: namely the production of sebacic acid (decanedioic acid) from castor oil and, the production of pelargonic (PA) and azelaic acid (AA) from oleic acid. It is important to note that ozonolysis is not a safe option since it is highly energy demanding and involves safety risks related to ozone handling during the reaction [27,28].

Hence, many scientists have looked for eco-friendly and safer ways for dicarboxylic acids production. Oxidative cleavage of UFAs is one of these ways. Most of the works related to this subject have been focused on the oxidative cleavage of oleic acid in the field of homogenous catalysis because it is easier to obtain high conversions and yields towards the desired products [29,30]. Although, heterogeneous catalysts can be recovered and reused for consecutive oxidative cleavage runs, works in this field are limited due to relatively poor results reached in terms of conversion and yield. However, some studies suggest that catalysts containing ruthenium and tungsten are the most promising transition metals in this reaction [31,32].

In this context, it is clear the necessity to dispose of suitable catalysts for the production of high-value products from UFAs. Therefore, the present work proposes a new catalytic system that combines the benefits of homogenous and heterogeneous catalysis towards the exploitation of UFAs through the oxidative cleavage reaction.

STATE OF ART

1. Unsaturated fatty acids in chemical industry

Among the most common biomass derivatives used nowadays, UFAs are considered as one of the most valuable compounds because of their versatility during oleochemical reactions [33]. Normally, these molecules are isolated in the form of fatty acids methyl esters (FAMES) after the hydrolysis of triglycerides within oils and fats [5,33]. The triglycerides which come from animal fats typically have more SFAs, while those that constitute vegetable oils have more UFAs [34]. The latter present long carbon chains with one or several carbon-carbon double bonds and a hydrophilic carboxyl group. UFAs can be classified 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 show a *cis* or *trans* configurations with the former configuration being the most common in nature [35].

The most abundant mono-UFA in nature is oleic acid (C18:1) which contains one carbon-carbon double bond on the ninth carbon atom. It is present in various vegetable and animal oils [16]. Mainly, it is the major component of olive oils (60-75%), giving rise to its name “oleic”, which means derived from olive [5,16]. Oleic acid is present as well in sunflower oil (45-64%), mustard oil (38-60%), palm oil (36-44%) among others [36,37]. As regards poly-unsaturated fatty acids, linoleic (C18:2) and linolenic (C18:3) acids are the most common examples. They can be found abundantly in mustard oil (30% and 16%), walnut oil (47% and 10%) and white chia seed oil (21% and 49%) respectively [37,38].

The double bond(s) in the carbon chain of UFAs and the acidic group are the two reactive sites available in these molecules. The length of the aliphatic chain and the number of unsaturation, play a crucial role in chemical processes that lead to the formation of a plethora of value-added products [39]. Figure 1 shows the main reactions that can be carried out using UFAs.

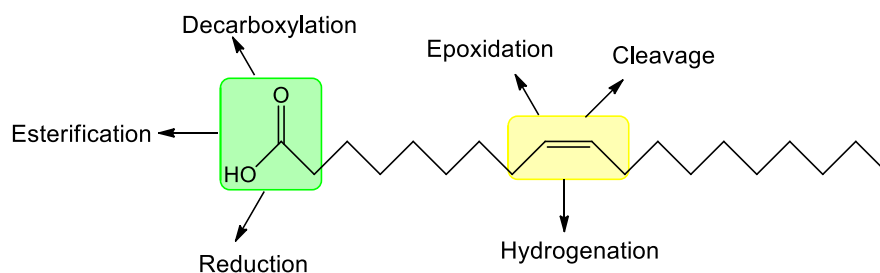
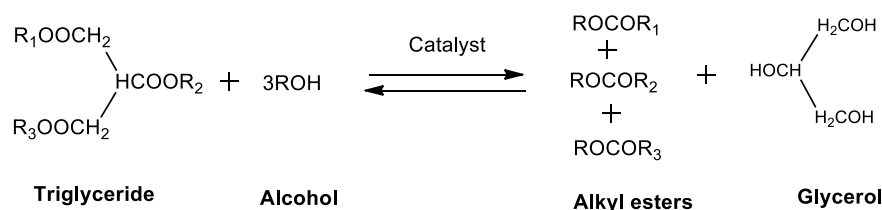


Figure 1. Main transformations for the valorization of UFAs

The majority of industrial reactions are performed at the carboxylic group site (> 90%) [5]. Remarkably, only very few reactions that involve carbon-carbon double bonds of UFAs are currently applied in the chemical industry (e.g. hydrogenation, oxidative cleavage, and epoxidation) [16]. On the other hand, the transformation of UFAs to valuable products is limited due to production costs of oleochemical processes which to date cannot compete efficiently with petrochemical industry [40]. To make the oleochemical industry more competitive, it is important to optimize the associated chemical processes for example via the employment of efficient catalysts. The most important reactions related to UFAs are summarized in the following.

1.1. Transesterification of fatty acids

The transesterification reaction between the carboxylic acid site of a fatty acid and an alcohol has been profited for the production of biodiesel [41]. Mainly a vegetable oil is employed for this process where triglycerides react with an alcohol (e.g. methanol) under the action of a base catalyst, to produce a mixture of long chain esters and glycerol as byproduct [41,42]. This reaction (Scheme 2) can be carried out with homogeneous base catalysts such as NaOH or KOH. However, they can also form soaps after neutralization of free fatty acids present in the oil or by saponification involving triglycerides [41,42]. On the other hand, heterogeneous base catalysts do not present this inconvenience and recent efforts have been targeted to the development of suitable solid catalysts for the valorization of vegetable oils into biodiesel [43,44]. For instance, Kojima and Takai used calcium oxide to perform the transesterification of soybean oil with methanol under ultrasound irradiation reaching 88% of yield in terms of methyl ester fatty acids production after 75 minutes of agitation [43]. Similar results were obtained by Liu *et al.*, who employed the same catalyst at 65 °C under conventional stirring [44].



Scheme 2. Transesterification of triglyceride oil to biodiesel

As observed in Scheme 2, glycerol is obtained as a byproduct of the transesterification reaction [45]. Pouilloux and co-workers have dedicated their efforts to develop suitable catalysts for the valorization of this molecule into valuable products [45,46]. Thus, different monoalkyl glyceryl ethers were produced after the reaction amid glycerol and alkyl alcohols with the intervention of acid organomodified silica [45]. As it was stated in the

beginning of this section, transesterification of triglycerides (within vegetable oils) is of great importance nowadays because biodiesel is a renewable fuel with lower CO₂ gas emissions than conventional diesel and gasoline [47]. According to the US government data base, the production of biodiesel has increased from 15 000 millions of liters in 2010 up to 35 000 millions of liters in 2016. This trend is expected to grow in order to limit the use of conventional fuels by 2050 [42,47].

1.2. Reduction of carboxylic acids

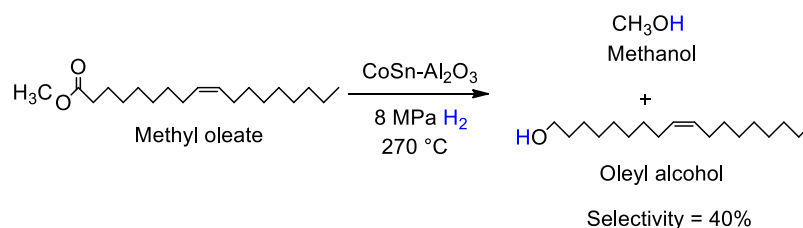
The reduction of the carboxylic group in UFAs leads to the production of fatty alcohols which are widely used as lubricants, surfactants in detergents, plasticizers in polymers, and additives in cosmetics [7,48]. Unsaturated fatty alcohols provide several advantages over the saturated ones such as a lower melting point, greater solubility in water and the possibility to functionalize the molecule at the carbon-carbon double bond [49]. Fatty alcohols of small carbon chain (C12-C14) can be produced using coconut and palm kernel oil as natural raw materials [50]. Soybean oil and palm oil are commonly used to synthesize C16-C18 fatty alcohols while long chain (C20-C22) unsaturated alcohols are obtained from rapeseed oil, linseed oil and fish oil. In addition, castor oil is a source of hydroxy acids employed for the production of diols [51].

The industrial production of fatty alcohols begins with the already mentioned hydrolysis of triglycerides in order to obtain FAMES. These methyl esters are submitted to a catalytic hydrogenation at high pressure and temperature to produce the fatty alcohols [48]. One industrial example involves a Cu-Cr alloy as a catalyst for the reduction of methyl dodecanoate ester into dodecanol at 250-350 °C under 10-20 MPa of H₂ pressure [52]. Although, the catalyst is effective in the reduction reaction, it represents a risk for the environment because of the use of Cr. On the other hand, the extreme conditions employed, promote the hydrogenation of the carbon-carbon double bonds in the UFAs chain [48,52].

Methyl esters are preferable since FAs are corrosive at high temperatures. In addition, FAs can also attack catalyst's surface and poison it. Nevertheless, methyl esters may produce undesired esterification reactions that require additional separation processes [48,52,53]. Thus, the deterioration of the equipment, low selectivity, toxic sub-products, and catalysts inactivation are the main drawbacks of this chemical reaction at industrial level [48,52,53].

Various efforts have been performed to promote the selective hydrogenation of UFAs (in form of FAMES) into unsaturated fatty alcohols preserving the carbon-carbon double bonds. For instance, methyl oleate has been transformed into oleyl alcohol, using bimetallic catalysts containing cobalt and tin. The tin content controls the transesterification side reaction between the methyl oleate and the alcohol formed (oleyl alcohol). By adjusting the

Sn/Co ratio it is possible to produce the desired fatty alcohol after 24 h of reaction under the conditions mentioned in Scheme 3 [54].



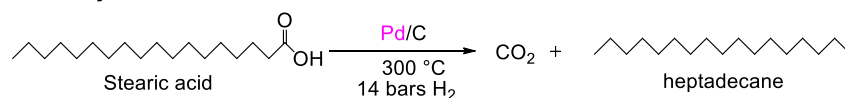
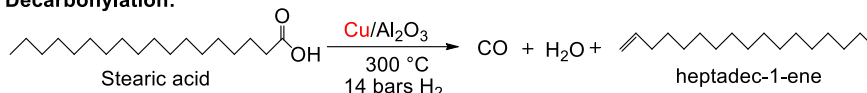
Scheme 3. Hydrogenation of methyl oleate with CoSn-Alumina catalyst at high pressure and temperature for the production of oleyl alcohol [inspired from 54]

Hence, it is clear that the current efforts must be directed to the development of suitable catalysts that favor the selective hydrogenation of UFAs into unsaturated fatty alcohols under milder conditions than those presented in the previous examples.

1.3. Decarboxylation of fatty acids

The decarboxylation of fatty acids is one of the eco-friendliest appealing alternatives for the production of long chain hydrocarbons from biomass derivatives [55,56]. The decarboxylation reaction implies the removal of the carboxylic acid site in the form of CO₂ producing long-chain alkanes with one carbon atom less than the original fatty acid [55-57]. The main challenge of this reaction lies in controlling the selectivity without using hydrogen (or a small amount of H₂) in order to optimize the cost-efficiency ratio of the process. The main application of this reaction is the production of alkanes for use as biofuels which is very appreciated nowadays [55-57]. In the last decades, many efforts have been conducted towards the synthesis of suitable catalysts for the decarboxylation of SFAs and UFAs. The latest evidence indicate that the decarboxylation pathway depends on transition metal employed [58].

For instance, Immer *et al.* demonstrated that Pd/C catalysts promote the decarboxylation reaction at 300 °C under 15 bar of He pressure. On the other hand, a Cu/Al₂O₃ catalyst can trigger the decarbonylation reaction under the same conditions [59-60]. While decarboxylation involves the release of the carboxylic acid functionality with the consequent production of an alkane, decarbonylation yields an alkene along with CO and H₂O (Scheme 4). It is important to mention that the decarbonylation reaction may occur at the early stages of the carboxylic acid removal as part of the whole mechanism of the decarboxylation reaction [58-60].

Decarboxylation:**Decarbonylation:**

Scheme 4. Decarboxylation and decarbonylation of stearic acid using Pd and Cu supported catalysts at 300 °C under H₂ atmosphere [inspired from 59 and 60]

On the other hand, the efficiency of the catalysts depends on the nature of the transition metal and support employed as well as on the method of preparation [59]. Carreon *et al.* demonstrated that the catalyst acidity, the dispersion of the transition metal and the pore diameter of the support are the main factors determining the selectivity for the decarboxylation of oleic acid [61]. High selectivity towards heptadecane from oleic acid was achieved using Pt over a zeolite (SAPO-34) with narrow pore diameters. Moreover, the degree of dispersion of Pt within the porous support influenced the catalytic activity significantly. Higher degrees of decarboxylation and selectivity to heptadecane were observed over catalysts with more uniform and well-dispersed Pt metal nanoparticles [61]. Therefore, a suitable method of catalysts preparation that yields high porosity and metal dispersion is of utmost importance for decarboxylation performance.

1.4. Hydrogenation of carbon double bonds

The hydrogenation of carbon-carbon double bonds in UFAs is a promising synthetic route for the development of biofuels. In this regard, biodiesel is constituted by FAMES coming from different vegetable oils such as soybean, palm, cotton seed among others [62]. The key aspect of a good commercial biodiesel is related to the chemical structure of FAMES since the nature of the fatty acids inside the biodiesel may influence its properties [63]. Two of the most important properties which are essential are the oxidative stability and fluidity in cold weathers. The first one depends on the degree of unsaturation in the FAMES chains [64]. It has been demonstrated that a high degree of unsaturation decreases the oxidative stability of the biodiesel which is detrimental for the engine while a low degree of unsaturation is desirable. Hence, biodiesel derived from palm oil is preferable over biodiesels from soybean or cottonseed since palm oil accounts with 50% of UFAs whereas soybean oil and cotton seed oil contain only 19%, and 28% of UFAs respectively [62].

On the other hand, it has been noted that the length of the hydrocarbon chains and the presence of unsaturation greatly affect low-temperature flow

properties [65,66]. In this matter a lower degree of unsaturation and shorter UFAs improve the lubricity at low temperatures [62, 65,66]. Therefore, new strategies that involve a partial hydrogenation of UFAs have been developed in order to improve their properties as biofuels in colder climates without affecting the oxidative stability of the bio carburant [67,68].

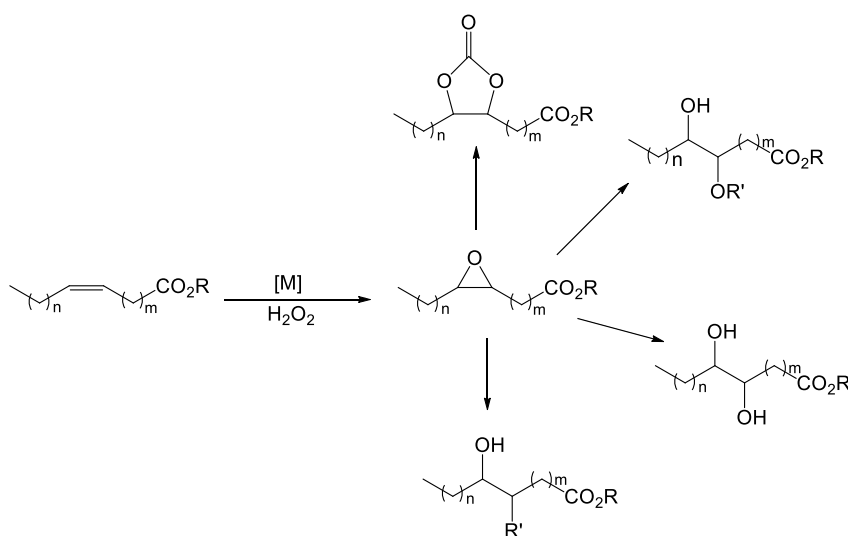
For instance, Pérez-Cardenas *et al.* explored the partial hydrogenation of FAMES from sunflower oil using Pd carbon-based monoliths as catalyst. The authors synthesized a monolithic support (HPM) which consisted of a classical square channel cordierite modified with $\alpha\text{Al}_2\text{O}_3$ with a uniform carbon layer applied by carbonization of a polyfurfuryl alcohol coating. After the deposition of Pd on the modified support, the catalyst resulted to be active in the hydrogenation of carbon-carbon double bonds contained in sunflower oil at 100 °C under 2 MPa of H_2 pressure. Compared to other commercial Pd/C catalysts, the synthesized catalyst presented a good performance in terms of *trans* double bonds formation which aids to meet the requirements of oxidative stability in biofuels. [67].

Another example of partial hydrogenation of UFAs was carried out by Zaccheria and co-workers. The authors employed a non-noble metal such as Cu supported on silicagel to perform the selective hydrogenation of various polyunsaturated FAMES under moderate conditions (2 wt% catalyst, 160 °C, 4 bar of H_2 pressure during 30-120 minutes) [69]. The catalyst transformed linolenic acid (C18:3) into linoleic acid (C18:2) after the hydrogenation treatment with an increase in the content of oleic acid (C18:1) inside the reaction mixture. Hence, the catalytic and selective hydrogenation of UFAs under mild conditions represents a valuable and efficient tool for feedstock equalization with industrial applications [67-69]. Apart from biofuel production, this procedure can be used for different purposes such as *trans* FAs reduction for healthier food production [70], stabilization against oxidation of esters blends from Camelina oil among others [71].

1.5. Epoxidation of unsaturated fatty acids

Epoxidation of the olefinic bond inside UFAs appears as one of the most versatile reactions that can be exploited in non-food industrial applications [72]. Through this reaction, it is possible to synthesize a plethora of necessary products such as plasticizers, lubricants, or painting components [73]. The epoxidation reaction implies the formation of an epoxide ring that can be profited as an intermediary for the development of several value-added products (e.g. polyol derivatives) [72,73]. Scheme 5 summarizes the epoxidation reaction and the possibilities after ring opening. At industrial scale, the epoxidation of UFAs is carried out with performic acid (CH_2O_3) with different yields according to the nature of the oil employed. Therefore, current efforts are focused on the development of efficient and eco-friendly catalyst for the epoxidation of UFAs and their derivatives [74].

Ti/Silica, CoCuAl double layered hydroxides, vanadium oxide supported catalysts are just few of the various examples that cover the epoxidation of UFAs [75-77]. These catalysts and so many others promote the oxygen transfer to the double bond using a single oxygen donor from different sources (e.g. H_2O_2 , organic hydroperoxides, peracids). For instance, Itthibenchapong *et al.* performed the epoxidation of oleic acid after generating *in situ* performic acid at mild conditions (45 °C and autogenous pressure). In this procedure H_2O_2 was mixed with formic acid for CH_2O_3 production which in turn yielded >98% of epoxidized oleic acid after 4h of agitation. No side reactions were reported and the ring-opening stage was possible after the addition of HBF_4 with a further esterification reaction [78].



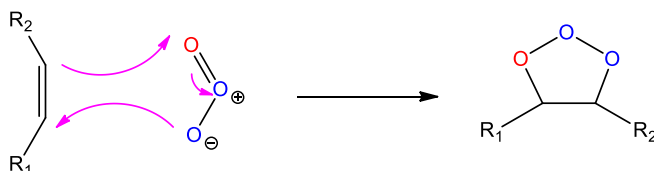
Scheme 5. Epoxidation of UFAs and possibilities after ring-opening [inspired from 72,73]

Current examples of epoxidation reactions catalyzed by transition metals involve metal complexes with oxo ligands. For example, a tungsten peroxocomplex $\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}^{3-}$ along with H_2O_2 achieved the epoxidation of methyl oleate under mild conditions (60 °C and atmosphere pressure). The presence of quaternary amines that act as phase transfer agents, allow the diffusion of the peroxo complex to the organic phase (methyl oleate itself) to trigger the epoxidation of the olefinic bond from the UFA. After 5 h of reaction, 85% of yield was accomplished which suggests that transition metal catalysts can provide a green alternative for the industrially relevant fatty acid oxidation processes [79]. In this group of oxidation reactions, oxidative cleavage of UFAs has acquired great importance recently; its principal characteristics are discussed hereunder.

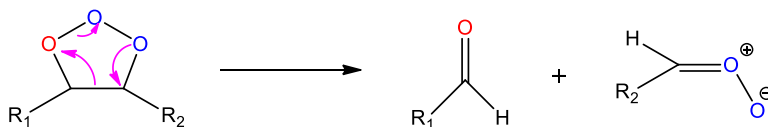
2. Oxidative Cleavage of Unsaturated Fatty Acids

The term oxidative cleavage refers to the rupture of carbon-carbon double bonds with the subsequent formation of carbonyl groups (aldehydes or carboxylic acids). Sometimes carbon-hydrogen bonds are also cleaved in addition to carbon-carbon bonds. As a consequence, a variety of products such as alcohols, aldehydes, ketones and carboxylic acids are obtained depending on the type of bond to be oxidized and the reaction conditions [80]. Generally, oxidative cleavage of olefins occurs via ozonolysis, where ozone (O_3), an allotrope of oxygen, interacts with the carbon-carbon double bonds through a pericyclic [3+2] reaction in order to form an ozonide intermediary. This ozonide, which is a cyclic peroxide formed by the three atoms of ozone plus the two carbon atoms of the olefin, evolves after a rearrangement of electrons towards a carbonyl compound and a carbonyl oxide. Subsequently, the latter suffer a dimerization or it may react with water to form hydrogen peroxide (Scheme 6).

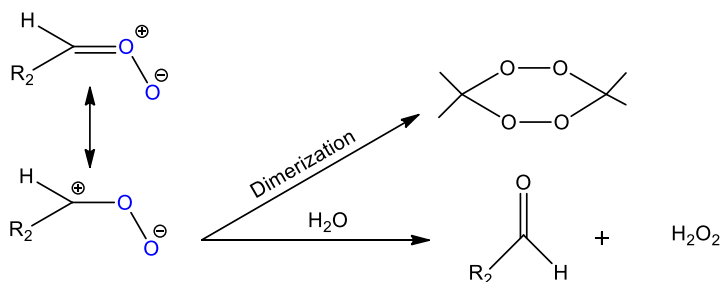
1) First stage: Perycyclic reaction [3+2]



2) Second stage: Decomposition of ozonide towards carbonyl compound and carbonyl oxide

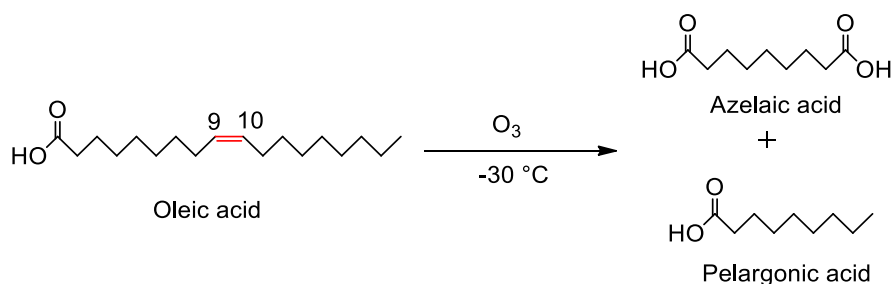


3) Third stage: Main possibilities for carbonyl oxide evolution



Scheme 6. Mechanism of ozonolysis for the oxidative cleavage of olefins [inspired from 80]

As regards the oxidative cleavage of UFAs, main efforts have been made to transform oleic acid into valuable products of industrial interest. The ozonolysis process requires the decrease of reactor temperature down to $-30\text{ }^{\circ}\text{C}$ while oleic acid adsorbs ozone supplied slowly. Since the olefinic bond of oleic acid is located in the middle of the molecule, two carbonyl compounds of nine carbon atoms are produced after the scission of the carbon-carbon double bond (Scheme 7) [27]. The first one is azelaic acid which is a dicarboxylic acid of 9 carbon atoms [27,81]. Azelaic acid (AA) can also be isolated from cultures of *Pityrosporum ovale* fungus. It is commonly used as main ingredient for creams and other cosmetics [82]. More important, azelaic acid is employed to cure cutaneous malignant melanoma since this dicarboxylic acid can destroy abnormal melanocytes [82]. Apart from medical applications, AA can be used as well for the production of polymers (nylon 6:9), adhesives, solvents, corrosion inhibitors among others [83,84]. The second product from the oxidative cleavage of C18:1 is pelargonic acid (PA). This carboxylic acid of 9 carbon atoms is also valuable for the production of lubricants, plasticizers, perfumes, herbicides, fungicides and resins [84].



Scheme 7. Oxidative cleavage of oleic acid [inspired from 27]

The two mentioned products are obtained after a complete oxidation of the carbonyl compounds resulted from the ozonide decomposition. Otherwise, ozonolysis of oleic acid yield only nonanal (precursor of pelargonic acid) and 9-oxononanoic acid (precursor of azelaic acid) [5].

Oxidative cleavage of UFAs through ozonolysis shows efficient results in terms of conversion and selectivity. However, the use of this method is highly energy demanding and not safe because of the handling of ozone [85]. The need of sophisticated equipment for ozone production and supply, the costs associated to handle large volumes of ozone and high electricity consumption, are some of the most important drawbacks related to this method [80,85]. Therefore, a safer, more economically feasible and eco-friendly process should be explored for the oxidative cleavage of UFAs. This alternative process should also maintain high conversion and yield towards the desired products. At this regard, catalytic systems based on transition metals have shown to be effective in the oxidative cleavage of UFAs [5].

These catalytic systems combine different metal complexes with oxidizing agents under several reaction conditions in order to accomplish high conversions and yields [5,85]. In this report the state of art of the oxidative cleavage of UFAs is divided between homogeneous and heterogeneous catalysis.

2.1. Homogeneous Catalysis in the oxidative cleavage of UFAs

Catalytic systems based on transition metals have attracted the attention of scientific community because of the possibility to use safer oxidants and the high efficiency achieved in terms of conversion and selectivity [5]. Mainly, ruthenium, osmium and tungsten complexes have been investigated but other transition metals such as iron, magnesium, cobalt and gold have demonstrated to be active in the oxidative cleavage reaction [86-88]. Most of the mentioned transition metals show high catalytic activity when they are present in the reaction medium in form of oxo or peroxy complexes. However, other types of metal complexes have been reported to be active as well. For instance, a catalyst formed by iron along with trifluoromethane sulfonate (OTf) and bis(2-picolyl)-2,2'-bipyrrrolidine) can produce aldehydes via oxidative cleavage employing H_2O_2 and NaIO_4 as oxidizing agents [87]. First, an epoxidation of the carbon-carbon double bond takes place with a subsequent ring opening in order to form a diol. Afterwards, the alcohol functionalities of the vicinal diol react with NaIO_4 in order to form a cyclic ester which is decomposed to yield two carbonyl compounds [87].

It is important to point out that the nature of the transition metal as well as the oxidizing agents and reaction conditions (e.g. temperature) employed, influence the mechanism and the type of products synthesized. In addition, undesired side reactions such as epoxidation, dihydroxylation or allylic oxidation, which are detrimental to selectivity, could take place as well [5,89]. In order to prevent or minimize these side reactions, an understanding of the mechanism associated to the catalyst employed must be collected. More important, the homogeneous catalysts synthesized so far have not been scaled-up at industrial level in order to replace ozonolysis because of their instability and because they cannot be easily recovered and reused once the reaction ends [5,87].

Nevertheless, due to high catalytic activity displayed, most of the investigations carried belong to this sub-domain of catalysis [90,91]. At lab-scale stage, researches focus on synthesizing selective homogeneous catalysts as well as on gaining understanding on how these transition metal complexes do perform the oxidative cleavage of olefinic bonds. In the literature, only a small fraction of the investigations refers to the oxidative cleavage of UFAs since the mechanisms involved are more complicated to understand than those that belong to aliphatic or cyclic alkenes [5]. As it was stated before, the most promising transition metals in the oxidative cleavage of UFAs are Os, W and Ru; therefore, in the following sections, recent

advances related to these mentioned transition metals complexes are presented.

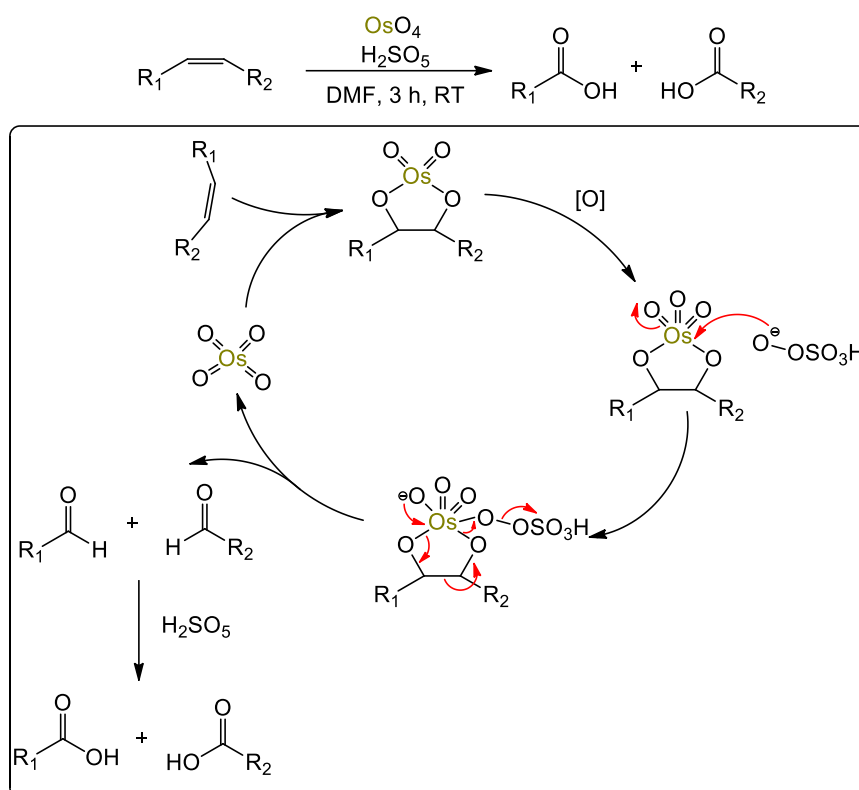
2.1.1. Osmium complexes

Osmium is a third-row transition metal which was the first one to be investigated in the oxidative cleavage of UFAs [92]. Mainly, Os is used in form of osmium tetroxide (OsO_4) in order to transform carbon-carbon double bonds into vicinal diols. After the addition of supplementary oxidants such as sodium periodate (NaIO_4) or potassium peroxydisulfate (KHSO_5), the diol can evolve towards carbonyl compounds [93]. OsO_4 can be directly applied to the oxidative cleavage of UFAs, or it can be generated *in situ* after the oxidation of an Os precursor salt with the aid of the abovementioned oxidizing agents [92,93]. Osmium tetroxide appears in form of pale yellow monoclinic crystals (M.P. 40.6 °C, B.P. 121.2 °C, density 4.906 g/cm³). The oxo complex is poorly soluble in water (0.072 g/mL at 25°C) and highly soluble in inert organic solvents (e.g. 3.5 g/mL in carbon tetrachloride). It can exist in the gaseous, solid or solution state as discrete molecular tetrahedra (Os-O distance 1.717 Å) [94].

An interesting example in literature about the performance of this transition metal complex involves 1 equivalent of methyl oleate along with 4 equivalents of oxone (H_2SO_5) and 0.01 equivalent of OsO_4 . After 3 hours of agitation in N, N-Dimethylformamide as solvent (DMF) the catalytic system produced PA and methyl azelate (the corresponding ester of azelaic acid) with 93% of yield [95]. Scheme 8 describes how OsO_4 interacts with the unsaturation within the hydrocarbon chain of methyl oleate via a pericyclic reaction [3+2] in order to form an osmate ester [95,96]. This cyclic ester is decomposed after the intervention of oxone in order to split methyl oleate into two molecules with carbonyl groups incorporated in the cleaved carbon atoms (aldehydes). Finally, oxone over-oxidizes aldehydes into the desired carboxylic acids [95,96]. Although OsO_4 is particularly known for its dihydroxylation capacity, it is not believed that a vicinal diol was formed in this example since that kind of molecules requires the hydrolysis of the osmate ester while no water was present in the reaction medium [95].

Although catalytic systems based on Os require minimal amounts of the homogenous catalyst, its applications have been restricted due to the significant toxic properties of this transition metal [94]. In order to find a safer way to employ Os in the oxidative cleavage of UFAs, organometallic complexes have been recently developed applying ligands for electronic and steric modulation. However, in oxidative cleavage reactions care should be taken since the ligand backbone can be decomposed or get oxidized by the strong co-oxidants used in this reaction [95]. For example, Samanta *et al.* synthesized a $[\text{OsO}(\text{N-aryl-1,2-arylenediamine})_2]$ complex which is less toxic than OsO_4 . This mono oxo Os^{VI} complex with N-aryl moieties as ligands is pentacoordinated with a distorted square pyramidal geometry and it can perform the oxidative cleavage of several alkenes in the presence of 5-6

equivalents of tert-butylhydroperoxide (TBHP) as co-oxidant at room temperature. After 6 h of agitation in acetonitrile, the 0.6 mol% of Os^{VI}-N-aryl complex produces carboxylic acids with ~80% yields [90]. The Os complex maintained its integrity throughout all the reaction confirming the ability of the N-aryl ligands to stabilize the mono oxo complex. Nevertheless, an excess of contact time (> 24 h) allows TBHP to decompose the Os⁶⁺-N-aryl complex [97]. This example clearly demonstrates that organometallic/coordination complexes may be an important tool to improve transition metals performances and security towards the oxidative cleavage of UFAs.

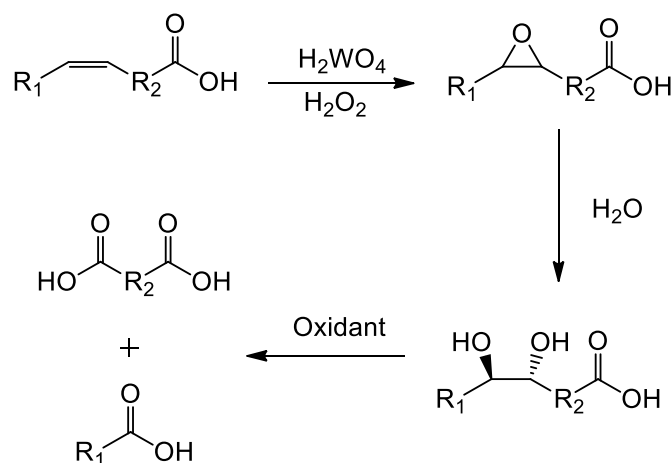


Scheme 8. Oxidative cleavage mechanism with OsO_4 and H_2SO_5 as co-oxidant [95]

2.1.2. Tungsten complexes

Tungsten oxo and peroxo complexes have been widely used in the oxidative cleavage of UFAs [5,96]. These tungsten complexes can perform the reaction in combination with softer oxidizing agents such as H_2O_2 [97]. This is the main reason why there are a greater number of applications of tungsten complexes as catalysts in the oxidation of UFAs than other transition metal compounds [96]. In addition, tungsten is cheaper and less

toxic compared to Os and Ru [96]. However, it is important to point out that side reactions (e.g. epoxidation or dihydroxylation) may arise during the catalytic oxidative cleavage reaction which may produce byproducts such as vicinal diols [96,98]. The principal example in this regard is the use of tungstic acid (H_2WO_4) along with H_2O_2 dissolved in *tert*-butanol for the oxidative cleavage of erucic acid (C22:1). After 4 days of stirring at 75 °C, the mentioned UFA was converted into the corresponding diol (13,14-dihydroxydocosanoic acid) which agrees with the proposed mechanism depicted in Scheme 9 [96]. In this pathway, the formation of an epoxide group takes place, followed by hydrolysis to *trans*-diols, and finally a further oxidation in order to obtain aldehydes or carboxylic acids [96]. Since only a 2% yield was observed for the desired products, tungstic acid combined with H_2O_2 turns out not to be enough to carry on the full oxidative cleavage of UFAs.



Scheme 9. Oxidative cleavage with tungsten [96]

In order to improve the performance of the catalytic system, it was necessary to add another catalyst to cleave the diol. $\text{Co}(\text{acac})_3$ (1 mol%), and N-hydroxyphthalimide (NHPI) along with O_2 and H_2O_2 as oxidants were employed to over-oxidize the diol intermediate into the desired carboxylic acids [99]. This modified catalytic system was tested in the oxidative cleavage of erucic acid with ~50% yields of pelargonic (C9) and brassylic acids (C13) after 3 h of stirring. Oleic acid was assessed as well, but the yields of PA and AA were very low (15%) [98]. Thence, many efforts have been made to eliminate the secondary oxidants when tungsten complexes are used in the oxidative cleavage of UFAs. For this purpose, catalytic systems that involve polyoxometalates (POMs) have been developed. Such systems mainly include phase transfer agents which are usually quaternary

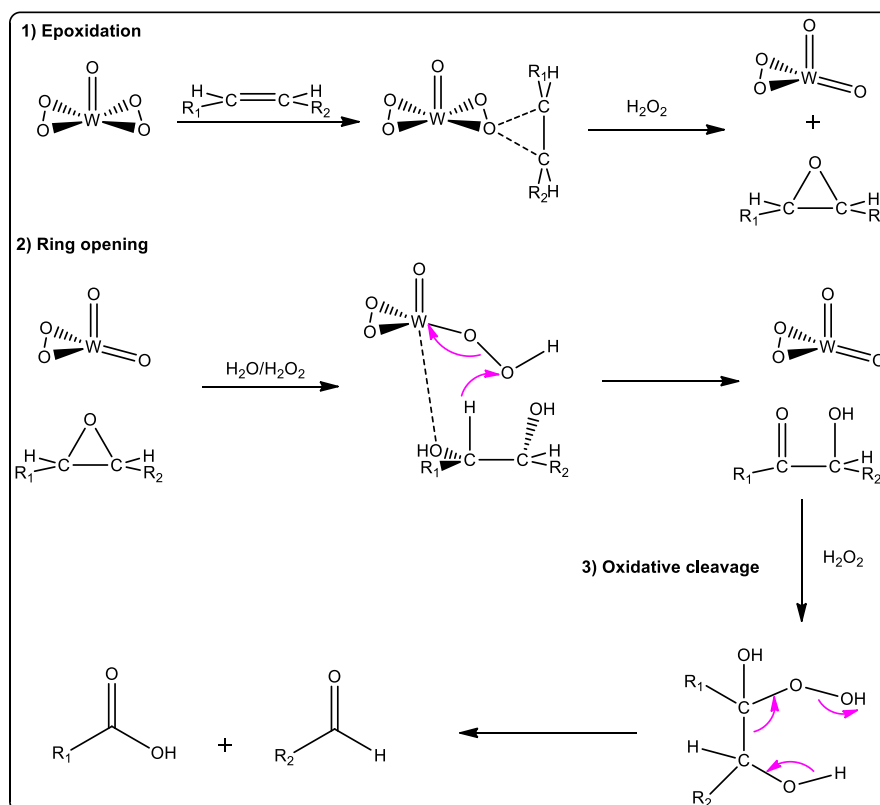
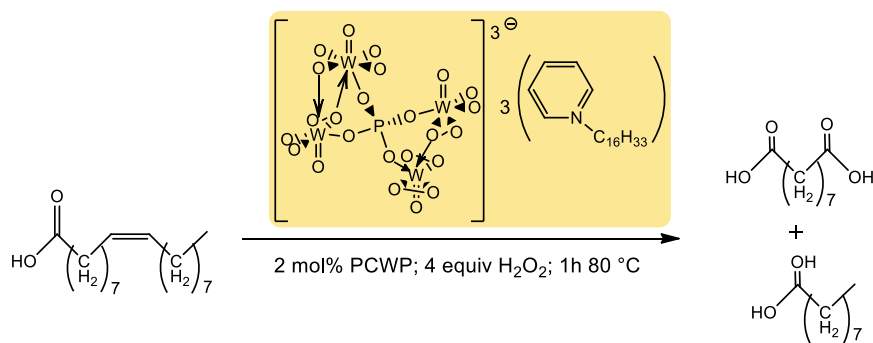
ammonium salts necessary to enhance the diffusion of POMs towards the UFA [84].

Normally the addition of H_2O_2 to a quaternary ammonium salt and a tungsten source such as tungstophosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$), leads to the formation of a peroxo tungsten complex in the form of $\text{Q}_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$, where Q is the cationic part of the quaternary ammonium salt. So far cetylpyridinium chloride (CPC), methyltrioctylammonium chloride (Aliquat® 336), tetrabutylammonium chloride and tetraoctylammonium chloride have been used for the production of tungsten POMs. One of the first examples of these peroxo-tungsten compounds in the oxidative cleavage of UFAs is attributed to a peroxo-tris (cetylpyridinium)12-tungstophosphate (PCWP) produced by Turnwald *et al* [84]. The authors developed a solvent free catalytic system where 1.3 mol% of PCWP transformed 1 mol of oleic acid into 54% of PA and 57% of AA yield after 5h of stirring at 90 °C. Although yields improved up to 64% when the reaction time was increased to 10 h, PCWP was decomposed [84]. On the other hand, Pai *et al.* achieved better results in the oxidative cleavage of oleic acid after increasing the ratio of PCWP/oleic acid (0.02 mole of catalyst per mole of substrate). In a shorter period of time (1 h of stirring) and lower temperature (80 °C), yields of PA and AA increased to 82% and 86% respectively [100]. These W based POMs boosted with phase transfer agents perform the oxidative cleavage reaction through an epoxidation/dihydroxylation mechanism shown in Scheme 10.

In first place, the peroxo complex transforms the carbon-carbon double bond into an epoxide linked to the POM. Then, the oxidizing agent (H_2O_2) releases the epoxide oxidizing the peroxo ligand [101]. The ring opening of the epoxide is carried out by the same catalysts that performed the epoxidation reaction along with water and H_2O_2 which results in the formation of a 1,2 diol [101]. The proposed mechanism for the oxidative cleavage of such diols involves the protonation of the peroxo moiety of the catalyst to yield a hydroperoxo group. Afterwards, an adduct between the diol and the hydroperoxo tungsten catalyst is formed which after a rearrangement of electrons yields a hydroxy ketone [102]. This ketone may undergo a nucleophilic attack by H_2O_2 in order to fragment the molecule into a carboxylic acid and an aldehyde. The aldehyde formed by this way can be further oxidized into a carboxylic acid by means of the tungsten catalyst and H_2O_2 [102].

Other W-based POMs with different phase transfer agents have been tested as well. For example, Khlebnikova *et al.* used Aliquat® 336 instead of CPC to synthesize a $[\text{Me}(n\text{-C}_8\text{H}_{17})_3\text{N}]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$ complex for the oxidative cleavage of methyl oleate. This new catalyst presented the same results achieved by PCWP under similar conditions (1 mol% of catalyst, 2 equiv. of H_2O_2 , 5h of agitation at 85 °C) [103]. Antonelli *et al.* applied the same catalytic system for the oxidative cleavage of pure oleic acid among other alkenes. The reaction was performed with 1.2 mol% of catalyst along with

5.5 equivalents of H_2O_2 at 80°C for 5 h. At the end, azelaic acid was produced with a 79% yield, which was slightly lower than the previous case [104].



Scheme 10. Proposed mechanism for the oxidative cleavage of UFAs with W based POMs [84]

In order to obtain a more precise comparison between the performances of the different phase transfer agents in the oxidative cleavage of UFAs,

Godard *et al.* synthesized different W-peroxo catalysts with four phase transfer agents such as: CPC, Aliquat® 336, tetra butyl and tetra octyl ammonium chlorides. All reactions were performed with 2 mol% of catalyst, 5 equivalents of H₂O₂, at 85 °C for 5 h [105]. Although the best results in terms of yield were accomplished with PCWP (the catalyst synthesized with CPC), the other tungsten compounds achieved yields close to that of the mentioned complex. Therefore, more important than the phase transfer agents, are the reaction conditions [105]. An adequate reaction time, to avoid the decomposition of the tungsten compound, as well as the amount of oxidizing agent, are essential to allow the catalyst to transform the substrates into the desired products. Therefore, the optimization of the reaction conditions plays a fundamental role in the oxidative cleavage of UFAs.

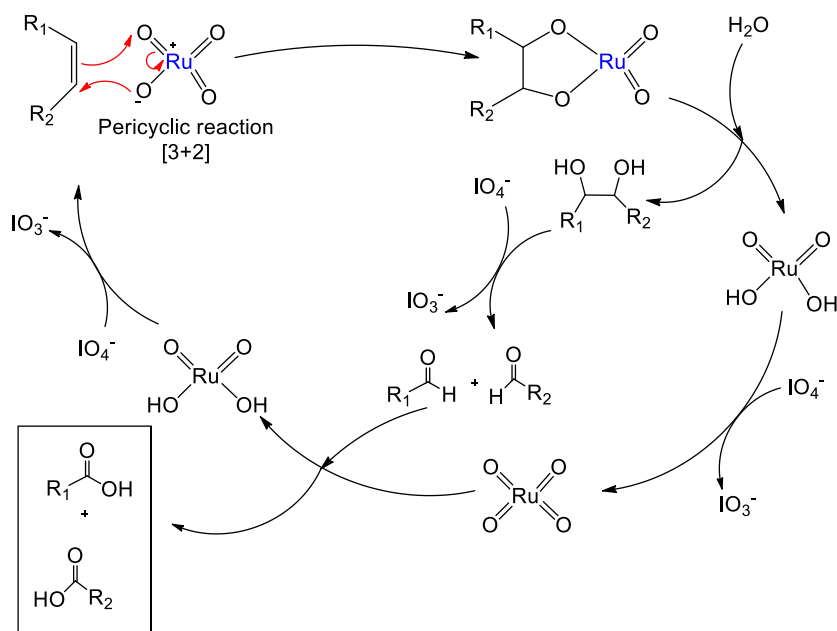
2.1.3. Ruthenium complexes

Ruthenium, along with osmium, is the oldest transition metal used for the oxidation of organic compounds. In fact, this transition metal is less toxic, less volatile, cheaper and more available than Os [106]. Like Osmium, the tetroxide form of ruthenium (RuO₄) is highly active and selective in the oxidative cleavage of alkenes [99,100]. RuO₄ can be isolated as yellow crystals at low temperatures (~0 °C). Its melting point is around 25 °C and its moderately soluble in aqueous phase (0.13 mole/L at 25 °C). Preferably, RuO₄ is stored in a suitable organic solvent such as carbon tetrachloride (CCl₄). Actually, the distribution coefficient between carbon tetrachloride and water is 58:1 [107-109]. For the oxidative cleavage of UFAs, Sharpless and co-workers developed a catalytic system where RuO₄ is generated *in situ* after the oxidation of a Ru precursor salt (e.g. RuCl₃ or RuO₂) by means of an oxidizing agent such as NaIO₄ or NaClO₄ as shown in Equation 1 [110,111].



The homogeneous Ru catalyst performs the oxidative cleavage reaction in a biphasic solution of H₂O/MeCN/CCl₄ (Scheme 11). First, a pericyclic reaction [3+2] takes place between RuO₄ and the carbon-carbon double bond of the UFA in order to form a cyclic perruthenate ester which is broken after its interaction with water [112]. The perruthenate ester evolves into a diol which in turn is cleaved by means of NaIO₄ producing carbonyl compounds. It is believed that these intermediates are oxidized by RuO₄ to yield the desired carboxylic acids [113]. As regards ruthenium, once the perruthenate ester is broken, the Ru^{VIII}O₄ is reduced to H₂Ru^{VI}O₄. Such reduced Ru species is then oxidized by NaIO₄ keeping the oxidative cleavage reaction ongoing [113]. Most of the works related to the use of RuO₄ towards the oxidative cleavage of UFAs, have obtained complete conversions in short periods of time along with high selectivity [29,30]. For instance, Zimmerman *et al.* employed the same solvent mixture as Sharpless and co-workers

(H₂O/MeCN/CCl₄) but they replaced the toxic CCl₄ by ethyl acetate (AcOEt) as organic solvent [30].



Scheme 11. Proposed mechanism for the oxidative cleavage of UFAs with Ru^{VIII}O₄ and NaIO₄ (inspired from [113])

It is worth to say that replacing CCl₄ is quite difficult because NaIO₄ may react violently with the most common solvents employed in organic chemistry. Zimmerman and co-workers found that the solvent system H₂O/MeCN/AcOEt in a proportion (3/2/2) along with 2.2 mol% of RuCl₃ and 4.1 equivalents NaIO₄ can perform completely the oxidative cleavage of oleic acid after 2 h of agitation at room temperature with the same results as the Sharpless catalytic system (PA yield 65% and AA yield 73%). In addition, the change of solvent allowed to reduce the reaction time from 4 h and 30 min with CCl₄ to 2 h with AcOEt [30].

In order to improve these results, Rup *et al.* performed the oxidative cleavage of oleic acid testing various mixtures of solvents under ultrasonic irradiation and with Aliquat® 336 as phase transfer agent [114]. They demonstrated the utility of each solvent within the biphasic system. Water is necessary for the dissolution of the Ru precursor salt as well as the oxidizing agent. On the other hand, AcOEt dissolves the UFAs along with RuO₄ to facilitate their interaction and the further formation of the perruthenate ester. Acetonitrile (MeCN) aids to maintain Ru species in the liquid medium avoiding their volatilization [111,114]. In fact, without MeCN, yields of PA

and AA decreases down to ~50%. After optimization of the solvent mixture, H₂O/MeCN/AcOEt (4/2/1), it was possible to achieve yields of 78% for AA and 88% for PA using 2.2 mol% RuCl₃, 4.1 equivalents of NaIO₄ and 2 mol% of Aliquat® 336 within 1 h of ultrasonic irradiation. In addition, Rup and co-workers found that a non-desired product (9,10-dihydroxystearic acid) was present in the reaction mixture. According to the authors, AcOEt may retain the 9,10-dihydroxystearic acid which prevents its cleavage by NaIO₄ in the aqueous phase [114,115].

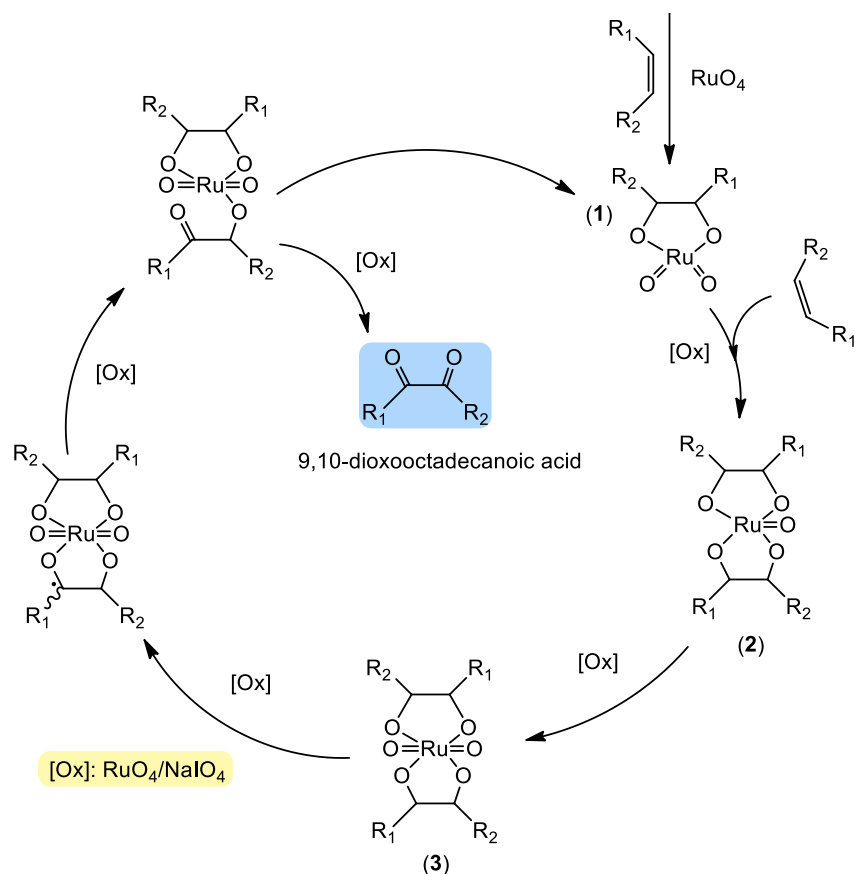
When only H₂O/MeCN was used the diol (9,10-dihydroxystearic acid) was not detected, but after increasing the amount of AcOEt in the solvent mixture, the diol concentration increased as well. Therefore, the amount of AcOEt must be adjusted in order to prevent low yields of the desired products due to an incomplete cleavage of the diol. In order to explore what does happen in the organic phase (where no H₂O is present to hydrolyze the perruthenate ester into a diol) Frunzke *et al.* demonstrated that the perruthenate ester (1) may interact with another olefin in order to produce a rutheniumoxo-(2,5-dioxolane) intermediate (2). This species is oxidized by free RuO₄ to yield a ruthenium dioxo bis(2,5-dioxolane) compound (3). The latter may evolve to 9,10-dioxooctadecanoic acid through a hydrogen atom abstraction mechanism as depicted in Scheme 12 [116].

Recently, efforts have been made to perform the oxidative cleavage reaction with softer oxidizing agents along with simple solvent blends. In this matter, Behr *et al.* tested the complexation of Ru by several organic compounds in combination with H₂O₂ instead of NaIO₄ [117]. The best results were achieved when Ru(acac)₃ was combined in situ with 2,6-dipicolinic acid (PDC) in a mixture of *tert*-butyl alcohol and water. The oxidative cleavage reaction required 1 mol% of Ru, 20 mol% of ligand and 8 equivalents of hydrogen peroxide at 80 °C for 24 h. Although yield related to AA was high (81%) when methyl oleate was the substrate, it decreased to 59% when pure oleic acid was tested. These results are clearly lower than the systems based on RuO₄ and NaIO₄ [117].

Behr and co-workers demonstrated that the performance of their organometallic Ru complex was significantly influenced by the Ru-precursor/ligand ratio, the reaction temperature, the solvent and the reaction time [117]. Conversely to RuO₄/NaIO₄ catalytic system, the Ru-PDC complex shows a mechanism very similar to those presented by W or Os complexes. In this case, the reaction proceeds through the epoxidation of the carbon-carbon double bond in order to yield a vicinal diol as intermediate. It is important to point out that acidic conditions are required (pH = 2.4) in order to promote the ring opening of the epoxide towards the vicinal diol [117,118]. Otherwise the reaction cannot proceed and AA yield may decrease [118].

Despite the level of performance of homogeneous catalysis in the oxidative cleavage of UFAs, this approach presents drawbacks that are worth to be

avoided. Besides the specific issues mentioned related to the nature of the transition metal, solvents, or the oxidizing agent, the main one is the difficulty to recover the dissolved catalysts after the reaction ends and separate them from the products that need to be washed intensively to get purified. Hence, recent efforts have been made to develop heterogeneous catalysts, easy to recover, in the oxidative cleavage of UFAs.



Scheme 12. Proposed mechanism for 9,10-dihydroxystearic acid synthesis in the organic phase [114]

2.2. Heterogeneous Catalysis in the oxidative cleavage of UFAs

The possibility of employing solid catalysts in liquid phase reactions has always been a promising route towards industrial scale production of value-added products [119]. The main characteristic of heterogeneous catalysts lies in the ease of recovering the solids once the reaction is completed [119,120]. Therefore, the possibility of recycling heterogeneous catalysts and reuse them several times makes them attractive for scale-up production

and commercialization. In the specific case of chemical reactions involving biomass derivatives such as oils; the application of heterogeneous catalysts has been restricted due to pore diffusion limitations, poor contact between the active site and the substrate, degradation and poisoning of the solid catalyst among other shortcomings [121].

In order to find solutions for these drawbacks, it is important first to comprehend the main characteristic of heterogeneous catalysts. Generally, a heterogeneous catalyst is present in a different phase (i.e. solid) than the substrates (i.e. liquid or gaseous). These catalysts are formed by a solid support which contain several active sites (organic functionalities or transition metal complexes) well dispersed over the solid's surface [122]. It is important here to clarify the difference between a heterogeneous supported catalyst and active species grafted and dispersed on the surface of a solid. Normally a supported classic catalyst possesses a transition metal in a metallic form over the surface of the support which is later submitted to a heating treatment (air or inert atmospheres) to enhance the interaction amid the surface and the transition metal. On the other hand, a functionalized catalyst is prepared after a transition metal complex is grafted on the surface of a support by means of different interactions (electrostatic or covalent). In addition, no heating treatments are applied after anchoring transition metal complexes on a support [121,122].

One of the most important features of heterogeneous catalysts is related to, their textural properties. In this matter, IUPAC has classified solids in three large groups according to their pore size distribution [123]. First, microporous materials (e.g. ZSM-5 zeolite) with pore diameters of less than 2 nm have generally high specific surface areas along with a crystalline structure and a uniform pore size distribution. Although such microporous solids are widely used in industrial applications (e.g. petrochemical industry), these materials seem not to be suitable for oxidation reactions of UFAs due to the large molecular size of these biomass derivatives [123-125]. On the other hand, macroporous materials with pore diameters larger than 50 nm, normally present low catalytic activity as a consequence of the low number of active sites caused by a low specific surface area [123,124]. It seems that mesoporous materials with pore diameters between 2 and 50 nm are suitable for oxidation reactions that involve large molecules such as UFAs. Nevertheless, novel and straightforward methodologies should be defined in order to produce mesoporous materials or to increase pore size of supports without sacrificing their specific surface area [123-125].

As a consequence of all the aforementioned inconvenient, the number of investigations carried out in the oxidative cleavage of UFAs is quite reduced compared to homogeneous catalysis examples [122]. So far, transition metal oxides, cation-exchanged zeolites, transition-metal complexes with cross-linked polymers or metal nanoparticles have been reported in literature among the most promising heterogeneous catalysts for the oxidative cleavage of alkenes and UFAs [96]. Environmental issues as well as the

need of recyclable catalysts are just some of the driving forces that encourage the search of suitable materials for performing the oxidation of UFAs [5,96]. In this section, the most important heterogeneous catalysts referred to Os, W and Ru for the oxidative cleavage are described.

2.2.1. Osmium supported catalysts

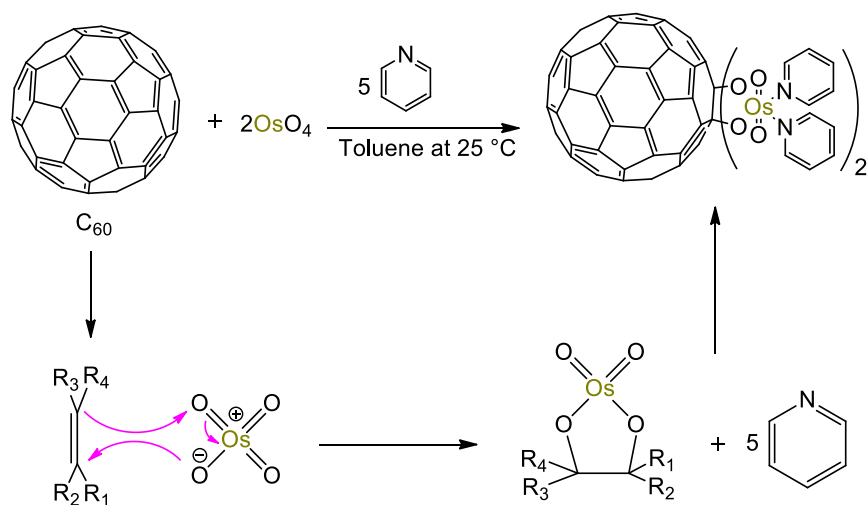
As stated in the previous section, Os complexes (mainly $\text{Os}^{\text{VIII}}\text{O}_4$) are highly active in dihydroxylation and oxidative cleavage of alkenes and UFAs. In order to take advantage of this coordination complex with four oxo ligands, different functionalization techniques have been employed to transfer Os species on several solids' surfaces [96,126]. For example, Ley *et al.* encapsulated osmium tetroxide into a polyurea matrix using an *in situ* interfacial polymerization approach. Such technique implies the mixture of isocyanates, surfactants and the desired metal complex. This mixture yields an oil-in-water microemulsion with a particle size range of 20-250 μm . The particles with OsO_4 entrapped inside the polymer matrix, were gently paddle-stirred for 36 h in order to obtain polyurea microcapsules which were thoroughly washed and dried [126,127].

Scanning electron microscopy (SEM) images showed a high degree of distribution of OsO_4 within the structure of the polymer. As regards catalytic tests, the synthesized heterogeneous catalyst performs the oxidative cleavage of various alkenes in two stages. First, 5 mol% of the catalyst performs the dihydroxylation of the substrate along with 1.5 mmol of N-methyl morpholine N-oxide (NMO) as co-oxidant. After 24 h of reaction, yields around 85% to the desired product was registered [126]. The oxidative cleavage of the produced diol is triggered after the addition of 3 equivalents of NaIO_4 . It is worth to know that the OsO_4 -polyurea catalyst can also cleave cis-7-tetradecene for heptanal production, an example which can be regarded as a mimic of UFAs [96,126].

In most cases, the incorporation of a transition metal complex on a solid support is intrinsically related to the nature of the ligating functional groups of the latter. However, it could be useful to employ the functionalities of the complex to react with the surface of the support in order to graft the active sites. Taking advantage of OsO_4 high reactivity, Brutchey and co-workers managed to fix this osmium oxide on fullerene surface through a pericyclic reaction (the same reaction used to interact with alkenes and UFAs double bonds) [128]. As described in Scheme 13, OsO_4 may react to carbon-carbon double bonds of fullerene through a pericyclic reaction [3+2] in order to form an osmate^{VI} ester (osmylation). When Os reacts with tetra substituted olefins, the resulting cyclic ester is resistant to hydrolysis [128,129].

Hence, it is possible to irreversibly bind a carbon support to a Os^{VI} pre-catalyst which can be further oxidized to $\text{Os}^{\text{VIII}}\text{O}_4$ by means of a soft oxidizing agent like NMO. X-ray photoelectron spectroscopy (XPS) and infrared spectroscopy confirmed the osmylation of fullerene as well as the

oxidation state of Os fixed on the carbon support. Moreover, this “soccer ball” Os catalyst has demonstrated to be active in the dihydroxylation of several olefins with yields ~80% after 24 h of stirring in a dichloromethane (DCM)/H₂O biphasic solution. Unfortunately, the fullerene-osmium structure was deteriorating at each recycle test putting in evidence the instability of the synthesized heterogeneous catalyst [128].

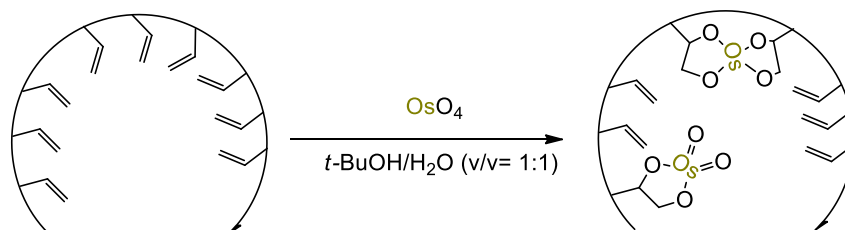


Scheme 13. OsO₄-Pyridine-C₆₀ heterogeneous catalyst for dihydroxylation of alkenes [128]

Continuing with the same strategy, Song *et al.* immobilized OsO₄ on a nonionic porous resin such as Amberlite XAD-4 (polystyrene-based) and XAD-7 (polyacrylate-based) through the same pericyclic reaction [3+2] between OsO₄ and vinyl functionalities along the polymer framework [130]. These synthetic polymers are mainly highly cross-linked macroporous resins bearing between 0.20 to over 0.40 mol of residual vinyl groups per mole of polymer repeating units [131]. After anchoring OsO₄ on the Amberlite resins (Scheme 14), the solid catalysts were tested in the hydroxylation of several alkenes. Unlike osmylated fullerene, 1 mol% of the OsO₄-Amberlite catalyst showed a high catalytic activity and stability using potassium ferricyanide as the co-oxidant instead of NMO or NaIO₄ [132].

No osmium was detected in the liquid phase after the extraction of the solid catalyst once the reaction ended. Although, the heterogeneous osmium catalyst maintained the same catalytic activity after 3 recycling tests, they started to lose their activity in the fourth and fifth run suggesting catalyst deterioration [130]. Most likely, the osmate ester formed with the vinyl moieties was not stable since the osmate requires a tetra substituted

unsaturation to form a stable complex as it was presented in the case of the fullerene osmium catalyst [128].



Scheme 14. Osmylation of Amberlite resin [130]

In summary, the abovementioned approaches have permitted to manage properly a toxic and dangerous complex such as OsO_4 . The high cost of osmium as well as its high toxicity and volatility have made large-scale industrial applications with this metal very difficult [126-130]. Nevertheless, the proposed osmylated heterogeneous catalysts are air-stable, nonvolatile, and much easier to handle than their soluble counterpart OsO_4 . Only the catalyst of Ley *et al.* was tested in the oxidative cleavage reaction suggesting that further research is required in the oxidative cleavage of UFAs with Os supported catalysts.

2.2.2. Tungsten supported catalysts

Unlike osmium heterogeneous catalysts, tungsten composites have been widely studied in the oxidative cleavage of UFAs. Since tungsten peroxo and oxo complexes have demonstrated to be active in this kind of reactions, various attempts have been made to transfer these compounds onto suitable solid supports. One of the first efforts related to evaluate a tungsten-based catalyst was performed by Nouredini and Kanabur [133]. The authors impregnated ammonium metatungstate $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$ by wet impregnation on alumina and silica supports followed by a calcination stage under air atmosphere at 400 °C for 2 h. Tungsten-silica catalyst with H_2O_2 as co-oxidant dispersed in *tert*-butanol showed high catalytic activity in the oxidative cleavage of oleic acid when the reaction temperature was adjusted at 130 °C. Just one hour was enough to achieve 96% of conversion after a slow performance in the first minutes of the reaction. During the monitoring of oleic acid conversion, the concentration of the products (i.e. PA and AA) increased up to reach a plateau followed by a decrease in their concentration when the reaction time was prolonged for more than 5 hours [133]. The reason of this decrease is associated to a prolonged heating process. Therefore, care should be taken when adjusting the reaction time at which the maximal concentration of desired products is obtained in order to prevent their decomposition [133]. According to the nature of the catalyst used and the reaction conditions applied, shorter or longer reaction times are required [119-122]. For supported tungsten oxide on silica, the highest

PA yield was 36% whereas AA yield corresponded to 32% after 1 h of stirring. Regarding the effect of the textural properties of the support, the authors performed the oxidative cleavage of oleic acid with unsupported tungsten oxide in order to compare its performance with its supported counterpart [133]. The kinetic curves showed that the unsupported catalyst possesses a higher catalytic activity than the supported one. Hence, the authors conclude that 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 one, especially at the early stages of the reaction [133]. It is worth to mention that yields of PA and AA were slightly lower with unsupported catalyst than the ones obtained with tungsten supported catalyst. In addition, the performances presented by solid tungsten oxide, supported or unsupported, were lower compared to tungsten homogenous catalysts discussed in the previous section.

More important is to understand what is the special characteristic that makes tungsten oxides active in the oxidations of alkenes and UFAs. It is known that tungsten oxide has different oxidation states, with which H_2O_2 may form different oxo and peroxy complexes active in the oxidative cleavage reaction. In fact, the W-OOH complex, produced after the activation of WO_x by H_2O_2 , has been reported as the active species in the oxidative cleavage of olefins [134-136]. Although the nature of active sites and their modifications are controversial among the scientific community, it is believed that the acid sites in the structure of tungsten oxide are highly dependent on the parameters of the preparation process which involve the nature of the tungsten precursor salt, the loading of tungsten oxide, and the calcination stage [137-139].

For instance, Do *et al.* tested various tungsten oxide nanoparticles in the oxidative cleavage of oleic acid [140]. Several structures from commercial tungsten trioxide (WO_3), $\text{WO}_3 \cdot \text{H}_2\text{O}$ to $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$ and $[(\text{WO}_2)\text{O}_2 \cdot \text{H}_2\text{O}]$ were synthesized through the oxidation of W powder with H_2O_2 followed by different calcination treatments. In addition, tungsten oxides were functionalized with different amounts of cetyltrimethylammonium bromide (CTAB) which works as a phase transfer agent [140]. Catalytic tests were performed using 1 g of oleic acid, 0.45 g of catalyst along with H_2O_2 dissolved in *tert*-butanol at 120 °C for 5 h. All tungsten oxide nanoparticles presented high catalytic activities (>99% after 5 h of stirring); however, a difference was evidenced in PA and AA yields. Commercial WO_3 achieved only 10 and 18% of PA and AA yields respectively whereas $[(\text{WO}_2)\text{O}_2 \cdot \text{H}_2\text{O}]$ presented higher yields of 71 and 67% related to the same oxidative cleavage products [140-142]. This high catalytic efficiency comes from the presence of peroxy functionalities which are responsible for triggering oxidative cleavage of UFAs (Figure 2).

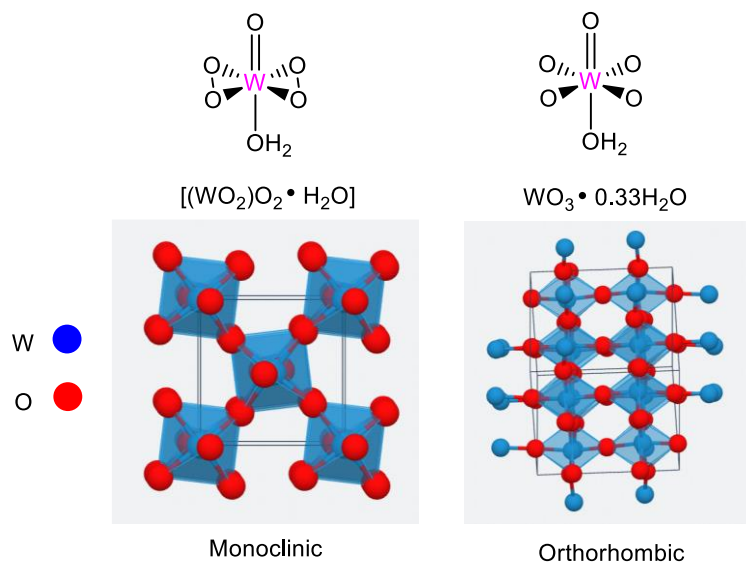
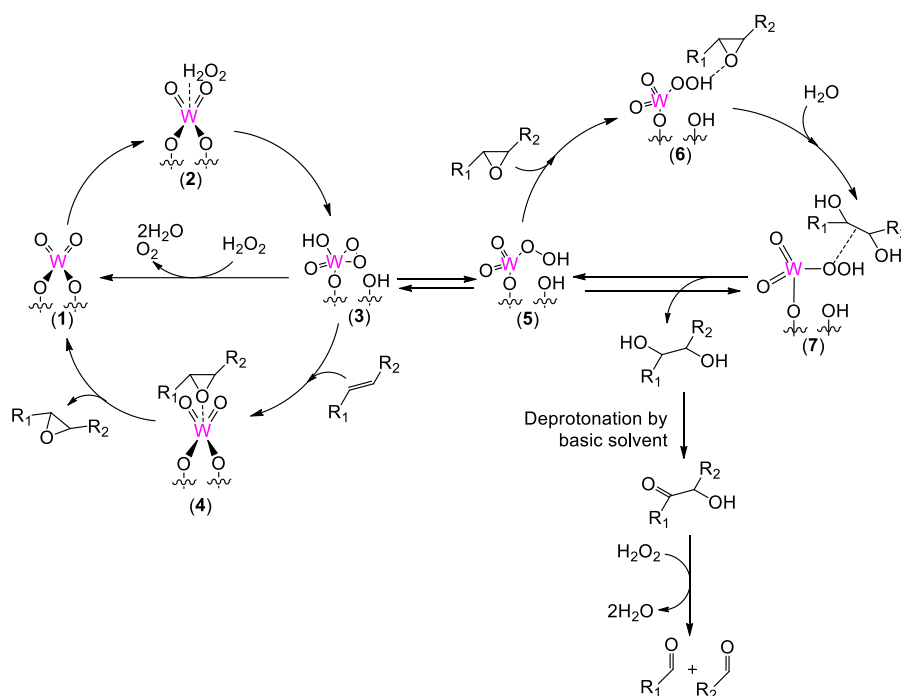


Figure 2. Tungsten oxides active in oxidative cleavage of UFAs [inspired from 141,142]

As regards $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$, the catalyst showed better results (yields of AA=77% and PA=69%) due to water linked molecules which promote the *in-situ* production of tungsten-peroxo groups during the oxidative cleavage reaction [143,144]. The influence of temperature was assessed as well, demonstrating that lower reaction temperatures decrease the catalytic activity of tungsten oxides. On the other hand, higher temperatures than 120 °C may cause H_2O_2 decomposition as well as PA and AA. Finally, recycling tests confirmed that only $[(\text{WO}_2)\text{O}_2 \cdot \text{H}_2\text{O}]$ lost catalytic activity after the first run due to a decomposition of the tungsten-peroxo structure [133]. The stability of the other tungsten oxides can be ascribed as a result of calcination treatments which provided them an unalterable crystalline structure to maintain their catalytic activity up to four recycling tests [140].

After assimilating the aforementioned information, the next step consisted in functionalizing a suitable support with these active tungsten oxides for the oxidative cleavage of UFAs. Therefore, a recent work carried out by Flaherty and co-workers was dedicated in grafting organometallic tungsten complexes on mesoporous γ -alumina (mean pore size = 3.8 nm, specific surface area = 364 m^2/g) [145,146]. Flaherty *et al.* dissolved bis(cyclopentadienyl)tungsten dichloride $(\text{C}_5\text{H}_5)_2\text{WCl}_2$ into chloroform under argon atmosphere. Afterwards, 3 equivalents of triethylamine $(\text{C}_2\text{H}_5)_3\text{N}$ were added to the mixture in order to deprotonate the hydroxyl groups of γ -alumina favoring the adsorption of $(\text{C}_5\text{H}_5)_2\text{WCl}_2$ on the mesoporous support. The mixture was stirred for another 12 h followed by filtration and a further calcination at 550 °C to promote the transformation of the organo-tungsten complexes into WO_x [145].

The synthesized catalysts were assessed in the oxidative cleavage of oleic acid along with H_2O_2 as conventional co-oxidant and MeCN as solvent. In addition, *in situ* Raman and UV-vis Spectroscopy was conducted to determine tungsten species during the oxidative cleavage reaction. The data collected allowed the authors to propose the mechanism described in Scheme 15 [145]. First, H_2O_2 activates $\text{WO}_x\text{-}\gamma\text{Al}_2\text{O}_3$ to form a $\text{W-(}\eta^2\text{-O)}$ intermediate (3) confirmed by UV-vis measurements. Then, (3) reacts either with a UFA molecule to form an epoxide (4) or react with a second molecule of H_2O_2 to decompose it into 2 molecules of H_2O and one molecule of O_2 with the consequent regeneration of the tungsten oxide (1). The probability to have (1) or (4) depends of the UFA/ H_2O_2 ratio present in the reaction medium. The (4) intermediate releases the epoxide which is ready to pursuit a catalyzed ring opening.



Scheme 15. Proposed mechanism of oxidative cleavage of UFAs with $\text{WO}_x\text{-}\gamma\text{Al}_2\text{O}_3$ heterogeneous catalyst [145]

The authors propose that (3) may evolve into an acidic W-OOH species (5) whose acid sites protonate and bind the epoxide to yield intermediate (6). After hydrolysis of the epoxide, a vicinal diol is formed which is desorbed from intermediate (7). Finally, the authors propose that the diol is deprotonated by the basic solvent and transformed into a α -hydroxy ketone which then is cleaved by a nucleophilic attack of H_2O_2 [145].

In spite of the high capability of W-peroxo sites to perform the oxidative cleavage of UFAs, yields of oxidative cleavage products are still low due to WO_3 agglomeration into nanoparticles yielding only epoxides [145]. Even though epoxidation and dihydroxylation of UFAs are easily promoted by W-OOH species, the limited number of protic sites and competitive adsorption of oleic acid to the W atoms on the WO_3 surface prevent the epoxide for reacting with W-OOH complexes as required for hydrolysis. Hence, efforts must be focused increasing dispersion of reactive tungsten complexes instead of WO_3 nanoparticles [145]. In addition, attention must be paid to the nature of the support since it can also determine the number of protonated intermediates required to assist the hydrolysis of the epoxide ring and the consequent increase of the catalytic activity and selectivity.

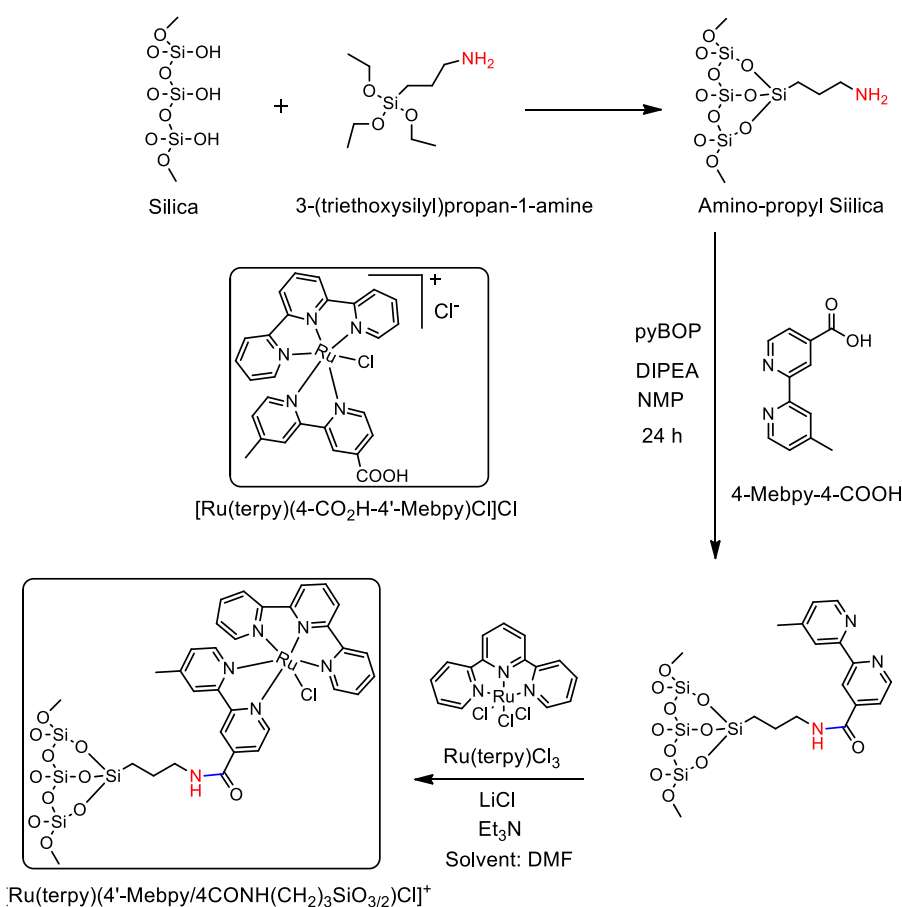
2.2.3. Ruthenium supported catalysts

RuO_4 , has shown great catalytic activity in the oxidative cleavage reaction as stated in the homogeneous catalysis section. Nevertheless, few examples are reported in literature related to the heterogenization of this Ru complex or similar, onto a suitable support for an easier handling in this kind of reaction. Among the few works presented so far, Yu and co-workers demonstrated the possibility to deposit Ru nanoparticles on hydroxyapatite (HAP) [146,147]. In this matter, RuCl_3 was dispersed in a 1,2-propanediol solution along with sodium acetate at 150 °C [148]. Upon reduction of ruthenium the resulted nanoparticles were put in contact with HAP to graft them on the support. X-ray diffraction (XRD) analysis confirmed HAP maintained the same phase after Ru nanoparticles deposition while transmission electron microscopy (TEM) displayed a high degree of dispersion of Ru nanoparticles on HAP surface. In addition, inductively coupled plasma mass spectrometry ICPMS confirmed a Ru loading of 5 wt % on HAP support whereas the Ca:P molar ratio was 1.66 which indicates no significant exchange of Ca^{2+} ions occurred during Ru nanoparticles deposition [149].

The synthesized nano-RuHAP catalyst was tested in the oxidative cleavage of several alkenes including methyl oleate. For this purpose, 4 mol% Ru of catalyst was added to 0.5 mmol of methyl oleate with 1 mmol of NaIO_4 in a 1,2-dichloroethane/ H_2O (5:1 v/v) solution at room temperature for 12 hours. After this time, a 16% conversion was achieved with high yields of PA and AA (84% and 79% respectively). Although poor conversion was obtained due to diffusional issues, the yields were higher than those obtained with tungsten oxides at higher temperatures. In addition, recycling tests were successful only with simple alkenes, but Yu and co-workers affirmed that Ru nanoparticles on HAP could behave similarly on large aliphatic alkenes such as oleic acid [147].

Not only metallic Ru has been deposited on a support, but other sophisticated Ru complexes have been grafted on other materials like silica for the oxidative cleavage reaction. For instance, Garoufis *et al.* attached a

Ru(terpy)Cl₃ complex on a modified amino-propyl-silica by means of a pseudo-peptide bond using a 4-Mebpy-4-COOH (4-methyl-2,2'-bipyridine-4-carboxylic acid) ligand as a connector between the Ru complex and the silica support (Scheme 16). Benzotriazol-1-yloxytris(pyrrolidino)phosphonium hexafluorophosphate (pyBOP) and diisopropylethyl-amine (DIPEA) were employed as coupling agents while N-methyl-2-pyrrolidone (NMP) was used as solvent [150].

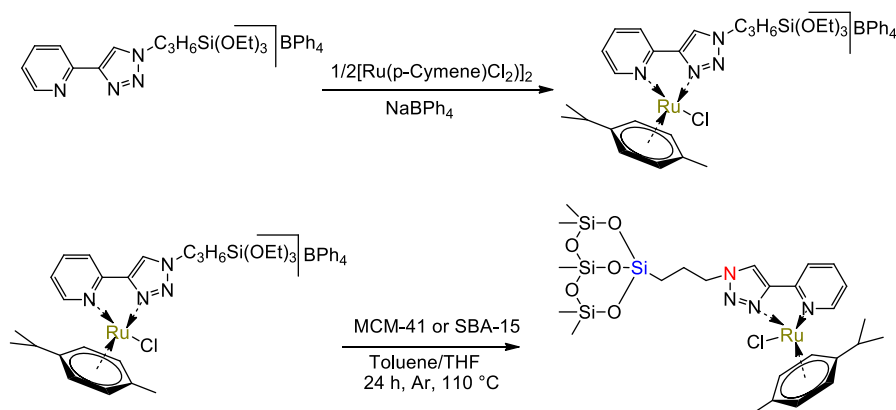


Scheme 16. Functionalization of silica with (4-methyl-2,2'-bipyridine-4-carboxylic acid) ligand for the chelation of Ru(terpy)Cl₃ complex [150]

Both the homogenous [Ru^{II}(terpy)(4-CO₂H-4'-Mebpy)Cl]Cl complex and the Ru-silica heterogeneous catalyst were assessed in the oxidative cleavage of various olefins with *tert*-butylhydroperoxide (TBHP) as oxidizing agent [150,151]. Catalytic tests were performed using 1 mol of substrate along with 0.1 mol% of catalyst and 0.1 mol of TBHP dissolved in *tert*-BuOH at room temperature under argon atmosphere. No UFAs were evaluated in this work but large molecules such as *cis*-stilbene were cleaved by both Ru catalysts

[150]. The Ru-silica catalyst shows a profile of oxidation products analogous as that of the Ru homogenous catalyst. However, in some cases (e.g. *cis*-stilbene) the Ru-containing modified silica showed increased activity providing total oxidation yields of 89% versus 48% produced by Ru homogeneous catalyst. In addition, it is worth to know silica does not provoke any steric hindrance which may prevent the substrate to access the active metal sites [150]. Although, the applied grafting process preserves the catalytic activity of the organometallic complex, the catalytic system requires an inert ambient to perform the reaction. Moreover, yields of the desired oxidative cleavage products (e.g. 25% of benzaldehyde and 64% of epoxide in the case of *cis*-stilbene) [150] were low compared to conventional RuO₄ homogenous catalytic system.

Following the same trend, Mapolie *et al.* functionalized mesoporous silica with Ru-triazole-arene complexes for the oxidative cleavage of various alkenes [152]. First a siloxane functionalized Ru complex was synthesized using a [Ru(*p*-cymene)Cl₂]₂ precursor along with NaBPh₄ and a pyridine N-oxide triazole ligand as described in Scheme 17. Then, silica (MCM-41 or SBA-15) was mixed with the functionalized complex in a solvent mixture formed by toluene and THF under inert atmosphere. The yellow mixture was refluxed at 110 °C under stirring for 24 h followed by filtration, washing with ether and drying in vacuum at 40 °C. Catalytic tests were carried out with 0.1 mol% catalyst and periodic acid (HIO₆) as oxidant in a H₂O/MeCN/CCl₄ solvent mixture [153].



Scheme 17. Preparation of silica modified with Ru-triazole-arene complex [152]

During the catalytic test the heterogeneous catalyst showed enhanced activity when compared to conventional homogeneous systems even when operating at a relatively low catalyst loading. According to the authors, this phenomenon is due to the synergism achieved between the silica support and the Ru-triazole-arene complex [152]. UV-visible measurements

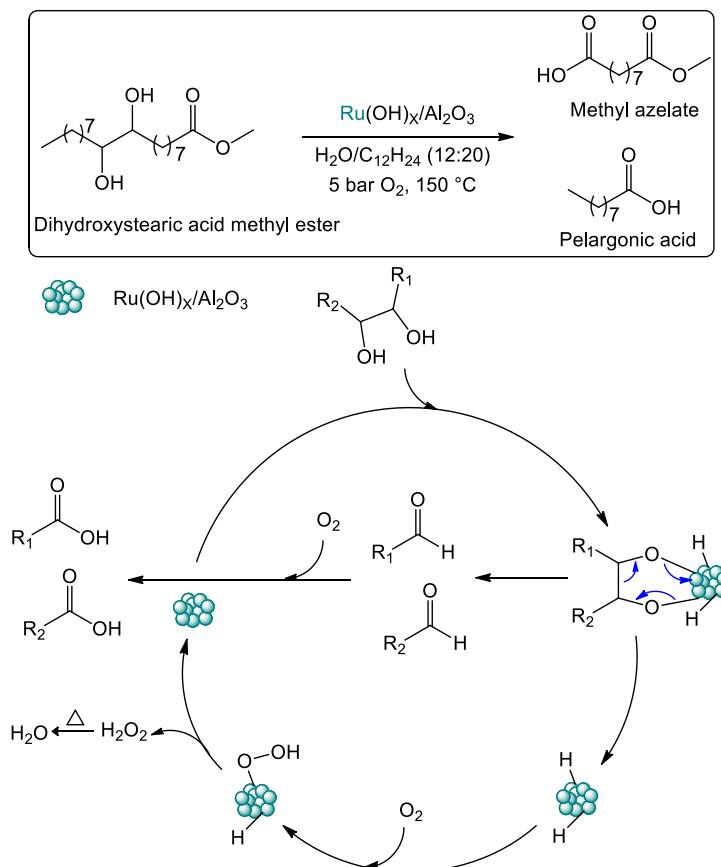
confirmed the presence of RuO₄ in the organic phase during oxidative cleavage tests with the immobilized Ru catalysts which means that Ru leaching occurred during these tests [153,154]. On the other hand, several authors claim that silica support operates as a phase transfer agent improving the diffusion of the Ru-triazole-arene pre-catalyst into the aqueous phase for its transformation in RuO₄ by periodic acid [155-157]. As regards the influence of the support, Mapolie *et al.* found evidence that larger micropores (SBA-15 SBET = 708 m²/g; Pore diameter = 40.6 nm) are more important than a high specific surface area (MCM-41 SBET = 1079 m²/g; Pore diameter = 28.6 nm) since SBA-15-Ru solid catalyst presented a better catalytic activity than its counterpart with MCM-41 [152]. To conclude, even if Mapolie *et al.* achieved great conversions (99% in 9 h) in the oxidative cleavage of small alkenes (1-octene), no recycling tests were carried out because of Ru leaching. Besides, no larger aliphatic alkenes (e.g. UFAs) were assessed in this work, so the scope of the proposed Ru-silica catalysts is limited.

A recent work carried out by Lemaire and co-workers achieved the oxidative cleavage of dihydroxystearic acid methyl ester (the vicinal diol of methyl oleate) using a Ru(OH)_x grafted on γ-alumina [158]. The solid catalyst was synthesized by putting in contact γ-Al₂O₃ previously calcined at 600 °C, with an aqueous solution of RuCl₃ (20 mM). After 15 minutes of stirring the pH solution was adjusted to 13.2 through the addition of a 1.0 M NaOH solution with continuous agitation up to 24 h. The solid Ru(OH)_x - γ-Al₂O₃ was obtained after filtration and drying as a green dark powder [159]. Unlike the previous cited examples, this time the oxidative cleavage reaction was performed in a stainless-steel autoclave with mechanical stirring and oxygen pressure (5 bar) as oxidizing agent. Dihydroxystearic acid methyl ester was added to water with 6 mol% of Ru catalyst at 150 °C. With the mentioned conditions 80% of conversion was achieved after 5 h of stirring with 45% and 43% yields of PA and AA respectively [158]. The presence of several by-products such as octanoic acid, 8-methoxy-8-oxooctanoic acid, methyl oleate ozonide and other epoxides were evidenced. The authors proposed that oxygen starvation in the solvent was the reason of such byproducts [160,161].

To solve this issue, CO₂ and dodecane were incorporated as diluents for oxygen in order to improve the catalytic performance of the Ru(OH)_x - γ-Al₂O₃ solid catalyst. Even 51 bars of oxygen pressure were not enough for attaining high yields (PA yield = 68%; AA yield=67%) when CO₂ was tested, but dodecane resulted to be a better diluent for oxygen since >99% conversion was achieved along with greater yields towards the oxidative cleavage products (PA = 85% and AA = 80%) [158]. According to Lemaire *et al.* dodecane contributed to a better dissolution of oxygen in the solvent which in turn promotes O₂ diffusion towards the substrate. On the other hand, an increase in the reaction temperature (from 150 °C to 170 °C) did not improve the catalytic activity of the solid catalyst while recycling tests confirmed that catalyst started to lose activity after 4 runs as a consequence of catalyst deterioration and small Ru leaching (< 0.03 wt % of initial Ru

content). However, Lemaire and co-workers were able to regenerate their catalyst after a sonification treatment with a 1.0 M NaOH solution [158].

As regards the pathway for the oxidative cleavage of the vicinal diol with ruthenium hydroxide – $\gamma\text{Al}_2\text{O}_3$ catalyst, the authors propose that the diol could be adsorbed on the catalyst surface forming a cyclic ester. After a rearrangement of electrons, the cyclic ester is cleaved into two aldehydes and a metal hydride. The solid catalyst is regenerated by means of O_2 , producing hydrogen peroxide that is decomposed into water under the experimental conditions used ($T > 130\text{ }^\circ\text{C}$). Other possibility could involve H_2O_2 as a radical initiator for the aerobic oxidation of aldehydes, leading to the desired carboxylic acids (Scheme 18) [158,162].



Scheme 18. Proposed mechanism for the oxidative cleavage of dihydroxystearic acid methyl ester with $\text{Ru(OH)}_x - \gamma\text{Al}_2\text{O}_3$ [inspired from 158]

To sum up, Ru heterogeneous catalysts are just being studying in depth and most of the works reported in the literature are related to aromatic or small

alkenes. The few examples about oxidative cleavage of UFAs with Ru based supported catalysts still present various shortcomings such as low catalytic activity, leaching issues, or the need of high temperatures and pressure as it was stated in the last example. Hence, new strategies must be applied in order to transfer active Ru complexes, mainly RuO_4 , on a suitable support for the oxidative cleavage of UFAs.

2.3. Conclusions from homogeneous and heterogeneous catalysis in the oxidative cleavage of UFAs

Throughout this compilation of works related to the oxidative cleavage of UFAs (Table 1), homogenous catalysts prepared with Os, Ru and W complexes have shown a better catalytic activity than their heterogeneous counterparts. As regards Os and Ru, their tetroxide form is quite active in the mentioned reaction. The main difference between them lies in the different pathway provided for each complex. While OsO_4 mainly leads to dihydroxylation reactions, RuO_4 can continue the reaction producing the desired carboxylic acids [5,96,108]. Other important aspect is OsO_4 volatility and toxicity which make it hard to handle at industrial level [89]. Although, Brutchey *et al.* [128] and Song *et al.* [130] have demonstrated interesting strategies for OsO_4 immobilization on fullerene and polymer resins respectively, only vicinal diols were producing through dihydroxylation reaction requiring an over oxidation to cleave the cited diol [128,130].

As regards tungsten, various efforts have been made to identify the active peroxo-tungsten species necessary for the oxidative cleavage of alkenes and UFAs [140-142]. The works of Turnwald *et al.* [84] as well as Do and coworkers [138] clearly demonstrated that tungsten oxides (e.g. $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$) is a promising candidate for the oxidation of carbon-carbon double bonds by means of an epoxidation-dihydroxylation and over-oxidation pathway [138]. In the last years, successful attempts on the immobilization of $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$ on different supports have been performed for oxidative cleavage applications [140]. Although great catalytic activity can be accomplished with tungsten oxide using a soft oxidizing agent like H_2O_2 , it is necessary a good control of the reaction conditions in order to avoid side reactions, products decomposition because of a prolonged heating period or leaching issues in supported catalysts [133]. It is important to remark that tungsten oxides require higher reaction temperatures than those required with RuO_4 or OsO_4 in order to attain the same catalytic results as with the mentioned transition metal complexes [133,140].

Finally, RuO_4 which is the oldest active species known for the oxidative cleavage of alkenes and UFAs, is more active and selective than Os and W oxides [96,111]. Normally the use of RuO_4 does not lead to byproducts. As indicated before, RuO_4 can carry out the reaction at room temperature [96,111,114]. Hence, the proper use of these Ru species may allow to produce value added products with high conversions and yields [111,114].

Table 1. Summary of catalysts reported in the literature active in the oxidative cleavage of UFAs

Catalyst	Substrate	Oxidant	Solvent	Conditions	Conv. (%)	Yield (%)	Reference
OsO ₄	Methyl oleate	H ₂ SO ₅	DMF	3 h; RT	>99	PA=80 MA= 93	95
H ₂ WO ₄ /Co(acac) ₃	Erucic acid	H ₂ O ₂ /O ₂	<i>t</i> BuOH	3 h; 75 °C	Not reported	PA=15 AA=15	98
PCWP	Oleic acid	H ₂ O ₂	Solvent free	3 h; 80 °C	Not reported	PA=82 AA=86	100
RuO ₄	Oleic acid	NaIO ₄	H ₂ O/MeCN/AcOEt	2 h; RT	>99	PA=65 AA=73	30
RuO ₄	Oleic acid	NaIO ₄	H ₂ O/MeCN/AcOEt	1 h; UI	>99	PA=78 AA=88	114
Ru(2,6-dipicolinate) ₂	Oleic acid	H ₂ O ₂	<i>t</i> BuOH/H ₂ O	24 h; 80 °C	>99	PA=59 AA=81	117
WO ₃ /SiO ₂	Oleic acid	H ₂ O ₂	<i>t</i> BuOH	1 h; 130 °C	96	PA=36 AA=32	133
WO ₃ .0.33H ₂ O	Oleic acid	H ₂ O ₂	<i>t</i> BuOH	5 h; 120 °C	>99	PA=69 AA=77	140
Ru/HAP	Methyl oleate	NaIO ₄	1,2dichloroethane/H ₂ O	12 h; RT	16	PA=84 MA= 79	147
Ru(OH) _x /A ₂ O ₃	dihydroxystearic acid methyl ester	O ₂	H ₂ O/C ₁₂ H ₂₄	5 bar, 150 °C	80	PA=45 MA= 43	157

DMF: Dimethylformamide; RT: room temperature; PA: pelargonic acid; MA: methyl azelate; AA: azelaic acid; MeCN: acetonitrile; AcOEt: ethyl acetate; PCWP: peroxo-tris (cetylpyridinium)12-tungstophosphate

The main drawbacks of RuO₄ are related to its toxicity as well as polluting solvents such as CCl₄ required for the normal ongoing of the oxidative cleavage reaction [96,111,114]. In order to overcome these issues, some efforts have been made to heterogenize RuO₄ on various supports. Most of the examples found in literature (and cited in the previous section) employed nitrogen ligands to connect the superficial functional groups of the selected support to a Ru complex [150,152]. Unfortunately, these grafting techniques have not produced the desired results in terms of yield and, in the case of Mapolie *et al.* Ru leaching arises as a major adversity [152]. Besides, most of the Ru-supported catalysts have been tested only with small alkenes [147,150,152]. The few examples related to heterogeneous Ru catalysts towards the oxidative cleavage of UFAs present low catalytic activity or require harsh conditions such as 5 bars of oxygen pressure along with high temperatures [147,158].

Therefore, the heterogenization of Ru on suitable supports for the oxidative cleavage of large aliphatic molecules like UFAs still requires a deep investigation. The above-mentioned works provide insights about the strengths and weaknesses of the Ru-supported catalyst in this oxidation reaction. It seems that the right path towards an efficient Ru supported catalyst is associated to a proper functionalization of a support in order to incorporate well dispersed active species without losing the catalytic activity they had in homogenous phase. In order to propose a solution in this direction, general and innovative approaches for support functionalization in catalysis applications are presented in the next section.

3. General approaches for the functionalization of supports towards catalysis

Functionalization of a material consists in modifying its surface by providing different physical, chemical, or biological characteristics from compounds not found in the original material's surface [163]. Thus, the functionalization process implies the introduction of desired groups on the surface mainly by means of chemical reactions or physical procedures [164]. As a consequence, the original characteristics of the material's surface are altered such as roughness, hydrophilicity, surface charge, surface energy, biocompatibility, and reactivity [165]. The functionalized materials can be profited for several applications in the chemical industry [164]. As regards catalytic applications, functionalized materials such as silica, alumina or carbon can be used as supports or reactors in several domains like heterogeneous catalysis, photocatalysis, petrochemistry and electrocatalysis, among others [166]. Since hydroxyl, amine, carbonyl or carboxylic groups are part of the surface of natural or synthetic carbonaceous, oxides or siliceous materials, most of the functionalization techniques use compounds with similar functional groups [166,167]. It is worth to know that recent functionalization techniques prioritize the use of non-hazardous compounds and solvents in order to align with the goals of green chemistry in today's global context [168]. Such functionalization

methodologies must contemplate less reaction steps which leads to reduced costs and low generation of wastes [168,169]. Generally, functionalization techniques are classified into two main groups: covalent and non-covalent functionalization methods [164,167]. Both types of techniques are here described emphasizing more on covalent functionalization since this technique is essential to develop Ru-supported catalysts for oxidation reactions.

3.1. Non-covalent functionalization

Non-covalent functionalization consists in a supramolecular complexation between the surface of a support and the modifying compounds using different adsorption forces such hydrogen bonds, Van der Waals forces, electrostatic interactions and π -stacking [170]. By this means it is possible to build highly dispersed materials applicable to catalysis applications [171]. Because of the weak forces associated to non-covalent functionalization techniques, the interaction between the surface of the material and the modifying molecules will be weak in most of the cases [170]. Nevertheless, the main advantage is that these techniques do not require complicated chemical procedures and appear straightforward, efficient and economic. As regards catalytic applications, non-covalent functionalization methods may contribute to the stereochemical outcome in a reaction by controlling the position of the active site with respect to the support [170,172]. Non-covalent functionalization methods can be classified in the following categories: electrostatic interactions, coordinative approach, adsorptive forces, and entrapment methods [170].

Electrostatic interactions depend on the surface charge of the support and the nature of the transition metal complex to be supported [173]. Normally, in this methodology an exchange between a metallic ion on the support with a counterion of the desired metal complex takes place which brings the transition metal complex on the support's surface [170]. The salt formed between the support's metallic ion and the complex counterion must be removed through a suitable solvent in order to avoid reversible electrostatic interactions [170,173]. According to the charge of the metal complex a cationic or an anionic support should be selected. For instance, an Al-Mg layered double hydroxide (LDH) was employed as an ion-exchanger for the immobilization of osmate in the hydroxylation of various alkenes [174]. The Os catalyst synthesized by this means resulted active in the mentioned reaction but the performance depends greatly on the type of solvent and oxidant used. In fact, when $K_3Fe(CN)_6$ or oxygen were used as the co-oxidants, the ferrocyanide ion or the phosphate anion from the phosphate buffer used in the case of oxygen, displaced the osmate anion from the support causing the catalyst deactivation due to Os leaching [174].

Another non-covalent functionalization technique is related to physisorption by means of Van der Waals forces and hydrogen bonds [170]. This kind of technique is quite important when the support to be functionalized

possesses a high surface area (e.g. activated carbon > 1000 m²/g) [175,176]. Although a great dispersion of the metal complex could be achieved, leaching issues cannot be overcome through this method [170,177]. For example, Inoue *et al.* performed the adsorption of [(DIOP)Rh(cod)Cl] and [(BPPM)Rh(cod)Cl] neutral complexes on charcoal. Both complexes were adsorbed from ethanol/water (1:1) solution. The catalyst was tested in the hydrogenation of (Z)-2-acetamidocinnamic acid and although Rh leaching was detected, the catalyst maintained 86% of its original loading after 4 recycling tests [178].

One interesting strategy related to non-covalent methodologies is the encapsulation technique. In this case, a catalytic metal complex is enclosed inside the structure of the support without the need for an additional support-complex interaction [170,179]. The pore size of the support must be smaller than the catalyst in order to avoid its diffusion toward the reaction medium, but not too small so the substrates may get inside the pore to interact with the metal complex during the catalytic tests. In the literature there are two types of encapsulations, a metal complex enclosed into a flexible polymer matrix or an entrapment into a rigid inorganic structure [170,179].

An example for the use of polymers was performed by Ishida and Kobayashi, when they attempted to encapsulate OsO₄ inside a cross-linked polystyrene matrix for dihydroxylation reactions [180]. For this purpose, OsO₄ was put in contact with polystyrene, and methanol was added slowly at 0 °C. After the catalyst was filtered and dried, it was tested in the dihydroxylation of small alkenes without losing catalytic activity after several recycles [180]. An example related to entrapment inside inorganic solids was performed by Owungumi and Bein using an EMT zeolite to encapsulate a manganese chiral complex for epoxidation reactions. The encapsulated complex was tested in the epoxidation of different alkenes in an aqueous NaClO solution [181]. In this case conversion and selectivity towards epoxides were much lower than those in solution. The explanation could be associated to diffusion restrictions which caused that a significant portion of the immobilized complex did not take part in the reaction [181].

In summary, non-covalent functionalization methods may contribute greatly to various catalytic applications in spite of their limitations. However, for the oxidative cleavage of UFAs, these kinds of techniques do not seem to be promising in the attachment of suitable metal complexes. As it was mentioned, OsO₄, which is active as well in the oxidative cleavage reaction, was not efficiently heterogenized by electrostatic or adsorptive methods. As regards to the encapsulation technique, it is important to point out that large molecules such as UFAs (e.g. oleic acid or linoleic acid) would not get inside the support in order to take contact with the catalyst [133]. Therefore, diffusion limitations would be the Achilles' tendon of this last heterogenization strategy.

3.2. Covalent functionalization

This kind of surface functionalization involves covalent bonds between the superficial functional groups of a support and the functional groups of the molecules to be grafted [167, 182]. These covalent bonds are more stable, and as consequence, more difficult to break than weak interactions discussed in the non-covalent functionalization section. The type of covalent bond will depend on the surface nature (e.g. oxide or a carbonaceous material) and the type of molecule to be grafted (e.g. amine, carboxylate, catechol) [182,183]. In the case of catalysis, covalent functionalization techniques could be classified in two groups: direct functionalization and indirect functionalization [167]. In the former, a covalent bond is formed between the superficial functional groups of the support and the ligands of the transition metal complex. In the latter, the catalyst and the support are covalently bonded through an organic linker [167,182].

Commonly various functionalization examples for the development of heterogeneous catalysts are found in literature. For instance, in the case of direct functionalization, Paredes *et al.* functionalized MoS₂ nanosheets with acetic acid groups towards the reduction of several nitroarenes [184]. The functionalization of MoS₂ surface was accomplished by putting in contact a dispersion of the nanosheets with iodoacetic acid for 5 days. After filtration and washing with different solvents, the functionalized MoS₂ nanosheets were dialyzed for 2 days against water to further remove unreacted species [184,185]. The functionalized nanosheets exhibited a long-term (> 6 months) colloidal dispersion in aqueous medium and a high retention of catalytic activity toward the reduction of nitroarenes such as 4-nitrophenol into 4-aminophenol [184].

A recent example of indirect covalent functionalization was carried out by Wu *et al.* where a Ru polypyridyl complex was attached on carbon nanotubes for water splitting [186]. In a first stage the carbon support was modified with 2,2'-bipyridine (bpy) in order to use this organic compound as a bridge between the carbon nanotubes and the Ru(tpy-OMe)Cl₃ complex. The resulting Ru-heterogeneous carbon catalyst shows good catalytic oxygen evolution performance due to the higher electrochemical activity provided by the carbonaceous structure and bpy ligands [186,187]. Hence, it is clear that modified surfaces by means of covalent functionalization can improve the properties of determined materials towards different applications including catalysis. More important, covalently bonding a transition metal complex (normally active in homogeneous catalysis) to a desired support, allows the easy recovery of the catalyst from the reaction medium decreasing the risk of losing the active species due to leaching [122,167].

In section 2.2.3, examples of covalent functionalization have been presented related to Ru supported catalysts [150,152]. It has been noticed that Ru-amino complexes, especially those with bpy ligands, show catalytic activity in the oxidative cleavage of alkenes. Therefore, the properties of this

aromatic ligand are detailed in the next section as a promising tool for the heterogenization of Ru in the oxidative cleavage of UFAs.

3.2.1. General aspects of bipyridine

In coordination chemistry 2,2'-bipyridine (bpy) is one of the most common and used ligands for metal complexes preparation [188,189]. This ligand presents a planar *trans*-conformation with respect to the inter-annular C–C bond. On the other hand, the monoprotonated bipyridine cation is usually close to a *cis*-coplanar conformation with both nitrogen atoms facing each other [188]. As regards its coordination behavior, bpy is a bidentate ligand which may form three different covalent bonds with a transition metal center: monodentate, chelation, and bridged bidentate (Figure 3) [188-190]. The most common coordination mode is the chelating bidentate way where both nitrogen atoms are bonded to the same metal center. Less reported in literature are complexes in which bpy ligand is monodentate [190,191]. It is worth to mention that bpy coordination complexes have played essential roles in various applications such as photochemistry, photophysics, electrochemistry and of course catalysis [188,189].

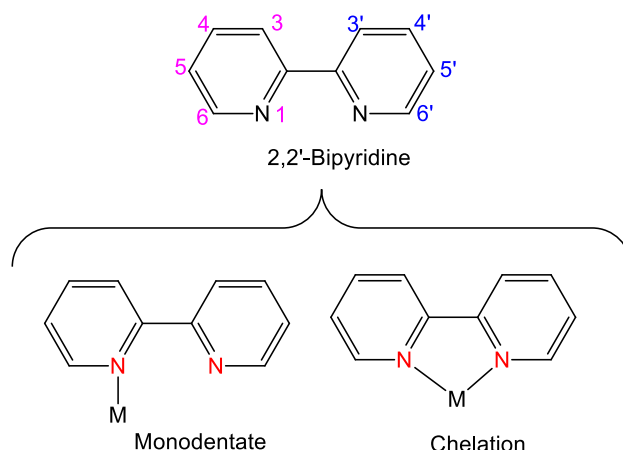
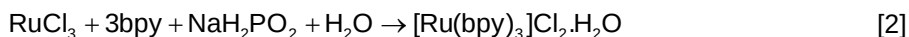


Figure 3. Structure of 2,2'-Bipyridine and its coordination modes

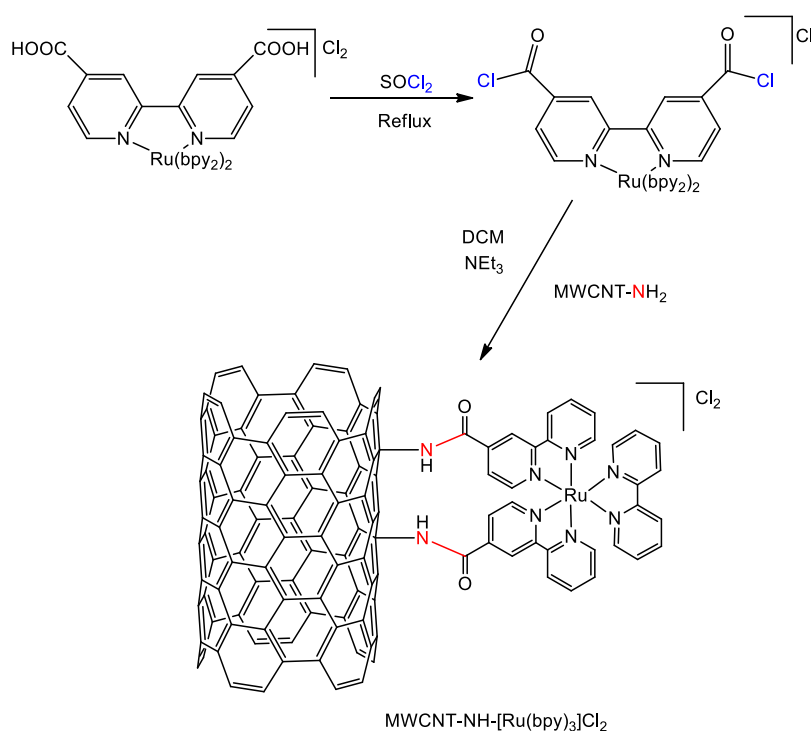
Usually, bpy forms stable complexes with transition metals of group 8 (Fe, Ru and Os). Most of the examples are related to Ru-bpy complexes which are significantly more stable than iron(II) and nickel(II) analogues [188]. For instance, RuCl_3 can be reduced by sodium phosphinate and then it can be chelated by bpy to form the $[\text{Ru}^{\text{II}}(\text{bpy})_3]\text{Cl}_2$ complex as follows [192]:



Ru-bpy complexes and their derivatives are known for being stable, with highly conductive properties and an enormous versatility for various catalytic applications [193,194].

3.2.2. Functionalization through bipyridine

Moreover, aromatic rings of bpy can be functionalized in order to add suitable functional groups for covalent bonding with the functionalities of different supports [195]. For instance, Rillema and co-workers tested several procedures to add carboxylic acids, phenols or esters in the aromatic structure of bpy involving oxidations with KMnO_4 , esterification with alcoholic solutions, among other procedures [196]. The functionalized bpy with COOH groups can be used to form a complex with a Ru precursor salt as described in Equation 2 [192]. Benrezzak *et al.* proposed a functionalization method where a Ru-bpy-COOH complex is modified by means of a thionyl chloride (SOCl_2) solution under argon atmosphere and reflux. As shown in Scheme 19, carbon nanotubes previously functionalized with amines (MWCNT-NH₂) form an amide bond with the Ru-bpy-COCl complex through an addition-elimination mechanism [197].



Scheme 19. Covalent functionalization of a $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ complex on MWCNT-NH₂ [197]

The reason why SOCl_2 is added to the Ru-bpy-COOH complex is to favor the amidation reaction since chlorine is a better leaving group than OH [197]. Through these kind of covalent functionalization strategies, it is possible to synthesize stable complexes which can be transferred to the surface of a support. It is worth to know that carbonaceous materials are easy to functionalize and their textural properties can be modulated by chemical or physical methods [186,197]. As it was stated in section 2.1, some Ru-arene complexes were active in the oxidative cleavage of alkenes [150,152]. Therefore, a Ru-bpy complex grafted on a suitable support could be useful in the oxidative cleavage of UFAs.

3.3. Polymer functionalization

This kind of functionalization involves the use of polymers for superficial functionalization either by covalent (grafting) or non-covalent methods (adsorption) [198]. In the case of a covalent approach, the polymer is attached to a surface by *in situ* polymerization of monomers in presence of the required initiators for triggering the polymerization. Thus, the polymer functional groups interact with superficial groups of the support while polymerization takes place at the same time [198]. The benefit of this methodology is that a polymer coating with high grafting density can be easily produced and deposited on the material to be functionalized [198,199]. For example, Hua *et al.* introduced styryl moieties onto MWCNTs surface previously treated with sodium carboxylate and chloromethylstyrene in toluene. Under ultrasonic treatment under N_2 atmosphere at 70 °C, the styryl-modified MWCNTs reacted as *in situ* radical copolymerization with free styrene in the reaction mixture [199,200]. The attachment of polystyrene on MWCNTs surface was confirmed through FTIR and UV-visible spectroscopy analyses while thermogravimetric (TGA) and differential scanning calorimetry (DSC) analyses demonstrated an enhanced thermal conductivity of the functionalized carbon material [199].

There is a plethora of examples in the literature about polymer functionalization on different kind of surfaces and most of them require complicated procedures with hazardous reagents and solvents [201-203]. On the other hand, the scientific community have oriented its attention to a natural polymer with outstanding properties which can be leveraged in several applications. Polydopamine (PDA) has been used as a polymer coating for almost all kind of materials from oxides to carbonaceous surfaces in the last years [204]. This polymer comes from the polymerization of dopamine which is a neurotransmitter responsible for transmitting signals between the nerve cells of the brain. In the world of medicine, dopamine is often called a chemical messenger that plays an essential role on our central nervous system [205]. When dopamine polymerizes into PDA, its structure and its functional groups make it a very advantageous material for the functionalization of different supports that can be exploited in various chemical applications including catalysis [204]. The most important features of PDA are summarized below.

3.3.1. Polydopamine

Polydopamine (PDA) is considered as a polymeric coating employed for the protection of materials from erosion, acidic, alkaline conditions or strong oxidizing agents [205]. This coating material has been used in the last years as a protective layer for many substrates such as metals, ceramics, carbonaceous materials among others. In addition, PDA is a major pigment of naturally occurring melanin [205,206]. Consequently, PDA possess similar properties as naturally occurring melanin in optics, electricity, and magnetics [205]. Above all, it presents an excellent biocompatibility which makes it suitable for medical applications [207]. Another important feature of PDA is related to its chemical structure which consists in an indole ring with amine and catechol groups (Figure 4). These functional groups may be used for covalent functionalization to different surfaces. In the case of graphene layers, a non-covalent functionalization can occur by π -stacking interactions via the aromatic indole rings. As regards coordination chemistry, functional groups of PDA may serve as anchor sites for complexation of transition metal ions [208].

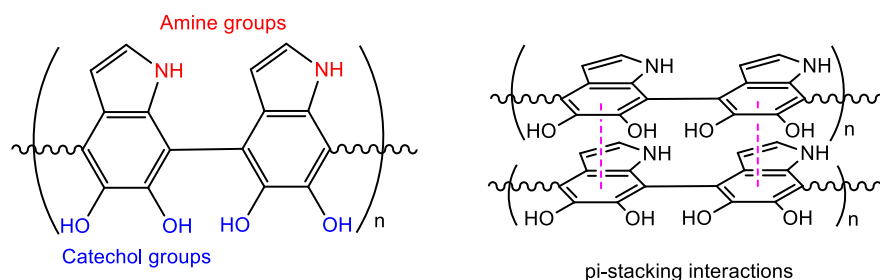


Figure 4. Main structure of PDA and π -stacking interactions between PDA layers [inspired from 205-208]

Thanks to its versatility related to the chemistry of its structure, PDA possess high capacity of adherence to various materials. Evidently, this feature may also depend on superficial functionalities present in each support which may lead to covalent or non-covalent interactions, or even both [209]. For instance, surfaces that contain amine or thiol groups on their surfaces may interact with catechol groups of PDA by Michael addition or basic Schiff reactions under alkaline conditions while, at ambient conditions, non-covalent bond interactions may take place [205,209]. As regards metal surfaces, it is important to mention that catechol groups of PDA can chelate metal ions as bidentate complexes [205,209]. Thus, different coordination interactions can play a central role in the adhesion of PDA to various materials and metal oxides [210]. For example, it has been reported that Fe_2O_3 , Al_2O_3 or ZrO_2 have been coated with PDA through the coordination between the oxide and the catechol group. In some cases, more than one interaction may be involved between PDA and the substrates [210,211]. In

the case of TiO₂ surface, the adherence mechanism between these two entities remains a controversial subject. Some authors have proposed that catechol groups interact with TiO₂ by bidentate chelating bond [210-212].

One of the most remarkable benefits of PDA is the ability to adhere to organic and hydrophobic surfaces; however, the adherence mechanism is still not well understood. Using atomic force microscopy (AFM), Lee and co-workers have demonstrated that the adhesion mechanism of PDA to organic surfaces relies on the oxidation of catechol groups to quinones which occurs in an alkaline environment. This oxidation leads to a covalent bond with organic surfaces via aryl-aryl coupling or possibly via Michael type addition reactions. Despite an incomplete understanding of the binding mechanisms, research on PDA has not stopped and the outstanding results of PDA adherence to various types of materials has encouraged the interest for the preparation of functional substrates and hybrid materials [213].

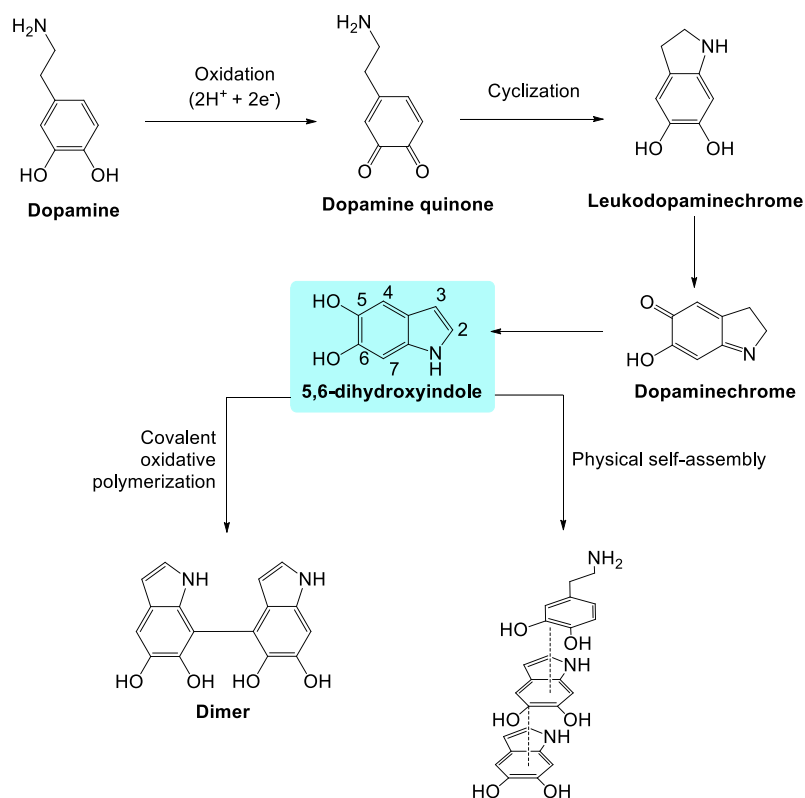
3.3.2. Dopamine polymerization

The solution oxidation method is the simplest and most widely used procedure for the preparation of PDA. Its monomer, dopamine hydrochloride (DA), can be oxidized and spontaneously self-polymerize under alkaline conditions (pH > 8.5) with oxygen as an oxidant. This self-polymerization reaction can be carried out at room temperature without the need of complicated instrumentation or hazardous reagents. During the DA polymerization, the solution changes from colorless to pale brown and finally dark brown particles start to precipitate [214,215]. PDA particles may interact with materials of different nature as well as between themselves by π -stacking or hydrogen bonds (Figure 4) [208].

The understanding of the polymerization mechanism of DA is still under exploration, but most of the works reported so far believes that DA present a polymerization mechanism similar to eumelanin due to its structural proximity. Under alkaline conditions, DA is first oxidized to dopamine-quinone followed by intramolecular cyclization via 1,4 Michael type addition yielding leukodopaminechrome. The latter evolves into 5,6-dihydroxyindole which readily oxidizes into 5,6-indolequinone. These two indole derivatives are capable of undergoing branching reactions through reverse dismutation at positions 2, 3, 4, and 7 (Scheme 20), leading to the formation of multiple dimers and eventually, higher oligomers which self-assemble to give a cross-linked polymer [216,217].

In contrast to the eumelanin model which envisions a polymer backbone based on the covalent bonds between the aryl rings of monomers, Dreyer and co-workers have used solid-state nuclear magnetic resonance (NMR) and crystallographic techniques to propose a new model for DA polymerization [218]. The authors confirmed the formation of cyclized nitrogen species such as indole and indole-like structures, consistent with the patterns shown in Figure 4. However, based on one-dimensional

solid-state NMR analysis, the cyclized nitrogen species were assigned to a saturated indole structure, rather than the unsaturated one appearing in the aforementioned models. Moreover, PDA was considered as an aggregate of monomers, which were mostly cross-linked by strong, non-covalent forces including hydrogen bonding, charge transfer, and π -stacking [218].

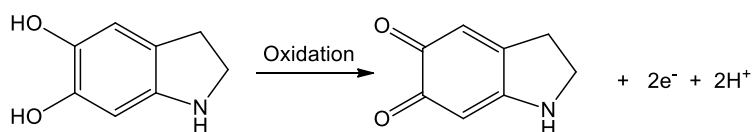


Scheme 20. Dopamine polymerization under alkaline conditions [210]

3.3.3. Applications of Polydopamine in catalysis

After having assimilated the benefits of this versatile polymer, it is clear that the main advantage of PDA in catalysis is associated to its adherence capacity (i.e. so a support functionalization is feasible) and chelation of metal ions thanks to PDA amine and/or catechol groups. In this regard, various multivalent metal ions such as Fe^{3+} , Cu^{2+} or Ru^{3+} have been impregnated to PDA through quinone, amine and catechol groups [219-221]. Moreover, different PDA binding sites can be activated under different pH conditions [220]. Froncisz and co-workers determined by electronic paramagnetic resonance spectroscopy (EPR) that Cu^{2+} ions are bidentately attached by catechol groups of PDA under alkaline conditions whereas under acid

conditions no catechol-copper complex was detected [220]. In addition to PDA capacity for chelating metal ions, it can also reduce certain noble metal ions such as Au^{3+} , Ag^+ and Pt^{2+} at basic conditions. The ability of PDA to act as a reducing agent is related to catechol groups capacity of releasing electrons when it is oxidized to its corresponding quinone analogue which in turn triggers the reduction of metal cations (Scheme 21). XPS analyses have demonstrated a slight increase in the density of quinone groups with a consequent slight decrease in catechol groups on the surface of PDA films [222].



Scheme 21. Catechol groups oxidation into quinones in PDA

Examples in the literature are abundant and most of them can be summarized in the functionalization of a support followed by the chelation of a metal ion or metal complex in order to be used in the desired catalytic application. For instance, Nicholas *et al.* functionalized silica and alumina surfaces with PDA films in order to perform the deoxydehydration of vicinal diols to terminal olefins after the complexation of Re with PDA to yield a (catecholato)oxorhenium complex [223]. On the other hand, Lu and co-workers functionalized a polyacrylonitrile fiber paper with PDA by just putting in contact the support with a dopamine aqueous solution in basic conditions. The coated support was impregnated with Ag for the reduction of 4-nitrophenol showing high catalytic activity and stability up to 4 recycling tests [224]. It is important to point out that PDA can also be used as a support. Cai *et al.* produced indeed PDA particles via the conventional self-polymerization procedure under basic conditions. Then, RuCl_3 was deposited in the polymer matrix by wet impregnation followed by filtration, washing, drying at room temperature and an annealing treatment at 800 °C under argon atmosphere [225]. It is curious that authors do not report PDA decomposition under such conditions and it is even more surprising that the PDA-Ru catalyst resulted active in H_2 production through water splitting presenting similar performances as other conventional catalysts in this electrocatalysis field [225].

To conclude, PDA is an interesting and versatile polymer which presents high adherence to several materials as well as different covalent and non-covalent types of interactions. In recent years, PDA has been used as a promising tool for the heterogenization of several transition metal complexes which can be targeted in various catalytic applications. In contrast to other conventional covalent functionalization techniques which involve several synthesis steps and toxic reagents, PDA can easily functionalize various supports under mild conditions without using hazardous products. Therefore,

PDA can be considered as a promising alternative for the complexation of transition metals in the oxidative cleavage of UFAs.

OBJECTIVES

As it was exposed in the previous sections, the search for **suitable solid catalysts active in the oxidative cleavage of UFAs is still under exploration**. Most of the works reported in literature employ transition metal complexes covalently linked to various oxide materials such as silica or alumina. However, most of them have been tested in the oxidation of small alkenes or present several drawbacks when large UFAs were assessed (e.g. leaching of the active species, pore diffusion limitations, poor contact between the substrate and the catalyst). Among all metal complexes screened in the last decades, **RuO_4** arises as the most efficient catalyst for the oxidative cleavage of UFAs because of its high catalytic activity and because it does not require high temperatures or pressures to perform the reaction. Unfortunately, attempts to heterogenize this Ru complex have not been reported.

Instead, the aforementioned examples in section 2.2 have demonstrated that it is possible to covalently bond Ru-arene complexes to different kind of supports by means of covalent functionalization methods. These solid Ru catalysts can be used for the catalytic oxidation of alkenes and UFAs with different oxidation profiles. Therefore, **the combination of covalent functionalization techniques with a suitable Ru complex** could be a promising way to prepare a heterogeneous catalyst for the oxidative cleavage of UFAs. The new heterogeneous catalyst should be active, selective and stable so it can perform the oxidative cleavage of UFAs for several consecutive cycles. Since the literature only mentions examples of solid catalysts using polymers or oxide based materials, published works with carbonaceous materials are extremely rare in this oxidation reaction. It is worth to know that **carbonaceous materials are easy to functionalize** and their textural properties can be modulated by chemical or physical methods [196,197]. So the functionalization of a suitable carbon support for the complexation of Ru is still a question in the oxidative cleavage of UFAs.

In light of the above mentioned information, the present thesis is organized according to the following objectives:

Design of a reliable process for the oxidative cleavage of UFAs using Ru heterogeneous catalysts

The main objective of this thesis consists in conceiving a new and robust catalytic system for the oxidative cleavage of UFAs. For this purpose, carbon is chosen as a support due to its ease to be functionalized and because its textural properties can be modulated by simple methods. Different functionalization procedures will be applied as well to anchor Ru onto a carbon surface to perform the oxidative cleavage of UFAs. At first oleic acid will be the targeted molecule to assess the different aspects associated to the synthesized Ru-carbon catalysts in the oxidative cleavage reaction. Thus, the main objective can be divided in the following secondary goals:

1. Evaluation of the textural properties in the oxidative cleavage reaction with Ru supported catalysts

Since no information is provided related to how carbonaceous materials behave in the oxidative cleavage of UFAs, activated carbon (microporous) and carbon black (macroporous) will be used as supports for Ru deposition and further assessment in the oxidative cleavage of oleic acid. The influence of the textural and chemical properties of these two carbonaceous materials will be evaluated to better understand the impact of different specific surface areas and pore size distribution in this reaction.

2. Assessment of supports functionalization for the construction of Ru heterogeneous catalysts towards oxidative cleavage

The carbon support that presents the highest catalytic activity in the previous evaluation will be covalently functionalized using 2,2'-bipyridine and polydopamine. The impact of these two functionalization techniques towards the oxidative cleavage of oleic acid will be assessed. The idea is to verify if the functional groups provided by the aromatic ligand and the polymer may enhance the stability of the Ru-carbon catalysts by avoiding Ru losses due to leaching.

3. Understanding the main features and the mechanism behind the oxidative cleavage of UFAs using Ru supported catalyst

How a catalyst works is always a question that all scientists want to answer in order to understand the strengths and the weaknesses of a catalytic system in a given reaction. The functioning of the synthesized Ru-carbon catalysts in the oxidative scission of the carbon-carbon double bond of oleic acid will be attempted through the available characterization techniques and using different approaches. The main objective of this section consists in determining the key aspects that govern the oxidative cleavage of UFAs when our synthesized Ru-carbon catalysts are employed.

4. Applying eco-friendly approaches in the Ru chemistry towards a greener oxidative cleavage process

As it was stated in section 2.1.3., Ru requires of strong oxidizing agents (e.g. NaIO_4) to efficiently perform the oxidative cleavage reaction. In order to propose greener alternatives, the possibility of using N-methylmorpholine N-oxide (NMO) will be assessed. In addition, our own carbon supports will be synthesized by using the eco-friendly hydrothermal carbonization method. The idea is to provide a green alternative to easily develop carbon supports ready to be functionalized and impregnated with Ru for the oxidative cleavage of oleic acid.

5. Evaluation of the synthesized Ru solid catalysts in the oxidative cleavage of UFAs within a real natural oil

Finally, the performance of the best synthesized Ru catalysts will be verified in the oxidative cleavage of UFAs which are found inside a real vegetal oil. The goal is to verify whether the carbon catalysts present the same catalytic activity in a natural oil where several SFAs and other components may interfere with the development of the reaction. For this purpose, Ecuadorian palm oil has been selected since this raw material contains a high content of UFAs and is largely underused in this south American country. The final and most ambitious objective of this research is to provide a novel route for the production of high value-added products from a cheap feedstock as palm oil. By this means, the development of poor countries where vegetal oils are abundant would be a reality using the proposed catalytic system.

STRATEGY

In order to meet the main objective of this research, dedicated strategies have been developed to address each secondary goal. The first three secondary objectives follow a linear sequence while the fourth one is independent. Figure 5 recapitulates the main strategies followed to accomplish the above mentioned goals.

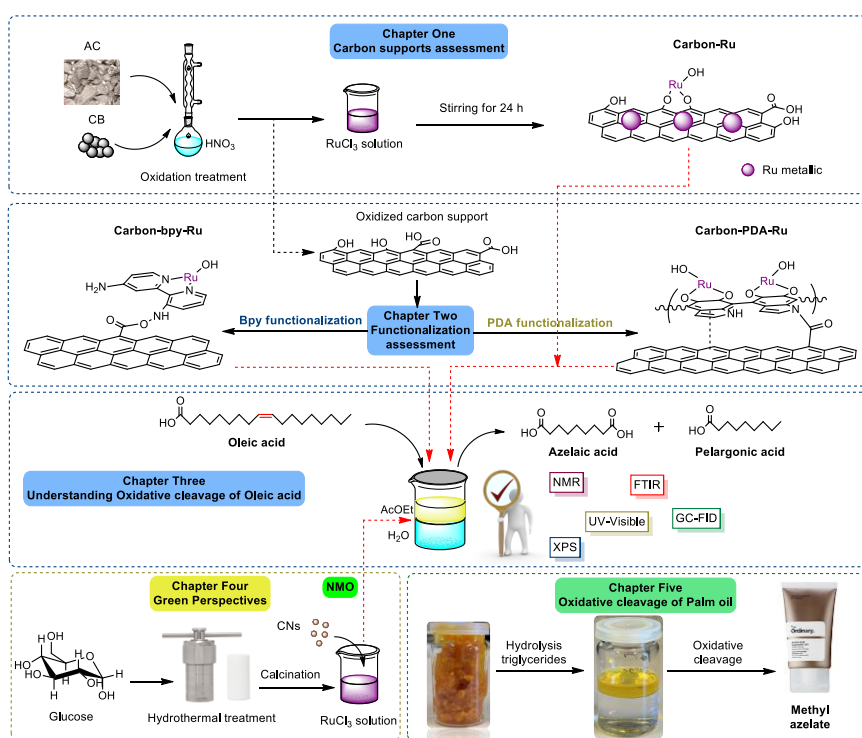


Figure 5. Global strategy of the thesis where schemes in blue dashed boxes are referred to chapters that are connected in a sequential way. Scheme in yellow box is independent while the scheme in a green box uses the background from the previous chapters to assess the oxidative cleavage of palm oil. Red dashed arrows indicate the synthesized catalysts to test in oxidative cleavage reaction

In the **first chapter** the influence of the textural properties towards the oxidative cleavage reaction will be evaluated. For this purpose, activated carbon, which is a microporous material with high surface area, and carbon black (a macroporous material) will be used as supports for the impregnation of Ru. The conventional wet impregnation method will be used to deposit this transition metal on the carbon supports and their textural properties will be determined by N_2 physisorption (specific surface area, pore volume and pore size distribution). The chemical features of both carbon supports will be

determined by FTIR, XPS and Boehm's titration method while the catalyst performance will be assessed in the oxidative cleavage of oleic acid. The conversion, yields and selectivity will be compared in order to determine **which carbonaceous material is more suitable for this reaction**. In addition, recycling tests will be carried out to verify the catalytic stability of the synthesized carbon catalysts. The obtained results will provide information about the strengths and weaknesses of these carbon supports towards the oxidative cleavage reaction.

The **second chapter** will be dedicated to determine the influence of covalent functionalization techniques in the performance of the previous synthesized Ru-carbon catalysts. First a traditional ligand **2,2'-bipyridine (bpy)** will be covalently bond to the best carbon support found in the previous chapter. The surface of the carbon support will be oxidized by an acidic treatment in order to generate carboxylic acid sites. These acid functionalities will be treated with SOCl_2 to produce acyl chlorides ready to react with amine groups of 4,4'-diamino-2,2'-bipyridyl ($\text{NH}_2\text{-bpy}$) via an addition-elimination mechanism. In the same context, **polydopamine (PDA)** will be also tested for the functionalization of carbon. In this case an *in situ* self-polymerization of dopamine in contact with the carbon material will take place under alkaline conditions. Both functionalized materials with $\text{NH}_2\text{-bpy}$ and PDA will be impregnated with Ru using the wet impregnation method. Following the previous methodology, the synthesized catalysts will be fully characterized to verify the influence of the grafted molecules on carbon's properties. In addition, catalytic tests will be conducted to observe the catalytic activity of the functionalized catalysts in the oxidative cleavage of oleic acid. Finally, hot filtration and recycling tests will be carried out to determine if the catalysts work only in the heterogeneous phase and to verify their **catalytic stability** respectively.

The **third chapter** of the thesis will be dedicated to understand how the synthesized Ru carbon catalysts perform the oxidative cleavage of oleic acid. To address this matter, the reaction will be monitored through different spectroscopic techniques to determine the main features in the development of this reaction. A monitoring of the catalyzed reaction will be performed by means of gas chromatography (GC) and nuclear magnetic resonance spectroscopy (NMR) to identify the intermediates throughout the oxidative cleavage reaction. In addition, UV-Visible spectrophotometry measurements will be performed to identify Ru species, if any, dissolved in the reaction medium. To complete the assessment, the catalysts will be characterized after the reaction ends to verify any potential change provoked by the components inside the reaction medium. Through the treatment of the data obtained, it will be possible **to highlight the key aspects** of the synthesized Ru-carbon composites towards an efficient performance in the oxidative cleavage of UFAs.

In order to find greener options to perform this reaction using Ru, the **fourth chapter** will focus on the development of eco-friendly alternatives. The first

approach is dedicated to the synthesis of our own carbon support which can be easily modulated by changing the conditions of a straightforward method such as hydrothermal carbonization. The strategy consists in submitting a glucose aqueous solution to heating under autogenous pressure inside an autoclave. By adjusting the glucose concentration, the temperature and the time of heating, it will be **possible to produce carbon nanospheres (CNs) with high content of oxygenated groups**. A calcination treatment will be evaluated as well to explore the possibility of increasing the specific surface area of the synthesized CNs. This new carbon support will be fully characterized and evaluated in the oxidative cleavage of oleic acid (catalytic tests, recycling tests, hot filtration tests) to verify its efficiency and stability in this reaction. Finally, NMO will be employed as a co-oxidant to determine whether this soft and green oxidizing agent may replace NaIO_4 in the oxidative cleavage of UFAs.

The **final chapter** of this thesis will cover the use of the best synthesized Ru-carbon catalysts, described in the previous chapters, for the oxidative cleavage of UFAs from **a natural feedstock such as Ecuadorian palm oil**. For this purpose, the targeted oil will be submitted to a derivatization process which consists in the hydrolysis of the triglycerides for releasing the FAs. Afterwards the oil will be characterized to identify and quantify all FAs present in this biomass derivative. Then, the FAs (SFAs and UFAs inside the oil) will be incorporated to our developed catalytic system to assess the **performance of our catalysts in the oxidative cleavage of UFAs**. Recycling tests will be carried out to determine whether the synthesized catalysts maintain a similar catalytic activity and stability as when they were tested in the oxidative cleavage of oleic acid.

EXPERIMENTAL SECTION

This section describes the main experimental methodologies employed throughout the development of this research. The procedures to functionalize the carbon supports as well as the additional techniques required are fully described in the corresponding chapters. Hereunder the general procedure used to impregnate Ru on the different carbon supports is provided.

1. General procedure for Ru impregnation on carbon supports

Normally, 500 mg of the corresponding carbon support was added into 20 mL of distilled water and further dispersed by ultrasonic treatment for 15 minutes. Afterwards, 10 mL of RuCl_3 (Ruthenium^{III} chloride hydrate, 99.9% $\text{RuCl}_3 \cdot \text{H}_2\text{O}$, Ru 38% from Alfa Aesar) solution (10 mM) was added drop by drop to the above suspension under stirring for the next 24 h [225,226]. Unless said otherwise, the amount of ruthenium was adjusted in order to obtain a Ru load of 2 wt% on the carbon support as exposed in Equation 3.

$$\text{Ru load (\%wt)} = \frac{m_{\text{Ru}}}{m_{\text{Ru}} + m_{\text{Carbon}}} \times 100\% \quad [3]$$

The solid was separated from the liquid by centrifugation in a Heraeus MultifugeX1R Centrifuge at 14 000 rpm (26 200 g) for at least 20 minutes. Finally, the Ru solid catalyst was washed with distilled water 3 times, and dried at room temperature before use.

2. Characterization techniques

2.1. Morphology and particle size

The morphology as well as particle size distribution of the synthesized carbon materials were determined by transmission electron microscopy (TEM) in a LEO 922 microscope with an acceleration voltage of 200 kV and equipped with a LaB6 thermal cathode. From each acquired image, the diameter of 20 to 25 particles was measured in order to obtain the mean particle size and the standard deviation after building a frequency distribution histogram.

2.2. Textural Properties

The textural properties were determined by N_2 physisorption at -196 °C in a Micromeritics Tristar 3000 equipment. Before the analysis, 50 mg of sample was degassed overnight under vacuum (~10.7 Pa) at 150 °C. The total surface area was calculated by the Brunauer-Emmet-Teller (BET) method

using the adsorption isotherm in the partial pressure (P/P_0) range from 0.05 to 0.30. In the case of microporous carbon materials, a lower P/P_0 range from 0.004 to 0.08 was employed for the BET method application [227]. In addition, the t-plot method was used to estimate the external surface area by the slope of the line drawn in the linear portion of $0.3 < P/P_0 < 0.8$. The micropore volume was determined after multiplying the intercept of the t-plot (in mol/g) by the density conversion factor = $34.53496 \text{ cm}^3/\text{mol}$. The micropore specific surface area was estimated by the difference between the BET area and the external surface area while the total pore volume was measured at $P/P_0 = 0.98$. Pore size distribution was estimated by Barrett, Joyner and Halenda method (BJH) using the data from the desorption isotherm branch [227,228]. For microporous materials the micropore volume was estimated with the Dubinin-Radushkevich (DB) method in a $P/P_0 < 0.1$ range whereas micropore size distribution was obtained by means of the Horvath-Kawazoe (HK) method [229,230].

2.3. Chemical Properties

Fourier transform Infrared spectroscopy (FTIR) was performed to characterize the different carbon supports employed in this thesis. It was also used to identify the characteristic peaks of bpy and PDA deposited on the corresponding carbonaceous materials. For this purpose, wafers were prepared by mixing 15 mg of sample with 300 mg of KBr beforehand dried overnight at 110°C [231]. All analyses were carried out in a Bruker Equinox 55 FTIR spectrometer in the transmission mode. One hundred scans were carried out in the range of 4000 to 400 cm^{-1} with a 4 cm^{-1} resolution.

Boehm's titration was achieved to quantify the amount of oxygenated groups of all carbon supports used in this thesis. For this purpose, three samples of 0.5 g were added to three 0.05 M solutions of NaOH, Na_2CO_3 and NaHCO_3 (50 mL each one). The suspensions were degassed for 1 hour under argon atmosphere and stirred for other 23 hours. Then, the solids were separated by vacuum filtration with the aid of a filter paper (pore size: $0.2 \mu\text{m}$). Next, 10 mL of the filtrate was taken from each suspension and were acidified with 20 mL of a 0.05 M HCl solution. The new solutions were agitated and continuously degassed for 2 hours under argon atmosphere. Finally, the solutions were titrated using a 0.05 M NaOH solution with phenolphthalein as indicator [232]. The three basic solutions allow to measure different oxygenated groups on carbon surfaces. Precisely, NaOH neutralizes all acidic functional groups of the in phenols, lactones and carboxylic types. Na_2CO_3 neutralizes lactones and carboxylic groups, whereas NaHCO_3 neutralizes only carboxylic groups. By subtracting the results obtained with each base, the amount of phenols, lactones and carboxylic groups on carbon materials can be estimated [232,233]. An example of calculation is explained in the Supporting information section.

X-ray photoelectron spectroscopy (XPS) analyses were carried out in a SSX 100/206 photoelectron spectrometer from Surface Science Instruments (USA) equipped with a monochromatized micro focused Al X-ray source (powered at 20 mA and 10 kV). The pressure in the analysis chamber was around 10^{-6} Pa and the flood gun was set at 8 eV. The angle between the surface and the axis of the analyzer lens was 55° . The analyzed area was approximately 1.4 mm^2 and the pass energy was set at 150 eV. Under these conditions, the full width measured at half maximum (FWHM) of the Au $4f_{7/2}$ peak for a clean gold standard sample was about 1.6 eV. Samples were prepared by pressing the powder in small stainless-steel troughs of 4 mm diameter and placed on a ceramic carousel with a Ni grid set above the sample surface for charge stabilization. The following sequence of spectra was recorded: survey spectrum, C 1s, O 1s, N 1s, Cl 2p, Ru 3p. For all samples, C 1s spectrum was recorded again to check the stability of charge compensation with time. The aromatic C-(C,H) component of the C1s peak of carbon was fixed at 284.8 eV to set the binding energy scale. Data treatment was performed with the CasaXPS program (Casa Software Ltd, UK). Carbon 1s peaks were decomposed with the least squares fitting routine provided by the software with a Gaussian/Lorentzian (85/15) product function and after subtraction of a non-linear baseline. The identification and quantification of Ru was performed with the $3p_{3/2}$ peak in order to avoid deconvolution problems associated with the C 1s peak (C 1s and Ru $3d_{5/2}$ peaks have similar binding energies) [234].

2.4. Ru loading on carbon catalysts

Ruthenium loading on each carbon catalyst was measured by inductively coupled plasma - atomic emission spectrometry (ICP-AES) in an ICP 6500 Thermo Scientific Instrument. For this matter, about 100 mg of each sample was placed in a vitreous carbon crucible and calcined overnight at 500°C in an oven to remove the organic matter. Then, 50 to 100 mg of the calcined sample were mixed with 2 g of sodium peroxide (Na_2O_2) along with 1 g of sodium hydroxide tablet (NaOH) and transferred to another vitreous carbon crucible. This solid mixture was molten under the flame of a Bunsen burner and after cooling, the crucible was immersed in 100 mL of HCl 11% (v/v) solution to dissolve all Ru along the carbonaceous matrix. Finally, the crucible was rinsed with distilled water and the obtained solution was diluted to 1000 mL prior analysis.

2.5. Ru dispersion on carbon catalysts

Ruthenium dispersion on the synthesized carbon catalysts was measured by CO chemisorption in a Micromeritics PulseChemiSorb 2705. For this purpose, 250 mg of each sample was reduced at 200°C for 2 h under hydrogen atmosphere (Air liquid; Purity > 99.999%) with a heat ramp of $10^\circ\text{C}/\text{min}$. After reduction, helium (Air liquid; Purity > 99.999%) was passed through for 1 h until the temperature decreased to 35°C . Under these conditions, CO pulses (20% of CO in helium as carrier gas) were introduced

so metallic Ru on the surface adsorbs CO molecules with a stoichiometric ratio of Ru:CO=1:1 [235]. After each injection, a TCD detector gives a signal which is transformed to a peak area (A_p) corresponding to the non-adsorbed CO. When the metallic surface is saturated, the peak area is maximum (A_{max}) and corresponds to the volume of the CO injected at each pulse ($V_{CO} = 185 \mu\text{L}$). To correlate the moles of non-adsorbed CO with the peak area, a calibration factor is calculated as follows:

$$F_c = \frac{1}{A_{max}} \left(\frac{PV_{CO}}{RT} \right) \quad [4]$$

The moles of adsorbed CO per catalyst gram ($n_{CO \text{ ads}}$) and Ru dispersion (D_{Ru}) were calculated as follows:

$$n_{CO \text{ ads}} = \sum (A_{max} - A_p) \frac{F_c}{\text{sample mass}} \quad [5]$$

$$D_{Ru} = \frac{n_{CO \text{ ads}} \times \text{Ru : CO} \times \text{Ru atomic weight}}{\text{Ru load}} \times 100\% \quad [6]$$

3. Catalytic tests

All tests were carried out in 20 mL closed glass vessels with magnetic agitation at room temperature. Two different amounts of oxidizing agent (NaIO_4 , >99% from Sigma Aldrich) were tested in the oxidative cleavage reaction: 4.1 equivalents (430 mg) and 8.2 equivalents (870 mg) with respect to oleic acid. The oxidant was dissolved in 8 mL of distilled water followed by 4 mL of acetonitrile (MeCN , $\text{C}_2\text{H}_3\text{N}$ >99.98% GC from Carl Roth) and 2 mL of ethyl acetate (AcOEt , $\text{C}_4\text{H}_8\text{O}_2$ > 99.9% GC from Carl Roth). Next, 0.5 mmol of oleic acid (OA , $\text{C}_{18}\text{H}_{34}\text{O}_2$, >99.9% GC from Carl Roth) along with 81.7 μL heptanoic acid ($\text{C}_7\text{H}_{14}\text{O}_2$, >98% GC from TCI chemicals) which acts as internal standard, were dissolved in the biphasic solvent system. After adding 100 mg of the catalyst (2 wt% of Ru), the reaction mixture was agitated at 1 500 rpm for 24 hours.

All solvents employed in this reaction were selected according to the fact that the aqueous phase is required for the dissolution of the oxidizing agent, while AcOEt is used for the dissolution of oleic acid and the internal standard. In addition, MeCN is added in order to stabilize RuO_4 species in the liquid medium and prevent its volatilization. At different time intervals, 0.1 mL from the organic layer was extracted with a filter-syringe (0.2 μm) and diluted in 1.4 mL of AcOEt . The diluted samples were analyzed by gas chromatography (GC) in order to separate, identify and quantify the reaction products and unreacted oleic acid. A constant and exact volume of 1 μL was injected each time, and the injection was repeated three times in a Varian 3800 Gas Chromatograph equipped with a flame ionization detector (FID). In

this study, a Stabilwax-DA Restek column, formed by a crossbond acid-deactivated Carbowax polyethylene glycol as stationary phase, was employed in order to analyze directly the samples without performing any derivatization process. Once an oxidative cleavage test ended, the solid catalyst was recovered after centrifugation at 14 000 rpm for 30 minutes. The organic layer was separated using a syringe while the aqueous layer was submitted to three subsequent extractions using 2 mL of AcOEt in order to recover all the reaction products that could have formed an emulsion in the aqueous phase. Since the internal standard (IS) was retrieved along with the extraction of the organic phase in the previous step, another 81.7 μ L of IS was added to each extract and they were injected in the GC in the same manner as before (0.1 mL from each extract diluted in 1.4 mL of AcOEt). The yields reported in the following are calculated by summing the quantities of PA and AA found in the reaction organic phase with those found in the three extracts from the aqueous phase.

3.1. Products Identification and Quantification

For the separation of the reaction products (pelargonic and azelaic acid) the GC-FID system was equipped with Stabilwax-DA Restek column (30 m $\times$ 0.53 mm $\times$ 0.25 μ m). Helium was used as a carrier gas with a flow rate of 12.6 mL/min with a column pressure of 10 psi. The injector temperature was established at 280 $^{\circ}$ C while a split ratio of 30:1 was set. An autosampler injected 1 μ L of each sample using a 10 μ L syringe (SGE removable needle, 5 cm 0.47 mm OD bevel tipped needle, Trajan) The oven temperature was maintained at 100 $^{\circ}$ C for 2 min and then, it was increased to 240 $^{\circ}$ C with a heat ramp of 8 $^{\circ}$ C/min. The final temperature was maintained for 10 more minutes to ensure that all compounds appear in the chromatogram. For the identification of unreacted oleic acid (OA) and the oxidative cleavage products, pure OA as well as pelargonic acid (PA, C₉H₁₈O₂, >98% GC) and azelaic acid (AA, C₉H₁₆O₄, >98% GC) were dissolved in AcOEt and analyzed in the GC-FID. The temperature program gave three peaks with different retention times (Rt) at 9.6 min, 19.4 min and 25.1 min which correspond to PA, OA and AA respectively (Figure 6).

The quantification of these organic compounds was performed via the internal standard (IS) method. This technique is based on the fact that within a certain concentration range, the ratio between chromatographic peak areas (A_c =area of the substrate; A_{IS} =area internal standard) and concentrations (C_c =concentration of the substrate; C_{IS} =concentration internal standard) is constant. This ratio is known as the response factor (F_R) which is used to build calibration curves for the concentration measurement of a compound [236,237].

$$F_R = \frac{A_c/C_c}{A_{IS}/C_{IS}} \quad [7]$$

possible to ease the calculations of yield and selectivity by adding the missing part of AA in the organic layer.

$$K_{AA} = \frac{C_{AA} \text{ Aqueous}}{C_{AA} \text{ Organic}} = 0.175 \pm 0.003 \quad [8]$$

Where $C_{AA} \text{ Organic}$ is the concentration of AA in AcOEt and $C_{AA} \text{ Aqueous}$ is the concentration of AA in water. The calculation of K_{AA} is described in the Supporting information (section E.3).

3.3. Conversion, Yield and Selectivity determination

To measure the catalytic performance of the synthesized Ru-carbon catalysts, the following indicators were calculated. Conversion was estimated through the ratio between OA reacted and OA fed in the reactor at the beginning of the reaction [238] as exposed in Equation 9:

$$\chi = \frac{n_0 - n_t}{n_0} \times 100\% \quad [9]$$

where n_0 correspond to the initial moles of OA and n_t refers to the moles OA at the given reaction time.

For the calculation of yield and selectivity, it is important to keep in mind that 1 mol of OA can produce 1 mol of PA and 1 mol of AA as was indicated in Scheme 6. Yield is defined as the ratio of moles of PA and AA produced and the theoretical amount of these products that could have been produced [238].

$$Y_{PA} = \frac{n_{PA}}{n_{OA} \times 1 \text{ mol PA/1 mol OA}} \times 100\% \quad [10]$$

$$Y_{AA} = \frac{n_{AA}}{n_{OA} \times 1 \text{ mol AA/1 mol OA}} \times 100\% \quad [11]$$

where n_{OA} is the initial moles of oleic acid while n_{PA} and n_{AA} are the produced moles of pelargonic and azelaic acid respectively.

Finally, selectivity refers to the moles of PA and AA produced versus the moles of OA reacted [238]. Therefore, selectivity can be calculated by incorporating conversion to the following equations:

$$S_{PA} = \frac{n_{PA}}{n_{OA} \times \chi \times 1 \text{ mol PA}/1 \text{ mol OA}} \times 100\% \quad [12]$$

$$S_{AA} = \frac{n_{AA}}{n_{OA} \times \chi \times 1 \text{ mol AA}/1 \text{ mol OA}} \times 100\% \quad [13]$$

3.4. Recycling tests

Once a catalytic test was finished, the catalyst was separated from the biphasic solution by centrifugation in a Heraeus MultifugeX1R Centrifuge at 14 000 rpm (26 200 g) for 20 minutes. The solid catalyst was washed three times with warm distilled water (~80 °C) and dried overnight at room temperature. Afterwards, the catalyst was re-inserted in a fresh reaction mixture to start the oxidative cleavage of oleic acid with the procedure explained at the beginning of this section. These steps were repeated five times in order to verify the catalytic stability of the synthesized catalyst by assessing conversion after each recycling test.

3.5. Hot filtration tests

In these tests, once the conversion in oxidative cleavage test arrived approximately to 50%, the catalyst was removed from the reaction medium by centrifugation at 14 000 rpm (26 200 g) in a Heraeus MultifugeX1R Centrifuge. Then, the reaction was further monitored (without the solid catalyst) by injecting samples of the organic layer in the chromatograph. The idea was to verify whether there was catalytic activity after the removal of the solid catalyst. An increase in conversion after the catalyst removal would suggest that the active sites (ruthenium species) have moved in the liquid phase leaving the composite and were exerting a catalytic effect therein.

CHAPTER I: CARBON SUPPORTS FOR THE OXIDATIVE CLEAVAGE OF OLEIC ACID: INFLUENCE OF TEXTURAL PROPERTIES

Abstract

The present chapter explores the potential use of carbon supports in the oxidative cleavage of unsaturated fatty acids. In spite of their promising properties such as tunable porosity, high chemical resistance to various conditions and easy surface modification/functionalization, there are no examples in the literature about oxidative cleavage of UFAs using carbonaceous materials. The vast majority of published works to date present different heterogeneous catalysts using oxide-type supports. However, they present various inconveniences that should be overcome like leaching of the active species, diffusional limitations, poor contact between the substrate and the transition metal, among others. For these reasons, activated carbon (a microporous material) and carbon black (macroporous) were evaluated in the oxidative cleavage of oleic acid in order to assess the influence of their textural properties in this reaction. Both carbon materials were treated with HNO_3 prior Ru deposition by wet impregnation method. Carbon materials were characterized by FTIR and Boehm's titration to identify and quantify the oxygenated groups incorporated to carbon surface thanks to acid treatment. Moreover, N_2 physisorption was conducted to determine their textural properties. ICP-AES confirmed that Ru bulk concentration matched with the nominal Ru load (2 wt%). In addition, the deconvolution of high resolution Ru 3p XPS spectra indicated that the transition metal was in a Ru(III) oxidation state. Catalytic tests clearly demonstrated that activated carbon catalyst was not suitable for the oxidative cleavage of oleic because of the low conversion (~53%) attained in comparison to carbon black catalyst (>99%). The molecular length of oleic acid (2.2 nm), estimated by *ab initio* Hartree-Fock calculation, resulted larger than micropores from activated carbon (~0.7 nm). Conversely, the interstitial spaces between carbon black nodules are large enough to welcome oleic acid which leads to a greater catalytic activity in the oxidative cleavage reaction. Therefore, a macroporous material like carbon black is a promising support for the heterogenization of Ru for the development of an efficient catalyst towards the oxidative cleavage reaction.

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1. Introduction

Since many years, carbon materials have been exploited as supports for the preparation of heterogeneous catalysts due to their flexibility at the moment to tailor their physical and chemical properties [239]. For instance, through thermic treatments, it is possible to develop a large surface area, being the first step to facilitate the dispersion of active species [240]. Moreover, pore size distribution can be tuned in order to improve the diffusion of reactants and products to and from the surface. Chemical treatments involving strong acids (e.g. HNO_3 or H_2SO_4) or oxidizing agents (e.g. KMnO_4) are commonly used to increase the number of chemical functionalities suitable to chelate transition metal cations [240,241]. In the literature many examples are reported of different carbon materials as catalyst supports. Mainly activated carbon (AC), carbon black (CB), carbon nanotubes (CNTs) and graphene have been widely exploited in the field of heterogeneous catalysis [240]. For instance, CNTs have been used in several applications from photocatalysis to recent open research areas like electrocatalysis (e.g. water splitting) [242,243].

Besides the mentioned properties, carbon materials present additional important advantages over other traditional supports. Amid them, their resistance to acidic and alkaline media makes carbons suitable for catalytic applications in all pH range [239,244]. Other interesting feature is related to their synthesis. Carbon materials can be prepared in various shapes (from nanoparticles to monoliths) to fit the requirements of the application targeted. Another advantage of carbon supports is the ease of recovering active metals after burning the support. It is worth to mention that the synthesis of carbon supports is usually cheaper than other traditional materials employed in different catalytic reactions [240,245]. In spite of the highlighted benefits of carbon materials, their use as supports for heterogeneous catalysis is not widely spread at industrial level. The main reason is related to one of the weaknesses of these materials, namely their thermal stability [240]. Carbon materials cannot be used in gas phase applications at temperatures beyond 500 °C since the carbonaceous matrix starts to decompose in different ways according to the reaction medium (oxidizing or reductive conditions) [240,244].

Apart from reactions at high temperatures, carbon materials can be profited in a great number of applications in liquid phase [246-248]. In this regard, oxidation reactions have been largely scoped by carbonaceous materials as is the case of activated carbon [249,250]. This amorphous carbon support that belongs to the family of graphite is highly microporous as a consequence of an activation process [240,241]. Commonly biomass lignin derivatives are carbonized at 600 °C under reducing atmosphere followed by a further activation process consisting in a heating at 900 °C under CO_2 or H_2O atmosphere. Under these conditions, CO_2 and/or H_2O vapor diffuse into the carbon matrix to react with carbon atoms generating CO/H_2 as well as porosity [251,252]. The shape and size of the pores in AC mainly depend on

the morphological, chemical and physical properties of the raw materials used as well as the kind of activation process employed [240,251,252]. Afterwards, a well-developed surface area with numerous oxygenated functional groups such as carboxylic acids, phenols, carbonyls and lactones can facilitate the adsorption of several transition metal ions widely used in catalysis [240,251]. Additionally, its high surface area, due to a well-developed porosity, contributes to high metal dispersions which is essential for high catalytic activity [241].

Another carbonaceous material used as a support in oxidation reactions is carbon black (CB) [253,254]. This carbon material has been mainly employed in the tire industry as a reinforcement in rubbers or as ink pigment and additive for coatings and polymers [240]. For instance, it is added to polypropylene because carbon black can absorb ultraviolet radiation in order to prevent material degradation [255,256]. Generally, carbon black is produced from the incomplete combustion of heavy petroleum products such as coal tar or liquid hydrocarbons [256]. This type of material consists of nanometric spheres which agglomerate to form aggregates (nodules) [256]. According to the aggregation degree of carbon black nodules it is possible to obtain high or low dispersive materials. Besides, this aggregation capacity of carbon black spherical particles influences directly their surface area (mostly macroporous/ non porous). Precisely, small particles normally promote high surface areas whereas a high degree of particles aggregation yields low surface areas [240].

As catalyst support, CB is preferable than other carbon materials such as carbon nanofibers or graphene for its accessibility and low cost. One of the main characteristics that makes CB attractive for catalytic applications, is its high surface area/volume ratio which is due to the small size of the spherical particles (approximately 50 nm) [240,257]. Other important characteristic of this carbon material is the presence of oxygenated groups which could be originated from the fabrication process or be incorporated in a subsequent oxidation treatment [258,259]. The modification of the CB surface chemistry may enhance the impregnation of several transition metals or oxides such as Pt, Pd or RuO₂ which are normally used in the catalytic oxidation of alcohols [257,260,261].

In spite of all aforementioned positive characteristics and properties of carbon materials, examples of oxidative cleavage of alkenes using these supports is extremely rare. Vijay Kumar *et al.* impregnated Ru on charcoal (Ru load= 5 wt%) to perform the oxidative cleavage of various alkenes and alkynes using oxone as oxidizing agent [262]. High conversions were obtained in short reaction times when small alkenes (aliphatic or aromatic) were assessed. Nevertheless, so far no UFAs have been analyzed with catalytic carbon systems. Therefore, in this chapter two carbon materials with different textural properties (AC and CB) are tested in the oxidative cleavage of oleic acid (C8:1). The main purpose is to verify the influence of different surface areas and pore sizes on the scission of a carbon-carbon

double bond of a large compound such as oleic acid. Through this assessment, it will be possible to identify a suitable material for this reaction.

2. Experimental section

Activated carbon was selected because it is a cheap and abundant microporous material while carbon black is a macroporous support. In this manner it was possible to assess two carbon supports with different textural properties. Carbon catalysts were prepared with a Ru load of 2 wt% according to the explanation given in the main Experimental section of this thesis. The way carbon materials were prepared before Ru impregnation as well as some other details of the materials preparation and characterization are explained below.

2.1. Preparation of carbon materials

Activated carbon (AC, coconut shell, 2–4 mm, basic) from Calgon Corporation and carbon black (CB: 95.73 wt.% C, 0.73 wt.% H, 3.5 wt.% O, specific surface area 154 m²/g and pore volume 0.56 cm³/g) from Degussa Printex ®G were submitted to an oxidation treatment with nitric acid (Carl Roth HNO₃ = 65%) in order to incorporate oxygenated functional groups (phenols, lactones and carboxylic acids) on their surfaces. For this purpose, a 150 mL round flask was used to add 4 g of AC/CB in 50 mL of 5.0 M HNO₃ solution. The suspension was magnetically stirred (1500 rpm) and heated at 90 °C for 8 hours under reflux in order to avoid nitric acid losses. As regards AC, agitation speed was maintained at 500 rpm to avoid an excessive attrition of the carbon matrix. Afterwards, oxidized activated carbon (ACO) was filtered to recover the solid on a Whatman filter paper while oxidized carbon black (CBO) was separated from the solution by centrifugation at 14000 rpm (26200 g) during 20 minutes in a Heraeus MultifugeX1R centrifuge. Both carbon materials were washed in a Soxhlet equipment for 48 hours in order to remove all nitric acid remainings inside the carbonaceous matrix [263,264]. Finally, oxidized carbon supports were dried for 48 h at 110 °C to ensure removal of the remaining water inside the carbonaceous materials [264].

RuCl₃ (Ruthenium^{III} chloride hydrate, 99.9% RuCl₃·H₂O, Ru 38% from Alfa Aesar), was used to deposit Ru on ACO and CBO by wet impregnation (Experimental section p. 59). In the case of ACO, the suspension was not submitted to ultrasounds since ACO grains size was in a 2-4 mm range. Only a magnetic agitation at 500 rpm was achieved when ACO grains were in contact with RuCl₃ solution. As regards CBO, it was added into 20 mL of distilled water and submitted to ultrasounds for 15 minutes to well disperse CBO particles. Then RuCl₃ solution (10 mM) was added drop by drop to each suspension under stirring for the next 24 h. Finally, the solids were recovered by filtration and centrifugation in the case of ACO and CBO respectively. Henceforth, activated carbon with Ru is denoted as ACO-Ru(2%) whereas carbon black catalyst is denoted as CBO-Ru(2%).

Both catalysts were characterized with the characterization techniques previously detailed and additional techniques hereunder explained.

2.1. Additional characterization techniques

Activated carbon morphology was observed by means of an optical microscope Olympus SZX16. For the estimation of AC particle size, a granulometric analysis (ASTM D 2862 82) was performed through sieving the material with a series of sieves of different opening sizes. [265]. Particle size was determined by d_{80} indicator (see Table S1.1) which refers to the mesh opening of the sieve through which 80% of the carbon material passed [266].

Superficial chemical characteristics of both carbon supports were evaluated by FTIR, Boehm's titration and XPS techniques explained in section 2.3 of the main Experimental section (p. 60). Additionally, the point of zero charge (PZC) was estimated. This indicator corresponds to the pH where there is not charge (whatever negative or positive) at all at the surface of the material [267,268]. Thus, at a pH below PZC the surface will be positively charged while over this value the surface will be negatively charged. PZC of both carbon materials was estimated by means of the Mass Titration method. Precisely, the pH of a 0.1 M NaNO_3 (>99% Merck) 50 mL solution was registered using a Hanna Checker® portable pH meter. Then, 0.2 g of each sample was immersed within the solution and stirred up to 2 hours or until pH of the solution did not change. The pH of the suspension was registered and then other 0.2 g of the same material was added again. This process was repeated until the pH of the suspension did not change anymore and the final value corresponds to the PZC [267,268].

2.3. Catalytic tests

The procedure detailed in the main Experimental section (p. 62) was applied for the assessment of ACO-Ru(2%) and CBO-Ru(2%) in the oxidative cleavage of oleic acid. In the case of carbon black catalyst, agitation was interrupted for 5 minutes to allow CBO particles decantation and extract the sample from the organic phase (upper layer) easily. To ensure that no solid particles were injected in the GC, the diluted aliquot was filtered using a Syringe Filters ROTILABO® PTFE 0.20 μm . Conversion, selectivity and yield were measured to assess the catalytic performance of ACO-Ru(2%) and CBO-Ru(2%), while recycling tests were performed to assess their catalytic stability in the oxidative cleavage of oleic acid. Recycling test were also performed with both carbon supports without the oxidation treatment. Thus, the benefit of the functionalization with HNO_3 can be assessed towards the oxidative cleavage reaction. Finally, tests were performed without NaIO_4 to verify the possibility of oleic acid adsorption on the carbon surface.

3. Results and Discussion

3.1. Characterization results

Figures 1.1a and 1.1b show optical microscopy images of activated carbon grains before and after the oxidation treatment respectively. These images demonstrate that acid treatment did not cause serious damages in the carbonaceous surface. TEM images (Figures 1.1c and d) show the same results as regards carbon black samples. It is worth to mention that the conditions specified in the Experimental section of this chapter were already the optimized ones. When higher concentration of HNO_3 was employed or longer exposing times were tested, AC grains started to break and they were recovered in form of powder requiring longer washing periods in the Soxhlet equipment to get rid of HNO_3 remainings. Similarly, when $> 5 \text{ M}$ HNO_3 was used, intense centrifugation (times $> 1\text{h}$) was necessary to recover the tiny carbon black nanoparticles produced because of nodules rupture. In fact, it was not possible to use these CBO nanoparticles in catalytic tests because it was impossible to separate them from the aliquot before injection in the GC. The mean particle size calculated for both carbon materials confirms that they maintained their initial particle size in spite of the oxidation treatment under the optimized conditions employed.

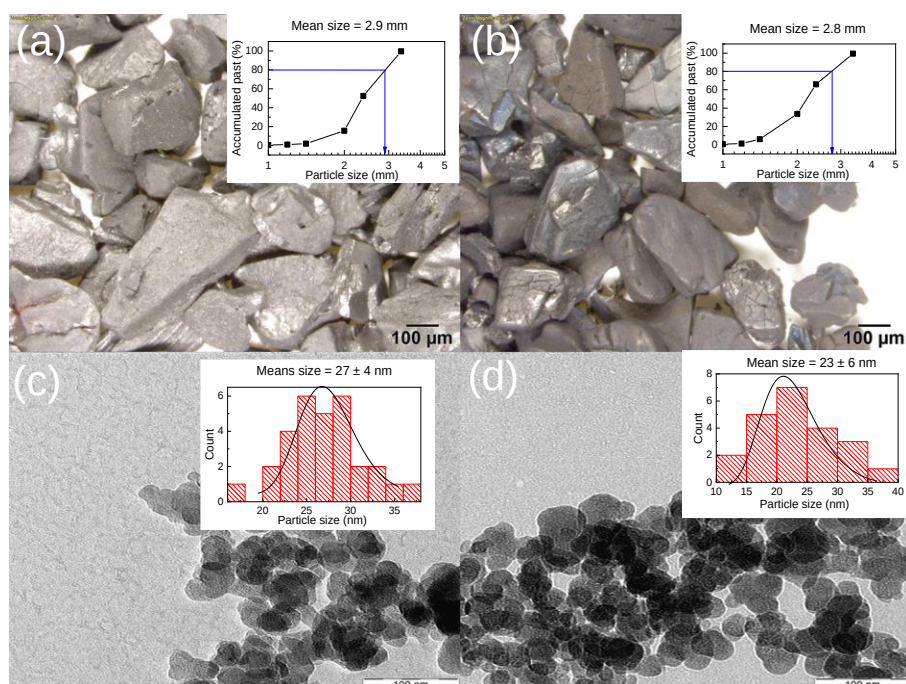


Figure 1.1. Images from optical microscopy of: a) AC; b) ACO. TEM images of c) CB; d) CBO

Figure 1.2 shows the IR spectra of activated carbon and carbon black. As regards AC, an intense band appears at 3440 cm^{-1} which belongs to O-H stretching vibration mode in hydroxyl groups [269]. A thin peak was observed at 1640 cm^{-1} which is characteristic of carbon materials and attributed to C=C stretching vibration in aromatic rings [269,270]. A broad band at 1200 cm^{-1} is attributed to C-O stretching vibration in lactone groups while the wide band at 767 cm^{-1} can be ascribed to C-H out-of-plane bending in the aromatic rings [271,272]. In the case of ACO the same peaks were observed with an additional band at 1717 cm^{-1} which is attributed to C=O stretching vibration in the carboxylic groups [269-272].

Carbon black presents similar peaks to those observed in activated carbon. A strong peak is also observed at 3432 cm^{-1} characteristic of O-H stretching vibration mode [269]. Unlike the AC case, two small bands appear at 2913 and 2850 cm^{-1} attributed to CH antisymmetric and symmetric stretching in aliphatic chains [273,274]. A medium peak at 1610 cm^{-1} can be ascribed to ring stretch vibration in aromatic compounds whereas a small band at 1200 cm^{-1} is assigned to lactone groups on the carbonaceous surface [269]. Conversely to AC, carbon black presents a strong peak at 1091 cm^{-1} that can be attributed to C-O stretch vibration of the C-OH bond in alcohols. Finally, a small band at 800 cm^{-1} is assigned to C-H out-of-plane bending in the aromatic rings [269,273]. After the oxidation treatment, CBO presents additional bands at 1726 cm^{-1} and 1380 cm^{-1} . The former belongs to C=O stretching vibration mode of carbonyl groups while the latter can be ascribed to NO_2 symmetric stretch as a consequence of the oxidation treatment with HNO_3 [274].

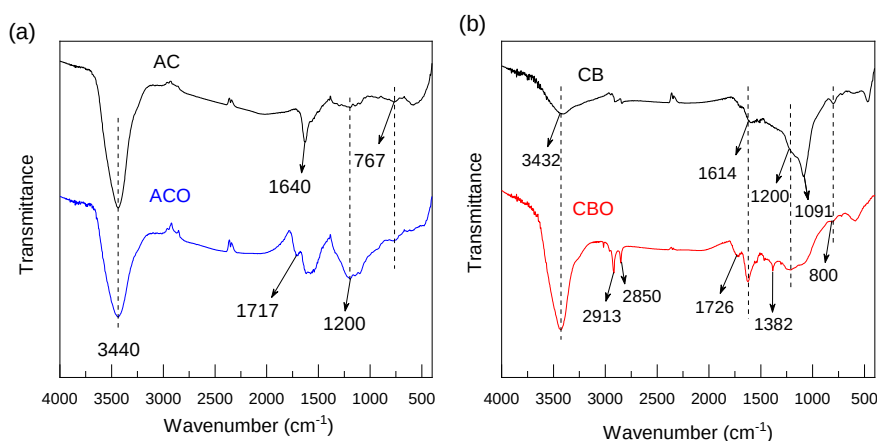


Figure 1.2. Infrared spectra of: a) AC and ACO; b) CB and CBO

The information provided by FTIR was confirmed by Boehm's titration results (Table 1.1). As a result of the oxidation with HNO_3 , both carbon materials increased their total acidity which means a greater amount of oxygenated

groups on their surfaces. Activated carbon resulted to be a basic material since its PZC (Figure S1.1) was quite high (PZC = 9.9); as a consequence; no acid sites were measured by Boehm's titration.

After the functionalization through HNO_3 , the amount of phenol groups and carboxylic acids increased greatly. As a result, the PZC of ACO decreased down to 4.1. The same trend was observed with carbon black. Initially, CB only possessed significantly lactones but the oxidation procedure provided additional $-\text{OH}$ and $-\text{COOH}$ groups to CBO surface. Since the total acidity of CBO is the highest of all assessed carbon materials, it also shows the lowest PZC because of the additional acid sites. These oxygenated functionalities on ACO and CBO surfaces can aid to the complexation of Ru during the impregnation process. In fact, the amount of phenol groups required to complex a Ru loading of 2 wt% was calculated in section S1.3 of the supporting information. Results show that ACO possesses around 4 times more OH groups than Ru atoms while CBO presents 2 times the amount of phenol groups required to reach a 2 wt% loading in Ru.

Table 1.1. Boehm's titration results and PZC of carbon materials

Support	PZC	Phenols (mmol/g)	Lactones (mmol/g)	Carboxylic acids (mmol/g)	Total Acidity (mmol/g)
AC	9.9	0.08	---	---	0.08
ACO	4.1	0.80	0.05	0.60	1.45
CB	6.9	0.06	0.54	0.04	0.64
CBO	2.9	0.43	0.52	1.02	1.97

Table 1.2 presents the textural properties of both carbon materials. Additionally, the catalysts synthesized through wet impregnation were assessed as well to verify the impact of Ru deposition on the textural properties of both supports. AC and CB present a typical type I isotherm, indicating presence of micropores, with a bit of type IV feature as a capillary condensation occurs at high pressure with a hysteresis with the desorption, indicating the presence of large mesopores (Figure 1.3) [228]. Most of AC surface area is formed by micropores created after its activation process. On the other hand, the porosity presented by CB is attributed to the interstitial spaces amid the carbon particles and nodules that form the material. AC shows a high specific surface area which is 7 times greater than that of CB. However, as regards the external surface area, the opposite is observed. The same trend is observed with pore size distribution (PSD). AC possesses pores between 0.5 and 1 nm while CB shows a wider PSD bearing pores from 2 nm to 75 nm. The difference of external surface area and PSD between the two assessed carbon materials is an important fact since most of AC total surface area can be wasted if oleic acid cannot diffuse inside microporosity to react with Ru in order to trigger the oxidative cleavage reaction.

Table 1.2. Textural properties of carbon materials

Carbon Material	BET surface (m ² /g)	External surface (m ² /g)	Pore Volume (cm ³ /g)	Mean Pore size (nm)
AC	1072	17	0.45	0.7
ACO	1017	24	0.45	0.7
ACO-Ru(2%)	994	19	0.43	0.7
CB	154	116	0.58	24.3
CBO	149	116	0.53	22.9
CBO-Ru(2%)	145	109	0.56	21.5

Concerning the oxidation treatment, it did not affect greatly the textural properties of both carbon materials since there was only a slight decrease of their specific surface area. In addition, PSD of ACO remains almost identical to that of AC while CBO shows a narrower PSD than CB presenting pores from 2 nm to 27 nm. Hence, in the case of carbon black the oxidation treatment aided to obtain a more uniform PSD. Thus, the conditions applied were ideal to incorporate oxygenated functional groups on both carbon materials without provoking great changes on their surfaces at physical level. Finally, the deposition of Ru did not produce pronounced changes on the textural properties of ACO and CBO either. As a result, two carbon catalysts with marked differences in terms of textural properties have been synthesized to evaluate their performance in the oxidative cleavage of oleic acid.

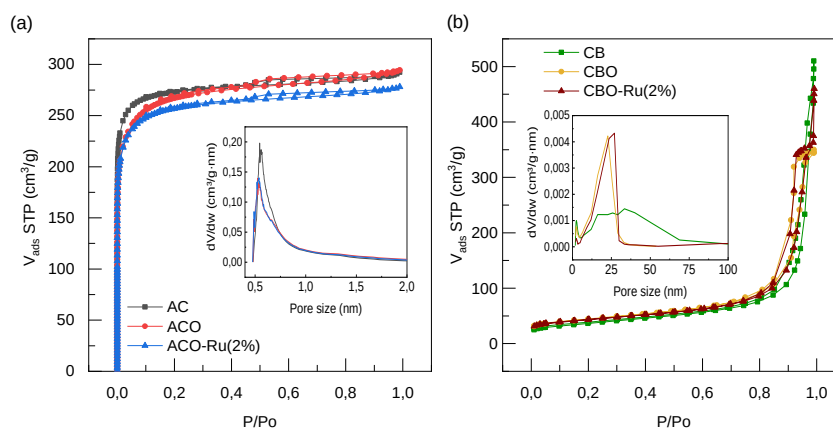
**Figure 1.3.** N₂ adsorption-desorption isotherms of: a) AC, ACO and ACO-Ru(2%); b) CB, CBO and CBO-Ru(2%)

Table 1.3 summarizes the main characteristics of the synthesized catalysts as regards Ru deposited on ACO and CBO samples. The total loading of Ru measured by ICP-AES matched with the nominal loading targeted by the

preparation of the catalysts. Hence, wet impregnation method was efficient for the deposition of Ru ions on both supports. On the other hand, the superficial Ru content (evaluated from XPS) was higher for both samples than their bulk content. It is impossible to decipher whether this observation results from the fact that Ru accumulates more on carbon external surface than it goes inside its porosity, or from the fact that a very good dispersion of Ru on external surfaces is attained, or a combination of both origins. Still CO chemisorption demonstrated that CBO catalyst possesses a greater Ru dispersion than ACO-Ru(2%). Both sets of results together allow to claim that for ACO, Ru being more abundant on a smaller external surface, it tends to agglomerate more, forming bigger particles displaying a lower dispersion. Thus for the ACO based catalyst, only a third of the impregnated Ru would be available to react with oleic acid in the oxidative cleavage reaction. Besides, Figures S1.2 and S1.3 show XPS survey and C 1s high resolution spectra of both carbon catalysts. After deconvolution of C 1s peaks and their disentangling from those of Ru, it was determined that Ru presented a doublet at 282.3 and 286.4 eV which corresponds to Ru[III] oxidation state [234]. Since no chlorine was detected in the survey spectrum, it is possible that the halogen was exchanged by OH groups during the impregnation process and afterwards eliminated along the several washings that the samples underwent after the impregnation.

Table 1.3. Ru loading on carbon catalysts

Catalyst	Nominal Ru (wt%) ^a	Superficial Ru (wt%) ^b	Ru loading (wt%) ^c	Ru dispersion (%) ^d
ACO-Ru(2%)	2.0	8.8	1.9	33.3
CBO-Ru(2%)	2.0	4.8	1.8	47.8

^aNominal composition corresponding to the precursor solution. ^bRu superficial content determined by XPS. ^cRu loading determined by ICP-AES. ^dRu dispersion determined by CO chemisorption.

3.2. Catalytic test results

First, the oxidative cleavage of oleic acid was carried out only with NaIO₄ (Table 1.4) in order to determine to what extent the oxidizing agent could perform the reaction by itself without the solid catalyst. Then, the same procedure was performed with ACO and CBO alone (i.e. in the presence of NaIO₄, but without Ru in the system). Conversions resulted to be lower than 1% in all the above cases and even more no products were detected on the chromatograms. These results demonstrate that is not possible to perform the reaction with only NaIO₄ or the carbon supports (i.e. without Ru). In addition, tests were performed with both catalysts but without NaIO₄ and in the presence of oleic acid to verify the possibility of adsorption of the substrate. After 24 h of stirring at room temperature, the same amount of oleic acid that was introduced at the beginning was detected at the end of

the test. Therefore, there is no risk of apparent consumption of UFA during the catalytic tests that would be just due to simple adsorption on the support.

Afterwards, CBO-Ru(2%) was assessed in the oxidative cleavage reaction but with hydrogen peroxide instead of NaIO₄. The idea was to verify whether it was possible to perform the reaction with a softer oxidizing agent which could oxidize Ru on CBO surface. However, results were very poor. Actually, hydrogen peroxide is not strong enough to oxidize surface Ru into the species with high oxidation state required to trigger the oxidative cleavage of the carbon-carbon double bond in oleic acid.

Table 1.4. Conversion and product distribution after 24 h of stirring

Catalyst	Conv. (%)	OA (%)	PA (%)	AA (%)
Blank	0.5	>99	---	---
ACO	0.4	>99	---	---
CBO	0.6	>99	---	---
CBO-PDA-Ru(2%) ^a	0.3	>99	---	---

^a3 mL of H₂O₂ instead of NaIO₄

Figure 1.4 shows the performances of both carbon catalysts in the oxidative cleavage of oleic acid with 4 and 8 equivalents of NaIO₄. According to previous tests conducted with RuO₄ in homogeneous phase, the oxidative cleavage reaction requires at least 4 equivalents relative to the substrate to oxidize the Ru precursor salt and to fully transform oleic acid into PA and AA [111,112,114]. In spite of ACO high surface area, its catalytic activity was much lower than the conversion attained with CBO-Ru(2%). When 8 equivalents of the oxidizing agent were employed, ACO-Ru(2%) showed a slight improvement in its catalytic activity.

CBO-Ru(2%) performance was also greater, reaching a complete conversion after 24 h of stirring, when using 8 equivalents of NaIO₄. The huge difference between the performances of the two catalysts was evidenced as well in yields and selectivity of the oxidative cleavage products. Even doubling the amount of oxidizing agent did not contribute to improve the poor yields of PA and AA when ACO-Ru(2%) was used. On the other hand, CBO-Ru(2%) shows 15% of improvement in terms of yield and selectivity after increasing the amount of NaIO₄ reaching values around 75%. These findings are related to the amount of nonanal and 9-oxononanoic acid present in the reaction medium. Both compounds are the precursors of PA and AA respectively. When the amount of NaIO₄ increased from 4 to 8 equivalents, the amount of both intermediates decreases in favor of the oxidative cleavage products. These findings confirm that the oxidizing agent plays an essential role in the over oxidation of the as mentioned intermediates after the cleavage of the oleic acid. It is worth to mention that the applied methodology (extractions, calibration curves and partition coefficient) agrees with the chemical reaction since one mole of oleic acid produces one mole of pelargonic acid and one mole of azelaic acid.

Therefore, it is normal to observe identical yields and selectivities for both oxidative cleavage products.

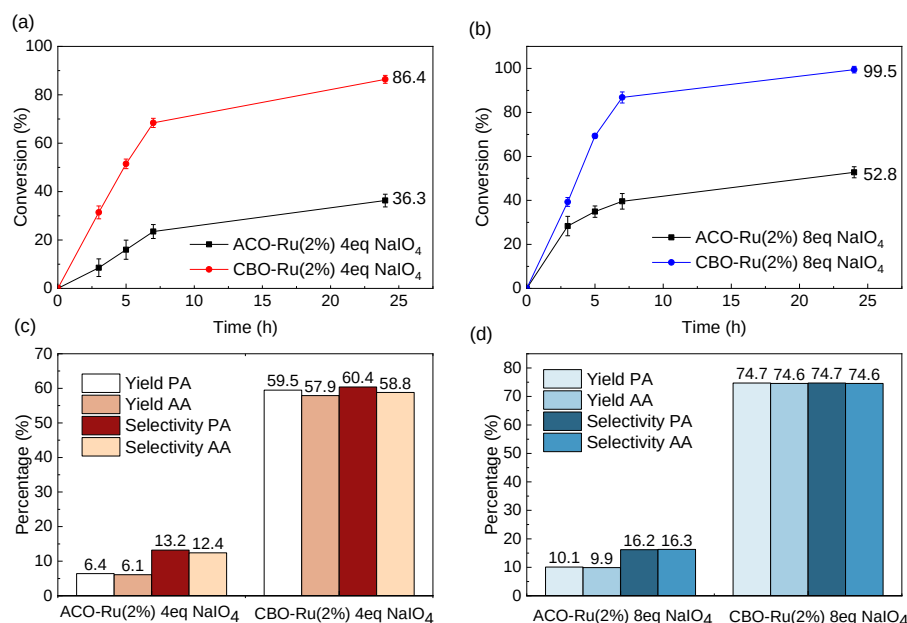


Figure 1.4. Catalytic activity of ACO-Ru(2%) and CBO-Ru(2%) with a) 4 equiv. NaIO_4 ; b) 8 equiv. NaIO_4 ; Yields and selectivity with c) 4 equiv. NaIO_4 ; d) 8 equiv. NaIO_4

To deepen the study of both carbon catalysts in the oxidative cleavage reaction, a hot-filtration test was conducted to verify whether the reaction was carried out by the solid catalysts. Figure 1.5 confirms that in both cases an increase of catalytic activity was observed after the removal of the solid catalysts. This fact demonstrates that Ru leached at least partially during the oxidative cleavage reaction and that leached Ru species (most likely RuO_4) performed the reaction. Although an increase of catalytic activity was detected after the removal of the catalysts, the conversion accomplished at the end of the hot-filtration test was lower than when the solid catalyst was kept in the reaction medium for the whole test. Also, if Ru was acting only in the liquid phase, the results for both ACO and CBO based catalysts should have been the same regardless the chemical nature and physical properties of the supports. Hence, these results suggest that the employed support plays a role in the oxidative cleavage reaction. Among the factors explored in this work, the Ru dispersion, PSD and external surface area influence the performance of the catalysts in this reaction. After observing the evolution with time of the yields and selectivities, it is clear that a macroporous material (and its large pore size) is preferable as compared to a support with micropores.

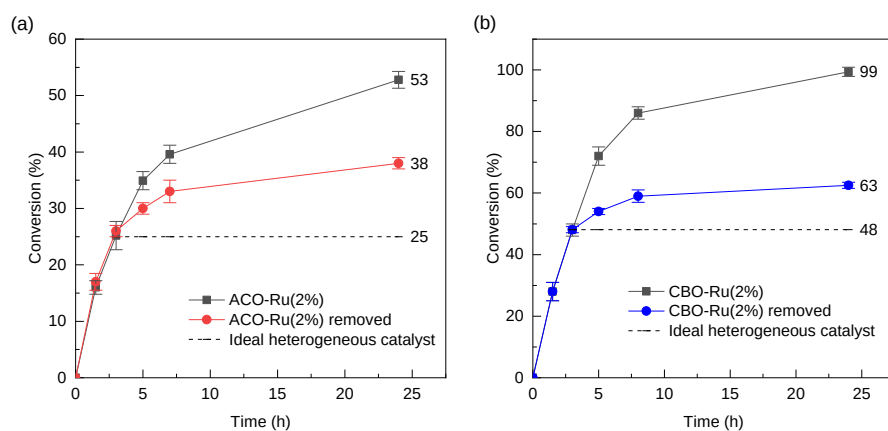


Figure 1.5. Hot-filtration tests a) ACO-Ru(2%) and b)CBO-Ru(2%)

To support this statement, the molecular size of oleic acid was estimated through an *ab initio* calculation using the Gaussian03 program. STO-3G minimal basis was chosen to perform the calculation with a Hartree-Fock level. The optimized molecular structure of oleic acid, depicted in Figure 1.6, shows a *cis* configuration with a minimal width of 0.83 nm. It is clear then that oleic acid would hardly diffuse inside micropores of ACO ($0.5 < \text{pore size} < 0.8 \text{ nm}$) to reach Ru located on the inner surfaces. Conversely, oleic acid molecules can diffuse easier amid the interstitial spaces of carbon black nodules improving the contact with Ru on CBO surface.

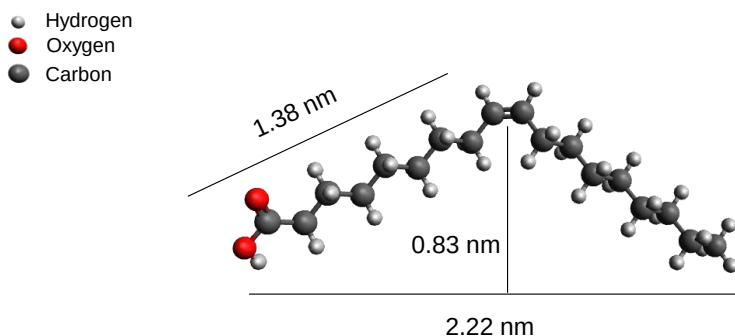


Figure 1.6. Optimized geometry of oleic acid after *ab initio* Hartree-Fock calculation

To assess the catalytic stability of both catalysts, recycling tests were conducted up to 5 times. Figure 1.7 shows that ACO-Ru(2%) and CBO-Ru(2%) lose catalytic activity after each recycle. The half of the catalytic activity of ACO-Ru(2%) is lost after two recycles but thenceforth conversion is maintained around 20%. The main reason for the decrease in

catalytic activity lies in Ru dissolution after its interaction with the oxidizing agent. Since the presence of Na and I was detected by XPS analysis of spent catalysts (Figure S1.4), NaIO_4 could be one of the reasons for Ru dissolution and further oxidation into $\text{Ru}^{\text{VIII}}\text{O}_4$ to trigger the oxidative cleavage reaction.

Moreover, no Ru anymore was detected by XPS after the recycling tests which demonstrates that all the available amount of the transition metal deposited on the external ACO surface got dissolved in the previous catalytic tests (Figure 1.8). However, conversions achieved from third to fifth recycle runs can be due to the presence of remaining Ru on external surface and/or Ru inside micropores. Most likely, Ru that was not leached in the previous catalytic tests was responsible for the activity while Ru in the micropores, which is a little more protected against leaching than when it is on the external surface, can diffuse into the medium to perform the reaction. More important, ICP analysis confirmed that Ru bulk concentration of both spent catalysts is quite low which is why they show poor performances in the last recycling tests (Table 1.5).

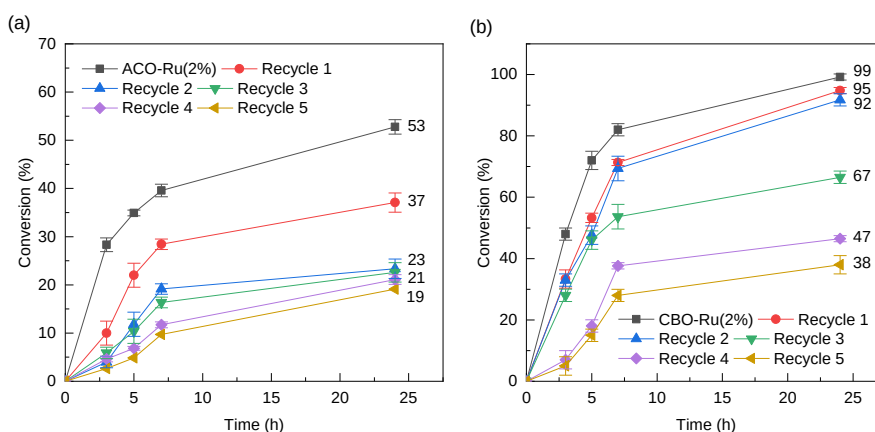


Figure 1.7. Recycling tests a) ACO-Ru(2%) and b)CBO-Ru(2%)

The same trend was observed in the case of CBO-Ru(2%). During the first three catalytic tests, the carbon black catalyst maintained a high conversion towards the oxidative cleavage of oleic acid. This observation shows that oxygenated groups of CBO managed to retain Ru on the surface up to three catalytic consecutive tests which is an advantage in respect to the homogeneous catalyst. Moreover, the catalysts made of supports without oxidation treatment were also submitted to recycling tests (Figure S1.6). These were not active anymore after 3 recycling tests which clearly demonstrates the benefits of carbon supports functionalization via an oxidation treatment. As regards, CBO-Ru catalyst, its catalytic activity

decreases down to 38% in the last two recycling tests which confirms that Ru leached throughout the previous oxidative cleavage tests.

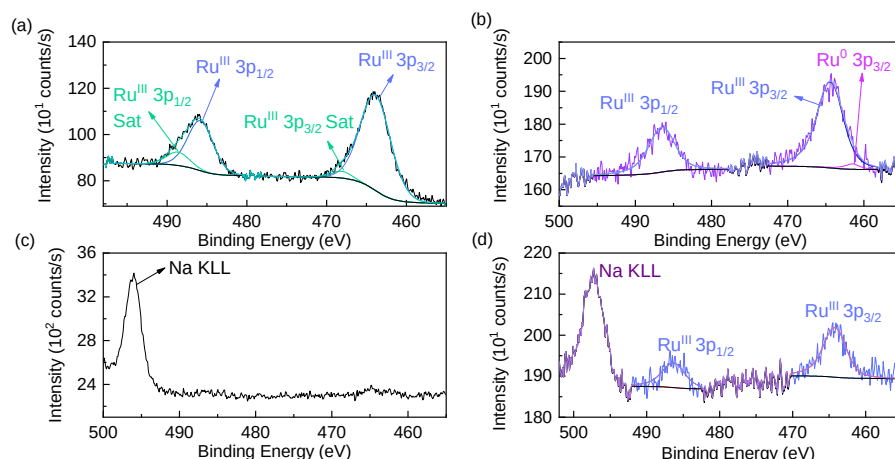


Figure 1.8. Ru 3p high resolution spectra of fresh catalysts: a) ACO-Ru(2%); b)CBO-Ru(2%) and spent catalysts: c) ACO-Ru(2%); d)CBO-Ru(2%)

Unlike activated carbon, XPS analyses confirmed that Ru was still on CBO surface but yet in a much smaller quantity than before its use in the reaction (Table 1.5). From the disentangling of the Ru 3p doublet it is possible to observe that Ru^{III} cations are on the surface of CBO. Since no chlorine was detected during XPS analysis, it is possible to conclude that oxygenated groups from CBO displaced Cl⁻ to form a Ru^{III} complex on the surface of the support.

Table 1.5. Ru loading on spent carbon catalysts

Catalyst	Nominal Ru (wt%) ^a	Superficial Ru (wt%) ^b	Ru loading (wt%) ^c
ACO-Ru(2%)	2.0	---	0.5
CBO-Ru(2%)	2.0	1.7	0.8

^aNominal composition corresponding to the precursor solution. ^bRu superficial content determined by XPS. ^cRu loading determined by ICP-AES.

4. Conclusions

To sum up, activated carbon and carbon black were successfully oxidized without affecting too much their textural properties. Infrared analyses along with Boehm's titration confirmed that oxidation with nitric acid allowed to increase the amount of oxygenated groups. These functionalities can be employed for Ru complexation during wet impregnation procedure. N₂ physisorption demonstrated that the selected activated carbon possesses a

high surface area with a narrow pore size distribution. On the other hand, carbon black shows a lower surface area with greater porosity which is ascribed to the interstitial spaces among carbon nodules.

A complete impregnation of Ru on both carbon supports was confirmed by ICP-AES analyses. In addition, the deconvolution of the XPS Ru 3p doublet allowed to estimate that Ru on carbon catalysts was present as Ru(III) for both CBO and ACO-based catalysts. Combined XPS and CO-chimisorption data showed that for ACO based catalyst, only a third of the impregnated Ru would be available to react with oleic acid in the oxidative cleavage reaction. This agreed with the observation that in the catalytic tests, CBO-Ru(2%) presented better catalytic activity than ACO-Ru(2%) confirming that a macroporous material is more suitable as a support than a microporous material. This claim was supported by the fact that oleic acid (*cis* configuration) has a bigger molecular size than the micropores of activated carbon which hinders the diffusion of the former inside the latter.

Hot-filtration tests demonstrated that Ru was present in the reaction medium after the solid catalysts were removed at approximately 50% of conversion. The characterization of spent carbon catalysts by ICP and XPS confirmed that Ru was dissolving during the oxidative cleavage reaction. As a consequence, the catalytic activity of both assessed catalysts decreased after each recycling test. Hence, the lack of homogeneity in the Ru deposition over the supports, pore sizes below the theoretical size of oleic acid and a low complexation of Ru conducted to poor performances in the oxidative cleavage of oleic acid.

For all these arguments, carbon black was selected as a support for the following of the thesis. Moreover, it turned obvious the necessity to functionalize this carbon support as its natural ability to retain Ru on its surface during the catalytic reaction was not strong enough. Therefore, we decided to assess the efficiency of covalent functionalization techniques oriented to maintain Ru on the solid phase without losing catalytic activity.

CHAPTER II: FUNCTIONALIZATION OF CARBON BLACK AS AN EFFICIENT TOOL FOR Ru COMPLEXATION TOWARDS OXIDATIVE CLEAVAGE OF OLEIC ACID

Abstract

In the previous chapter, we have shown the supremacy of oxidized carbon black (CBO)-based Ru catalysts, compared to oxidized active carbon ones, in the oxidative cleavage of oleic acid. Yet, we also highlighted the necessity to functionalize the CBO as its natural ability to retain Ru on its surface during the catalytic reaction was not strong enough. To achieve so, we report in this chapter on functionalization methodologies that lie in the complexation of Ru. Precisely, 4,4'-diamino-2,2'-bipyridine (NH₂-bpy) and polydopamine (PDA) were used as complexation agents for the functionalization of CBO. NH₂-bpy was covalently bonded to COOH groups on CBO surface by amidation through an (1) acylation along with SOCl₂ or by (2) N-hydroxysuccinimide/1-ethyl-3-(3-dimethylaminopropyl)carbodiimide cross-linking method (NHS/EDC). On the other hand, (3) dopamine was self-polymerized in contact with CBO to deposit PDA particles containing hydroxyl and amine groups able to complex Ru species. The functionalization of CBO by NH₂-bpy and PDA was confirmed by FTIR, TGA, and N₂ physisorption, while Ru loading was determined by ICP and XPS. The three catalysts were then assessed in the oxidative cleavage of oleic acid. The Ru-based catalyst containing PDA resulted to be the most promising of them after reaching a complete conversion at 7 h with yields of pelargonic and azelaic acid about 95%. Although hot-filtration tests confirmed the presence of Ru species in the reaction medium, the PDA catalyst remained active even after five runs. Actually, post-test characterization of the catalysts revealed that catechol groups of PDA re-adsorb Ru species once the reaction ends, thereby ensuring the reusability of this heterogeneous catalyst.

1. Introduction

As it was stated in section 3 (p. 38), several functionalization techniques have been employed to graft transition metal complexes onto a support [167,182]. The main purpose of such techniques is related to maintain attached the active species on supports surface throughout the catalytic reaction [167,182]. If this approach is successful, the synthesized catalyst would then be ready to be reused in several successive catalytic tests. As regards carbon supports, the most common functionalization techniques are oxidation treatments which develop different acid sites suitable to interact with transition metal ions [240,241]. Nevertheless, in the previous chapter, it was demonstrated that a random distribution of oxygenated functionalities on carbon black surface is not enough to maintain Ru grafted on the solid during the oxidative cleavage reaction. To address this issue, it is proposed that carbon black surface is covalently functionalized by two different ways. The first one consists in binding the traditional 2,2'-bipyridine (bpy) ligand (p. 38) onto the carbon surface in order to use this chelating agent for the complexation of ruthenium [196,197]. The other strategy implies the use of polydopamine (PDA) which is a versatile polymer that can be grafted on carbon surface (p. 41) and that can at the same time complex Ru using its catechol and amine groups [223-225]. Through these two chelating agents, we hypothesized that it would be possible to build robust and reusable heterogeneous catalysts for the oxidative cleavage of UFAs.

Indeed, ruthenium is a transition metal than can be chelated by several different ligands such as phosphines, CO, chlorides and, of course $\text{NH}_2\text{-bpy}$ [277-280]. Among all these ligands, $\text{NH}_2\text{-bpy}$ was chosen because (1) it has a high affinity for Ru, (2) it is resistant to highly oxidative environments and because (3) it can react with carboxylic moieties on CBO to form resistant and stable amide bonds [281]. The latter is the key to form a covalent interaction between carboxylic acids on carbon black support and the amine groups of the aromatic ligand. Then, the pyridinic nitrogens of bpy are available for the complexation of Ru ions. For this purpose, an oxidation treatment must be applied to the carbonaceous support in order to create carboxylic acids on its surface [282]. In addition, these acid groups should be activated to trigger the amidation reaction with $\text{NH}_2\text{-bpy}$. Mainly this activation involves the chlorination of CBO carboxylic acids by means of SOCl_2 [283]. Through this method, acyl chlorides (more reactive than other carbonyl compounds) are formed which are better leaving groups than hydroxyl groups [283,284]. Indeed, acyl chlorides inductively withdraw electrons from the carbonyl carbon, leading to more positively charged and electrophilic carbon atoms [283,284]. Therefore, acyl chloride can undergo a nucleophilic attack from amines of $\text{NH}_2\text{-bpy}$ [285].

Another approach consists in anchoring $\text{NH}_2\text{-bpy}$ on CBO surface by the activation of carboxylic groups through N-hydroxysuccinimide/1-ethyl-3-(3-dimethylaminopropyl)carbodiimide cross-linking method (NHS/EDC) [286]. This strategy has been commonly used in biochemistry to bind proteins or

antibodies to functionalized nanoparticles [287]. Normally, this crosslinking method proceeds via a condensation reaction between COOH and NH₂ groups. In a first step, EDC reacts with COOH groups forming an O-acylisourea intermediate, which can be easily hydrolyzed [288]. This is why sulfo-NHS is used to form a second more stable intermediate via the formation of active ester with the carboxylates. One of the main advantages of the NHS/EDC coupling method is the solubility of EDC and sulfo-NHS in water [289], avoiding the use of polluting organic solvents. However, this method is very sensitive to pH changes during the reaction [287] which is why it has not been fully developed yet.

On the other hand, polymer functionalization of CBO surface through PDA is a promising and easy route to anchor transition metals like Ru [290-292]. Mainly, dopamine requires alkaline conditions (pH ~ 8.5) to undergo a self-polymerization reaction yielding PDA in the form of particles [286]. Normally, a buffer solution formed by tris(hydroxymethyl)aminomethane (TRIS) is used to attain and maintain basic conditions during the self-polymerization of dopamine [213,216,294]. The structure of the polymer involves an indole ring with catechol and amine groups which possess a high adherence capacity to several types of surfaces such as oxides, metals and carbons [295,296]. As regards the latter, PDA can cover CBO surface by forming covalent bonds with oxygenated groups or by π - π stacking interactions. Besides, depending on the polymerization time, thinner PDA layers can be formed on the material to be functionalized strengthening the deposition of the polymer [297,298]. Other benefit of PDA is related to its chelation capability [292]. Through its amine and catechol groups, PDA can incorporate transition metal ions for effluents depuration or for catalytic applications [223, 225,297]. For instance, Cai *et al.* impregnated Ru on PDA particles and achieved an H₂ production through water splitting with similar performances as those of other conventional catalysts in electrocatalysis [225].

Hence, in this work we propose the functionalization of oxidized carbon black surface with 4,4'-diamino-2,2'-bipyridine and polydopamine as chelating agents for Ru complexation towards the oxidative cleavage reaction. The NH₂-bpy ligand will be covalently attached to carboxylic sites on carbon black surface by means of (1) conventional chlorination and (2) NHS/EDC crosslinking methods. In addition, (3) dopamine will be self-polymerized in contact with CBO particles leading to PDA deposition on this carbon material. Ru will then be impregnated on the three functionalized supports through wet impregnation and all catalysts will be assessed in the oxidative cleavage of oleic acid.

2. Experimental section

Carbon black (CB Degussa Printex ®G: 95.73 wt.% C, 0.73 wt.% H, 3.5 wt.% O, BET area 154 m²/g and pore volume 0.56 cm³/g) was first oxidized with nitric acid (Carl Roth HNO₃ = 65%) as was explained in the

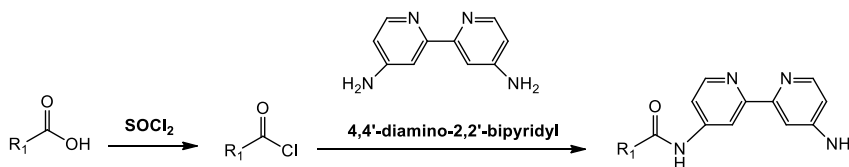
previous chapter (p. 70). Oxidized carbon black (CBO) was used for different functionalization procedures herein detailed. Afterwards, functionalized carbons catalysts were prepared with a Ru load of 2 wt% through wet impregnation (p. 59). The following Ru compounds were analyzed by XPS to better characterize the Ru chemical environment of the carbon catalysts synthesized in this chapter: Ruthenium(III) chloride hydrate 99.9% and Potassium perruthenate(VII) 97% from Alfa Aesar; Ruthenium(IV) oxide hydrate 99.9% and Tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate from Sigma-Aldrich.

2.1. Functionalization of carbon black with bipyridine

Commercial 4,4'-diamino-2,2'-bipyridine ($\text{NH}_2\text{-bpy}$, $\text{C}_{10}\text{H}_{10}\text{N}_4$ > 98.5% from TCI chemicals) was selected because it already contains primary amine groups for the amidation reaction with carboxylic acids on CBO surface.

2.1.1. Conventional chlorination

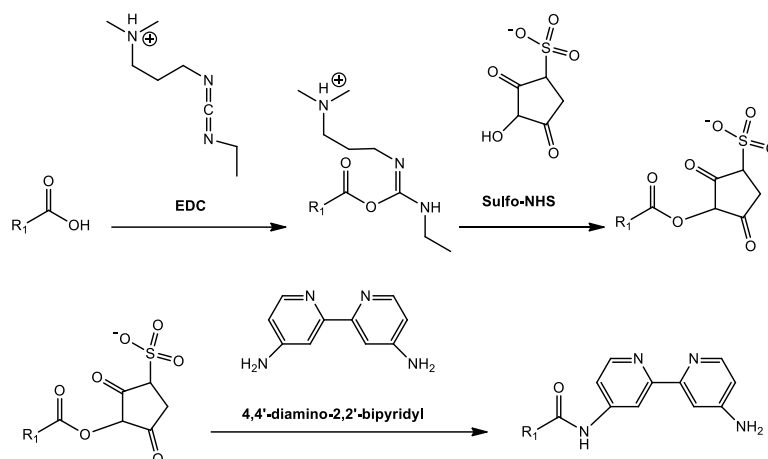
In a 500 mL triple-necked round-bottom flask, 4 g of CBO was introduced along with 130 mL of toluene (>99.5% from Carl Roth) and 12 mL of SOCl_2 (97% from Sigma Aldrich). The suspension was heated at 120°C for 5 hours under reflux to avoid losses of toluene. Then the solid (CBO-Cl) was separated by means of vacuum filtration using a MF-Millipore paper filter (pore size = $0.025\ \mu\text{m}$) and dried at 40°C under vacuum ($\sim 10^{-2}$ bar) overnight. Next, CBO-Cl was introduced in a 50 mL twin-necked round-bottom flask, together with 25 mL of toluene and 1.3 equivalent of 4,4'-diamino-2,2'-bipyridine relative to the amount of carboxylic sites on CBO measured by Boehm's titration (Table 1.1, p. 74). The mixture was refluxed at 120°C for 4 hours to obtain the functionalized CBO-bpy(SOCl_2). The solid was recovered by vacuum filtration and extensively washed with toluene in a Soxhlet apparatus with Whatman® thimbles. Finally, CBO-bpy(SOCl_2) was dried at 40°C under vacuum ($\sim 10^{-2}$ bar) overnight (Scheme 2.1).



Scheme 2.1. Functionalization of CBO with 4,4'-diamino-2,2'-bipyridyl through chlorination with SOCl_2

2.1.2. NHS/EDC method

In a 500 mL round-bottom flask, 4 g of CBO was added to 250 mL of distilled water and magnetically stirred at 1000 rpm. The suspension was mixed with 1.5 g of EDC (>99%, 1-ethyl-3-(3-dimethylaminopropyl-carbodiimid)-hydrochlorid from Carl Roth) and 1.5 g of sulfo-NHS (>98%, N-hydroxysulfosuccinimide sodium salt from TCI). The pH of the solution was fixed at 5.5 by adding a 2.0 M NaOH solution. After 1 hour of agitation, 1.3 equivalent of 4,4'-diamino-2,2'-bipyridine was added and the pH was adjusted to 7.5 using NaOH solution. The solid was recovered by centrifugation (30 minutes, 14000 rpm, 26200 g) in a Heraeus Multifuge X1R Centrifuge from Thermo Scientific. The CBO-bpy(NHS/EDC) solid was extensively washed with hot water (100°C) in a Soxhlet apparatus with Whatman® thimbles for 24 hours. Finally, CBO-bpy(NHS/EDC) was dried at 40°C under vacuum ($\sim 10^{-2}$ bar) overnight (Scheme 2.2).



Scheme 2.2. Functionalization of CBO with 4,4'-diamino-2,2'-bipyridyl through NHS/EDC coupling

2.2. Functionalization of carbon black with polydopamine

The self-polymerization method of dopamine was employed using tris(hydroxymethyl)aminomethane (TRIS $C_4H_{11}NO_3$ >99%, from TCI) for producing a buffer solution at alkaline conditions. As a reference material, pure polydopamine was prepared as detailed below.

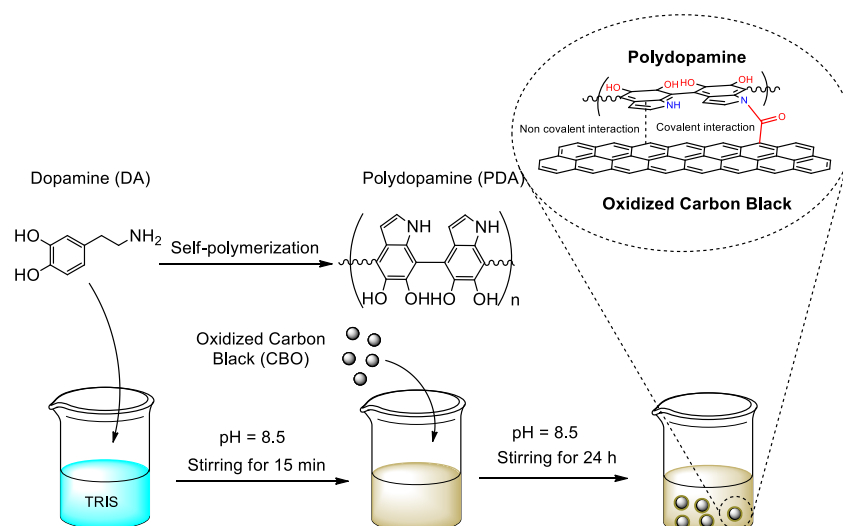
2.2.1. Polydopamine synthesis

First, 0.24 g of TRIS was dissolved in 200 mL of distilled water (10 mM) and magnetically stirred for 15 minutes at 1500 rpm. Then, 1 g of dopamine hydrochloride (> 98%, dopamine hydrochloride from TCI) was dissolved in

the TRIS solution at a pH of 8.5. At the beginning the solution is transparent, then it turns pink and finally it becomes dark brown which means that dopamine self-polymerized. The solution was stirred for 24 h at room temperature to allow a complete polymerization of dopamine. Afterwards, PDA particles were separated by centrifugation in a Heraeus Multifuge X1R Centrifuge at 14000 rpm (26200 g) for 30 minutes. PDA particles were washed 3 times with distilled water and dried in ambient air overnight at room temperature.

2.2.2. Polydopamine deposition on carbon black

For the impregnation of PDA on CBO surface, 100 mL of a 10 mM buffer solution of TRIS was prepared in an open vessel and magnetically stirred for 15 minutes at 1500 rpm. Afterwards, 350 mg of dopamine hydrochloride was dissolved in the buffer solution at a pH of 8.5. It is important to mention that the amount of dopamine added is that required to form a theoretical monolayer of the polymer on 1 g of support. This amount was estimated on the basis of the section of a dopamine molecule as detailed in Supporting information section Figure S2.1) and of the specific surface area of the CBO (Table 1.2, p. 75). Dopamine started to self-polymerize when the solution passed from colorless to pale brown. At this moment, 1 g of dried CBO was added to the solution and stirred for further 24 h at room temperature in order to ensure a complete deposition of PDA on the support. Next, the CBO-PDA composite was removed by centrifugation at 14000 rpm (26200 g) in a Heraeus MultifugeX1R Centrifuge, washed 3 times with distilled water and dried in ambient air overnight at room temperature (Scheme 2.3).



Scheme 2.3. Functionalization of CBO with PDA

2.3 Additional characterization techniques

Thermogravimetric analysis (TGA) was employed to determine the amount of PDA or bpy deposited on CBO surface. All analyses were carried out under a nitrogen flow from 50 °C to 900 °C in a Mettler Toledo TGA/SDTA851e Thermogravimetric Analyzer. About 2 mg of each sample was introduced into 70 μL Al_2O_3 crucibles. The heating ramp was kept at 10 °C/min and the N_2 flow rate was adjusted to 40 mL/min. With this technique it was possible to calculate the amount of PDA or bpy deposited on CBO surface by estimating the difference in the weight loss during the heating process. The nominal amount of each compound (see supporting information) was compared to the experimental amount obtained by TGA in order to calculate the yield of deposition as follows:

$$\text{Yield} = \frac{\text{Amount of PDA/bpy (TGA)}}{\text{Nominal amount of PDA/bpy}} \times 100\% \quad [2.1]$$

3. Results and Discussion

3.1. Characterization results

At first, 4,4'-diamino-2,2'-bipyridyl was characterized by infrared spectroscopy in transmission mode (Figure 2.1). The most representative bands of this ligand appear in the range from 1700 to 1200 cm^{-1} and correspond to stretching vibrations in-plane deformations of pyridyl rings [300,301]. Most of these peaks are overlapped with those from CBO when bpy is impregnated on CBO surface. This carbon support shows two small bands at 2913 and 2850 cm^{-1} attributed to CH antisymmetric and symmetric stretchings in aliphatic chains [273,274]. A small peak at 1714 cm^{-1} is assigned to C=O stretching vibration mode in carbonyls [269] whereas a band at 1610 cm^{-1} is associated to ring stretching vibration characteristic of aromatic compounds. Finally, a strong peak at 1091 cm^{-1} is attributed to C–O stretch vibration of the C-OH bond in alcohols. [269]. After the covalent impregnation of bpy on CBO via amide bond, the band at 1714 cm^{-1} disappears and small bands at 1580 and 1402 cm^{-1} arise. Both peaks can be attributed to N-H deformation and C-N stretching vibration in amides respectively [269].

As regards pure PDA (Figure 2.1c), a broad and intense band appears at 3250 cm^{-1} which is assigned to the stretching vibration mode of O-H bond in catechol groups [302]. Two more bands arise at 1618 and 1512 cm^{-1} ascribed to stretching vibration modes from N-H located in the indole ring [303]. At 1291 cm^{-1} another band appears which is related to stretching vibration of C-N bond in aromatic rings [303,304]. PDA spectrum observed here agrees with those reported in the literature [302-304]. Like the composites functionalized with bpy, the band at 1714 cm^{-1} , that corresponds to carbonyl groups, disappears when PDA is deposited over CBO surface.

Instead, the CBO-PDA solid shows small bands at 3220 and 1618 cm^{-1} which are characteristic of O-H stretching vibrations and aromatic ring stretching vibrations respectively [269,302]. Two additional peaks, similar to those found in PDA infrared spectrum, appear at 1514 and 1280 cm^{-1} as well. They belong to the stretching vibrations in N-H and C-N bonds of catechol and amine groups respectively [302-304]. Hence, the spectroscopic evidences aforementioned confirm the impregnation of NH_2 -bpy and PDA on CBO surface.

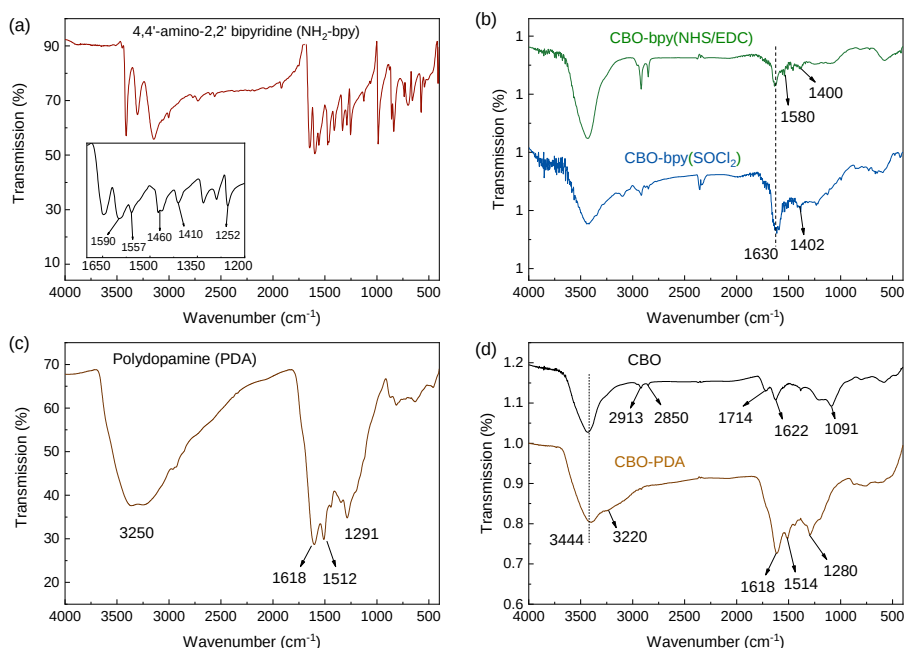


Figure 2.1. FTIR spectra of: a) 2,2' Bipyridine, b) CBO-bpy(SOCl_2) and CBO-bpy(NHS/EDC); c) Polydopamine; d) CBO and CBO-PDA

XPS measurements were carried out to elucidate the chemical environment of oxidized carbon black surface after its functionalization with NH_2 -bpy and PDA. Table 2.1 recapitulates surface elemental composition of all synthesized carbon materials while Figure 2.2a displays their XPS survey spectra. As regards CBO, two main peaks are clearly observed: C 1s (284.8 eV) and O 1s (533 eV) with an O/C ratio of 0.26. As was observed in FTIR analysis, CBO shows several oxygenated groups such as phenols (286.5 eV), carbonyls (288.3 eV), carboxylic groups (289.5 eV) which are observed in the deconvolution of C 1s peak (Figure S2.2a). In addition, a shake-up peak is observed due to the aromatic layers of the carbonaceous support. As a consequence of NH_2 -bpy deposition on CBO surface, O/C ratio decreases to 0.07 and 0.10 after using NHS/EDC and SOCl_2 techniques respectively. In both cases, a small N 1s peak arises which is attributed to nitrogen atoms within the bipyridine structure. Moreover, the

nitrogen content in CBO-bpy(SOCl₂) was higher than in the case of CBO-bpy(NHS/EDC) suggesting a greater deposition of NH₂-bpy with the chlorination technique. The possible chemical species on each carbon material were estimated after deconvolution of C 1s and N 1s peaks. In addition to the mentioned species found on CBO surface, Figures S2.2b and S2.2c present a sub peak at 288.5 eV associated to amides produced after the reaction between amines from bpy and carboxylic acids from CBO surface [305,306].

Table 2.1. Surface composition (wt%) of functionalized carbon black

Functionalized carbon	C 1s (%)	O 1s (%)	N 1s (%)	Cl 2p (%)
CBO	79.3	20.7	---	---
CBO-bpy(NHS/EDC)	92.1	6.7	1.3	---
CBO-bpy(SOCl ₂)	87.8	8.4	2.1	1.7
CBO-PDA	69.8	24.6	5.6	---

As illustrated in Figure 2.2b, the N 1s peak of CBO-bpy(NHS/EDC) is deconvoluted into two peaks at 398.8 and 400.7 which are attributed to pyridinic nitrogens and amides respectively [306,306]. These values agree with those published in literature [305-309].

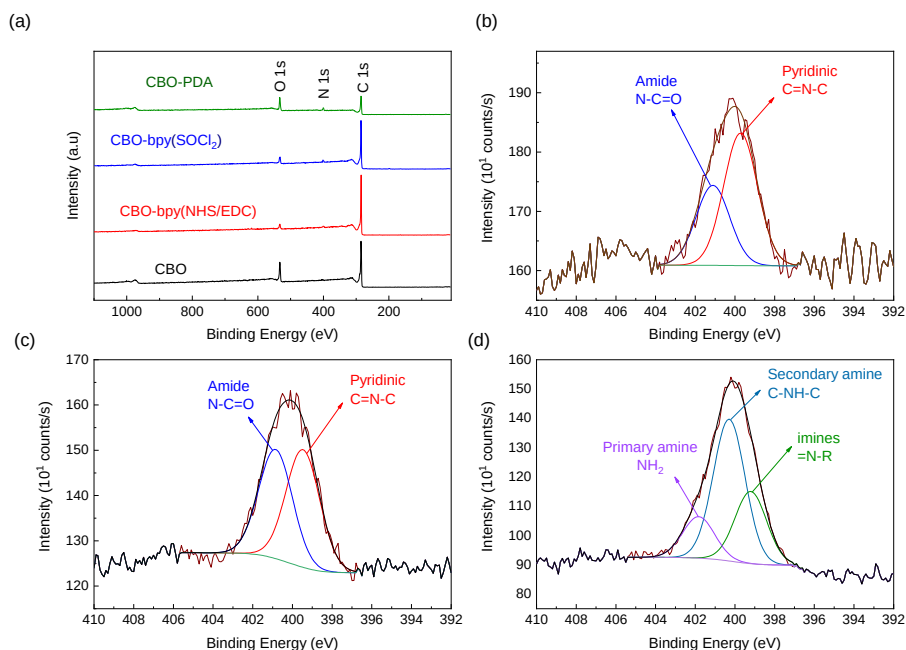


Figure 2.2. a) Survey XPS spectra of CBO and functionalized composites; N 1s spectra of b) CBO-bpy(NHS/EDC); c) CBO-bpy(SOCl₂) and d) CBO-PDA

In addition, CBO-bpy(SOCl₂) in Figure 2.2c shows an equal content between amides and pyridinic nitrogens confirming that the two amine groups in NH₂-bpy molecule formed an amide bond with carboxylic groups on carbon support. Thus, half of nitrogen atoms form amide bonds while pyridinic nitrogens are ready to chelate Ru ions. C 1s high resolution spectrum of CBO-PDA (Figure S2.2d) presents 5 contributions corresponding to C-(C,H) bonds (284.8 eV), C-OH of catechol groups (286.1 eV), C=O of quinones (287.1 eV), C-N bonds in the aromatic ring (288.4 eV), carboxylic acids from CBO (289.3 eV) and a shake-up peak at 290.1 eV which is characteristic of aromatic structures [225,305]. On the other hand, N 1s peak from CBO-PDA (Figure 2.2d) was deconvoluted assuming three species: an imine (=N-R at 398.5), a secondary amine (C-NH-C at 399.9 eV) and a primary amine (NH₂ at 401.8 eV) [225,305]. Imines and secondary amines are evidences that dopamine cyclization took place during the formation of the indole ring of PDA. However, the presence of primary amines demonstrates that this cyclization was not complete and PDA layers over CBO surface possess aliphatic chains with amine groups. In addition, the O/C ratio in CBO-PDA increases to 0.35 which is related to additional catechol groups provided by PDA.

TGA was employed in order to measure the amount of PDA and bpy deposited on CBO surface. The PDA thermogram (Figure 2.3a) clearly demonstrates that the decomposition of the polymer begins at a temperature higher than 250 °C. From 50°C to 250 °C, humidity is evaporated and then PDA starts to decompose through the entire range of temperature up to 900 °C.

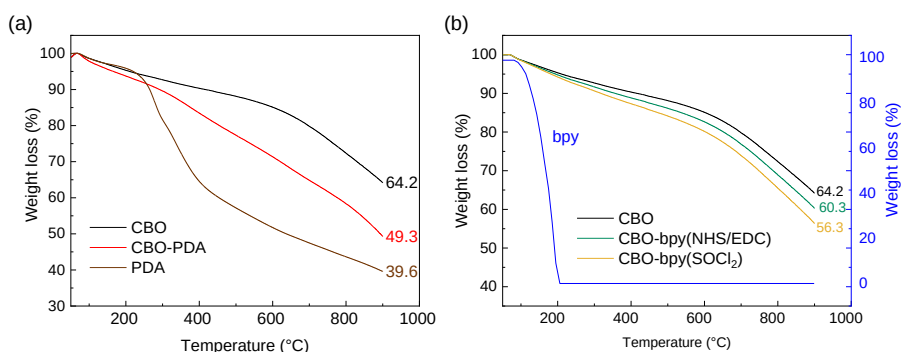


Figure 2.3. TGA of a) CBO, CBO-PDA and PDA; b) CBO, CBO-bpy(NHS/EDC) and CBO-bpy(SOCl₂)

Hence, in the case of CBO-PDA, the additional weight loss observed is attributed to the thermal decomposition of PDA. Based on this evidence, a 15% of PDA content on CBO surface was estimated by subtracting the weight loss of CBO from the weight loss of CBO-PDA composite. By calculating the yield of deposition through Equation 2.1, it was possible to estimate that 57% of the initial amount of dopamine was polymerized and

deposited on CBO surface during the functionalization of the support (Table 2.2). Most likely, PDA layers can interact with themselves and CBO surface by covalent interactions and π - π stacking. As regards NH_2 -bpy, the thermogram displayed in Figure 2.3b shows a swift thermal decomposition of the ligand in a temperature range from 85 °C to 200 °C. Therefore, CBO-bpy(NHS/EDC) and CBO-bpy(SOCl_2) present more pronounced weight losses from 85 °C. The solid functionalized with the conventional chlorination method presented a greater weight loss than its counterpart obtained by the NHS/EDC crosslinking method. This gap in weight loss amid both solids is attributed to a lower amount of NH_2 -bpy deposited when the NHS/EDC method was employed. Table 2.2 compares the expected amount of NH_2 -bpy to be deposited versus the experimental amount obtained by TGA.

Table 2.2. PDA and NH_2 -bpy deposition performance on CBO surface

Functionalized Carbon	Theoretical content of PDA/bpy (wt%)	Experimental content of PDA/bpy (wt%)	Deposition yield (%)
CBO-bpy(NHS/EDC)	8.5	3.9	46
CBO-bpy(SOCl_2)	8.5	7.9	93
CBO-PDA	26.1	14.9	57

The reason why the NHS/EDC method was the less efficient for the deposition of NH_2 -bpy can be related to the ligand solubility. This method was conducted in aqueous solutions and the low solubility of NH_2 -bpy could have prevented a good contact between the amine groups of the ligand and carboxylic acid sites of the carbon support. Thus, only 46% of the expected amount of NH_2 -bpy remained attached to CBO surface after washing the solid. On the other hand, the chlorination method allowed a better deposition (93%) of the ligand due to a higher solubility of NH_2 -bpy in toluene during its linking with acyl chlorides on CBO surface. Hence, TGA confirms the results obtained from FTIR and XPS analyses.

Nitrogen physisorption tests were carried out to determine how PDA and NH_2 -bpy influence the textural properties of CBO. Figure 2.4 demonstrates that all functionalized carbon materials possess a quasi-type 2 isotherm with a narrow hysteresis loop H3 which is characteristic of materials displaying big mesopores. These should be understood as pores located in between the carbon black nodules since nodules themselves are not porous [228]. Table 2.3 recapitulates textural properties of the assessed carbon materials. In the case of the CBO-PDA composite, the specific surface area diminished as compared to CBO from 149 to 80 m^2/g as a result of polymer deposition. The pore volume also decreased by a factor 1.6, due to the filling of the gaps in between particles by the PDA. Comparatively, CBO-PDA specific surface area and pore volume did not decrease after Ru impregnation due to the low loading of this transition metal employed. Pore size distribution (PSD) of

CBO and CBO-PDA (Figure 2.3b) shows pore sizes between 5 nm up to 38 nm.

Table 2.3. Textural properties of functionalized carbon black

Carbon Material	Specific surface area (m ² /g)	External surface (m ² /g)	Pore Volume (cm ³ /g)	Mean Pore size (nm)
CBO	149	116	0.53	22.9
CBO-bpy(NHS/EDC)	90	89	0.44	22.0
CBO-bpy(NHS/EDC)-Ru(2%)	87	80	0.43	21.4
CBO-bpy(SOCl ₂)	90	89	0.43	20.1
CBO-bpy(SOCl ₂)-Ru(2%)	92	84	0.42	20.7
CBO-PDA	80	65	0.33	16.8
CBO-PDA-Ru(2%)	81	62	0.30	16.7

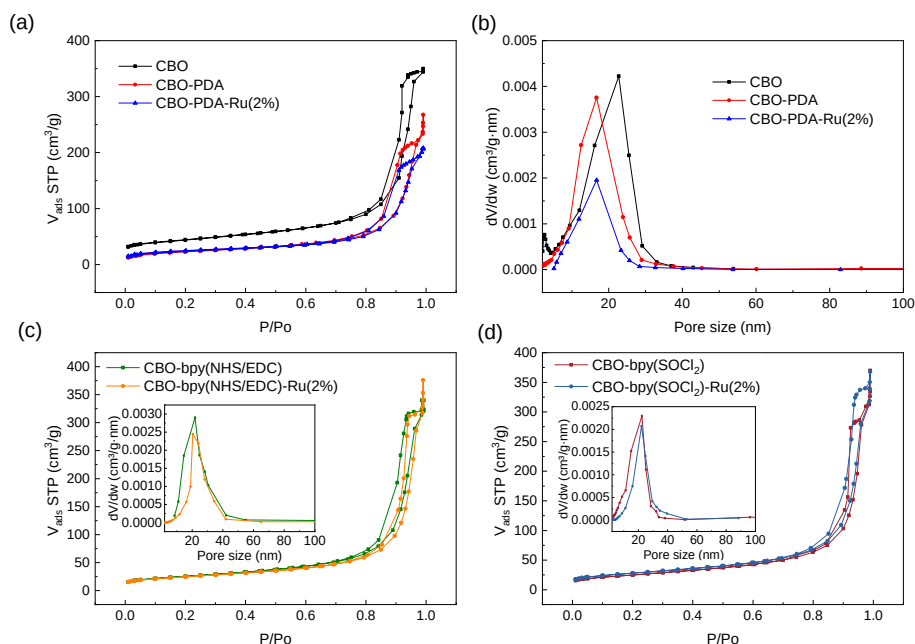


Figure 2.4. a) N₂ physisorption isotherms of: CBO, CBO-PDA and CBO-PDA-Ru(2%); b) PSD of CBO, CBO-PDA and CBO-PDA-Ru(2%); c) N₂ physisorption isotherms and PSD of CBO-bpy(NHS/EDC) and CBO-bpy(NHS/EDC)-Ru(2%); d) CBO-bpy(SOCl₂) and CBO-bpy(SOCl₂)-Ru(2%)

The average pore diameter of CBO decreases from 22.9 nm to 16.8 nm as a result of PDA particles deposition among CBO nodules. Following the same trend, NH₂-bpy deposition on CBO surface causes the decrease of its specific surface area as well as of its pore volume. In this case, aromatic

rings of bpy cover the gaps between CBO particles in the same manner as PDA particles do. More important, Ru impregnation did not cause significant modifications on the textural properties of all functionalized supports.

To confirm Ru dispersion, CO chemisorptions were conducted. Unfortunately, samples containing NH₂-bpy were not assessed by this technique since it requires a reduction pretreatment at 200 °C; a higher temperature than what NH₂-bpy can tolerate (see thermogram Figure 2.3b). On the other hand, PDA can stand the reduction treatment with H₂ allowing CBO-PDA-Ru(2%) to be submitted to CO chemisorption. Table 2.4 points out an extreme low Ru dispersion when this transition metal is impregnated on CBO-PDA surface. Conversely, Ru surface concentration (from XPS) matches with Ru load obtained by ICP-AES.

Table 2.4. Ru loading on functionalized carbon catalysts

Catalyst	Nominal Ru (wt%) ^a	Superficial Ru (wt%) ^b	Ru loading (wt%) ^c	Ru dispersion (%) ^d
CBO-bpy(NHS/EDC)-Ru(2%)	2.0	4.9	1.8	---
CBO-bpy(SOCl ₂)-Ru(2%)	2.0	3.5	1.8	---
CBO-PDA-Ru(2%)	2.0	2.2	1.9	7.8

^aNominal composition corresponding to the precursor solution. ^bRu superficial content determined by XPS. ^cRu loading determined by ICP-AES. ^dRu dispersion determined by CO chemisorption.

In order to explain these results, it is important to know that CO forms covalent bonds with Ru when it is already reduced to its metallic form. However, high resolution spectra of Ru 3p and O 1s of CBO-PDA-Ru(2%) in Figure 2.5 show that Ru is forming a complex. For guidance, high resolution Ru 3p spectra of different Ru compounds (i.e. [Ru^{II}bpy₃]Cl₂, Ru^{III}Cl₃, Ru^{IV}O₂, KRu^{VII}O₄) are given in Figure S2.3. The Ru 3p core level appears as a doublet that corresponds to Ru 3p_{3/2} and Ru 3p_{1/2} peaks [234]. These contributions at 463.6 eV and 485.8 eV could be interpreted as Ru^{III} [310-312]. In addition, the presence of Ru-O bond was determined through the deconvolution of O 1s peak (Figure 2.5b). The first peak at 529.8 eV is attributed to metal-oxygen bonds or in this case, the formation of a Ru^{III}-catecholate species [310,314]. While the peaks at 531.4, 533.3 and 534.2 eV are ascribed to quinones, phenols and water respectively [313-315]. On the other hand, no conclusive evidence was found about covalent bonds between Ru and nitrogen atoms from PDA (Figure S2.4a). To complete this information, a weak peak at 1140 cm⁻¹ was found during FTIR analysis of the mentioned catalyst (Figure S2.5). This band is attributed to metals forming catecholate complexes [310]. Thus, the spectroscopic evidences provided suggest that Ru^{III} is forming a catecholate complex with PDA functionalities which is why it is very unlikely that the transition metal may form a covalent

bond with CO under the conditions in which the chemisorption experiment was conducted.

As regards bpy functionalized carbon catalysts, Ru surface concentration on CBO-bpy(NHS/EDC) and CBO-bpy(SOCl₂) was higher than their bulk Ru concentrations provided by ICP analyses. In addition, the high resolution spectrum of Ru 3p core level from CBO-bpy(NHS/EDC)-Ru(2%) displays a doublet at 463.9 eV and 486.3 eV (Figure 2.5c). These binding energies can be assigned to Ru^{III} as well [234]. However, unlike CBO-PDA-Ru(2%), this Ru^{III} complex can be attributed mostly to oxygen groups of CBO that complex the transition metal. In addition, the presence of N-Ru bond at 399.9 eV which was identified after the deconvolution of the N 1s peak displayed in Figures 2.5d and 2.5f can be attributed to bpy complexation of Ru ions [309-311].

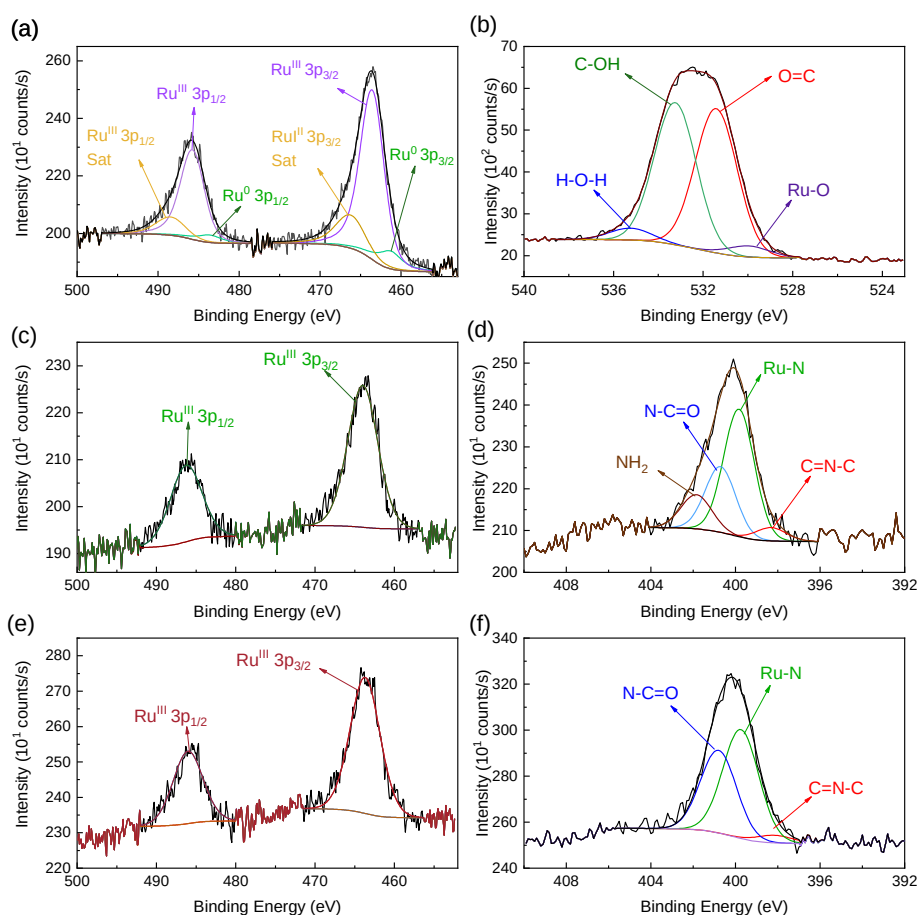


Figure 2.5. a) Ru 3p and b) O 1s spectra of CBO-PDA-Ru(2%); c) Ru 3p and d) N 1s spectra of CBO-bpy(NHS/EDC)-Ru(2%); e) Ru 3p and f) N 1s spectra of CBO-bpy(SOCl₂)-Ru(2%)

The pyridinic nitrogen peak (398.4 eV) decreased ostensibly as a result of the covalent interaction of bpy with Ru while the peaks at 400.7 and 401.8 eV are attributed to amides formed during the functionalization process and free amines which did not react to carboxyl acids on CBO surface respectively [298,299,311]. Similar peaks were observed in CBO-bpy(SOCl₂)-Ru(2%) with the only difference that no free amines were found. High resolution spectra of Cl 2p core level plotted in Figure S2.4 provide additional information about Ru chemical environment in the synthesized catalysts. First, the deconvolution of Cl 2p of CBO-bpy(NHS/EDC)-Ru(2%) yields two peaks associated to Cl 2p_{3/2} and Cl 2p_{1/2} at 198.8 and 199.9 eV respectively which can be assigned to Ru-Cl bond [318,319]. In the case of CBO-bpy(SOCl₂)-Ru(2%), an additional peak is observed at 202.5 eV which is attributed to organic chlorine, most likely to few acyl chloride groups that did not react with amines from NH₂-bpy during the amidation process [319]. Since the estimated Cl/Ru ratio = 0.5 was lower than the expected value = 3 (as in the precursor used, namely RuCl₃), it is believed that chlorine ligands were replaced by OH from the aqueous solution during the wet impregnation procedure. As regards CBO-PDA-Ru(2%), no chlorine was detected confirming that ligand substitution occurred between RuCl₃ and the catechol groups of PDA on CBO surface.

3.2. Catalytic test results

The three characterized catalysts were assessed in the oxidative cleavage of oleic acid along with 4 and 8 equivalents of NaIO₄ (Figure 2.6). With 4 equivalents of the oxidizing agent, CBO-bpy(NHS/EDC)-Ru(2%) shows a higher catalytic activity than the other two catalysts since it reaches almost complete conversion after 7 h of stirring. CBO-bpy(SOCl₂)-Ru(2%) and CBO-PDA-Ru(2%) require 24 h of agitation in order to attain the same results as the NHS/EDC catalyst.

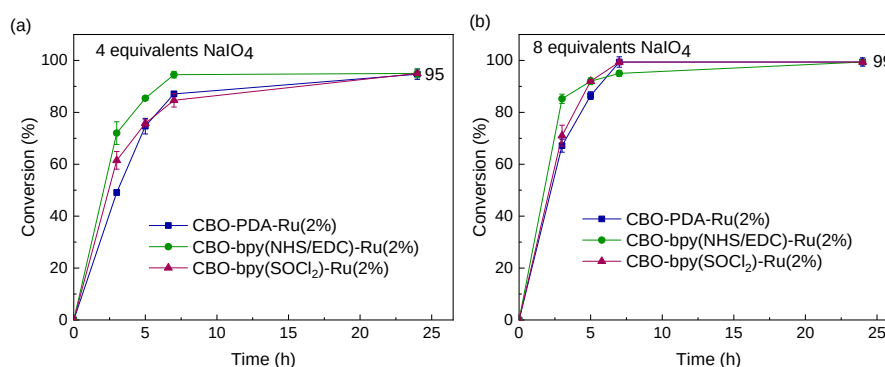


Figure 2.6. Catalytic activity of CBO-PDA-Ru(2%), CBO-bpy(NHS/EDC)-Ru(2%) and CBO-bpy(SOCl₂)-Ru(2%) in the oxidative cleavage of oleic acid along with: a) 4 equivalents and b) 8 equivalents of NaIO₄

However, when 8 equivalents of NaIO_4 were employed, all synthesized catalysts present similar results in terms of catalytic activity demonstrating the influence of the oxidant in the oxidative cleavage reaction. Moreover, Table 2.5 shows that the increase in the amount of oxidizing agent has a beneficial effect on yield and selectivity of the oxidative cleavage products as well. CBO-PDA-Ru(2%) and CBO-bpy(NHS/EDC)-Ru(2%) present similar yields and selectivities towards pelargonic (PA) and azelaic acids (AA) when the minimal amount of NaIO_4 was employed. After increasing NaIO_4 to 8 equivalents, about 95% of yield and selectivity to PA and AA was accomplished for both catalysts. Figure S2.6 shows the components distribution in the reaction medium after 24 hours. Nonanal and 9-oxononanoic acid (precursors of PA and AA respectively) were still present in the mixture with 4 equivalents of NaIO_4 .

Conversely, when 8 equivalents of NaIO_4 was used, the mentioned intermediates almost disappear in favor of PA and AA. Therefore, these results suggest that a higher amount of oxidizing agent favors the complete oxidation of the intermediates in the oxidative cleavage reaction. In the specific case of CBO-bpy(SOCl_2)-Ru(2%), yields and selectivities were lower than with the other catalysts (~76%). Although, CBO-bpy(SOCl_2)-Ru(2%) attained a complete conversion after 24 h of stirring there is an incomplete transformation of oleic acid into the desired oxidative cleavage products. This breach in catalytic performances between the tested composites suggests that the synthesized catalysts behave differently in the oxidative cleavage reaction. However, since CBO-bpy(NHS/EDC)-Ru(2%) and CBO-bpy(SOCl_2)-Ru(2%) catalysts possess the same aromatic ligand and the same amount of Ru on their surfaces, the results thus seem to contradict themselves. To fully understand the main differences in both mentioned catalysts, their catalytic stability was evaluated through recycling tests.

Table 2.5. Yields and selectivities to Pelargonic (PA) and Azelaic (AA) acids of the synthesized catalysts with 4 and 8 equivalents of NaIO_4

4 equivalents NaIO_4	Y_{PA} (%)	Y_{AA} (%)	S_{PA} (%)	S_{AA} (%)
CBO-PDA-Ru(2%)	82.2	81.7	83.4	82.6
CBO-bpy(NHS/EDC)-Ru(2%)	78.4	79.2	83.0	83.8
CBO-bpy(SOCl_2)-Ru(2%)	66.8	67.9	69.7	70.9
8 equivalents NaIO_4				
CBO-PDA-Ru(2%)	94.8	94.9	94.8	94.9
CBO-bpy(NHS/EDC)-Ru(2%)	96.2	96.7	96.2	96.7
CBO-bpy(SOCl_2)-Ru(2%)	76.0	76.4	76.0	76.4

Figure 2.7a clearly points out that CBO-PDA-Ru(2%) catalyst maintains its catalytic activity up to 5 recycling tests. In fact, in the first 4 catalytic tests, the catalyst shows the same kinetic behavior throughout the reaction. Loss of catalytic activity was evidenced only at the fifth run which is attributed to mass losses of the catalyst due to sampling and attrition after several runs. These results confirm that the CBO-PDA-Ru(2%) composite is a robust and

efficient catalyst in the oxidative cleavage of large UFAs such as oleic acid. Conversely, CBO-bpy(NHS/EDC)-Ru(2%) resulted to be the least stable of all tested composites in this reaction. Figure 2.7b demonstrates a pronounced decrease of its catalytic activity after each catalytic test reaching only 47% of conversion at the end of the fifth run. An intermediate catalytic stability is displayed by CBO-bpy(SOCl₂)-Ru(2%) (Figure 2.7c) since after two runs, conversion remained almost the same, but then in the last three recycling tests, it was observed a drop in the catalytic activity with a final conversion of 75% after 24 h of agitation.

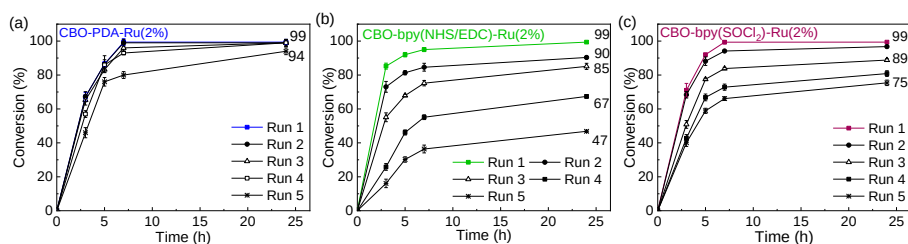


Figure 2.7. Recycling tests of a) CBO-PDA-Ru(2%); b) CBO-bpy(NHS/EDC)-Ru(2%) and c) CBO-bpy(SOCl₂)-Ru(2%)

After comparing these results, it is clear that CBO-bpy(NHS/EDC)-Ru(2%) presented high conversion and yields in the first run due to Ru leaching. A suitable explanation implies that Ru was released in the reaction medium from the CBO-bpy(NHS/EDC) support to perform the oxidative cleavage reaction in the liquid phase. Then, the catalytic activity of the mentioned catalyst decreased after each run due to cumulative Ru losses. This asseveration was confirmed during the hot-filtration tests (Figure 2.8). CBO-bpy(NHS/EDC)-Ru(2%) still shows 22% of increase in catalytic activity after catalyst removal from the liquid phase. If Ru had remained on the catalyst surface, no catalytic activity increase would have been registered. CBO-bpy(SOCl₂)-Ru(2%) presented similar results as well as CBO-PDA-Ru(2%). Although the PDA catalyst demonstrated to be stable after 5 recycles, hot-filtration test demonstrated that Ru was dissolved in the solvent system during the catalytic reaction.

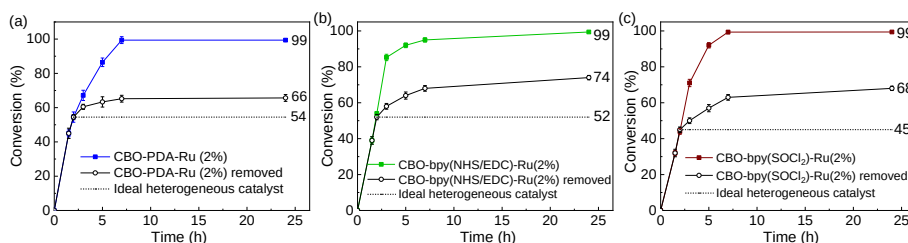


Figure 2.8. Hot-filtration tests of: a) CBO-PDA-Ru(2%); b) CBO-bpy(NHS/EDC)-Ru(2%) and c) CBO-bpy(SOCl₂)-Ru(2%)

To deepen more in the functioning of the synthesized catalysts, post-tests characterization was performed and recapitulated in Table 2.6. ICP analyses confirmed that Ru bulk concentration did not diminish after 5 catalytic tests in the case of CBO-PDA-Ru(2%). XPS analyses confirmed the presence of Ru on CBO-PDA surface, which means that the catalyst remained almost intact after performing the recycling tests. Even though Ru was dissolved in the liquid phase, this indicates that the functionalized support managed to recover Ru at the end of the reaction. The explanation to this event is attributed to the capability of catechol groups for re-adsorbing Ru from the reaction medium. By this way, it was possible to achieve great catalytic performances in terms of conversion and yields (by homogeneous catalysis) while the catalyst remained reusable thanks to the chelating capability of PDA functional groups for recovering the active species (heterogeneous catalysis).

This was not the case in the NH₂-bpy functionalized catalysts. In both cases there was a decrease in Ru bulk concentration with respect to the initial Ru loading. These results demonstrate that NH₂-bpy was not able to maintain the transition metal attached to the support along the catalytic tests nor capable of re-adsorbing Ru species after the oxidative cleavage reaction finished, as PDA does. Superficial Ru concentration was also lower than the concentration in the fresh catalysts confirming the departure of the transition metal from the NH₂-bpy functionalized supports.

Table 2.6. Ru loading on spent catalysts

Catalyst	Nominal Ru (wt%) ^a	Ru loading (wt%) ^b
CBO-PDA-Ru(2%)	2.0	1.8
CBO-bpy(NHS/EDC)-Ru(2%)	2.0	0.7
CBO-bpy(SOCl ₂)-Ru(2%)	2.0	1.4

^aNominal composition corresponding to the precursor solution. ^bRu loading determined by ICP-AES.

In addition, XPS survey spectra (Figure 2.9a) and surface composition (Table S2.2) show a decrease in nitrogen content as regards CBO-bpy(NHS/EDC)-Ru(2%) and CBO-bpy(SOCl₂)-Ru(2%) solids. In fact, in the former N 1s peak almost disappeared and the presence of Na 1s along with I 3d peaks arises as a proof that the oxidizing agent aided to detach NH₂-bpy from CBO surface. These evidences support the fact that the NHS/EDC method was not efficient to covalent link this ligand through amidation with carboxylic acids on the carbonaceous surface. The presence of amines on the initial catalyst characterization (Figures 2.2 and 2.5) suggested that part of bpy was only physisorbed on CBO surface. Therefore, during oxidative cleavage tests, NH₂-bpy weakly deposited on the carbon support departed along with Ru, thus diminishing the catalytic activity of the catalyst in the subsequent catalytic runs.

Spent CBO-bpy(SOCl₂)-Ru(2%) also presented less amount of Ru and nitrogen than the corresponding fresh solid. No sodium was detected (Figures 2.9a and 2.9d) but the high resolution spectrum of N 1s peak (Figure S2.7) reveals the presence of amines after the recycling tests. These findings suggest that indeed the amide bonds were cleaved and, as a consequence, NH₂-bpy was detached from the support. Most likely the amide bond was broken by the oxidizing agent releasing NH₂-bpy in the reaction medium producing Ru losses after each run [320,321]. Hence, the amidation strategy to deposit NH₂-bpy was not suitable in the oxidative cleavage reaction with strong oxidizing agents. On the contrary, CBO-PDA-Ru(2%) surface composition remained almost intact. In this case, Ru was present as Ru^{IV} and Ru^{III} on CBO-PDA surface. The explanation of how the mentioned Ru reduced species are present on the modified support surface is related to the redox activity of PDA. There are evidences in the literature that PDA may accept and donate electrons yielding different catechol, semi-quinone radicals and quinone groups [322-324]. Instead of breaking bonds, NaIO₄ may oxidize catechol groups to yield quinones which can also chelate and reduce Ru species dissolved in the reaction medium [222,322,323,324]. By this way, PDA can contribute to recover the active species, maintaining the catalyst reusability for several runs.

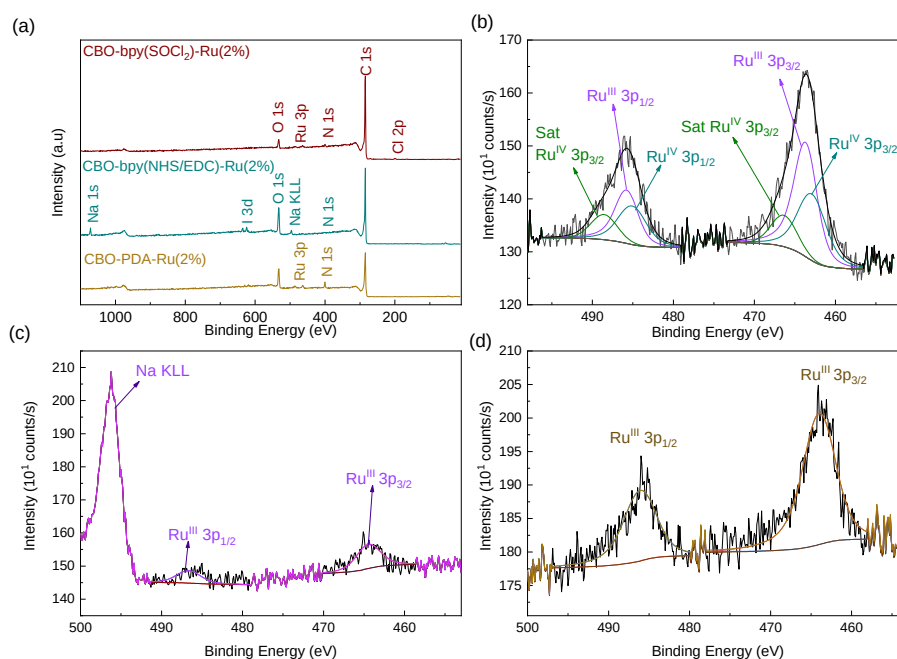


Figure 2.9. a) XPS survey spectra of spent catalysts; Ru 3p high resolution spectra of spent catalysts: b) CBO-PDA-Ru(2%); c) CBO-bpy(NHS/EDC)-Ru(2%) and d) CBO-bpy(SOCl₂)-Ru(2%)

4. Conclusion

4,4'-amino-2,2'-bipyridyl and polydopamine were employed for the functionalization of macroporous oxidized carbon black surface. NH₂-bpy was deposited on the carbonaceous support by activating its superficial carboxylic acids through NHS/EDC and SOCl₂ chlorination methods. TGA analyses demonstrated that only 46% of the total NH₂-bpy added initially was incorporated on CBO surface while XPS analyses provided evidence that not all the ligand was covalently bond to the support. Although it is more pollutant, the standard chlorination method resulted to be more efficient in the functionalization of CBO with NH₂-bpy. Textural properties assessment confirmed the decrease of specific surface area due to NH₂-bpy deposition over carbon black nodules while ICP-AES analyses indicated that Ru was successfully impregnated on functionalized supports. Despite great performances at the beginning of the oxidative cleavage of oleic acid, CBO-bpy(NHS/EDC)-Ru(2%) and CBO-bpy(SOCl₂)-Ru(2%) lost catalytic activity after each recycling test. XPS and ICP characterization on both spent catalysts demonstrated that this drop in catalytic activity is related to NH₂-bpy detachment and Ru leaching. These results point out that functionalization through amidation between the amine groups of NH₂-bpy and the carboxyl sites on the support is not a satisfying enough strategy for building a heterogeneous catalyst in the oxidative cleavage of UFAs achieved with strong oxidizing agents such as NaIO₄.

On the other hand, PDA resulted to be a promising option in this matter. Dopamine was easily polymerized and deposited on CBO surface at mild conditions without the need of hazardous reagents as in the case of NH₂-bpy functionalization through SOCl₂ chlorination. FTIR and XPS analyses confirmed PDA deposition on the carbonaceous support while N₂ physisorption showed a decrease in specific surface area as a consequence of the PDA particles filling the gaps between CBO nodules. In addition, TGA analysis determined that 57% of the initial amount of dopamine polymerized and was attached on CBO particles. XPS and FTIR analyses showed that catechol groups of the polymer play an essential role in complexing Ru. The synthesized CBO-PDA-Ru(2%) catalyst displayed high conversions and yields (~95%) in the oxidative cleavage of oleic acid along with NaIO₄. Moreover, the catalyst kept its catalytic activity even after 5 recycling tests in spite of observing Ru in the liquid phase during hot filtration tests. ICP analysis of the spent catalyst confirmed that Ru bulk concentration was the same as in the fresh catalyst. These findings suggest that catechol groups release Ru in the reaction medium to perform the oxidative cleavage reaction, but after the reaction ends, PDA functional groups re-adsorb Ru species and reintegrate them to the catalyst. This allowed subsequent uses in the oxidative cleavage of UFAs. Therefore, it is clear that PDA functionalization is a suitable technique to develop a stable and efficient catalyst in the oxidative cleavage reaction. To fully understand how the catalyst functions, the next chapter will be focused on exploring more in details the working mechanism of CBO-PDA-Ru(2%) in the oxidative cleavage of oleic acid.

CHAPTER III: ELUCIDATING THE MECHANISM OF CARBON BLACK-POLYDOPAMINE-Ru CATALYSTS IN THE OXIDATIVE CLEAVAGE OF OLEIC ACID

Abstract

This chapter goes further in the understanding of how the best catalyst pointed in chapter 2 works in the oxidative cleavage of oleic acid. Namely, it is based on Ru species supported on a carbon black that was previously oxidized and then functionalized with polydopamine. Being a polymer with hydroxyl and amine groups polydopamine provides moieties acting as tweezers able to complex Ru species. The latter may also induce a boomerang mechanism in the oxidative cleavage of oleic acid with our CBO-PDA-Ru(2%) solid catalyst. For this reason, the reaction mechanism was explored with different spectroscopic techniques (i.e. gas chromatography, IR spectroscopy, UV-Vis spectrophotometry and NMR spectroscopy) along with recyclability and hot centrifugation tests to confirm the boomerang behavior in our functionalized Ru-carbon catalyst. The solid catalyst was indeed recyclable at least 5 times without activity loss, but at the same time Ru species were shown performing the reaction in homogeneous phase namely in a dissolved state. Actually, polydopamine was confirmed to recover Ru species once the reaction ends, guarantying the recyclability of the catalyst. Therefore, the composite catalyst combines the advantages of homogeneous and heterogeneous catalysis in the investigated reaction.

The results presented in this chapter have been published in:

Gámez, S., de la Torre, E., & Gaigneaux, E. M. Carbon black-polydopamine-ruthenium composite as a recyclable boomerang catalyst for the oxidative cleavage of oleic acid. *Chemical Engineering Journal*, **2022**, 427.



1. Introduction

Here we focus on exploring the reaction mechanism behind the oxidative cleavage of oleic acid with our heterogeneous solid catalyst formed by oxidized carbon black (CBO) functionalized with polydopamine (PDA) and impregnated with Ru. In the previous chapter, it was demonstrated that PDA on CBO surface was able to adsorb Ru forming a catechol complex. In addition, CBO-PDA-Ru maintained its catalytic activity up to 5 consecutive oxidative cleavage tests in spite of hot-filtration essays suggesting that Ru was present in the liquid phase due to leaching. In order to acquire a better understanding about the catalyst functioning in this reaction, it is imperative to enlighten the nature of these catechol complexes as well as how Ru performs the oxidative cleavage of UFAs in homogeneous phase.

Metal-catechol species consist in coordination complexes formed when two or more oxygen atoms each donate a nonbonding electron pair to empty orbitals in a transition metal ion [311]. Normally, molecules bearing catechol groups, such as those found in PDA, form hexadentate mononuclear triple metal coordination complexes while bi and quadridentate complexes can also be produced by modifying the synthesis conditions [325,326]. For instance, Pierpont *et al.* synthesized a Ru-catechol/semiquinone complex using 3,5-di-*tert*-butylbenzoquinone in a RuCl_3 solution under basic conditions [327]. Electron paramagnetic resonance (EPR) spectroscopy as well as crystallographic data from X-ray diffraction indicated that Ru charge was in between Ru^{III} and Ru^{IV} when the transition metal was chelated by catechol groups forming a complex with an octahedral geometry [327] (Figure 3.1).

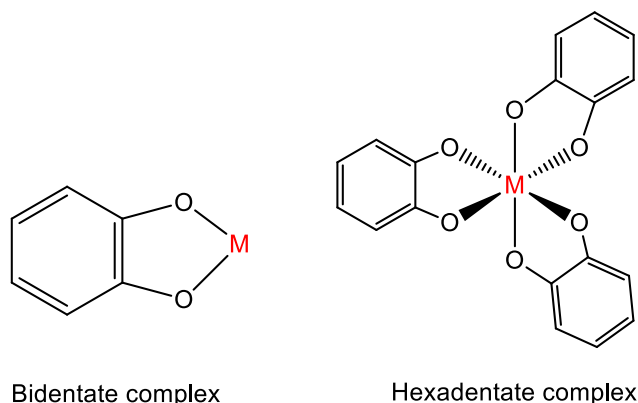


Figure 3.1. Metal a) bidentate and b) hexadentate catechol complexes

On the contrary, Öhrström and Michaud-Soret reported the existence of low-spin $[\text{Fe}^{\text{0}}\text{-catechol}]^{2-}$ and $\text{Fe}^{\text{III}}\text{-(catechol)}_3$ complexes with 12 and 17 electrons according to the 18-electron rule respectively. The authors thus

confirm that catechol groups may form bi and hexadentate complexes with transition metals from group 8 of periodic table. This asseveration was also supported by Bhattacharya *et al.* in the specific case of Ru [328,329].

As regards the binding nature in these kinds of metal complexes there is evidence that M-O link possesses a covalent and an ionic character at the same time. This duality makes the M-catechol bond reversible in spite of the high chelating capability of the bidentate ligand. The bonding nature between metal ions and oxygen atoms in catechols depends on the type of metal. In this regard, Xu studied the nature of the M-O bond by means of Electron Localization Functions (ELF) calculated using the Density Functional Theory (DFT) [311]. It turns out that iron (Fe-O bond length = 2.02 Å) [328] and ruthenium (Ru-O bond length = 1.98 Å) [327] are located in the middle of this electrostatic-covalent scale. This feature is important since the metal-catechol complex is not a rigid structure and therefore, Ru can be released from the chelating compound.

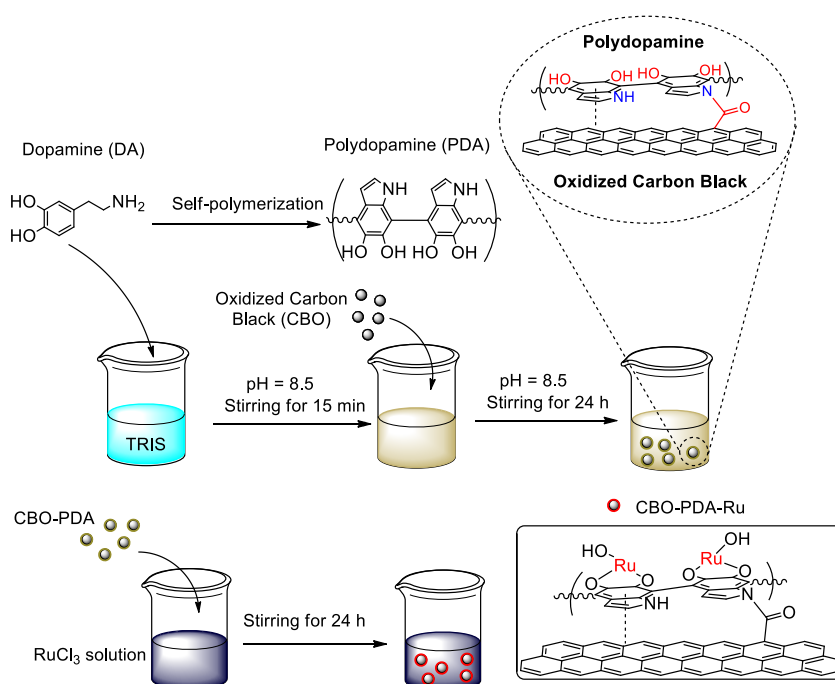
Concerning Ru behavior in the oxidative cleavage of oleic acid, it is known that this transition metal is active in the form of $\text{Ru}^{\text{VIII}}\text{O}_4$. This Ru species can achieve fast conversions with high selectivity toward the desired oxidative cleavage products (pelargonic and azelaic acids). The oxidative cleavage mechanism with ruthenium involves the *in situ* formation of $\text{Ru}^{\text{VIII}}\text{O}_4$ in liquidphase after the addition of a strong oxidizing agent (e.g. sodium periodate or sodium hypochlorite) to a precursor like RuCl_3 or RuO_2 . Then, a pericyclic reaction [3+2] takes place between the $\text{Ru}^{\text{VIII}}\text{O}_4$ and the carbon-carbon double bond of the UFA [119,121]. The resultant product is a cyclic perruthenate ester which is broken after its interaction with water (Scheme 11, p. 21). Next, the UFA is transformed into a diol after the rupture of the perruthenate ester, and then the diol is cleaved by the oxidizing agent to form aldehydes. It is believed that these aldehydes can be oxidized by $\text{Ru}^{\text{VIII}}\text{O}_4$ and yield carboxylic acids. Nevertheless, it is important to know which Ru species are present during the reaction and how they interact with all the intermediates present in the solvent.

With this background, we explored the reaction mechanism of the oxidative cleavage of oleic acid by monitoring the reaction medium and the solid catalyst at different time intervals. The CBO-PDA-Ru catalyst was characterized by FTIR and XPS spectroscopy at different moments of the reaction in order to assess whether the catalyst suffers changes during the catalytic test. The identification of Ru species in the liquid phase was achieved through UV-Vis spectrophotometry while Nuclear Magnetic Resonance spectroscopy (NMR) along with gas chromatography (GC) were employed to identify and quantify intermediates during the oxidative cleavage of oleic acid respectively. Finally, a dedicated boomerang catalysis protocol was implemented to verify whether the synthesized catalyst indeed works in that way, as suggested by data shown in chapter 2.

2. Experimental section

Carbon black from (CB Degussa Printex ®G: 95.73 wt.% C, 0.73 wt.% H, 3.5 wt.% O, BET area 154 m²/g and pore volume 0.56 cm³/g) was first oxidized with nitric acid (Carl Roth HNO₃ = 65%) as was explained in the first chapter (p. 70). The Ru-carbon functionalised catalyst (i.e. CBO-PDA-Ru) was prepared in the same manner as explained in the previous chapter. A brief summary of the catalyst preparation is represented in Scheme 3.1.

In addition, pure PDA was synthesized as explained in chapter 2 (pp. 87-88) and used as support for Ru impregnation. The same characterization techniques applied in chapter 2 were used as well. Transmission electron microscopy (TEM) was performed to assess the morphology of oxidized carbon black functionalized with PDA. For this matter, a LEO 922 microscope with an acceleration voltage of 200 kV and equipped with a LaB6 thermal cathode was employed for all tests. In addition, the diameter of 20-25 spheres from each sample was measured to build a frequency distribution histogram with the aim to determine the mean particle size of CBO and CBO-PDA.



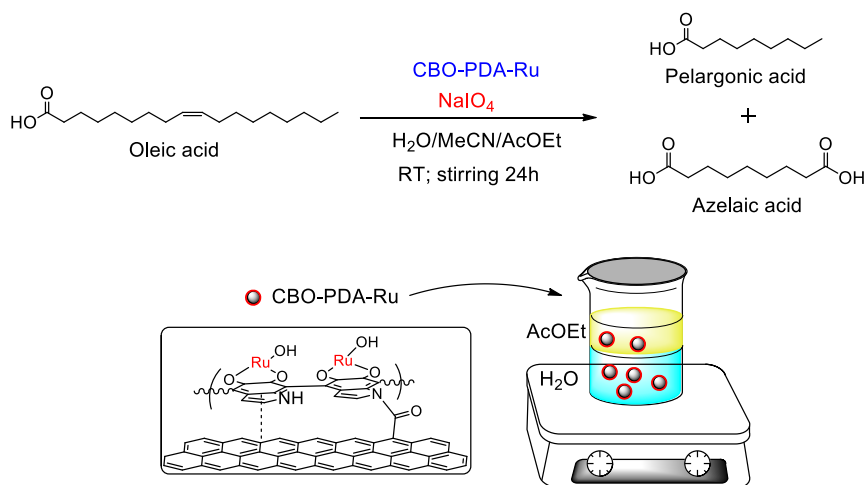
Scheme 3.1. Preparation of Ru heterogeneous catalyst based on oxidized carbon black with polydopamine (CBO-PDA-Ru)

2.1. Catalytic tests

The same protocol detailed in the main Experimental section of this thesis was followed to assess the catalytic activity of the PDA catalyst (pp.62-63). In this chapter three different Ru loadings (1 wt%, 2wt% and 4 wt%) on CBO-PDA surface were employed to evaluate the influence of the Ru content in the oxidative cleavage of oleic acid (Scheme 3.2). In addition, 9,10-dihydroxystearic acid (diol, $C_{18}H_{36}O_4$, 95% from abcr GmbH) which is the diol resulting from the hydrolysis of the perruthenate ester, was analyzed by GC to verify whether this intermediate was present during the catalytic tests. Nonanal (NA, $C_9H_{18}O$, >95% GC from TCI chemicals) and 9-oxononanoic acid (Oxo, $C_9H_{16}O_3$, 95% from abcr GmbH) were also analyzed in the same manner as the diol. Their calibration curves (Figures E.4-E.6) are found in the supporting information as well as their characterization by NMR spectroscopy (Figures S3.1-S3.6).

2.1.1 GC-FID monitoring

The same sampling procedure (detailed in the main Experimental section) was applied to monitor the oxidative cleavage of oleic acid with CBO-PDA-Ru as catalyst and $NaIO_4$ as oxidizing agent. In this chapter, the peaks displayed on each chromatogram (at different times of the reaction) were compared to those belonging to each intermediate (diol, NA and Oxo) and each product (PA and AA) in order to identify the components within the reaction mixture. Calibration curves were used to quantify components distribution at every moment of the reaction.



Scheme 3.2. Oxidative cleavage of oleic acid with Ru catalyst and $NaIO_4$

2.1.2. NMR spectroscopy monitoring

The same procedure was performed to verify the presence of intermediates and products throughout the oxidative cleavage of oleic acid with CBO-PDA-Ru catalysts by Nuclear Magnetic Resonance (^1H -NMR) spectroscopy. For this purpose, deuterated solvents: deuterated water (D_2O , 99.9% from Euristop), acetonitrile- d_3 ($\text{C}_2\text{D}_3\text{N}$, 99.9% from Euristop) and deuterated chloroform (CDCl_3 , 99.8% from Euristop) were used to prepare the same solvent mixture as before (4/2/1 respectively). At the same interval times, samples were extracted from the organic phase to analyze them in a Liquid-state Nuclear Magnetic Resonance Bruker Avance II 300 MHz equipped with a BBFO 5 mm NMR probe z-gradient coil. For each experiment, ^1H spectra were recorded after 16 scans. The spectral window was set at 16 ppm with a relaxation delay of 3 seconds. The calibration procedure was performed using CDCl_3 signal. All data was treated with MestReNova software.

2.1.3. UV-Vis spectrophotometry monitoring

In addition, oxidative cleavage of oleic acid with CBO-PDA-Ru was monitored by UV-Vis spectrophotometry in a UV-3600 Plus Shimadzu spectrophotometer equipped with a deuterium lamp (light source for the ultraviolet range) and a W1 halogen lamp (light source for the visible and near infrared range). Samples from the aqueous and organic phases were extracted separately at different time intervals and placed in quartz cells to be analyzed by UV-Visible spectroscopy in absorbance configuration. The idea was to verify the presence of Ru species in both phases during the reaction and after it was completed. In the case of the aqueous phase, a solution of NaIO_4 was used as reference while ethyl acetate was used as reference for the organic phase. In addition, the consumption of NaIO_4 was determined by measuring the absorbance of the peak at 222 nm corresponding to the oxidizing agent [328,329]. The calibration curve is shown in Figure S3.7. All tests were carried out from 600 to 200 nm range and spectra were recorded with a resolution of 0.5 nm.

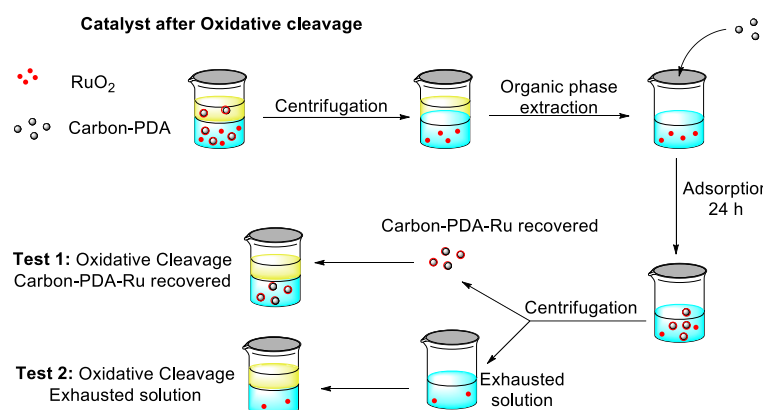
2.1.4. FTIR and XPS monitoring

In this case, the catalyst was studied by infrared and XPS spectroscopy to gather information about the surface chemical environment of the catalyst throughout the oxidative cleavage of oleic acid. For these analyses, the reaction was stopped at different time intervals to recover the solid catalyst by centrifugation at 14 000 rpm (26 200 g) in a Heraeus MultifugeX1R Centrifuge for 40 minutes. Then, the solid was dried at 100 °C for 1 hour to be analyzed. As regards FTIR, a Bruker Equinox 55 FTIR spectrometer in the transmission mode was employed. XPS analyses were carried out in an SSX 100/206 photoelectron spectrometer from Surface Science Instruments (USA) equipped with a monochromatized micro focused Al X-ray source

(powered at 20 mA and 10 kV). The procedures to analyze samples using both techniques are detailed in the main Experimental section (pp. 60-61).

2.2 Boomerang catalysis assessment protocol

The possibility that Ru ions could be released from the CBO-PDA support and return to it once the oxidative cleavage reaction ends, was verified by following the protocol depicted in Scheme 3.3. After an oxidative cleavage test finished, the solid catalyst was removed by centrifugation. The organic phase was separated from the aqueous layer by a syringe. Then, a fresh support (CBO-PDA, without Ru) was added to the aqueous phase in order to adsorb the eventually leached Ru ions from the original solid catalyst. After 24 h of adsorption, the solid was removed from the aqueous solution by centrifugation. The aqueous phase before and after adsorption was analyzed by ICP-AES spectrophotometry to determine the presence of Ru ions. Finally, both the CBO-PDA that has been used to recover the eventually leached Ru, and the aqueous layer were respectively submitted to one more oxidative cleavage test.



Scheme 3.3. Boomerang catalysis assessment protocol

3. Results and Discussion

3.1. Characterization results

In addition to characterization results presented in the previous chapter, TEM microscopy was carried out to visualize the morphology of CBO after PDA deposition (Figure 3.2). TEM images confirm that oxidized carbon black appears as aggregates of particles with average particle size of 27.8 ± 10.7 nm. On the other hand, PDA appears as a layer that covers CBO nanoparticles, increasing their average particle size to 41.2 ± 7.3 nm. Boehm's titration results (Table S3.1) demonstrated that the amount of

phenol groups increased from 0.43 to 0.66 mmol/g after PDA deposition. The amount of phenol groups available on CBO-PDA surface is in principle higher than the amount of Ru atoms required to obtain a load of 4 wt%, and more than enough to chelate Ru atoms corresponding to Ru loadings of 1 wt% and 2 wt%. CBO-PDA catalysts bearing Ru loadings from 1% to 4% showed a *quasi*-type 2 isotherm with a narrow hysteresis loop H3 which is characteristic of materials with big mesopores (Figure S3.8).

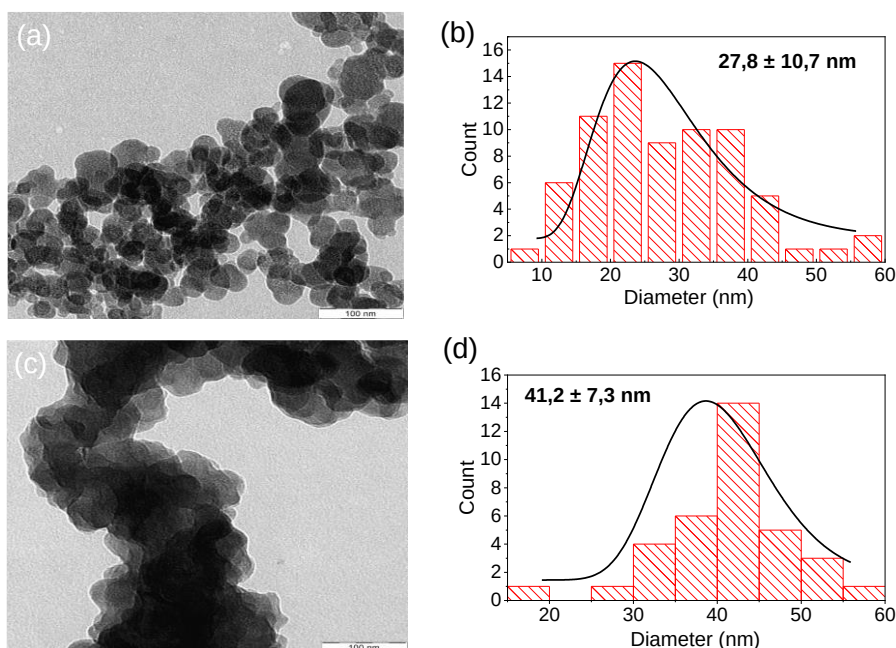


Figure 3.2. TEM images of a) CBO; b) particle size distribution of CBO; c) CBO-PDA; d) particle size distribution of CBO-PDA

Moreover, their specific surface area ($80 \text{ m}^2/\text{g}$) did not change even after the impregnation of 4 wt% of Ru (Table S3.1). ICP results summarized in Table 3.1 demonstrated the efficiency of the wet impregnation method in the preparation of the cited Ru base catalysts. The Ru bulk concentration agreed with their respective nominal values as well as with those reported by XPS confirming that PDA functional groups succeeded in complexing Ru even with higher Ru loadings (i.e. 4 wt%).

As regards CO chemisorption results, it could be interpreted that PDA induced a decrease of Ru dispersion on the support as compared to the catalyst without PDA (Table 1.4, p. 77). However, this would be misleading as the same result is more likely indicating the chelation of Ru atoms by functional groups of PDA. Indeed, if Ru atoms are interacting with catechol groups it is less probable that CO could form a covalent bond with Ru during

chemisorption analysis, which would then bring an apparent decrease of Ru dispersion as observed.

Table 3.1. Ru loading on functionalized carbon catalysts

Catalyst	Nominal Ru (wt%) ^a	Superficial Ru (wt%) ^b	Ru loading (wt%) ^c	Ru dispersion (%) ^d
CBO-PDA-Ru(1%)	1.0	1.1	1.0	8.4
CBO-PDA-Ru(2%)	2.0	2.2	1.9	7.8
CBO-PDA-Ru(4%)	4.0	4.3	3.8	4.8

^aNominal composition corresponding to the precursor solution. ^bRu superficial content determined by XPS. ^cRu loading determined by ICP-AES. ^dRu dispersion determined by CO chemisorption.

Therefore, the values reported in Table 3.1 may correspond to only the small fraction Ru ions that did not form a complex with PDA, but formed clusters on CBO surface instead and thus were titrable by CO.

3.2. Elucidating the oxidative cleavage mechanism with CBO-PDA-Ru

The oxidative cleavage of oleic acid was carried out only with PDA and CBO-PDA along with 8 equivalents of NaIO₄ (Table 3.2) in order to determine to what extent the functionalized support may contribute to the development of the reaction. Conversions resulted to be lower than 1% in all cases and no product was detected on the chromatograms. Therefore, it is not possible to perform the reaction with only the oxidant agent and the functionalized support. PDA was also employed as support for Ru impregnation. Catalytic tests were performed with 4 and 8 equivalents (with respect to oleic acid) of NaIO₄ and displayed 39% and 98% of conversion respectively. These results are lower than those obtained with CBO-PDA-Ru(2%). With 4 equivalents of the oxidizing agent, CBO-PDA-Ru(2%) reached a complete conversion at room temperature after 24 h of stirring. These results indicate that Ru and NaIO₄ are not the only responsible actors involved in a good performance in the oxidative cleavage of UFAs. The support plays also a main role in this reaction specifically via its textural properties. The specific surface area of PDA is about 14 m²/g (Figure S3.9) while a larger surface was reached in the case CBO-PDA-Ru (81 m²/g). Clearly the textural properties of the support affect the performance of the reactions since both catalysts possess the same chemical functionalities (i.e. catechol and amine groups). A complete conversion of oleic acid was also achieved with CBO-PDA-Ru(2%) and 8 equivalents of NaIO₄, but the difference lies in the compounds found within the reaction mixture.

During GC monitoring, it was possible to detect peaks in the chromatograms that did not match with those corresponding to oleic acid or to the desired reaction products (pelargonic and azelaic acids). Besides, since yields were not complete in the case with 4 equivalents of NaIO₄, the presence of

intermediates became a possibility. The reaction mechanism illustrated in Scheme 11 (p. 21), shows that a diol and aldehydes can be formed during the oxidative cleavage stages. Therefore, 9,10-dihydroxystearic acid (the corresponding diol of oleic acid), nonanal (NA, namely the aldehyde of PA) and 9-oxononanoic acid (Oxo, the precursor of AA) were analyzed by GC. The peaks fall exactly at the same positions of the unidentified peaks in the chromatograms of the catalytic tests. Figure S3.10 illustrates the chromatogram with the peaks of all products involved in this reaction.

Table 3.2. Conversion and product distribution after 24 h of stirring

Catalyst	Conv. (%)	OA (%)	PA (%)	AA (%)	NA (%)	Oxo (%)	Diol (%)
PDA	0.6	>99	---	---	---	---	---
CBO-PDA	0.7	>99	---	---	---	---	---
PDA-Ru(2%) ^a	39	66	3.3	4.5	10.7	9.2	6.1
PDA-Ru(2%) ^b	98	1.6	20.6	20.3	25.2	26.6	5.8
CBO-PDA-Ru(2%) ^a	>99	0.4	38.2	37.2	10.3	11.2	---
CBO-PDA-Ru(2%) ^b	>99	0.3	49.9	49.7	---	---	---

^a4 equivalents of NaIO₄; ^b8 equivalents of NaIO₄

In the catalytic test with 4 equivalents of oxidant, nonanal and 9-oxo nonanoic acid were present in the reaction medium even after 24 h of agitation (Figure 3.3a). However, these intermediates were not detected anymore after increasing the amount of NaIO₄ to 8 equivalents (Figure 3.3b). These results can be ascribed to the complete oxidation of both intermediates into PA and AA thanks to the extra equivalents of NaIO₄ added to the reaction medium. It is important to mention that PA and AA as well as nonanal and 9-oxo nonanoic acid are in equal amounts to each other. This is due to the fact that the oleic acid molecule is broken in the middle producing equal amounts of each oxidative cleavage product as observed in selectivity monitoring (Figure 3.3c and 3.3d). The GC monitoring of this reaction with CBO-PDA-Ru(2%) and 4 equivalents of NaIO₄ showed that nonanal and 9-oxononanoic acid are the major components in the solvent mixture in the early stages of the catalytic test. At 5 hours both intermediates reach their highest concentration and then it starts to decrease in contrast with the increasing concentration of PA and AA. In addition, 9,10 dihydroxystearic acid (diol) was detected as well. The presence of the latter in the reaction medium confirms that the oxidative cleavage pathway proceeds via the formation of a vicinal diol most likely after the hydrolysis of a perruthenate ester as was stated in the literature [111-114].

As regards the catalytic test with 8 equivalents of NaIO₄, the diol is barely detected suggesting that the hydrolysis of this intermediate proceeded really fast yielding nonanal and 9-oxononanoic acid. From the third hour of reaction, intermediates concentration decreased being almost totally consumed after 7 hours of stirring. From these monitoring analyses, it is clear that the oxidative cleavage reaction takes place in several steps: (1) the production

of the 9,10 dihydroxystearic acid which is (2) rapidly cleaved into nonanal and 9-oxononanoic acid. While oleic acid is still transformed into the mentioned diol, (3) both intermediates are in turn being oxidized into pelargonic and azelaic acid. According to the amount of oxidizing agent added to the solvent mixture, the solid catalyst can accomplish total conversion and yields in shorter or longer reaction periods.

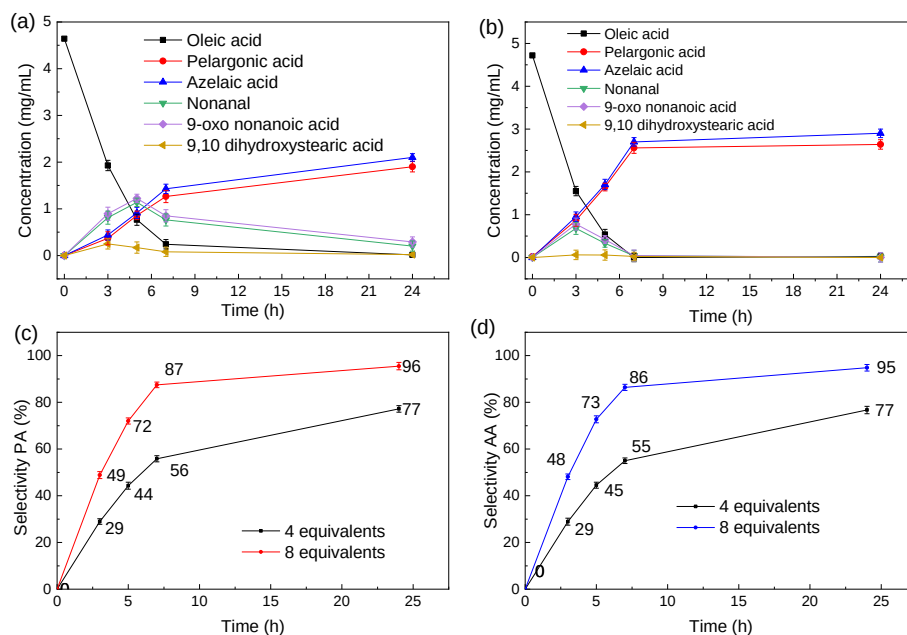


Figure 3.3. GC monitoring of oxidative cleavage reaction on CBO-PDA-Ru(2%) with a) 4 equiv. NaIO₄ and b) 8 equiv. NaIO₄; c) pelargonic acid selectivity with CBO-PDA-Ru(2%) and 4 equiv. NaIO₄; d) azelaic acid selectivity with CBO-PDA-Ru(2%) and 4 equiv. NaIO₄

To corroborate the evidences found in GC analyses, a NMR spectroscopy monitoring was performed using 4 equivalents of NaIO₄ to observe all abovementioned intermediates. Figure 3.4a shows the whole NMR spectrum at the beginning of the oxidative cleavage reaction in a deuterated solvent mixture. Since the reaction was not yet started, only peaks corresponding to oleic acid were observed. The multiplets from 0.88 to 2.35 ppm are ascribed to protons located throughout the aliphatic chain of the UFA as was confirmed during its NMR characterization (Figure S3.1). The doublet of triplets at 5.34 ppm is characteristic of olefinic protons which in this case is assigned to protons in the carbon-carbon double bond of oleic acid. Figures S3.2-S3.6 show ¹H spectra of all intermediates and products detected by GC in the narrow region from 0 ppm to 11 ppm in order to visualize their characteristic peaks.

Since all products are formed mainly by methylene protons, almost all peaks in the ^1H spectra are constrained to the alkanes region (0-3 ppm). Nevertheless, each product showed distinctive peaks that permitted to differentiate between them. For instance, hydroxyl protons of the 9,10-dihydroxystearic acid appeared at 4.0 and 4.6 ppm while the aldehyde proton of nonanal and 9-oxononanoic acid was observed at 9.7 ppm. With this in mind, it was possible to follow the oxidative cleavage reaction by just observing the distinctive peaks in the narrow region from 3.5 ppm to 11 ppm.

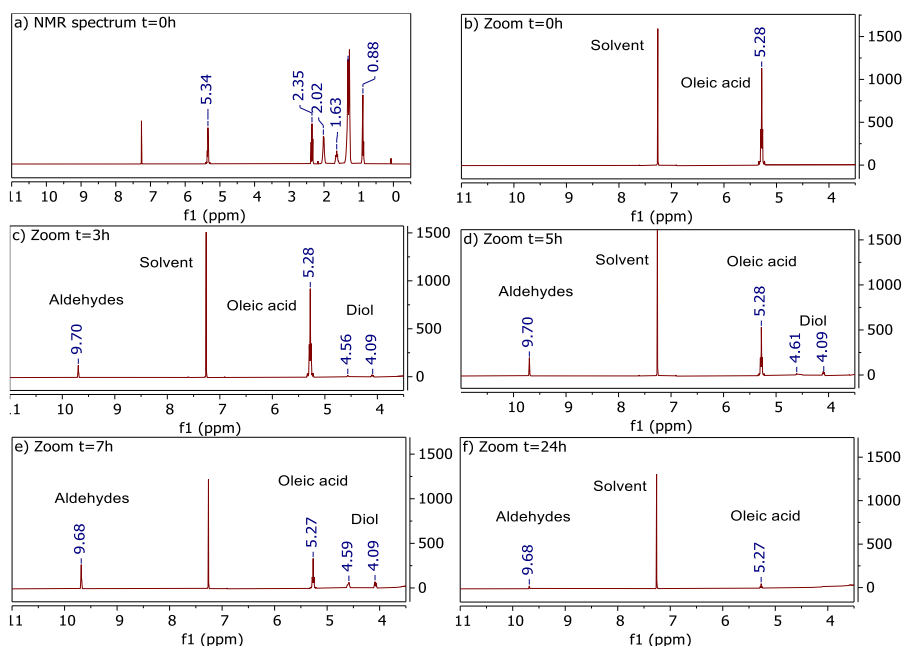


Figure 3.4. NMR spectroscopy monitoring of oxidative cleavage of oleic acid with CBO-PDA-Ru(2%) a) NMR full spectrum $t=0$ h; b) zoom olefinic region $t=0$ h; c) zoom olefinic region $t=3$ h; d) zoom olefinic region $t=5$ h; e) zoom olefinic region $t=7$ h and f) zoom olefinic region $t=24$ h

Thus, Figure 3.4b shows an expanded spectrum from this region where only the solvent (CDCl_3) and olefinic protons are observed. After 3 hours of agitation three new peaks were observed at 4.1, 4.6 and 9.7 ppm. Those peaks correspond to hydroxyl protons on 9,10-dihydroxystearic acid and to aldehydes respectively. The multiplet at 5.34 ppm (corresponding to olefinic protons) decreased in intensity as the reaction time progressed. At the same time, the triplet at 9.7 ppm (proton from aldehydes) increased in intensity while the multiplets of the diol protons were barely detectable. These ^1H spectra confirmed that indeed the mentioned intermediates were in the reaction mixture during the oxidative cleavage of oleic acid. Finally, at 24 hours all the mentioned peaks almost disappeared as a consequence of 9,10-dihydroxystearic acid transformation into NA and Oxo and their further over-oxidation towards PA and AA.

To sum up, it is clear that neither the functionalized support nor the oxidizing agent can trigger by themselves the oxidative cleavage reaction. Hence, Ru is indispensable for the transformation of oleic acid to 9,10-dihydroxystearic acid and after that into carbonyl intermediates and carboxylic acids (i.e. PA and AA). However, the question remains on how ruthenium achieves the aforementioned pathway. Moreover, hot-filtration analyses from the previous chapter demonstrated that Ru was present in the reaction medium. This is an evidence that oxidative cleavage was carried out by a Ru species in the liquid phase. Based on this result UV-Visible spectrophotometry was applied on samples from the solvent mixture in order to detect potential Ru species in high oxidation states that could perform the reaction.

Figure 3.5 shows UV-Vis spectra of the organic (ethyl acetate) and aqueous phases after 3 h and 24 h of agitation. At three hours, three defined peaks at 295, 375 and 455 nm were observed. According to literature, $\text{Ru}^{\text{VIII}}\text{O}_4$ characteristic peaks are at 300 and 380 nm whereas peaks at 380 and 455 nm correspond to $\text{H}_2\text{Ru}^{\text{VI}}\text{O}_4$ species [332-337]. Therefore, both Ru species are present in the organic phase (where oleic acid is located) during the catalytic tests. $\text{Ru}^{\text{VIII}}\text{O}_4$ performs the pericyclic reaction in first, and after the perruthenate ester is broken, the Ru species is reduced to $\text{H}_2\text{Ru}^{\text{VI}}\text{O}_4$. Then, the latter is oxidized again by means of NaIO_4 .

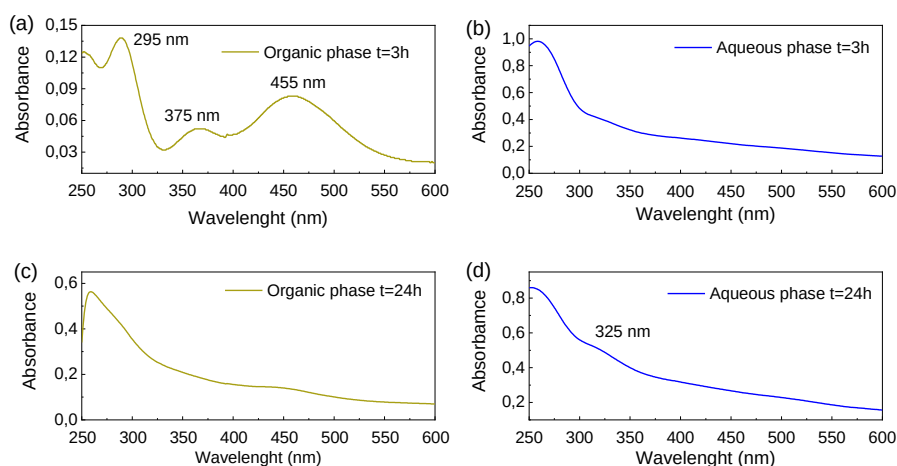
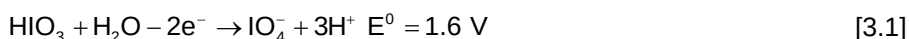


Figure 3.5. UV-Visible monitoring of oxidative cleavage reaction with CBO-PDA-Ru(2%) spectrophotometry: a) organic phase at t=3h, b) aqueous phase at t=3h, c) organic phase at t=24h, d) aqueous phase at t=24h

In addition, at 24 hours all the mentioned characteristic peaks disappear indicating that Ru species were no longer present in the organic phase. As regards the aqueous phase, it is possible to observe a small peak at 325 nm at 3 and 24 hours of agitation. This peak is characteristic of $\text{Ru}^{\text{III}}/\text{Ru}^{\text{IV}}$ species which may be present in the aqueous phase when $\text{Ru}^{\text{VIII}}\text{O}_4$ is reduced after the oxidative cleavage ends. In the aqueous phase, no Ru at

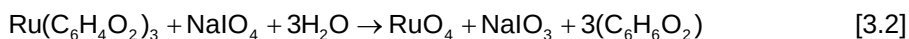
high oxidation state was detected. These results suggest that Ru^{III} is released from the CBO-PDA support once the oxidative cleavage reaction begins. Next it is oxidized by means of NaIO₄ and performs the oxidative cleavage as a homogeneous catalyst. These findings confirm that Ru^{VIII}O₄ is the active species responsible for producing 9,10-dihydroxystearic acid after the perruthenate ester is broken.

As a result, one aldehyde (nonanal) and one acid (9-oxononanoic acid) are formed, which in turn are transformed into carboxylic and dicarboxylic acids either by means of NaIO₄ or by Ru^{VIII}O₄. The former is a strong oxidizing agent widely used in several organic reactions (i.e. oxidative cleavage of diols, oxidation of sulfides and others). Sodium periodate is cheaper than RuO₄ and is synthesized through the electrochemical oxidation of iodates at industrial scale [338,339]:



In order to elucidate which one of the above oxidants may oxidize both intermediates, the following experiment was performed. First, 0.5 mmol of nonanal was dissolved in the absence of any Ru species in our biphasic solvent system along with 4 equivalents of NaIO₄. The same procedure was performed with 4 equivalents of NaIO₃ to explore the possibility that the reduced form of NaIO₄ may still oxidize the intermediates during the catalytic tests. In addition, 5 mg of RuCl₃·H₂O was added to the solvent mixture along with 4 equivalents of NaIO₄ in order to form Ru^{VIII}O₄ in the reaction medium. NaIO₃ was also mixed with the Ru precursor salt but Ru^{VIII}O₄ was not formed as in the case with NaIO₄. With this finding, it is possible to affirm that only NaIO₄ can form the Ru active species (i.e. Ru^{VIII}O₄) during the catalytic tests and NaIO₃ (formed after the cleavage of the diol) cannot contribute to the re-oxidation of H₂Ru^{VI}O₄.

The results plotted in Figure 3.6 demonstrate that all oxidizing agents can oxidize nonanal into pelargonic acid under the same conditions of oxidative cleavage tests. A difference is however observed in the kinetics of each oxidizing agent. While Ru^{VIII}O₄ completely oxidizes nonanal in 5 hours, NaIO₄ requires more time, with 24 hours not being enough to completely oxidize this aldehyde. Conversely, NaIO₃ barely contributes to the oxidation of nonanal, since a 6% of conversion was achieved after 24 h of stirring. Therefore, it is confirmed that the reduced species of NaIO₄ have a negligible influence in the oxidative cleavage of oleic acid. The presence of NaIO₄ is essential since it intervenes several times in different steps of the oxidative cleavage mechanism. In first, the oxidizing agent facilitates the oxidation of the Ru^{III}-catecholate[(C₆H₄O₂)₃] complex on solid catalyst surface into Ru^{VIII}O₄.



Next, $\text{Ru}^{\text{VIII}}\text{O}_4$ in the organic phase reacts with the carbon-carbon double bond of oleic ($\text{C}_{18}\text{H}_{34}\text{O}_2$) acid to produce a perruthenate ester. After its hydrolysis, 9,10-dihydroxystearic acid ($\text{C}_{18}\text{H}_{36}\text{O}_4$) was produced with the consequent reduction of $\text{Ru}^{\text{VIII}}\text{O}_4$ to $\text{H}_2\text{Ru}^{\text{VI}}\text{O}_4$.

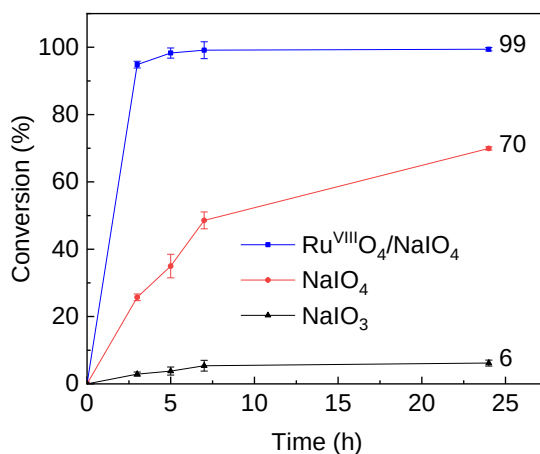
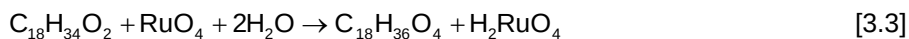
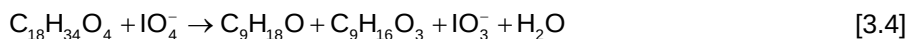


Figure 3.6. Oxidation of nonanal with NaIO_4 , NaIO_3 and $\text{Ru}^{\text{VIII}}\text{O}_4/\text{NaIO}_4$

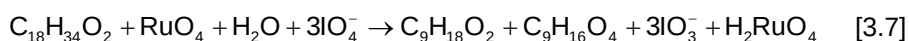
Afterwards, NaIO_4 also cleaves the 9,10-dihydroxystearic acid through a nucleophilic addition attack from OH groups of the diol to the iodine forming a cyclic iodate ether which eventually evolves into nonanal ($\text{C}_9\text{H}_{18}\text{O}$) and 9-oxononanoic acid ($\text{C}_9\text{H}_{16}\text{O}_3$) [340].



At the same time, NaIO_4 re-oxidizes $\text{H}_2\text{Ru}^{\text{VI}}\text{O}_4$ into $\text{Ru}^{\text{VIII}}\text{O}_4$ in order to maintain the catalytic process. Finally, NaIO_4 can also take part in the over-oxidation of nonanal and 9-oxo nonanoic acid into pelargonic ($\text{C}_9\text{H}_{18}\text{O}_2$) and azelaic ($\text{C}_9\text{H}_{16}\text{O}_4$) acids.



Thus, the proposed global reaction of the oxidative cleavage of oleic acid is as follows:



According to the later reaction, only 3 equivalents of the oxidizing agent are required to completely transform oleic acid in the desired carboxylic acids. Nevertheless, during the catalytic tests it was demonstrated that 4 equivalents of NaIO_4 were not enough to accomplish the complete oxidative cleavage of oleic acid. Therefore, the consumption of NaIO_4 was measured in three different scenarios. First, the monitoring of a catalytic test with $\text{Ru}^{\text{VIII}}\text{O}_4$ in homogeneous phase (without a carbon support) demonstrated that only a third of the initial amount of the oxidizing agent was consumed (Figure 3.7). The same monitoring was conducted with CBO-Ru(2%) and CBO-PDA-Ru(2%) showing that NaIO_4 concentration in the aqueous phase decreased ostensibly with both supports. After 24 h of stirring at room temperature, NaIO_4 was totally consumed in the case of CBO-PDA-Ru(2%).

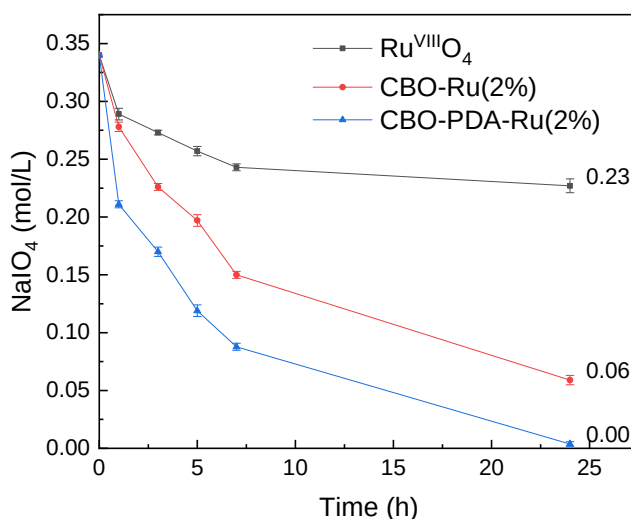


Figure 3.7. NaIO_4 monitoring through the oxidative cleavage of oleic acid with 8 equivalents (0.34 mol/L) of the oxidizing agent

To assess the possibility that the oxidizing agent can interact with the catalyst surface, an infrared spectroscopy monitoring was conducted. Figure 3.8a shows how a small peak at 1722 cm^{-1} appears during the oxidative cleavage reaction. This peak agrees to the stretching vibration mode of carbonyl groups, which in this case, can be attributed to the presence of quinones [269]. XPS analyses were carried out as well to corroborate the results obtained from FTIR spectroscopy. C 1s high resolution spectra (Figure 3.8b) show the influence of the oxidizing agent on CBO-PDA surface. The spectrum from the beginning of the reaction ($t = 0\text{ h}$) shows the main carbon peak at 284.8 eV assigned to C-H bonds in the aromatic structure of PDA over CBO surface. In addition, a small peak at 281.7 eV appears which is ascribed to Ru^{III} species on catalyst surface. At the third

and seventh hour of the catalytic test, the C 1s peak broadens with an increase in intensity at 287.4 eV.

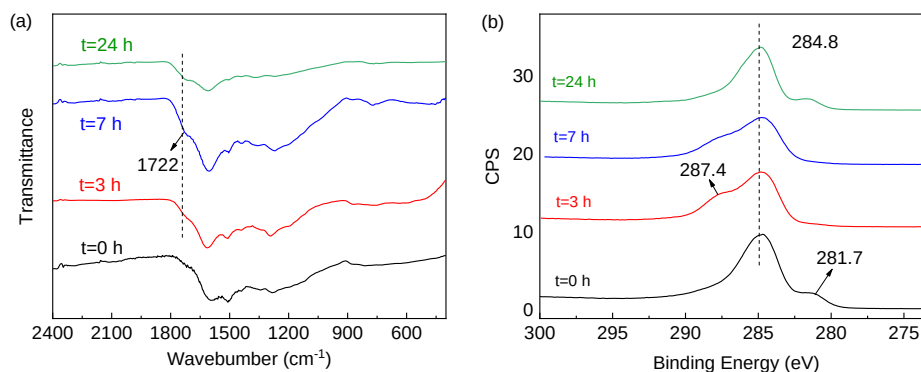


Figure 3.8. Characterization of CBO-PDA-Ru(2%) solid catalyst during oxidative cleavage tests by a) FTIR and b) XPS spectroscopy (C 1s high resolution spectra)

This change of the C 1s peak is ascribed to the increase of C=O groups population which is attributed to the oxidation of catechol groups to quinones. Based on the evidences provided by both spectroscopy techniques, it is possible to affirm that NaIO_4 not only intervenes in the aforementioned steps of the oxidative cleavage of UFAs but it also oxidizes catechol functionalities on CBO-PDA surface. This is why 4 equivalents of NaIO_4 were not enough to fully transform oleic acid into PA and AA and so 8 equivalents can enhance CBO-PDA-Ru performance in this reaction.

3.2. Influence of Ru loading on oxidative cleavage of oleic acid

Since it is now known how Ru and NaIO_4 function in the oxidative cleavage of oleic acid, we wanted to assess the influence of different Ru loadings on CBO-PDA surface in this catalytic reaction. For these experiments 8 equivalents of oxidizing agent were employed. Figure 3.9a indicates that the higher the quantity of Ru on catalyst surface, the higher is the catalytic activity. In the catalytic test with 1 wt% of Ru, it was possible to achieve a complete conversion but only after 24 h of stirring. Conversely, with 4 wt% of Ru only 3 hours were necessary to attain a complete conversion in comparison with the 7 h required with CBO-PDA-Ru(2%).

The same trend was observed as regards products distribution (Figure 3.9b). Indeed, Ru loadings higher than 2 wt% are more than enough to totally transform oleic acid into pelargonic and azelaic acid. Conversely, the catalytic test carried out with CBO-PDA-Ru(1%) catalyst still presented ~8.5% of nonanal and 9-oxononanoic acid in the reaction medium even if 8 equivalents of NaIO_4 were used. Therefore, an excess of NaIO_4 was not enough to oxidize the intermediates into the oxidative cleavage products.

These results confirm that Ru loadings greater than 2 wt% are required to fully transform oleic acid into PA and AA under the reaction conditions employed.

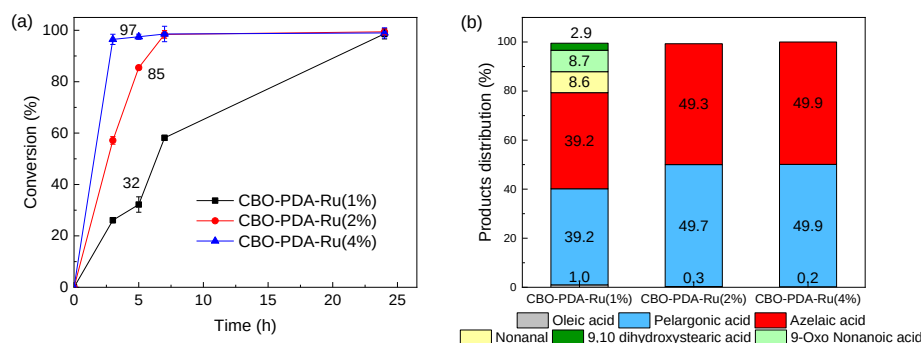


Figure 3.9. Influence of Ru load in the oxidative cleavage of oleic acid a) catalytic activity and b) products distribution

Recyclability tests were performed with CBO-PDA-Ru(4%) catalyst in order to verify their reusability. The solid catalyst was reusable after 5 catalytic tests (Figure 3.10a). Nevertheless, conversions decreased after the 3rd oxidative cleavage test probably due to a progressive physical loss of support (and therefore also of Ru) accumulating at each recyclability test. Another reason is related to the continuous extraction of samples for monitoring the reaction by GC. In any case, the functionalized Ru-carbon catalyst presented a high catalytic activity after 5 recycling tests despite the fact that Ru species were found during UV-Visible monitoring tests. In addition, hot-filtration test was performed on the mentioned catalyst.

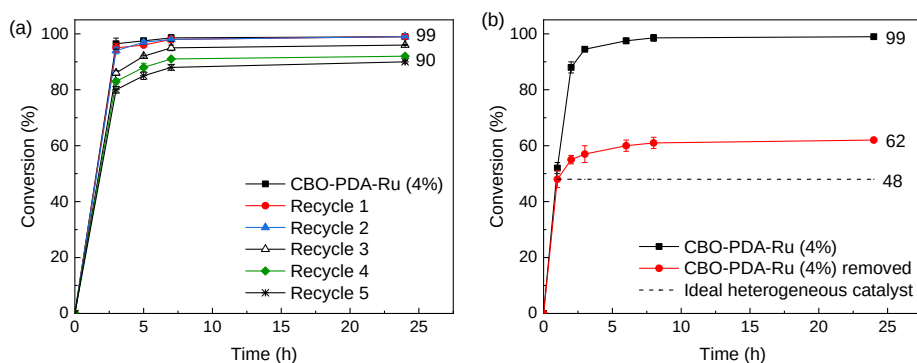


Figure 3.10. a) Recycling tests and b) Hot filtration tests with CBO-PDA-Ru(2%) along with 8 equivalents of NaIO_4

When conversion reached approximately 50%, the CBO-PDA-Ru(4%) was removed from the reaction mixture by centrifugation. Afterwards, the reaction

mixture (without the solid catalyst) was agitated and samples were extracted from the organic layer in order to monitor the reaction up to 24 hours. Figure 3.10b demonstrates that the oxidative cleavage of oleic acid proceeded after the catalyst removal with an increase of 14% in catalytic activity. This finding corroborates the understanding reached from UV-Vis spectra that a leaching occurred, since Ru species are the only ones capable to perform the reaction. The only way to reconcile the facts that a leaching of active Ru species occurred, but still that the catalyst maintained the same catalytic activity after 5 recycling tests, is to evoke the possibility that the CBO-PDA-Ru system behaves along a boomerang catalytic mechanism.

3.3. Boomerang Catalysis

This kind of catalytic system combines the benefits of heterogeneous and homogeneous catalysis [341-343]. The strategy of the boomerang catalysis consists in the development of a support that allows the release of the active species in the liquid reaction medium and once the reaction is completed, these active species are recaptured by the support in order to re-use them in subsequent catalytic cycles [341-344]. Thereby, on one hand, it is possible to obtain the advantages of a homogenous catalyst (high catalytic activity and selectivity) and the advantages of a heterogeneous catalysts (easy separation and recycling) on the other hand [341-346]. In order to assess this possibility with our catalytic system, the protocol explained in the experimental section (Scheme 3.3) was carried out.

After performing an oxidative cleavage test with 100 mg of CBO-PDA-Ru(2%) for 24 hours, the solid catalyst was removed by centrifugation. Then, the organic layer was removed along with three subsequent extractions with fresh ethyl acetate in order to ensure that all the products were removed from the aqueous phase. The ICP analysis (Table 3.3) determined that 0.043 mg of Ru remained in the aqueous phase after the oxidative cleavage reaction which means a loss of Ru of 2.2% from the original catalyst (which initially contained 2 mg of Ru). Next, a fresh support (100 mg CBO-PDA) was added to the aqueous layer to adsorb the leached Ru for 24 hours. The new composite CBO-PDA-(Ru recovered) adsorbed 75% of the Ru left in the aqueous layer.

Table 3.3. Mass balance (mg) of Ru in the Boomerang assessment protocol

Fresh catalyst (mg)	Spent catalyst (mg)	Aqueous phase (mg)	CBO-PDA after adsorption (mg)	Exhausted solution (mg)
2.00	1.95	0.043	0.032	0.011

The catalytic test shown in Figure 3.11a confirms that the residual amount of Ru that remained in the aqueous phase after the first catalytic test was not enough to perform the oxidative cleavage of oleic acid (only 3% of conversion was reached). The composite CBO-PDA-(Ru recovered)

achieved a 14% of conversion. The same procedure was conducted with CBO-PDA-Ru(4%) to verify if the same behavior was observed with higher Ru loading. Figure 3.11b confirms that PDA covered CBO surface managed to recover Ru from the liquid phase in the same manner as with CBO-PDA-Ru(2%). Functional groups of PDA can act as redox ligands yielding different catechol, semi-quinone radicals and quinone groups which can recapture Ru ions forming Ru^{III} and Ru^{IV} complexes on the surface of the support [322-324].

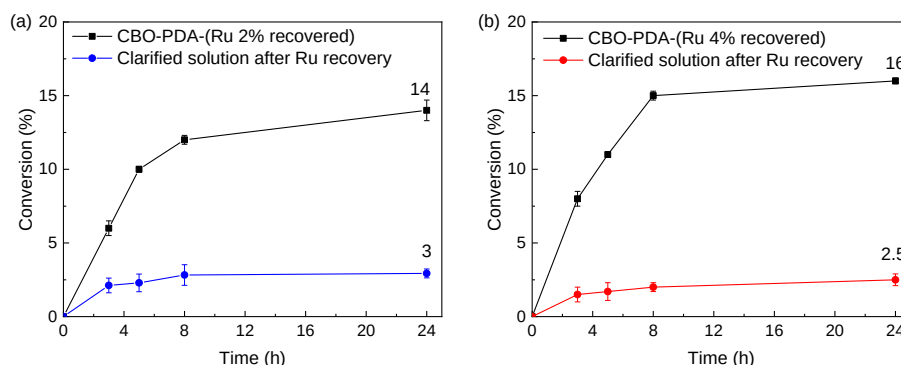
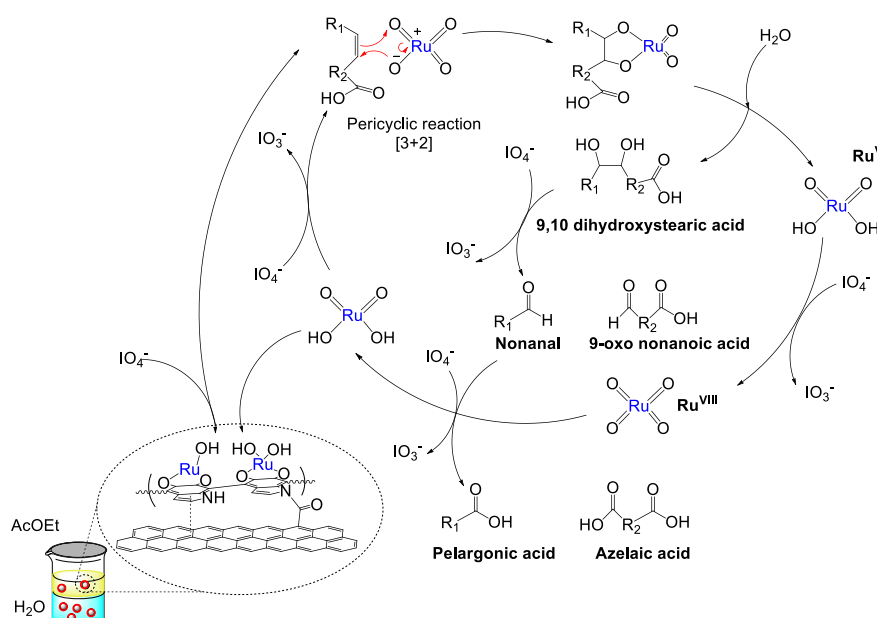


Figure 3.11. Catalytic activity of CBO-PDA after adsorption of Ru within reaction medium with a) 2 wt% and b) 4 wt% of Ru loading

These evidences explain how the composite can complete subsequent catalytic tests reaching conversions >99% without losing catalytic activity. In addition, it is possible to affirm that the real benefit of PDA lies in its capability to chelate Ru species after an oxidative cleavage test finishes. Thus, functional groups of the polymer may form complexes with Ru ions, then release them in the reaction medium to perform the oxidative cleavage along with NaIO_4 and when the reaction ends, PDA may recapture Ru species to maintain the integrity of the solid catalyst. Hence, the synthesized CBO-PDA-Ru composites combine the benefits of homogeneous catalysis (high catalytic activity) with those of heterogeneous catalysis (recycling of the solid catalyst). Finally, after considering all the findings shown and discussed in this section, the mechanism for the oxidative cleavage of oleic acid with CBO-PDA-Ru is illustrated in Scheme 3.4.

To sum up the proposed pathway, Ru is released into the reaction medium and it is oxidized by NaIO_4 into to $\text{Ru}^{\text{VIII}}\text{O}_4$. Then, a pericyclic reaction takes place between the carbon-carbon double bond of oleic acid and $\text{Ru}^{\text{VIII}}\text{O}_4$ in order to form a cyclic perruthenate ester. The cyclic ester is broken by water and ruthenium is reduced to $\text{H}_2\text{Ru}^{\text{VI}}\text{O}_4$ whereas at the same time 9,10-dihydroxystearic acid is formed. NaIO_4 transforms the resulted diol into nonanal and 9-oxo nonanoic acid. Simultaneously, ruthenium is oxidized again to $\text{Ru}^{\text{VIII}}\text{O}_4$ which in turn oxidizes the intermediates into pelargonic and azelaic acids. It is important to remind that NaIO_4 can perform the latter

reaction only in a minor extent. When the reaction ends, Ru species (most likely reduced RuO_2) is readsorbed by PDA functional groups which maintains the catalytic activity of the catalyst in subsequent runs.



Scheme 3.4. Proposed mechanism for the oxidative cleavage of oleic acid with CBO-PDA-Ru

4. Conclusions

Our synthesized Ru-carbon catalyst functionalized with polydopamine presented a boomerang behavior in the oxidative cleavage of oleic acid along with NaIO_4 as oxidizing agent. Through different spectroscopic techniques it was possible to confirm that Ru species were indeed performing the reaction in the liquid phase while functional groups of PDA were able to recover these species once the reaction ends. Thus, CBO-PDA could re-incorporate all Ru on its surface maintaining the integrity of the designed solid catalyst.

PDA was not detrimental for this kind of reaction and higher Ru loadings (i.e. 4 wt%) increased the selectivity towards pelargonic and azelaic acids. NMR and GC analyses demonstrated the presence of intermediates such as 9,10-dihydroxystearic acid, nonanal and 9-oxo-nonanoic acid. When the reaction was performed with 4 equivalents of NaIO_4 , a complete transformation of the mentioned intermediates into the desired products was not possible requiring 8 equivalents of the oxidizing agent to complete the oxidative cleavage reaction.

UV-Visible spectroscopy tests confirmed the presence of $\text{Ru}^{\text{VIII}}\text{O}_4$ and $\text{H}_2\text{Ru}^{\text{VI}}\text{O}_4$ in the reaction medium during catalytic tests. However, once the reaction ends, the presence of these Ru species was not detected anymore. On the other hand, recyclability tests demonstrated that CBO-PDA-Ru catalysts did not lose catalytic activity even after 5 runs. ICP analyses confirmed that almost all Ru is recovered by PDA functional groups once the reaction ends. Hence, these findings suggest that the synthesized composite functions as a boomerang catalyst combining the advantages of homogeneous and heterogeneous catalysis in order to produce high value products from renewable raw materials like oleic acid.

CHAPTER IV: ECO-FRIENDLY PERSPECTIVES: GREEN CARBON PARTICLES AND N-METHYLMORPHOLINE-N-OXIDE

Abstract

Although the carbon black catalyst possesses a high catalytic activity in the oxidative cleavage reaction, we wanted to verify if it was possible to improve the performance of the catalyst by increasing its specific surface area. At the same time, the possibility to conceive an eco-friendlier catalytic system was explored. For this purpose, our own carbon supports were synthesized by submitting a glucose aqueous solution to hydrothermal carbonization into a stainless-steel reactor under autogenous pressure. Through this procedure, well distributed carbon submicrometric spheres were produced and characterized by TEM microscopy, TGA, FTIR and XPS spectroscopy. The as prepared solids were then calcined under air atmosphere in order to create porosity in their carbonaceous matrix. The latter was confirmed through N_2 physisorption while Boehm's titration demonstrated that calcined carbon particles possess a great amount of oxygenated groups. Polydopamine (PDA) was also deposited on calcined carbon particles to improve their ability to complex Ru ions. The as prepared Ru-carbon catalysts were tested in the oxidative cleavage of oleic acid with $NaIO_4$ as oxidizing agent at room temperature and showed complete conversion after 7 h of stirring. Recycling tests demonstrated that in this system again PDA was able to re-adsorb Ru species from the reaction medium ensuring the same catalytic activity up to five recycles. Finally, the addition of N-Methylmorpholine N-oxide (NMO) which is a green oxidizing agent was tested as an alternative to the less green $NaIO_4$ that was employed in previous catalytic tests. NMO allowed to diminish the excess of $NaIO_4$ needed. Although $NaIO_4$ could not be replaced totally by NMO, a synergistic effect was found between when they were used as a mixture of oxidizing agents, which led to complete the transformation of oleic acid into pelargonic and azelaic acids in a faster way than when $NaIO_4$ was used alone.

The results presented in this chapter have been published in:

Gámez, S., de la Torre, E., & Gaigneaux, E. M. (2022). Ru on Modified Carbon Submicrometric Spheres as Novel Catalysts for the Oxidative Cleavage of Oleic Acid with N-Methylmorpholine-N-Oxide as Green Oxidizing Agent. Accepted. ChemCatChem.



1. Introduction

In the previous chapters it was demonstrated that a macroporous material is necessary to perform the oxidative cleavage reaction of large UFAs such as oleic acid. Although macroporous carbon black displayed a low surface area, the carbon support functionalized with polydopamine and Ru showed a complete conversion of oleic acid into pelargonic and azelaic acids after 7 hours of agitation. Despite the efficiency of this Ru-carbon catalyst, we wanted to employ a different carbon material with higher surface area in order to improve the catalytic activity towards the oxidative cleavage reaction. In this matter we explored (i) the possibility to develop our own carbon supports and (ii) the modification of their textural properties by simple thermal treatments. To avoid polluting methodologies and to conceive a greener catalytic system, a hydrothermal eco-friendly carbonization procedure was selected to synthesize carbon submicrometric particles. This methodology uses different biomass derivatives (e.g. glucose, xylose, maltose, fructose, hydroxymethylfurfural) diluted in aqueous solutions which are heated under autogenous pressure inside sealed recipients [347,348].

The most common and simple example is the hydrothermal carbonization of glucose which isomerizes into fructose during the autogenous heating process [349-352]. The latter decomposes into different organic derivatives such as acetic, lactic, propenoic, levulinic and formic acids [353,354]. Fructose and glucose molecules may also undergo dehydration reactions (i.e. ring opening and C-C bond breaking) leading to the formation of several soluble products like 1,6-anhydroglucose, erythrose, 5-hydroxy methylfurfural, furfural, acetaldehyde among others [355-357]. The next stage of the hydrothermal carbonization process involves a polymerization of the previous intermediates via aldol condensation. These reactions lead to the formation of several oligomers with different oxygenated groups [344]. Finally, an aromatization process takes place by means of intermolecular dehydration of the growing oligomers. During this step, various carbonyl groups (e.g. quinones, ketones, aldehydes) as well as C=C bonds arise due to the dehydration of hydroxyl groups along the monomer units [358,359].

When the concentration of aromatic units in the aqueous solution attains the critical point of saturation, a burst nucleation takes place. These nuclei grow outwards incorporating different species dissolved in the solution through stable oxygen bonds (i.e. ether or quinone bonds) [347,359]. Throughout the whole carbonization process, these nuclei grow in the form of spheres with several aromatic layers increasing their particle size. When the heating stops, the outer surface of these carbon spheres exposes several oxygen groups (such as hydroxyls, aldehydes or carboxylic acids) while the inner layers possess less reactive oxygenated species [347,359]. Hence, the particle size of these carbon spheres can be controlled by adjusting the hydrothermal carbonization time. Longer residence times lead to an extensive polymerization of the aromatic units which produces carbon spheres with bigger particle sizes.

Other parameters that influence the production of carbon particles are the substrate concentration in the aqueous solution and the carbonization temperature [360]. The former is related to the yield of carbon spheres. The higher the concentration of the substrate in the aqueous solution, the higher the amount of produced carbon particles. As regards the carbonization temperature, it can also influence the size of carbon spheres. Higher carbonization temperatures contribute to extensive polymerization which leads to bigger carbon particles [360,361]. In order to modify the textural properties of these carbon particles, a calcination step under oxygen atmosphere can be applied. Joula and Farbod demonstrated that a post-calcination treatment at 350-420 °C can remove the outer layers of carbon particles through their combustion [348]. Then, the CO₂ generated during this combustion process can react with superficial carbon layers producing CO as well as porosity (which increases the specific surface area) in carbon particles [251,252]. Therefore, by combining a hydrothermal carbonization technique and a post-calcination treatment, it would be possible to easily synthesize nanoscale carbon particles with high surface area and a great amount of oxygen groups suitable for the complexation of metal cations.

Keeping the environment in mind, the possibility to replace NaIO₄ by a softer and greener oxidizing agent was explored in the oxidative cleavage of oleic acid. Although NaIO₄ is an efficient oxidizing agent in this reaction, it is also polluting for the environment. It has been reported that NaIO₄ is toxic for the aquatic life [362,363]. In this matter, amine oxides specifically N-methyl morpholine N-oxide (NMO), appear as a greener alternative. This organic compound is a heterocyclic amine oxide and morpholine derivative which is used in organic chemistry as a co-oxidant along with osmates and perruthenates [364,365]. From the chemistry of osmium, it is known that NMO can give its oxygen atom to regenerate H₂Os^{VI}O₄ into Os^{VIII}O₄ during the dihydroxylation of olefins. The ability of NMO to oxidize this osmium species could also be used in the oxidation of Ru species during oxidative cleavage reactions [365,366]. Moreover, NMO is not bioaccumulative nor toxic for the aquatic life [367].

Therefore, in this work we propose the synthesis of our own carbon supports by submitting a glucose aqueous solution to a hydrothermal carbonization under autogenous pressure to produce carbon spheres. The latter will be calcined under air atmosphere to increase the specific surface area of the new carbon support. After a functionalization with polydopamine (PDA), Ru will be impregnated on calcined carbon particles (CCN) surface to assess the catalytic activity of the new carbon catalyst in the oxidative cleavage of oleic acid using NMO as oxidizing agent.

2. Experimental section

Carbon based supports were synthesized by hydrothermal carbonization followed by a post calcination treatment under air atmosphere. The

preparation of our new green catalytic system for the oxidative cleavage of oleic acid proceeds as follows:

2.1. Synthesis of carbon particles by hydrothermal carbonization

In a typical procedure, 3.6 g of D(+)-glucose ($C_6H_{12}O_6$, >98% anhydrous from Carl Roth) was dissolved in 100 mL of distilled water to prepare a 0.2 M aqueous solution. This solution was then transferred into a 120 mL Teflon lined stainless steel autoclave which was sealed and put inside an electric MEMMERT GmbH oven at 180 °C for 24 hours. The autoclave was afterwards allowed to cool down to room temperature and then the synthesized carbon submicrometric particles (CNs) were recovered by vacuum filtration using Whatman® PTFE membrane filters (diameter 47 mm, pore size 0.22 μ m). The solids were washed thoroughly with distilled water and ethanol until the recovered solution was colorless. Next, CNs were dried at 100 °C for three hours. CNs were calcined under air in a Vecstar furnace already preheated at 420 °C for 20 minutes in order to produce calcined carbon nanoparticles (CCNs).

2.2. Polydopamine deposition on calcined carbon nanoparticles

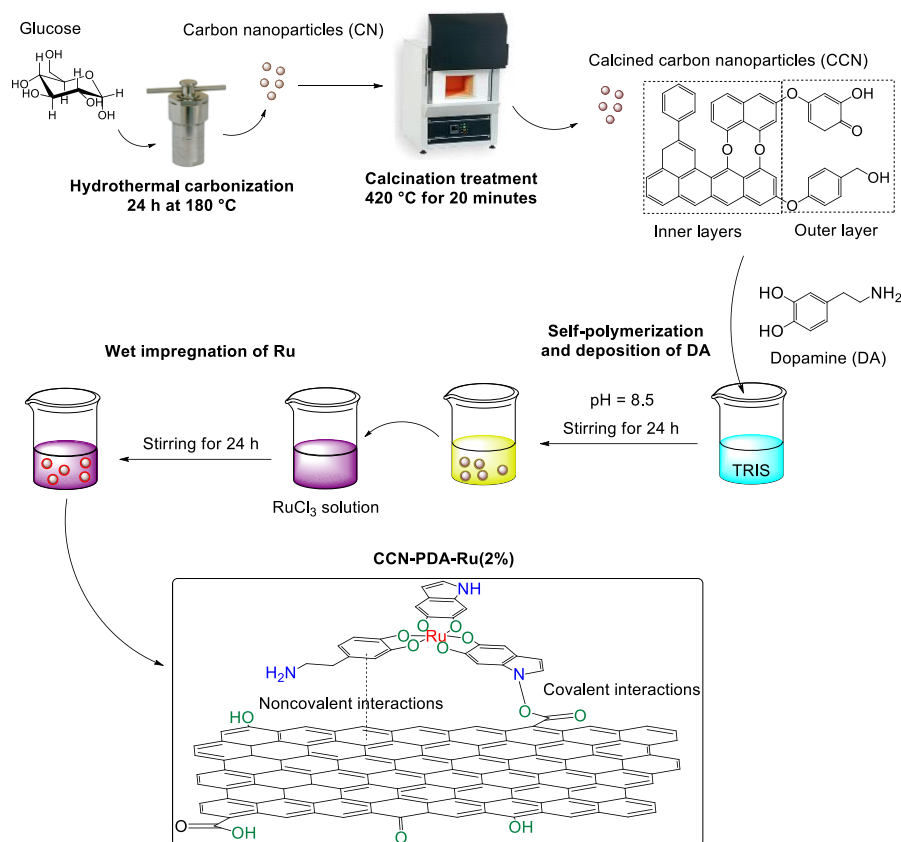
PDA was deposited on the surface of the synthesized CCNs as it was detailed in the previous chapters for CBO. An amount of 110 mg of dopamine hydrochloride per 1 g of dry CCN was employed for the deposition of the polymer.

2.3. Catalysts preparation

All carbon catalysts were prepared with a Ru loading of 2 wt% according to the wet impregnation method explained in the main Experimental section of this thesis. From now carbon particles impregnated with Ru are denoted as CN-Ru(2%) while calcined carbon particles with the same transition metal are assigned as CCN-Ru(2%). Finally, this carbon material functionalized with polydopamine and Ru is denoted as CCN-PDA-Ru(2%). A summary of the whole catalyst preparation is depicted in Scheme 4.1.

2.4. Catalytic tests

Oxidative cleavage of oleic acid (OA, $C_{18}H_{34}O_2$, >99.9% GC from Carl Roth) was performed in the same manner as it was explained in the Experimental section. The only change is the replacement of sodium periodate ($NaIO_4$, >99% from Sigma-Aldrich) by a greener oxidizing agent such as 4-Methylmorpholine N-oxide monohydrate (NMO, $C_5H_{11}NO_2 \cdot H_2O$, 98+% from Alfa Aesar).



Scheme 4.1. Carbon nanoparticles synthesis by hydrothermal carbonization followed by a calcination treatment and functionalized with PDA and Ru

3. Results and Discussion

3.1. Characteriation of synthesized carbon materials

TEM images displayed in Figure 4.1 demonstrate that the hydrothermal carbonization method produced very regular carbon spheres with a mean diameter of 336 nm. After the calcination treatment, the mean particle size of CNs decreased down to 221 nm confirming that combustion of CNs outer layers led to smaller carbon particles.

As onion layers, the external films of CNs are removed during the calcination process under air. On the other hand, when PDA was added to calcined carbon particles (CCNs), the mean particle size increased by about

20 nm. Figure 4.1e shows PDA a layer of polymer that glues the carbon spheres confirming the adherence capability of this polymer on carbon materials.

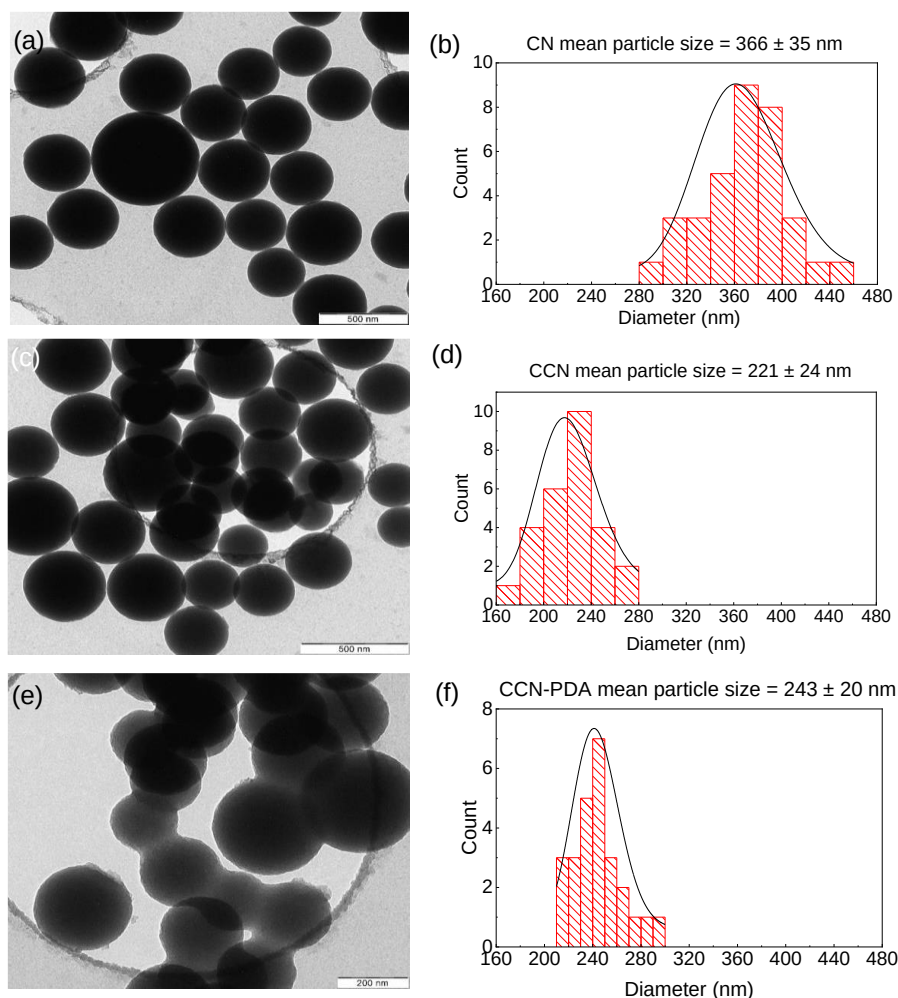


Figure 4.1. a) TEM image and b) particle size distribution of carbon nanoparticles (CNs); c) TEM image and d) particle size distribution of calcined carbon nanoparticles (CCNs) and e) TEM image and f) particle size distribution of CCN-PDA

As regards the textural properties obtained through N_2 physisorption, CNs displays a type II isotherm which is characteristic of macroporous/non porous materials (Figure 4.2a). As a consequence, CNs present a low surface area as well as a low pore volume (Table 4.1). The mean pore size (~ 25 nm) should be understood as that of the spaces between carbon nanoparticles. On the contrary, CCNs display a type I isotherm which is

assigned to microporous materials. Moreover, the specific surface area increased greatly (668 m²/g) with respect to carbon particles without calcination. The CO₂ generated after the combustion of the outer layers on CNs surface can react with external carbon atoms that remained after the combustion [347,368]. In consequence, CO is generated while oxygen atoms can be incorporated on the carbonaceous matrix yielding surface oxygenated complexes represented by C(O) as follows:



Then the adsorbed oxygen C(O) may evolve into C-O bonds or they can be gasified in the form of CO [369]. Therefore, the most reactive and disorganized carbons are gasified generating spaces in the carbon matrix. Thus, the loss of carbon atoms due to this gasification creates porosity in the treated material [368,369]. This asseveration was confirmed after estimating the mean pore size of CCNs. The pore size distribution of CCNs displayed mostly micropores (1.0-1.5 nm) which are still larger than the estimated dimensions of oleic acid (0.8 nm). These micropores are smaller than the gaps between carbon particles observed during TEM microscopy which confirms that CO₂ created ruptures in the carbonaceous matrix through carbon gasification (i.e. creation of porosity).

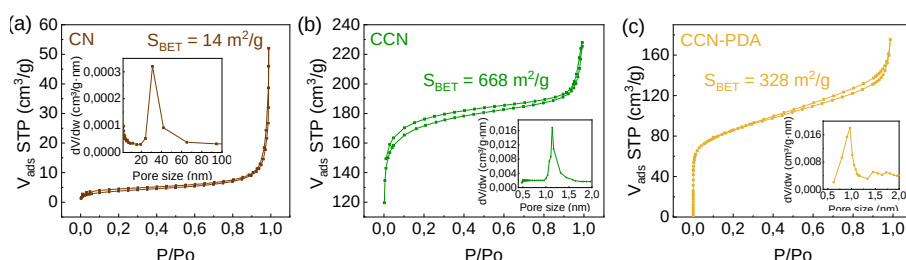


Figure 4.2. N₂ adsorption-desorption isotherms and pore size distribution of: a) CN; b) CCN and c) CCN-PDA

The most important fact of the calcination process is related to the increase of external surface area which is the real surface that can be exploited for the deposition of PDA and the further impregnation of Ru. As is shown in Table 4.1, the external surface area of CCNs increased by a factor of 3 with respect to CNs. Finally, PDA deposition on CCNs decreased their specific surface area as a consequence of micropores blocking. Polymer layers covered the surface of carbon particles filling the spaces between particles as well as blocking most of their micropores created after calcination. It is important to note that despite this event, the external specific surface area was maintained, preserving the benefit of CCNs on CNs. About the chemical properties of the synthesized carbon materials, Figure 4.3 shows the main functional groups determined by FTIR spectroscopy. Carbon particles shows

a broad peak at 3426 cm^{-1} which is assigned to the stretching vibration of hydroxyl groups.

Table 4.1. Textural properties of carbon nanoparticles

Carbon Material	BET surface (m^2/g)	External surface (m^2/g)	Pore Volume (cm^3/g)	Mean Pore size (nm)
CN	14	12	0.03	24.9 ^a
CCN	668	37	0.33	1.2 ^b
CCN-PDA	328	38	0.25	1.1 ^b

^aBarrett-Joyner-Halenda method. ^bHorvath-Kawazoe method

Two more peaks at 1726 cm^{-1} and 1612 cm^{-1} were also detected. The former is ascribed to carbonyl groups on CNs surface while the latter is characteristic of aromatic compounds [269]. Finally, a broad peak at 1220 cm^{-1} is also detected and can be attributed to stretching vibrations in ethers [269]. These findings agree with the dehydration and aromatization processes ongoing during the hydrothermal carbonization.

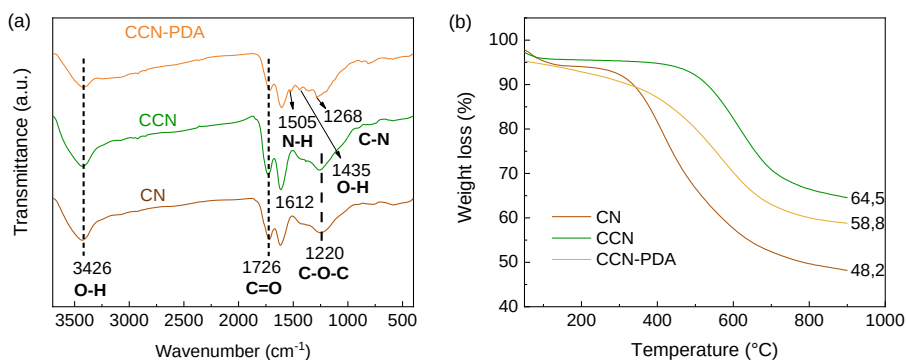


Figure 4.3. a) FTIR spectra of CN, CCN and CCN-PDA; b) TGA of CN, CCN and CCN-PDA

The same characteristic peaks were also observed in the CCNs infrared spectrum. The presence of hydroxyl and carbonyl groups on CCNs confirms the fact that oxygen atoms can be incorporated on carbon particles during the calcination treatment. On the other hand, PDA deposition contributed with three additional peaks along with a decrease in intensity of the band associated to carbonyl species (1726 cm^{-1}). Two bands at 1505 and 1435 cm^{-1} are ascribed to stretching vibration modes from N-H in the indole ring and O-H in aromatic rings respectively [303]. The peak at 1268 cm^{-1} is related to the stretching vibration of C-N bond in the same indole ring of PDA units [303,304]. Hence, these spectroscopic findings confirm the deposition of the polymer on CCNs surface.

Boehm's titration results summarized in Table 4.2 confirm the findings in FTIR spectra. CNs showed the highest total acidity of all carbon materials employed in this research work, even higher than oxidized carbon black treated with HNO₃. This outcome is due to the presence of oxygenated groups on carbon particles surface generated during the hydrothermal carbonization. Therefore, this green and simple method allowed to produce a carbon material with a great number of oxygenated groups suitable for transition metals complexation without using hazardous reagents which are detrimental for the environment. On the contrary, calcination treatment diminished the total acidity of carbon particles due to the gasification of carbon implying the elimination of oxygenated functional groups. After the deposition of PDA, the amount of hydroxyl groups increased because of the extra catechol groups provided by the polymer.

Table 4.2. Boehm's titration results of carbon nanoparticles

Carbon material	Phenols (mmol/g)	Lactones (mmol/g)	Carboxylic acids (mmol/g)	Total Acidity (mmol/g)
CN	1.30	0.80	1.05	3.15
CCN	0.88	0.67	0.83	2.38
CCN-PDA	1.23	0.05	0.24	1.52

Thermogravimetric analyses displayed in Figure 4.3b indicated that the thermal stability of carbon particles increased after the calcination treatment. Most likely, tar and unpolymerized moieties produced after the hydrothermal carbonization were eliminated by combustion during the calcination treatment. In addition, by subtracting the weight loss of CCN-PDA from the weight loss of calcined carbon particles, it was possible to estimate that about 6% of PDA was deposited on CCN surface. According to the values presented in Table S4.1, around 56% of the dopamine incorporated in the deposition process was polymerized. PDA layers can interact with calcined carbon particles functional groups or with their aromatic layers by π -stacking interactions.

XPS survey spectra displayed in Figure 4.4a show the main characteristic peaks at 284.8 and 532 eV which correspond to C 1s and O 1s respectively. As regards CCN-PDA, it is possible to observe a small contribution at 399 eV assigned to N 1s peak. The presence of the latter in the CCN-PDA XPS spectrum is attributed to nitrogen atoms within the indole ring of polydopamine which is deposited on CCN surface. The deconvolution of the C 1s peak of carbon particles displayed in Figure 4.4b was performed assuming 5 contributions. The main sub-peak at 284.8 eV is attributed to aromatic carbons on the graphene layers and carbon contamination while the contribution at 286.4 eV is assigned to carbon bonded to hydroxyl groups. Three sub peaks at 287.6, 288.9 and 291.3 eV were also estimated which are ascribed to carbonyl compounds (C=O), carboxylic acids (COOH) and the shake-up peak typical of aromatic structures respectively. The same carbon species were detected in the C 1s high resolution spectrum of CCNs

(Figure 4.4c); however, the amount of oxygenated groups was lower than the that found for CNs. These findings agree with Boehm's titration results and with the explanation provided by literature (i.e. losses of carbon and oxygenated groups are caused by carbon gasification during the calcination treatment).

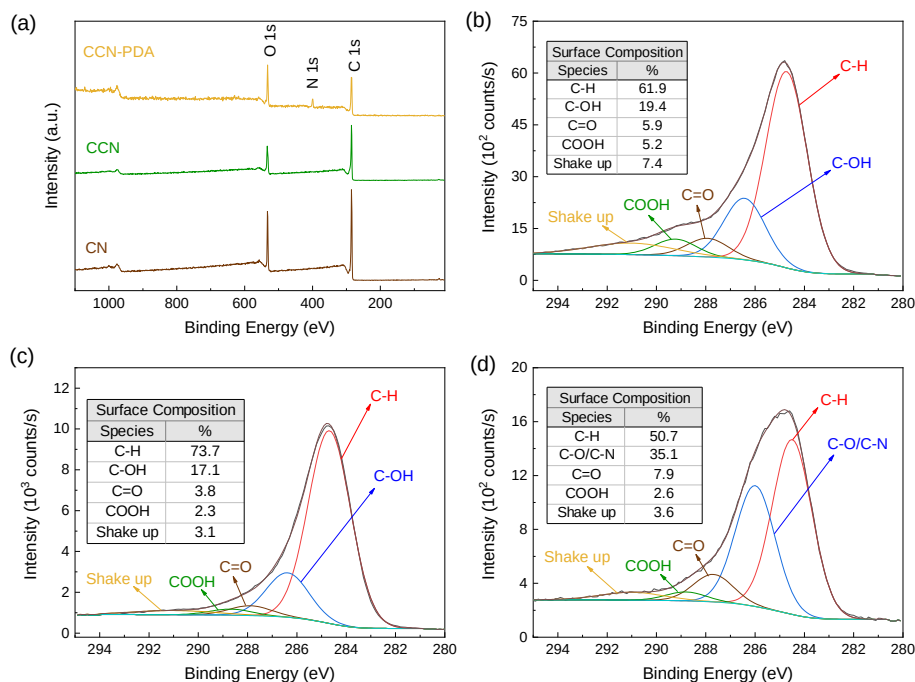


Figure 4.4. a) XPS survey spectra of CN, CCN and CCN-PDA; C 1s high resolution spectrum of b) CN, c) CCN and d) CCN-PDA

The deposition of PDA on CCN surface broadens the C 1s peak displayed in Figure 4.4d. The contribution at 286 eV is attributed to catechol groups and/or C-N bonds from secondary amines within the indole ring of the polymer. This contribution was greater than carbonyl compounds or carboxylic acids confirming that the deposition of PDA provided supplementary catechol groups on CCNs surface. This contribution was also evidenced in the elemental surface composition recapitulated in Table S4.2 where the oxygen/carbon ratio increased from 0.29 (CCNs) to 0.48 (CCN-PDA). To sum up, PDA provided suitable functional groups for Ru complexation.

This assumption was verified by measuring the amount of Ru incorporated on the abovementioned carbon materials by ICP-AES spectrophotometry analyses. Indeed, Table 4.3 shows that Ru nominal value matched with ICP values confirming that functional groups of CN, CCN and CCN-PDA managed to chelate Ru ions from the aqueous medium during the wet

impregnation process. On the other hand, Ru surface concentration obtained by XPS spectroscopy was higher than the nominal value because all the transition metal is distributed on the surface of each carbon support.

Table 4.3. Ru loading on carbon nanoparticles

Catalyst	Nominal Ru (wt%) ^a	Superficial Ru (wt%) ^b	Ru loading (wt%) ^c
CN-Ru(2%)	2.0	10.4	1.7
CCN-Ru(2%)	2.0	11.0	1.8
CCN-PDA-Ru(2%)	2.0	2.5	1.8

^aNominal composition corresponding to the precursor solution. ^bRu superficial content determined by XPS. ^cRu loading determined by ICP-AES.

As regards Ru oxidation state on carbon particles surface, the deconvolution of the O 1s peak from CCN-PDA-Ru(2%) in Figure 4.5a shows a contribution at 528.9 eV which is attributed to Ru-O bonds. The same contribution was also observed in the cases of CN-Ru(2%) and CCN-Ru(2%) shown in Figures S4.1a and S4.1b respectively. On the other hand, the Ru 3p core level of CCN-PDA-Ru(2%) presented a doublet at 463.3 and 485.5 eV which corresponds to an oxidation state of Ru^{III} (Figure 4.5b).

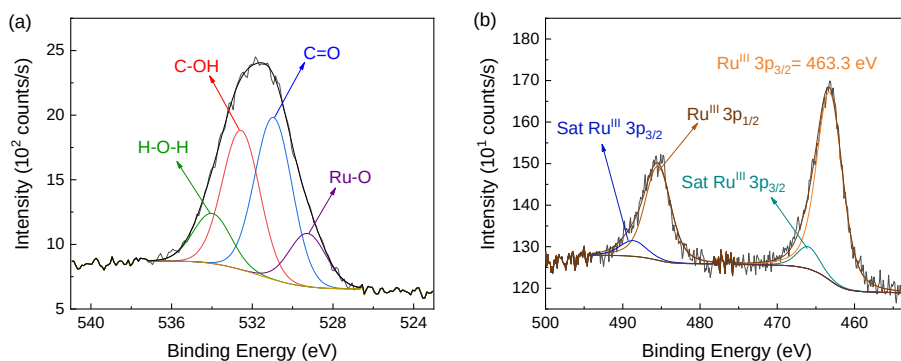


Figure 4.5. a) O 1s and b) Ru 3p high resolution spectra of CCN-PDA-Ru(2%)

Since no Cl 2p was detected during the XPS analyses, it is proposed that the transition metal is forming a Ru^{III}-catecholate complex with catechol groups of PDA on calcined carbon particles surface.

3.2. Catalytic test results

The synthesized carbon catalysts were assessed in the oxidative cleavage of oleic acid using 8 equivalents of sodium periodate as oxidizing agent. Figure 4.6a shows that CCN-Ru(2%) displayed a greater catalytic activity

than carbon particles without the calcination treatment (CNs). This fact is important because in the previous chapter it was demonstrated that the oxidative cleavage reaction with Ru-carbon catalysts took place mostly in the reaction medium. Thus, it would not matter what type of support was used for this reaction since the catalytic activity should have been the same. However, in this case, it is observed that the catalyst with the lowest specific surface area has the lowest conversion requiring 24 h to complete the reaction. On the other hand, the catalyst with a higher specific surface area completes the oxidative cleavage reaction in only 7 hours. This allows to conclude that the textural properties of the support (mostly the external surface area and pore size distribution) play a role in the oxidative cleavage of large UFAs such as oleic acid. The addition of PDA on CCNs was not detrimental for the performance of the functionalized catalyst. Actually, CCN-PDA-Ru(2%) completed the oxidative cleavage of oleic acid after 7 h of agitation as well.

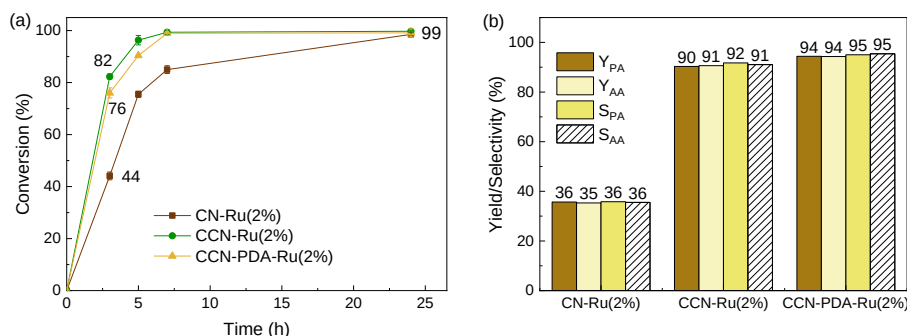


Figure 4.6. a) Catalytic activity of CN-Ru(2%), CCN-Ru(2%) and CCN-Ru(2%) in the oxidative cleavage of oleic acid with 8 equiv. of NaIO_4 ; b) Yields and selectivity towards pelargonic (PA) and azelaic acid (AA) achieved with carbon catalysts

The same trend was also observed in the production of pelargonic (PA) and azelaic (AA) acids. Figure 4.6b demonstrates that yields and selectivity towards both desired oxidative cleavage products are improved when a carbon support with higher surface area than CNs is employed. It is important to remind that oleic acid evolves into PA and AA through different intermediates during the oxidative cleavage reaction. Briefly, oleic acid is transformed into 9,10 dihydroxystearic acid which is cleaved into nonanal and 9-oxononanoic acid. Both intermediates are over-oxidized into PA and AA by means of the oxidizing agent or by $\text{Ru}^{\text{VIII}}\text{O}_4$. These intermediates were still present after 24 h of stirring when CN-Ru(2%) was employed as catalyst (Figure S4.2). This was not the case when CCN-Ru(2%) or CCN-PDA-Ru(2%) were used in the catalytic tests suggesting that the textural properties of the carbon support may also intervene in the transformation of oleic acid into the desired carboxylic acid products.

The stability of the synthesized carbon catalysts was evaluated by means of recycling tests. Figure 4.7a shows that CN-Ru(2%) loses catalytic activity after each oxidative cleavage test. The same trend was observed in the case of CCN-Ru(2%) where the conversion after 24 h of agitation diminished down to 72% at the fifth recycle (Figure 4.7b). On the other hand, the carbon catalyst functionalized with polydopamine maintained its catalytic activity almost intact after five recycling tests (Figure 4.7c). Only a slight decrease in conversion (about 5%) was registered when CCN-PDA-Ru(2%) was used. This small drop in catalytic activity can be ascribed to losses of the solid material due to attrition or because of the extensive sampling carried out during the consecutive catalytic tests.

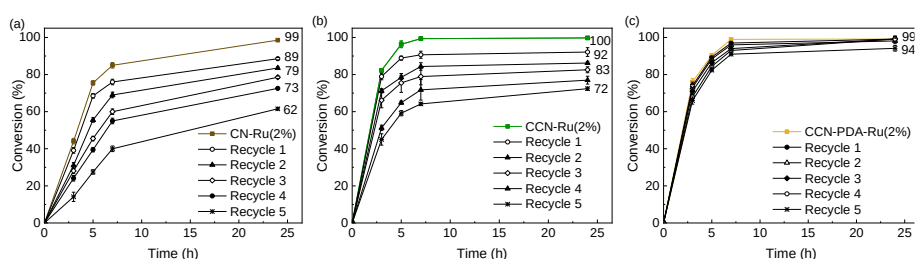


Figure 4.7. Recycling tests of: a) CN-Ru(2%); b) CCN-Ru(2%) and c) CCN-PDA-Ru(2%)

The reason why CN-Ru(2%) and CCN-Ru(2%) lost of their catalytic activity after each recycling test is attributed to the leaching of Ru. Since $\text{Ru}^{\text{VIII}}\text{O}_4$ is the only species capable of transforming oleic acid into PA and AA, it is believed that a continuous loss of Ru was the main reason for the poor performances of both Ru-carbon catalysts during the last recycling tests. This assumption was confirmed by ICP-AES analyses which showed a reduction of Ru loading on the mentioned solid catalysts after performing the subsequent catalytic tests (Table 4.4). This was not the case for CCN-PDA-Ru(2%) since the functionalized catalyst with polydopamine maintained almost the same Ru loading as before performing the successive oxidative cleavage runs. From our previous experiences with oxidized carbon black functionalized with PDA, we know that the polymer has the capability to recover Ru ions instead of keeping attached Ru during the whole catalytic test.

Table 4.4. Ru loading on spent carbon catalysts

Catalyst	Nominal Ru (wt%) ^a	Ru loading (wt%) ^b
CN-Ru(2%)	2.0	0.9
CCN-Ru(2%)	2.0	1.1
CCN-PDA-Ru(2%)	2.0	1.7

^aNominal composition corresponding to 2 wt%. ^bRu loading determined by ICP-AES.

This asseveration was confirmed by hot-filtration tests (Figure 4.8) where conversion increased after the extraction of the three different solid catalysts tested in this work. Therefore, it is demonstrated that CCN-PDA-Ru(2%) behaves in the same manner as our previous carbon black-PDA-Ru catalyst. The oxidizing agent transforms the Ru^{III} -catecholate complex into $\text{Ru}^{\text{VIII}}\text{O}_4$ which reacts in the liquid phase with oleic acid via a pericyclic [3+2] reaction. The UFA evolves into 9,10 dihydroxystearic acid while the Ru species is reduced into $\text{H}_2\text{Ru}^{\text{VI}}\text{O}_4$. The latter is re-oxidized by means of NaIO_4 and it is re-adsorbed by catechol groups of PDA on CCNs surface (i.e. boomerang catalysis). By this way it is possible to maintain almost the same catalytic activity throughout several catalytic tests.

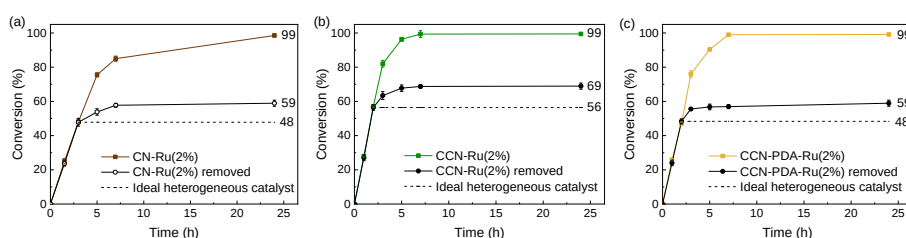


Figure 4.8. Hot-filtration tests of: a) CN-Ru(2%); b) CCN-Ru(2%) and c) CCN-PDA-Ru(2%)

Although carbon submicrometric particles before and after the calcination treatment possessed a greater amount of oxygenated groups than carbon particles with polydopamine, the former supports did not manage to re-incorporate Ru species as polydopamine did. This shows that a random distribution of several oxygenated functional groups was not enough to re-capture Ru ions once the oxidative cleavage test ended. On the contrary, a periodic distribution of catechol groups within PDA monomers ensured the recovery of Ru species to maintain the catalytic activity of the synthesized catalyst. Hence the real benefit of the polymer is related to its capability to complex Ru through its well organized functional groups.

3.3. Influence of NMO in the oxidative cleavage reaction

CCN-PDA-Ru(2%) was selected to verify the influence of N-methylmorpholine N-oxide (NMO) as a green oxidizing agent in the oxidative cleavage of oleic acid. When NaIO_4 was completely replaced by NMO no catalytic activity was detected at all (Figure 4.9a). The reason is related to NMO capability to only regenerate $\text{H}_2\text{Ru}^{\text{VI}}\text{O}_4$ into $\text{Ru}^{\text{VIII}}\text{O}_4$ as is depicted in Figure S4.3. This means that NMO cannot oxidize the Ru^{III} -catecholate complex on CCN surface to transform it into the Ru active species. As a consequence, the oxidative cleavage reaction does not take place with only NMO. This fact was confirmed during UV-visible analyses (Figure S4.4) where $\text{Ru}^{\text{VIII}}\text{O}_4$ was not produced after the addition of NMO in the reaction medium. Hence, it is not possible to completely replace sodium

periodate as the main oxidizing agent in the oxidative cleavage reaction with our Ru-carbon catalysts.

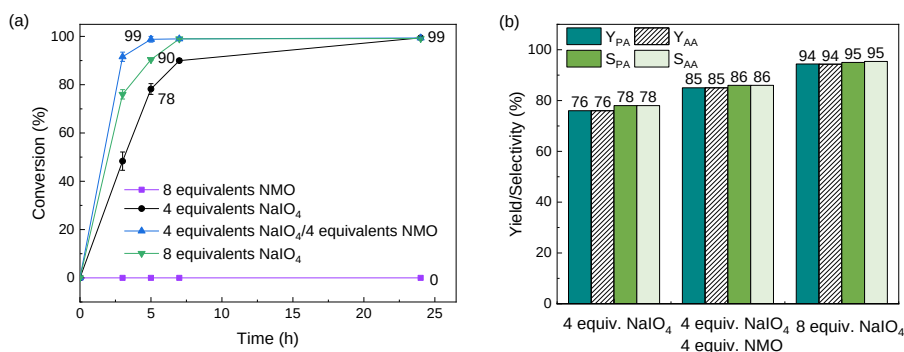


Figure 4.9. a) Catalytic activity of CCN-PDA-Ru(2%) in the oxidative cleavage of oleic acid with different combinations of oxidizing agents. b) Yields and selectivity achieved with different combinations of oxidizing agents

When 4 equivalents of NMO were combined with 4 equivalents of NaIO₄, the transformation of oleic acid was faster than with 8 equivalents of NaIO₄. Actually, with the NMO/NaIO₄ combination the greatest catalytic activity was achieved which led to a total conversion after 5 h of stirring (instead of 7 h with only NaIO₄). To understand these results it is necessary to keep in mind at what stages of the oxidative cleavage reaction the oxidizing agent can intervene. According to the pathway already explained and detailed in the previous chapter (Scheme 3.5), the oxidizing agent reacts with: 1) the Ru^{III}-catecholate complex on the carbon support surface for its transformation into Ru^{VIII}O₄; 2) in the liquid phase, it can also take part in the oxidation of H₂Ru^{VI}O₄ into Ru^{VIII}O₄ to maintain the catalytic activity of Ru in the oxidative cleavage of UFAs; and 3) it can also intervene in the oxidation of nonanal and 9-oxononanoic acid towards pelargonic and azelaic acids. It was already demonstrated that NMO cannot transform the Ru^{III}-catecholate complex into Ru^{VIII}O₄ while it is well known from the literature the ability of NMO to re-oxidize Ru^{VI} species into Ru^{VIII}O₄ [365,366]. Then, to verify if NMO can transform oxidative cleavage intermediates into carboxylic acids, nonanal oxidation was carried out with this amine oxide. Nevertheless, NMO cannot perform the oxidation of nonanal into pelargonic acid either (Figure S4.5). Hence, NMO is only useful for the re-oxidation of reduced Ru^{VI} species into Ru^{VIII}O₄ which is the active species responsible for oxidative cleavage of oleic acid.

Based on these results and explanations, it is possible to affirm that there is a synergistic effect when NMO and NaIO₄ are used in equal amounts. While NaIO₄ can intervene in the oxidation of the Ru^{III}-catecholate complex on CCN surface as well as the oxidation of nonanal and 9-oxononanoic acid into PA and AA, NMO can focus in the re-oxidation of the Ru^{VI} species into

$\text{Ru}^{\text{VIII}}\text{O}_4$ to improve the catalytic activity during the oxidative cleavage reaction. On the contrary, NaIO_4 by itself is distributed among the abovementioned stages of the oxidative cleavage reaction. Thus, with less NaIO_4 (i.e. 4 equivalents) the production of PA and AA is not complete as observed in Figure 4.9b, and only with a greater amount of this oxidizing agent (i.e. 8 equivalents), yields and selectivity of both oxidative cleavage products are almost complete.

Although NMO mixed with NaIO_4 completely transformed oleic acid within 5 h of stirring, yields and selectivity of PA and AA were 10% lower than the test with 8 equivalents of NaIO_4 . This reduction in selectivity is ascribed to the lesser amount of NaIO_4 and the inability of NMO to oxidize intermediates into the desired oxidative cleavage products. Nevertheless, with the addition of NMO, it was possible to diminish the excess of NaIO_4 (which has detrimental effects on the environment) without ostensibly sacrificing the catalytic activity of the designed carbon catalyst. Finally, recycling tests were carried out using 4 equivalents of NaIO_4 mixed with 4 equivalents of NMO in the reaction medium. Figure 4.10a shows that CCN-PDA-Ru(2%) catalyst was still active even after 5 consecutive catalytic tests as when 8 equivalents of NaIO_4 was used.

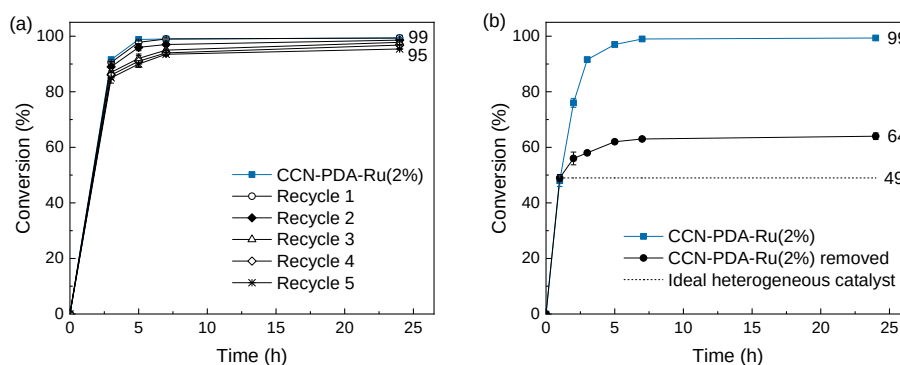


Figure 4.10. a) Recycling tests with CCN-PDA-Ru(2%) along with 4 equiv. NaIO_4 /4 equiv. NMO; b) Hot-filtration test with CCN-PDA-Ru(2%) along with 4 equiv. NaIO_4 /4 equiv. NMO

The hot-filtration test (Figure 4.10b) confirmed the presence of Ru species in the reaction medium due to the increase of conversion after the removal of the solid catalyst. In the same way as with NaIO_4 , the functionalized support can recapture Ru species from the liquid phase and maintain the catalytic activity of the solid catalyst. Hence, the addition of NMO was not an impediment for polydopamine functional groups capability to recover Ru species from the reaction medium.

4. Conclusions

Hydrothermal carbonization of an aqueous glucose solution led to the production of very regular carbon submicrometric spheres which possess a great number of different functional groups *a priori* suitable for transition metals complexation. TEM analyses confirmed the spherical shape of the as synthesized carbon particles while Boehm's titration determined the total acidity of this carbon support. By means of this simple and eco-friendly methodology, it was possible to generate several oxygenated groups on carbon particles surface in a greater amount than with other dangerous and polluting procedures such as oxidations with HNO_3 or $\text{KMnO}_4/\text{H}_2\text{O}_2$. Hence, hydrothermal carbonization is a green alternative for the development of new carbon supports suitable for various applications including catalysis.

The post-calcination treatment was beneficial for the reduction of carbon particles size and for the increase of their specific surface area. The oxygen inside the oven reacted with the outer layers of the carbon particles producing CO_2 . The latter in turn reacts with carbon atoms on the outer surface producing CO and oxygenated groups. The loss of carbon atoms during this gasification process led to the creation of porosity (mostly micropores) which increases the specific surface area of the support. This aspect was verified by N_2 -physisorption which confirmed that CCNs possessed a type I isotherm characteristic of microporous materials with pores sizes from 1.0-1.5 nm. Our work thus demonstrates that it was possible to modify the textural properties of carbon submicrometric particles through a simple calcination treatment in a short period of time (i.e. 20 minutes).

After the impregnation of Ru on carbon particles with and without calcination, the oxidative cleavage reaction of oleic acid was carried out. The catalytic tests demonstrated that the textural properties of the carbon support have an important impact in the catalytic activity of the as prepared solid catalysts. Although in the previous chapters it was demonstrated that the reaction is mostly carried out in the liquid phase, the results reported in this chapter confirm that a carbon material with higher surface area possessed a greater catalytic activity than a macroporous/non porous material. This was demonstrated that the textural properties of the support play an important role in the oxidative cleavage of UFAs.

The deposition of polydopamine on calcined carbon particles surface was demonstrated by FTIR, TGA and XPS analyses. The real benefit of the polymer coating was observed during the oxidative cleavage tests. After performing 5 recycling tests, the functionalized catalyst maintained its catalytic activity almost intact. Although Ru species were dissolved in the reaction medium, functional groups of polydopamine manage to re-adsorb Ru and regenerate the solid catalyst. By this way, the CCN-PDA-Ru(2%) catalyst remained active up to five catalytic tests with great yields and selectivity towards pelargonic and azelaic acids.

Finally, the possibility to completely replace NaIO_4 as oxidizing agent in the oxidative cleavage reaction by N-Methylmorpholine N-oxide (NMO) was explored. The latter is a green oxidant which is active in the re-oxidation of $\text{H}_2\text{Ru}^{\text{VI}}\text{O}_4$ into $\text{Ru}^{\text{VIII}}\text{O}_4$ species. Although it was not possible to perform the oxidative cleavage reaction with only NMO, a combination of NaIO_4 and NMO (4 equiv./4 equiv.) increased the catalytic activity of CCN-PDA-Ru(2%) by reducing the reaction time needed to achieve complete conversion. While NMO focused in the re-oxidation of Ru species, NaIO_4 can intervene at other stages of the oxidative cleavage reaction (i.e. oxidation of the Ru^{III} -catecholate complex as well as the intermediates). Hence, the synergistic effect of the NaIO_4 /NMO combination allowed to reduce the excess of NaIO_4 (which is detrimental for the environment) used in previous catalytic tests without losing the catalytic activity in the oxidative cleavage of oleic acid.

CHAPTER V: ECUADORIAN PALM OIL VALORIZATION THROUGH THE OXIDATIVE CLEAVAGE OF UFAs FOR AZELAIC ACID PRODUCTION

Abstract

In all previous chapters, the oxidative cleavage reaction was carried out only with pure oleic acid without other compounds which may be detrimental for the normal ongoing of the catalytic test. However, in Nature that is not the case, since a vegetable oil possesses several compounds apart from UFAs, that could impact detrimentally on the efficiency of the catalysts. Therefore, we wanted to check how the catalysts we have developed until now could maintain their performance with a real oil. In this purpose Ecuadorian palm oil was selected for carrying out the oxidative cleavage reaction because of its abundance and its high content in UFAs. The fatty acids composition of this feedstock showed that it possesses 41% and 9% of oleic (C18:1) and linoleic (C18:2) acids respectively. Both UFAs can be exploited through their carbon-carbon double bonds scission for the production of azelaic acid (AA). To achieve so, triglycerides within the vegetable oil were hydrolyzed and transformed into fatty acids methyl esters (FAMES). Then, along with other minor components from palm oil, the FAMES were incorporated in our catalytic system ($\text{H}_2\text{O}/\text{MeCN}/\text{AcOEt}$, 4/2/1). Our best catalysts (i.e. CBO-PDA-Ru and CCN-PDA-Ru) were tested in the oxidative cleavage reaction with 4 equivalents of N-Methylmorpholine N-oxide (NMO) and 4 equivalents of NaIO_4 at room temperature. The catalysts achieved complete conversion after 5 h of reaction with yields around 85% towards azelaic acid. Although Ru species were found in the solvent during UV-Visible spectroscopy monitoring, the solid catalysts maintained the same catalytic activity for 5 consecutive catalytic tests. ICP-AES analyses confirmed that PDA on carbon surface recovered Ru species once the reaction ended, assuring the recyclability of the functionalized carbon materials. Therefore, our study revealed that our best catalysts maintained their high performance when used to convert a complex substrate directly originating from a real oil and open a novel route for the production of a high value-added product with medicinal applications from a cheap feedstock.

1. Introduction

So far, all oxidative cleavage tests reported in this thesis have been carried out with pure synthetic oleic acid. By doing so, it was possible to identify all intermediates that intervene in the transformation of oleic acid into pelargonic (PA) and azelaic (AA) acids. It was verified that carbon supports functionalized with polydopamine (PDA) may anchor Ru ions in order to perform the oxidative cleavage reaction. The synthesized carbon-PDA-Ru solids behave as boomerang catalysts by releasing Ru species in the liquid phase to trigger the oxidative cleavage of oleic acid, and once the reaction ends, catechol groups of PDA recapture these Ru species thus allowing to maintain the integrity and reusability of the carbon catalysts. The designed catalytic system is quite active since oleic acid is totally transformed into PA and AA after 7 hours of reaction at room temperature. Considering this performance, we wanted to go beyond and challenge our catalytic system in the oxidative cleavage of UFAs in a real natural vegetal oil. This natural feedstock indeed contains several components apart from UFAs such as saturated fatty acids (SFAs), carotenoids among others [370-373]. These components may, or may not, interfere in the normal ongoing of the oxidative cleavage reaction. Therefore, we wanted to verify if our designed catalytic system is still active (i.e. in terms of conversion and yield) in the oxidative cleavage of UFAs inside a natural blend. For this purpose, palm oil was selected as raw material since this vegetable oil possesses a high concentration of UFAs and is abundant in Ecuador, the country where the first year of this research work was carried out.

Palm oil is extracted from a fruit called *Elaies guineensis* which is normally produced in tropical areas of Africa and South America [372]. This feedstock is one of the most important vegetable oils because of its abundance, low price and its high versatility towards the synthesis of value-added food products such as margarines or shortenings [370,371]. After its extraction from the *Elaies guineensis* fruit, the oil shows a reddish brown coloration with a semisolid consistency at ambient temperature [372]. This vegetable oil is constituted mostly by triglycerides which are formed by glycerol molecules covalently bonded to three fatty acids (FAs). These FAs vary in their length and the number of unsaturations but, in average, palm oil present a ratio of saturated FAs (SFAs): unsaturated FAs (UFAs) = 1 [373,374]. The lipidic profile of different palm oils from several locations around the world have shown that roughly they possess 40% of mono-UFAs (of which a major part is oleic acid) and a 10% of poly-UFAs. Palm oil also contains other components in minor quantity (less than 1%) such as carotenoids, tocopherols, sterols, phosphatides, triterpenic, and aliphatic alcohols [372,374]. Although these constituents are in minority within this feedstock, they contribute to the stability and refinability of the oil, increasing its nutritive value at the same time [373].

Traditionally, palm oil has been widely employed for the development of several food products, such as margarines, cooking oils, confectionery and

baking fats [373]. However, in the last two decades, several oils and fats, like palm oil, have been used in non-food applications for the synthesis of value-added products [5,17]. Recently, UFAs within several oils, have been employed as a novel raw material for the synthesis of plasticizers, polymers, biodiesel through hydrogenation, decarboxylation or esterification reactions [375-377]. Since palm oil possesses around 40% of oleic acid and a 10% of other poly-UFAs, it would be possible to submit them to the oxidative cleavage reaction for the synthesis of value-added products such as azelaic acid. In addition, there are no examples in the literature about the oxidative cleavage of UFAs from a real vegetable oil.

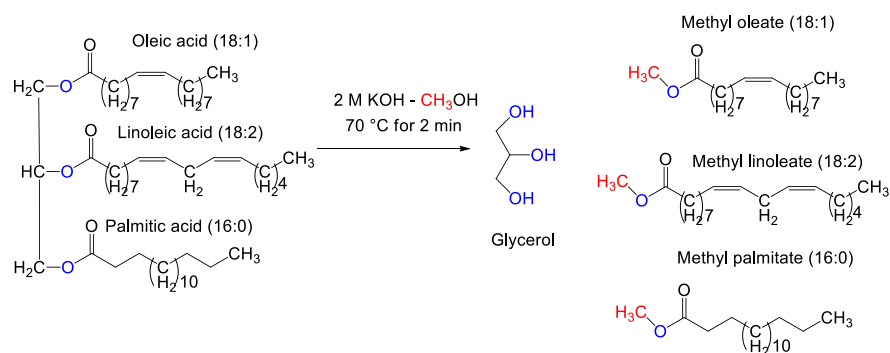
The Ru-carbon heterogeneous catalysts functionalized with polydopamine that we have developed in the preceeding chapters of the thesis, have proven to be efficient and reusable in the oxidative cleavage of pure oleic acid. However, one should check now if this very promising behavior is maintained when the catalysts are used in the same reaction with UFAs extracted from a real and complex palm oil. Therefore, our best synthesized carbon catalyst (i.e. CBO-PDA-Ru and CCN-PDA-Ru) were tested in the oxidative cleavage of UFAs from Ecuadorian palm oil. To perform this reaction, triglycerides in palm oil were first hydrolyzed to release FAs (including UFAs) and to transform them into methyl esters. This procedure facilitated the availability of UFAs (in form of esters) for the oxidative cleavage reaction. The fatty acids methyl esters (FAMES) were then incorporated to our catalytic system in order to verify if the “non UFAs” components of palm oil may be detrimental for the production of azelaic acid.

2. Experimental section

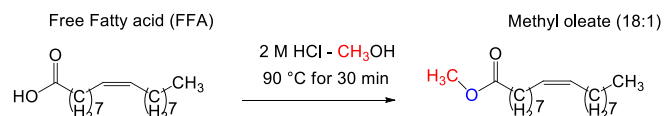
2.1. Palm oil derivatization

First, 0.3 g of palm oil was dissolved in 2 mL of n-hexane (C_6H_{14} , > 96% from TCI chemicals) and mixed with 1 mL of 2 M KOH-methanol solution (KOH, 99% from Acros Organics; CH_3OH , 99% from TCI chemicals) in order to hydrolyze the triglycerides and to release all fatty acids. The mixture was vortexed for 30 seconds and then heated at 70 °C for 2 minutes. Then the organic layer was extracted and mixed with 1.8 mL of a 2 M HCl-methanol solution (HCl, 37% from Carl Roth) to ensure the complete transformation of all FAs into their respective methyl esters (Scheme 5.1). The new solution was heated at 90 °C for 1 h and then it was allowed to cool down at room temperature with the further addition of 1 mL of distilled water. Afterwards, the solution was vortexed for 30 seconds and the organic layer was extracted and placed in a 50 mL round flask. To determine the lipidic profile of palm oil, 0.1 mL of the organic layer was dissolved in 1.4 mL of n-hexane and injected in a Varian 3800 Gas Chromatograph equipped with a Flame Ionization Detector (FID), a data base of the main FAs and a Stabilwax-DA Restek column. Finally, the organic phase in the round flask

was evaporated in a rotary evaporator (50 °C) to obtain the fatty acids methyl esters (FAMES) as a pasty solid.



Acidic treatment to ensure transformation of FFAs into FAMES



Scheme 5.1. Derivatization of triglycerides from palm oil

2.2. Catalytic tests

The FAMES pasty solid (300 mg of which ~150 mg are UFAs) was dissolved in 2 mL of ethyl acetate (AcOEt, C₄H₈O₂ > 99.9% GC from Carl Roth) and incorporated in a mixture of 8 mL of distilled water and 4 mL of acetonitrile (MeCN, C₂H₃N > 99.98% GC) to form a biphasic solution. Afterwards, 8 equivalents (870 mg) of NaIO₄ (sodium metaperiodate, >99% from Sigma-Aldrich) along with 100 mg of either CBO-PDA-Ru(2%), or CCN-PDA-Ru(2%), were introduced in the reactor and stirred for 24 h at room temperature. In another series of tests, 4 equivalents (291 mg) of Methylmorpholine N-oxide monohydrate (NMO, C₅H₁₁NO₂·H₂O, 98+% from Alfa Aesar) was combined with 4 equivalents of NaIO₄ and used at the place of the 8 equivalents of NaIO₄ to assess the influence of NMO in the oxidative cleavage reaction. Catalytic tests were monitored by gas chromatography (GC) after injecting samples from the organic phase at different time intervals. Methyl azelate (MA) and pelargonic acid (PA) are obtained from the oxidative cleavage of methyl oleate while MA, malonic and hexanoic acids are produced from methyl linoleate (Scheme 5.2). Calibration curves of methyl oleate (MO, C₁₉H₃₆O₂, >99.9% GC from Carl Roth), methyl linoleate (ML, C₁₉H₃₄O₂, >99.9% GC from TCI chemicals) and monomethyl azelate (MA, C₁₀H₁₈O₄, >97% GC from TCI chemicals) are displayed in Figures S5.1-S5.3 while conversion, yield and selectivity are detailed in the section S.2 of the corresponding supporting information. Recycling tests were performed in order to assess the stability of the synthesized catalysts in the

oxidative cleavage of UFAs from palm oil. The reaction was also monitored by UV-Visible spectrophotometry in a UV-3600 Plus Shimadzu spectrophotometer in order to determine the presence of Ru species during catalytic tests.

2.3. Azelaic acid isolation

Once a catalytic test ended, the organic layer was separated by means of a syringe. Then, three consecutive extractions were conducted with 2 mL of AcOEt in order to ensure that all MA and PA were recovered from the aqueous phase. Then, the AcOEt layer was evaporated using a rotary evaporator at 50 °C in order to obtain the oxidative cleavage products as a paste. The latter was incorporated in 5 mL 2 M KOH-MeOH solution to transform all methyl esters into carboxylic acids. The reaction was quenched with the addition of 5 mL of distilled water and the suspension was heated at 90 °C for 15 minutes in order to dissolve all azelaic acid in warm H₂O (only AA is soluble in warm water [107]). The aqueous solution was separated from the organic phase with a syringe and placed in a vessel. Once the aqueous solution cooled down at room temperature, azelaic acid precipitated. The as obtained product was weighed and dissolved in 3 mL of deuterated chloroform (CDCl₃, 99.8% from Euristop) to confirm the extraction of azelaic acid by means of Nuclear Magnetic Resonance (NMR) spectroscopy. For this purpose, the sample was analyzed in a Liquid-state Nuclear Magnetic Resonance Bruker Avance II 300 MHz equipped with a BBFO 5 mm NMR probe z-gradient coil. The ¹H spectrum was recorded after 16 scans using a spectral window up to 16 ppm with a relaxation delay of 3 seconds using the singlet signal of CDCl₃ for the zero calibration. The ¹H spectrum was treated with MestReNova software.

3. Results and Discussion

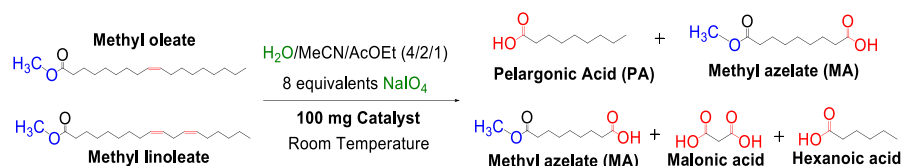
3.1. Lipidic profile of Ecuadorian palm oil

The lipidic profile of palm oil was obtained thanks to the assistance of Prof. Yvan Larondelle group in the Louvain Institute of Biomolecular Science and Technology. Table 5.1 shows FAs concentration inside Ecuadorian palm oil. The main component is oleic acid, which means that this vegetable oil can be used for the production of azelaic acid through the oxidative cleavage reaction of this UFA. Moreover, palm oil also contains a significant fraction of linoleic acid which is a poly-UFA with two unsaturations in C9 and C12. The presence of this UFA is interesting since through the scission of its carbon-carbon double bonds, it would be possible to synthesize azelaic acid as is demonstrated in Scheme 5.2. Therefore, the valorization of this palm oil by means of the oxidative cleavage of oleic and linoleic acids would yield a surplus of a value-added product such as azelaic acid. The chromatogram in Figure S5.4 shows the peaks which correspond to the different SFAs and UFAs within palm oil. Around 50% of FAs composition are related to SFAs being palmitic acid the most abundant of them.

Table 5.1. Fatty acids concentration in Ecuadorian palm oil

Fatty acid	Composition (wt%)
Myristic acid (C14:0)	0.5
Palmitic acid (C16:0)	40.1
Stearic acid (C18:0)	6.2
Oleic acid (C18:1)	41.5
Linoleic acid (C18:2)	9.1
Others	1.8

Stearic and myristic acids are in minor extent but the key question is if these SFAs can interfere with the normal ongoing of the oxidative cleavage of oleic and linoleic acids. To answer this question, triglycerides in palm oil were hydrolyzed as was stated in the experimental section and all FAs in form of FAMES were incorporated to our catalytic system formed by H₂O/MeCN/AcOEt (4/2/1).



Schem 5.2. Oxidative cleavage of oleic and linoleic acids

3.2. Catalytic tests

Figure 5.1a shows the catalytic activity displayed by CBO-PDA-Ru(2%) and CCN-PDA-Ru(2%) in the oxidative cleavage of UFAs within palm oil (conversions calculated based on the amount of methyl oleate and methyl linoleate within the oil). These reactions were carried out with 8 equivalents of sodium periodate and, as in the case of catalytic tests with pure oleic acid, both catalysts accomplished almost a complete conversion after 7 hours of reaction at room temperature. CCN-PDA-Ru(2%) presented a higher catalytic activity than CBO-PDA-Ru(2%) at the early stages of the catalytic test. This phenomenon is attributed to the higher surface area of calcined carbon particles (CCN) compared to CBO ones. These results demonstrate that other palm oil components (e.g. SFAs or minor components like carotenoids) were not detrimental to catalyst's performances in the oxidative cleavage reaction. In addition, yields and selectivity of PA were around 78% while MA yields were around 95%. It is worth to mention that a 20% of surplus is expected with MA since this product can be produced from methyl oleate (41% in palm oil) and from methyl linoleate (9% in palm oil). These results confirm that both carbon-polydopamine-Ru catalysts are as active and selective as in the case with pure oleic acid. Products distribution in Figure S5.5 confirms that a 6% surplus of MA is obtained because this product comes from the oxidative cleavage of both UFAs (i.e. methyl oleate and methyl linoleate).

When 4 equivalents of NaIO_4 along with 4 equivalents of NMO were incorporated to the reaction medium, the catalytic activity of CBO-PDA-Ru(2%) and CCN-PDA-Ru(2%) was greater than in the case with 8 equivalents of NaIO_4 (Figure 5.2a). In fact, the CCNs catalyst finished the oxidative cleavage reaction after only five hours of stirring at room temperature.

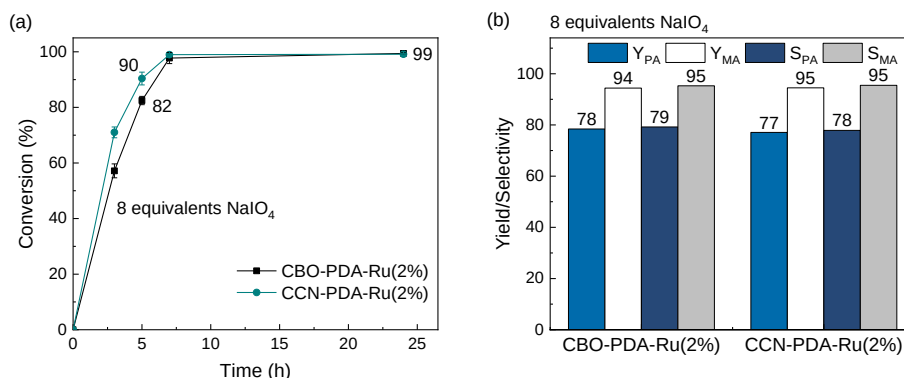


Figure 5.1. a) Catalytic activity and b) yields of PA and MA with of CBO-PDA-Ru(2%) and CCN-PDA-Ru(2%) along with 8 equivalents of NaIO_4

Hence, as with pure oleic acid, the addition of a greener co-oxidant allowed to improve the performance of both carbon catalysts without using great amounts of a strong oxidizing agent such as NaIO_4 . As regards the production of PA and MA, Figure 5.2b shows yields and selectivity ~90% ascribed to pelargonic acid and yields/selectivities around 74% as regard methyl azelate. These results were also similar to those observed when pure oleic acid was used in the oxidative cleavage tests. Therefore, the evidences displayed in Figures 5.1 and 5.2 confirm that it is possible to perform efficiently the valorization of palm oil with our catalytic system without any concern about interferences from SFAs or other minor components within this vegetable oil.

During the catalytic assessment of Ru-carbon catalysts in the oxidative cleavage of pure oleic acid, it was demonstrated that Ru got dissolved in the liquid phase during the catalytic tests. To verify this possibility with palm oil, UV-Visible monitoring analyses were conducted on the organic phase during catalytic tests with CBO-PDA-Ru(2%) and CCN-PDA-Ru(2%). The spectra displayed in Figure S5.6 confirm that both $\text{Ru}^{\text{VIII}}\text{O}_4$ and $\text{H}_2\text{Ru}^{\text{VI}}\text{O}_4$ species are present in the organic phase at early stages of the reaction. The former species is that responsible for triggering the oxidative cleavage of UFAs by means of a pericyclic [3+2] reaction yielding a perruthenate intermediate. On the other hand, $\text{H}_2\text{Ru}^{\text{VI}}\text{O}_4$ species is the outcome from the perruthenate decomposition. This Ru^{VI} species can be re-oxidized to $\text{Ru}^{\text{VIII}}\text{O}_4$ by means of NMO or NaIO_4 . Moreover, both Ru species are no longer present in the

organic phase at the end of the catalytic tests. These findings suggest that PDA functional groups on CBO and CCN surface re-adsorbed Ru from the reaction medium as it was observed in the previous catalytic tests with pure oleic acid.

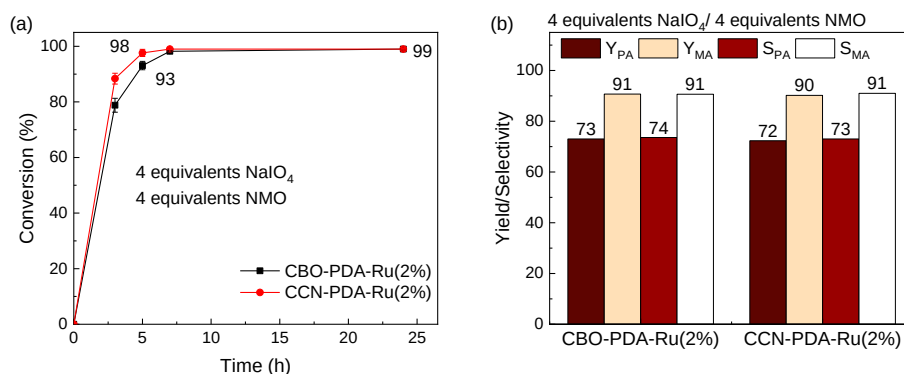


Figure 5.2. a) Catalytic activity and b) yields of PA and MA with of CBO-PDA-Ru(2%) and CCN-PDA-Ru(2%) along with 4 equiv. NaIO₄ + 4 equiv. NMO

The stability of both carbon catalysts was verified through recycling tests. Figure 5.3 demonstrates that CBO-PDA-Ru(2%) and CCN-PDA-Ru(2%) maintain their catalytic activity up to five consecutive catalytic tests. Only a slight drop of performance is noted, as likely due to unavoidable loss of catalyst when transferring it from one run to the next one.

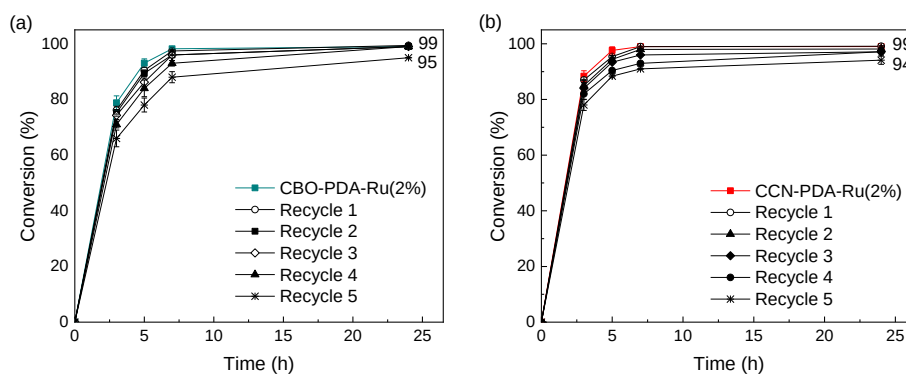


Figure 5.3. Recycling tests of a) CBO-PDA-Ru(2%) and b) CCN-PDA-Ru(2%) with 4 equiv. NaIO₄ / 4 equiv. NMO

These results along with Ru loadings on spent catalysts (Table 5.2) confirm that the real benefit of polydopamine lies in its capability to recover Ru species from the reaction medium. In this manner, the same catalytic activity

is assured in subsequent catalytic tests. In addition, all the information gathered in this work suggest that SFAs and other minor components of palm oil did not hinder the interaction of Ru species with UFAs. This is in line with the fact that the catalyst performances with this vegetable oil were similar as in the case with pure oleic acid.

Table 5.2. Ru loading on spent catalysts

Catalyst	Nominal Ru (wt%) ^a	Ru loading (wt%) ^b
Fresh CBO-PDA-Ru(2%)	2.0	1.9
Fresh CCN-PDA-Ru(2%)	2.0	1.8
Spent CBO-PDA-Ru(2%)	2.0	1.8
Spent CCN-PDA-Ru(2%)	2.0	1.7

^aNominal composition corresponding to the precursor solution. ^bRu loading determined by ICP-AES.

Isolated yields of azelaic acid with our two Ru-based functionalized carbon catalyst are reported in Table 5.3. The obtained white product was characterized by NMR spectroscopy (Figure S5.7) confirming that indeed azelaic acid was separated from the organic phase. These results demonstrate that both catalysts are efficient towards the production of this added-value product from UFAs in palm oil. Therefore, the methodology applied to isolate azelaic acid from the rest of components within the organic phase was efficient since the isolated yields are close to those calculated from GC results. Table 5.4 recapitulates the performances achieved by all catalysts discussed in this thesis and compared with the most promising ones found in literature. Yields of PA and AA reached in this work by our best carbon catalysts are better than those reported by Rup *et al.* [114] (78% AA) in homogeneous catalysis, or those obtained by Ho and co-workers [147] (79% AA) in heterogeneous catalysis.

Table 5.3. Isolated yields of azelaic acid

Catalyst	Conversion (%)	Azelaic acid (wt%)
CBO-PDA-Ru(2%)	>99	81±2
CCN-PDA-Ru(2%)	>99	80±3

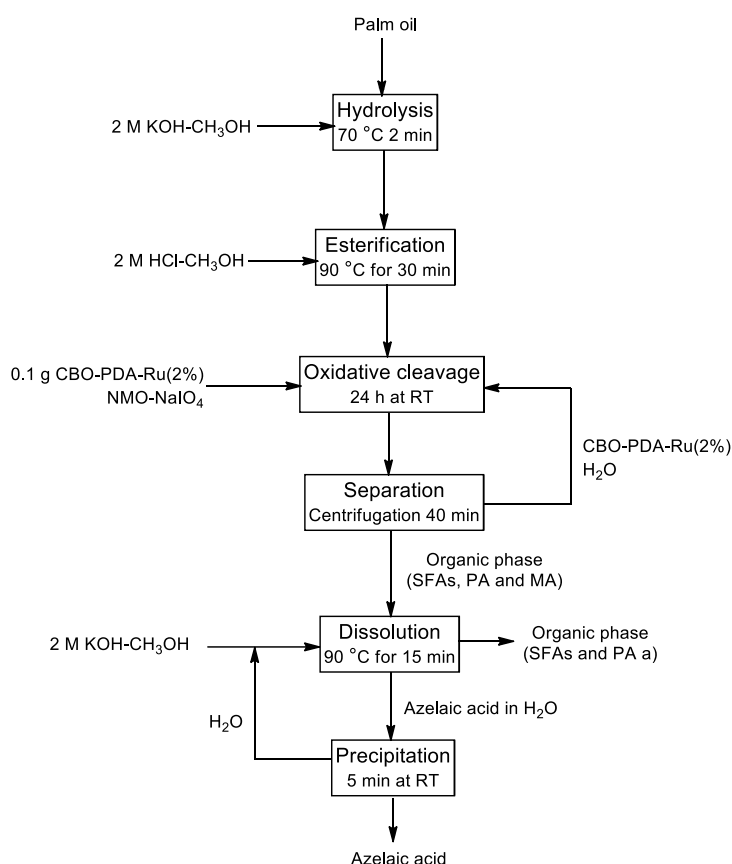
By this way, it is possible to propose a simple process to produce azelaic acid from a cheap and abundant feedstock such as palm oil. Scheme 5.3 recapitulates the main steps required for the production of this dicarboxylic acid without the need to separate UFAs from the vegetable oil. First, palm oil is submitted to hydrolysis along with a 2 M KOH-methanol solution in order to release all FAs within the feedstock. During this process some FAs can be transformed into FAMES. To standardize the blend, all free FAs from the previous step were transformed into FAMES by means of a 2 M HCl-MeOH solution.

Table 5.4. Summary of all catalysts synthesized in this work

Catalyst	Substrate	Oxidant	Solvent	Conditions	Conv. (%)	Yield (%)	Reference
ACO-Ru(2%)	Oleic acid	8 equiv. NaIO ₄	H ₂ O/MeCN/AcOEt	RT, 24 h	53	PA=10 AA=10	This work
CBO-Ru(2%)	Oleic acid	8 equiv. NaIO ₄	H ₂ O/MeCN/AcOEt	RT, 24 h	>99	PA=75 AA=75	This work
CBO-bpy(NHS/EDC)-Ru(2%)	Oleic acid	8 equiv. NaIO ₄	H ₂ O/MeCN/AcOEt	RT, 24 h	>99	PA=96 AA=96	This work
CBO-bpy(SOC ₁₂)-Ru(2%)	Oleic acid	8 equiv. NaIO ₄	H ₂ O/MeCN/AcOEt	RT, 7 h	>99	PA=76 AA=76	This work
CBO-PDA-Ru(2%)	Oleic acid	8 equiv. NaIO ₄	H ₂ O/MeCN/AcOEt	RT, 7 h	>99	PA=95 AA=95	This work
CN-Ru(%)	Oleic acid	8 equiv. NaIO ₄	H ₂ O/MeCN/AcOEt	RT, 24 h	>99	PA=36 AA=35	This work
CCN-Ru(%)	Oleic acid	8 equiv. NaIO ₄	H ₂ O/MeCN/AcOEt	RT, 7 h	>99	PA=90 AA=91	This work
CCN-PDA-Ru(%)	Oleic acid	8 equiv. NaIO ₄	H ₂ O/MeCN/AcOEt	RT, 7 h	>99	PA=94 AA=94	This work
RuO ₄	Oleic acid	4 equiv. NaIO ₄	H ₂ O/MeCN/AcOEt	1 h, UI	>99	PA=88 AA=78	114
WO ₃ /SiO ₂	Oleic acid	11 equiv. H ₂ O ₂	tBuOH	130 °C, 1 h	96	PA=36 AA=32	133
WO ₃ .0.33H ₂ O	Oleic acid	14 equiv. H ₂ O ₂	tBuOH	120 °C, 5 h	>99	PA=69 AA=77	140
Ru/HAP	Methyl oleate	2 equiv. NaIO ₄	1,2dichloroethane/ H ₂ O	RT, 12 h	16	PA=84 MA= 79	147

RT: room temperature; PA: pelargonic acid; MA: methyl azelate; AA: azelaic acid; MeCN: acetonitrile; AcOEt: ethyl acetate;

Next, all FAMES (which include saturated and unsaturated ones) along with minor components (e.g. carotenoids) are incorporated to the catalytic system (i.e. the biphasic solution of $\text{H}_2\text{O}/\text{MeCN}/\text{AcOEt}$: 4/2/1). The oxidative cleavage reaction takes place during 24 h at room temperature using our Ru-carbon catalysts functionalized with PDA. Although the complete transformation of UFAs into carboxylic and dicarboxylic acids can be accomplished in five hours using NMO-NaIO_4 (4 equiv-4equiv), the reaction must proceed in order to ensure a complete recovery of Ru species from the reaction medium by PDA functional groups. In this way, the catalyst maintains the same catalytic activity for several runs.



Scheme 5.3. Proposed procedure for palm oil valorization through oxidative cleavage of UFAs for azelaic acid production

Then, the solid catalyst and the aqueous phase should be separated by physical means and recycled into the next oxidative cleavage process to reuse the catalyst and avoid losses of Ru (which can be also detrimental for the environment). The organic phase is then treated with a 2 M KOH-MeOH solution in order to transform all FAMES into carboxylic acids. Finally, the

organic phase is mixed with distilled H₂O at 90 °C to solubilize AA in the aqueous phase. After separating water from the organic phase, the aqueous solution is allowed to cool down at room temperature to promote the precipitation of azelaic acid as white crystals. Thus, this proposed and simple methodology can be implemented for the valorization of palm oil in regions where these natural feedstock is abundant and cheap, yielding high value products such as azelaic acid.

4. Conclusions

Oxidized carbon black (CBO) and calcined carbon submicrometric particles (CCN) were functionalized with polydopamine (PDA) and Ru in order to perform the oxidative cleavage of UFAs contained in a real natural vegetable oil, precisely Ecuadorian palm oil. Both Ru based carbon catalysts successfully produced pelargonic and azelaic acids in high yields from UFAs. The addition of NMO as a co-oxidizing agent decreased by about 30% the time required to complete the transformation of UFAs into the desired oxidative cleavage products. The monitoring of the catalytic tests by means of gas chromatography demonstrated that the valorization of Ecuadorian palm oil through the oxidative cleavage of UFAs can be performed under soft and sustainable conditions using our developed carbon catalysts.

The lipidic profiling indicated that several SFAs were inside the Ecuadorian palm oil. Although these SFAs and other minor compounds (e.g. carotenoids) were significantly present in the blend, they were not an impediment for the normal ongoing of the oxidative cleavage reaction. Recycling tests demonstrated that conversions were greater than 95% even after 5 consecutive catalytic tests along with high yields towards the oxidative cleavage products. UV-Visible monitoring showed that Ru^{VIII}O₄ and H₂Ru^{VI}O₄ were in the reaction medium performing the oxidative cleavage reaction in the same way as in the case with pure oleic acid. These combined results clearly confirm that SFAs and other minor components in palm oil do not interfere in the oxidative cleavage reaction with Ru-carbon catalysts.

To submit a vegetable oil to the oxidative cleavage of UFAs, it is advisable to conduct a hydrolysis step with a KOH-MeOH solution to break triglycerides and to release all FAs. Since in this step some FAs can be transformed into FAMES, an esterification is advised to complete the transformation of all FAs into FAMES using a HCl-MeOH solution. Then, the whole blend can be incorporated to the biphasic solution made of H₂O/MeCN/AcOEt (4/2/1) to perform the reaction using our carbon-PDA-Ru(2%) solid catalysts along with 4 equivalents of NMO and 4 equivalents of NaIO₄. The reaction takes place at room temperature and after 24 h of agitation, azelaic acid can be separated quite easily from the rest of the blend by adding a 2 M KOH-MeOH solution (to transform monomethyl azelate into azelaic acid) and the

addition of distilled H₂O with a subsequent heating at 90 °C for 15 minutes (to solubilize AA in the aqueous phase).

This new proposed process with our Ru-carbon catalysts opens a novel route to the production of a high value-added product such as azelaic acid with medicinal applications from a cheap feedstock as palm oil.

GENERAL CONCLUSIONS

At the beginning of this research project, we wanted to design a reliable process for the oxidative cleavage of UFAs using Ru heterogeneous catalysts. For this purpose, two carbon supports, activated carbon (microporous material with high surface area) and carbon black (macroporous material with low surface area) were oxidized and impregnated with Ru to verify if they were adequate for the oxidative cleavage reaction. Oxidized activated carbon (ACO) was not suitable for this matter since Ru dispersion on this microporous material was lower than in the case of oxidized carbon black (CBO). Besides, the mean pore diameter of ACO is smaller than oleic acid molecular length which hinders the diffusion of UFAs inside micropores. Although CBO displayed greater performances in terms of conversion and yield than ACO, this macroporous catalyst started to lose catalytic activity after several catalytic tests. ICP-AES and XPS analyses confirmed that both carbon supports lost Ru after each oxidative cleavage test which diminished their performances. Therefore, it turned obvious the necessity to functionalize macroporous carbon black in order to improve its natural ability to retain Ru on its surface during the catalytic reaction. Thus, we decided to assess the efficiency of covalent functionalization techniques oriented to chelate Ru on the solid phase without losing catalytic activity.

Two functionalization techniques were applied on CBO surface: covalent functionalization using 4,4'-amino-2,2'-bipyridyl ($\text{NH}_2\text{-bpy}$) and a polymer functionalization with polydopamine (PDA). Through different spectroscopic techniques, it was demonstrated that $\text{NH}_2\text{-bpy}$ was indeed deposited on CBO surface through the binding between carboxylic acid groups on CBO surface and amines from bpy. In this way, pyridinic nitrogens were free to form a complex with Ru in order to form a heterogeneous catalyst. As regards PDA, dopamine chloride was successfully polymerized under alkaline conditions using trishydroxymethyl aminomethane as buffer. The formation and deposition of the polymer on CBO surface was confirmed as well as the Ru impregnation of the functionalized solid. CBO-bpy-Ru(2%) and CBO-PDA-Ru(2%) were both active in the oxidative cleavage of oleic acid but only the latter was stable throughout the recycling tests. Post-characterization tests revealed that $\text{NH}_2\text{-bpy}$ was detaching after several catalytic tests. As a consequence, the catalytic activity of CBO-bpy-Ru(2%) diminished little by little after each run due to Ru losses. On the other hand, the catalyst bearing PDA maintained its catalytic activity up to 5 consecutive catalytic tests confirming the stability of CBO-PDA-Ru(2%). Thus, the latter catalyst was thoroughly studied to determine the key aspects related to its performance towards the oxidative cleavage of oleic acid.

Monitoring tests carried out with gas chromatography and NMR spectroscopy determined that several intermediates were formed during the oxidative cleavage of oleic acid. In addition, UV-Visible monitoring tests showed that $\text{Ru}^{\text{VIII}}\text{O}_4$ and $\text{H}_2\text{Ru}^{\text{VI}}\text{O}_4$ species were present in the organic

liquid phase during the catalytic tests. These findings confirmed that the oxidative cleavage with CBO-PDA-Ru(2%) takes place mostly in the liquid phase through the Ru species already mentioned. The proposed mechanism begins with the transformation by NaIO_4 of the Ru^{III} -catecholate complex on the catalyst support into soluble $\text{Ru}^{\text{VIII}}\text{O}_4$. This Ru species reacts with double bond from oleic acid to produce a perruthenate ester which is hydrolyzed into a diol (9,10 dihydroxystearic acid) and $\text{H}_2\text{Ru}^{\text{VI}}\text{O}_4$. The latter is then re-oxidized by the oxidant while the diol is transformed into nonanal and 9-oxononanoic acid by a second intervention of the same oxidizing agent. Both intermediates are over-oxidized by $\text{Ru}^{\text{VIII}}\text{O}_4$ and/or NaIO_4 into pelargonic and azelaic acids respectively. As regards the solid catalyst, FTIR and XPS analyses revealed that NaIO_4 oxidizes catechol groups of PDA into quinones. Finally, it was also confirmed that all Ru in the reaction medium returned to CBO-PDA surface after the reaction. Therefore, we concluded that CBO-PDA-Ru(2%) functions as a boomerang catalyst as it releases Ru in the reaction medium to perform the oxidative cleavage reaction along with the oxidizing agent and once the reaction ends, the functionalized support recaptures Ru species to maintain the same performance for several runs.

In order to improve the performance of CBO-PDA-Ru(2%), calcined carbon submicrometric particles (CCNs) were synthesized and functionalized with PDA. This new carbon support was synthesized by hydrothermal carbonization of an aqueous glucose solution under autogenous pressure. Well distributed carbon spheres were synthesized and displayed the highest amount of oxygenated groups of all tested carbon materials in this thesis. After a calcination step under air, the mean particle size of these carbon spheres diminished along with the creation of some porosity which increased their specific surface area. The functionalization of CCNs with PDA was confirmed as well as the deposition of Ru. During the oxidative cleavage tests, CCN-PDA-Ru(2%) catalysts yielded similar results in terms of conversion and selectivity than the previously tested CBO-PDA-Ru(2%) catalyst. Moreover, CCN-PDA-Ru(2%) remained active after 5 recycles confirming the benefit provided by PDA functional groups. In order to produce a greener catalytic system, N-Methylmorpholine N-oxide (NMO) was combined with NaIO_4 to decrease the excess of the latter in previous catalytic tests. NMO is an amine oxide which can re-oxidize $\text{H}_2\text{Ru}^{\text{VI}}\text{O}_4$ into $\text{Ru}^{\text{VIII}}\text{O}_4$ during the oxidative cleavage reaction. Moreover, NMO is not considered as toxic (whereas NaIO_4 is toxic for aquatic life) nor bioaccumulative. Whereas making the process more sustainable, the addition of this amine oxide into the catalytic system contributed to reduce the reaction time by about 30% with yields of pelargonic and azelaic acids still around 85%.

Finally, CBO-PDA-Ru(2%) and CCN-PDA-Ru(2%) were assessed in the oxidative cleavage of real Ecuadorian palm oil. The lipidic profile of this natural feedstock revealed the presence of 41% of oleic acid and 9% of linoleic acid. To carry out the oxidative cleavage reaction, palm oil triglycerides were first hydrolyzed to transform all FAs into their corresponding methyl esters (FAMES). The whole blend (i.e. FAMES of SFAs

and UFAs along with minor components of palm oil) were incorporated to our conventional biphasic H₂O/MeCN/AcOEt system to perform the oxidative cleavage reaction with our two best mentioned carbon catalysts and the combination NMO / NaIO₄ as oxidizing agents. Both Ru-carbon catalysts achieved >99% conversion within 5 h of reaction at room temperature with yields towards monomethyl azelate around 85%. These results confirmed that the oxidative cleavage reaction can take place with a complex blend formed by different components without any concern that one of them would hinder carbon catalysts performances. Recycling tests also demonstrated that our carbon-PDA-Ru catalysts maintained the same catalytic activity after several runs confirming that functional groups of PDA can recover Ru species even if other compounds are present in the reaction medium.

All the findings gathered throughout this thesis have permitted to design reliable and robust carbon catalysts that combine the advantages of homogeneous (high activity) and heterogeneous (reusability) catalysis. The deposition of polydopamine on support surface improved the ability of carbon materials to complex Ru species. Nevertheless, the main contribution of PDA lies in the boomerang mechanism which enables the catalyst to release Ru into the reaction medium to perform the reaction and to recover it once it ends, so maintaining the integrity of the catalyst regardless the presence of big molecules such as SFAs and other natural components vegetable oils.

This new catalytic system which uses NMO and NaIO₄ as oxidizing agents, opens a new route for the synthesis of value-added products (e.g. azelaic acid) from an abundant, renewable and cheap feedstock like palm oil. We believe that the new established procedure for the valorization of vegetable oils might have societal consequences especially for the development of poor countries where this kind of biomass derivatives are abundant.

FUTURE WORK

The work carried out during this thesis has demonstrated that the functionalization of carbon supports with polydopamine can contribute enormously to the performance and stability of Ru-carbon catalysts in the oxidative cleavage of UFAs. Nevertheless, some aspects could be studied to improve the knowledge of these catalysts' performances in this reaction. For instance, carbon-PDA-Ru catalysts have been tested with 4 and 8 equivalents of NaIO_4 . In both cases Ru was present as $\text{Ru}^{\text{VIII}}\text{O}_4$ and PDA functional groups were able to recover Ru species from the liquid phase. However, no tests were conducted to verify the PDA capability to recover Ru at higher NaIO_4 concentrations (i.e. > 8 equivalents). In addition, the effect of greater NaIO_4 concentrations over Ru species during the oxidative cleavage tests should be investigated as well. These proposed studies can give some clues about the limits of carbon-PDA-Ru catalysts in the oxidative cleavage of UFAs.

Other aspect to investigate is related to the scope of raw material submitted to the oxidative cleavage. In this work we focused in Ecuadorian palm oil because it was abundant and cheap in the region from where the authors of this thesis originates. Therefore, it could be interesting to verify the behavior of our carbon-PDA-Ru catalysts in the oxidative cleavage of UFAs from different vegetable oils. For instance, olive oil, sunflower oil, coconut oil among others can be exploited for the production of different carboxylic and dicarboxylic acids beyond pelargonic and azelaic acids. For example, brown flaxseed oil possesses about 56% of linolenic acid (C18:3) and through its oxidative cleavage it could be possible to produce malonic as well as azelaic acids.

During the monitoring of the reaction, it was possible to determine that several intermediates were present in the reaction medium. Among them, aldehydes were formed as a consequence of the carbon-carbon double scission. These aldehydes were transformed into their corresponding carboxylic or dicarboxylic acids by means of the oxidizing agent. However, it could be interesting to adjust the reaction conditions in order to obtain aldehydes (which are also quite valuable in organic synthesis) instead of the final carboxylic acids. The decrease of temperature, the reaction time along with lower Ru loadings and less NaIO_4 equivalents are the key parameters to explore in order to produce aldehydes from UFAs.

Although PDA managed to recover Ru from the reaction medium, this transition metal is not well considered by green chemistry because of its toxicity and shortage. To date, scientists look for non-noble transition metals to carry out the different catalytic reactions with biomass derivatives. Since Os and Ru (group eight elements) have shown to be quite active in the oxidative cleavage of UFAs, it could be interesting the assess Fe or Mn in this matter. There is evidence that Fe and Mn oxides are active in the oxidative cleavage of aromatic alkenes such as styrene to yield

benzaldehyde. No attempts have been made to assess the suitability of such iron compounds in the oxidative cleavage of larger molecules such as UFAs. Therefore, it could be interesting to design a new heterogeneous system made with iron spinels towards the valorization of vegetable oils through the carbon-carbon double bond scission of UFAs.

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LIST OF PUBLICATIONS AND COMMUNICATIONS

1. Publications

Gámez, S., de la Torre, E., & Gaigneaux, E. M. (2022). Carbon black-polydopamine-ruthenium composite as a recyclable boomerang catalyst for the oxidative cleavage of oleic acid. *Chemical Engineering Journal*, 427. <https://doi.org/10.1016/j.cej.2021.131820>.

Gámez, S., de la Torre, E., & Gaigneaux, E. M. Carbon supports for the oxidative cleavage of oleic acid: influence of textural properties. Accepted, *Molecular Catalysis*. <https://doi.org/10.1016/j.mcat.2022.112797>.

Gámez, S., Magerat, A., de la Torre, E., & Gaigneaux, E. M. Functionalization of carbon black for Ru complexation towards the oxidative cleavage of oleic acid. Submitted.

Gámez, S., de la Torre, E., & Gaigneaux, E. M. (2022). Ru on Modified Carbon Submicrometric Spheres as Novel Catalysts for the Oxidative Cleavage of Oleic Acid with N-methylmorpholine-N-oxide as Green Oxidizing Agent. Accepted, *ChemCatChem*. <https://doi.org/10.1002/cctc.202201134>.

Gámez, S., de la Torre, E., & Gaigneaux, E. M. Palm oil valorization through the oxidative cleavage of unsaturated fatty acids with Ru-carbon catalysts. Submitted.

2. Oral communications

1. Ru carbon catalyst for the oxidative cleavage of UFAs in Palm oil

Sebastian Gamez, Ernesto de la Torre and Eric Gaigneaux

Oral presentation at th World Congress on Oxidation Catalysis Oxidation for a Sustainable Future and Clean Environment, Cardiff, (UK), September 4-8, 2022.

2. Carbon-Polydopamine-Ru composites towards Palm oil valorization

Sebastian Gamez, Ernesto de la Torre and Eric Gaigneaux

Oral presentation at the Carbon congress 2022, London, (UK), July 3-8, 2022.

3. Carbon black-Polydopamine-Ruthenium composite as a recyclable boomerang catalyst for the oxidative cleavage of oleic acid.

Sebastian Gamez, Ernesto de la Torre and Eric Gaigneaux

Oral presentation at the 5th International Symposium on Green Chemistry (ISGC 2022), La Rochelle, (France), May 16-20, 2022.

4. Carbon nanoparticles-Ru composites as an eco-friendly catalyst for the valorization of oleic acid.

Sebastian Gamez, Ernesto de la Torre and Eric Gaigneaux

Oral presentation at the 5th International Symposium on Green Chemistry (ISGC 2022), La Rochelle, (France), May 16-20, 2022.

5. Palm Oil valorization through azelaic acid production on Ru-carbon catalysts.

Sebastian Gamez, Ernesto de la Torre and Eric Gaigneaux

Oral presentation at the 5th International Symposium on Green Chemistry (ISGC 2022), La Rochelle, (France), May 16-20, 2022.

6. Carbon Black-Polydopamine-Ruthenium composite as an efficient and recyclable boomerang catalyst for the oxidative cleavage of oleic acid

Sebastian Gamez, Ernesto de la Torre and Eric Gaigneaux

Oral presentation at the European Federation of Catalysis Societies (EFCATS), Ljubljana, (Slovenia), September 15-19, 2020.

3. Poster communications

1. Carbon Black-Polydopamine-Ruthenium composite as an efficient and recyclable boomerang catalyst for the oxidative cleavage of oleic acid.

Sebastian Gamez, Ernesto de la Torre and Eric Gaigneaux

Poster presentation at the International Conference of Environmental Catalysis Congress (ICEC), Manchester, (UK), September 7-9, 2020.

2. Elucidating the mechanism of oleic acid oxidative cleavage on carbon black-polydopamine-Ru composites

Sebastian Gamez, Ernesto de la Torre and Eric Gaigneaux

Poster presentation at the PhD Students's Day 2021, Louvain-la-Neuve, (Belgium), 21th May, 2021.

3. Carbon Black-Polydopamine-Ru composite as a boomerang catalyst for the valorization of oleic acid

Sebastian Gamez, Ernesto de la Torre and Eric Gaigneaux

Poster presentation at the Journée scientifique de la Société Royale de Chimie (RSC), Brussels, (Belgium), 14th october, 2021.

SUPPORTING INFORMATION

Experimental section

E.1. Boehm's titration example

In Table E.1.1. the information relative to concentrations and volumes of each reagent employed in this methodology is provided.

Table E.1. Bases concentration and volumes employed

Base	nHCl/nBase	[Base] (mol/L)	V _{Base} (L)	V _{aliquot} (L)
NaOH	1	0.05	0.05	0.01
Na ₂ CO ₃	2	0.05	0.05	0.01
NaHCO ₃	1	0.05	0.05	0.01

Unlike the other bases, the ratio nHCl/nNa₂CO₃ = 2 because this base requires 2 moles of HCl to be completely neutralized. The data gathered for the calculation of oxygenated groups from ACO is described below.

Table E.2. Acidified and titration volumes

Base	[HCl] (mol/L)	V _{HCl} (L)	[NaOH] _t (mol/L)	V _{NaOHt} (L)
NaOH	0.057	0.02	0.05	0.0157
Na ₂ CO ₃	0.057	0.03	0.05	0.0155
NaHCO ₃	0.057	0.02	0.05	0.0140

As it was stated in the main Experimental section, NaOH provides the total acidity while Na₂CO₃ yields the moles of lactones and carboxylic acid. Moles of just carboxylic sites are obtained from NaHCO₃ titration. Thus, the moles of each oxygenated group can be calculated as follows:

$$n_{\text{Base}} = ((n_{\text{HCl}} / n_{\text{Base}}) \times [\text{Base}] \times V_{\text{Base}}) - ([\text{HCl}] \times V_{\text{HCl}} - [\text{NaOH}]_t V_{\text{NaOHt}}) \times (V_{\text{Base}} / V_{\text{Aliquot}}) \quad [\text{E.1.}]$$

Equation E.1. can be expressed in mmol/g of carbon material by dividing the previous results by the sample mass (0.5 g). Finally, the amount of phenol groups, lactones and carboxylic acids is obtained through the following equations:

$$n_{\text{NaOH}} = \text{Total Acidity} \quad [\text{E.2}]$$

$$\text{Phenols} = n_{\text{NaOH}} - n_{\text{Na}_2\text{CO}_3} \quad [\text{E.3}]$$

$$\text{Lactones} = n_{\text{Na}_2\text{CO}_3} - n_{\text{NaHCO}_3} \quad [\text{E.4}]$$

$$\text{Carboxylic acids} = n_{\text{NaHCO}_3} \quad [\text{E.5}]$$

The results obtained through this calculation procedure are summarized in Table 1.1.

E.2. Calibration Curves

Response factors (F_R) of all oxidative cleavage products including the intermediates found during the catalytic tests are summarized in Table E.2.1.

Table E.2.1. Response factors of organic compounds identified in the oxidative cleavage of oleic acid

Compound	F_R (mol C/mol IS)	Standard deviation
Oleic acid (OA)	0.75	0.08
Pelargonic acid (PA)	1.02	0.04
Azelaic acid (AA)	0.31	0.09
Nonanal (NA)	1.17	0.09
9-oxo nonanoic acid (Oxo)	0.41	0.08
9,10 dihydrixysearic acid (Diol)	0.79	0.08

With these values, calibration curves were calculated as follows:

$$\frac{C_C}{C_{IS}} = \frac{1}{F_R} \times \frac{A_C}{A_{IS}} \quad [\text{E.6}]$$

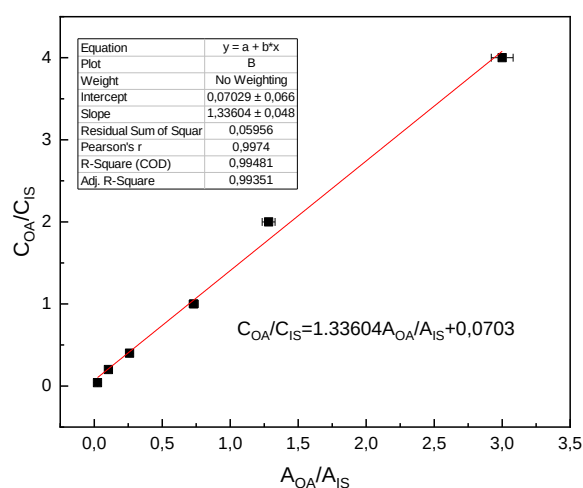


Figure E.1. Calibration curve of oleic acid

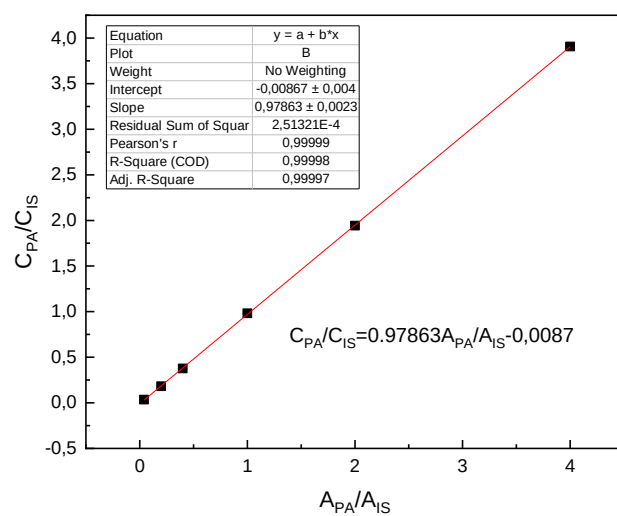


Figure E.2. Calibration curve of Pelargonic acid

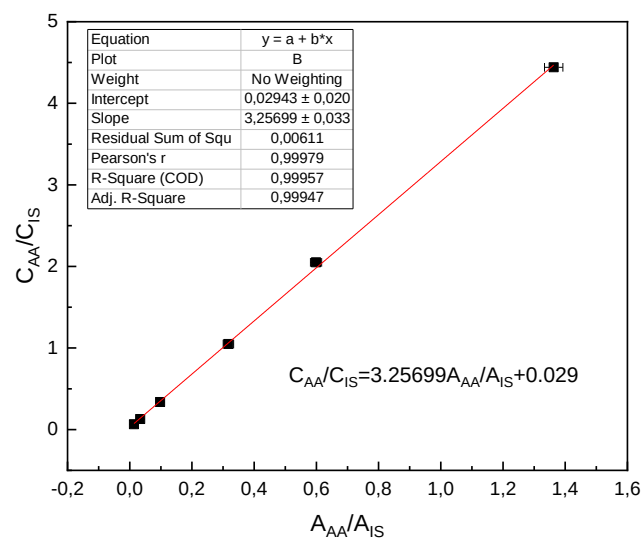


Figure E.3. Calibration curve of Azelaic acid

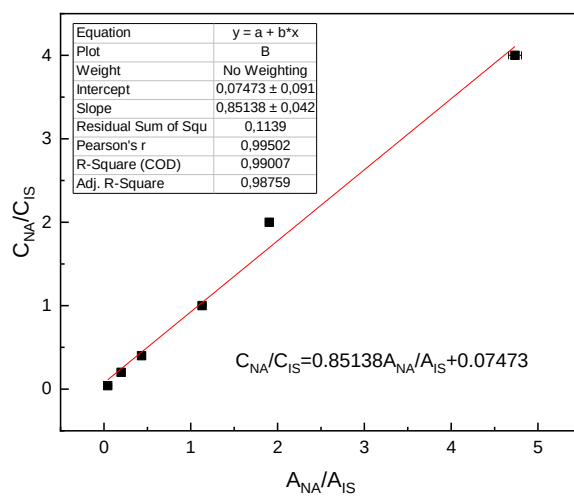


Figure E.4. Calibration curve of Nonanal

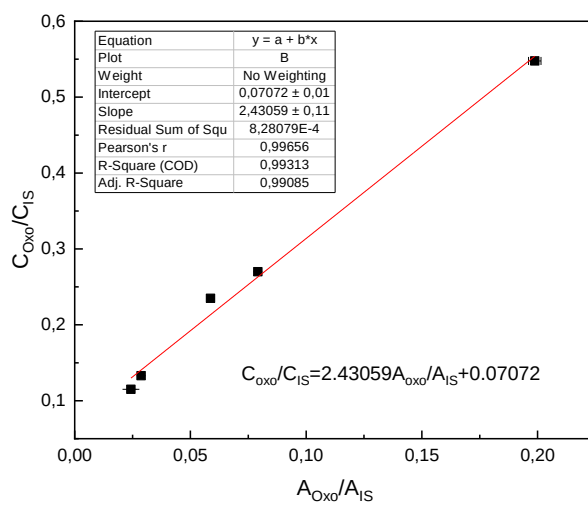


Figure E.5. Calibration curve of 9-oxo nonanoic acid

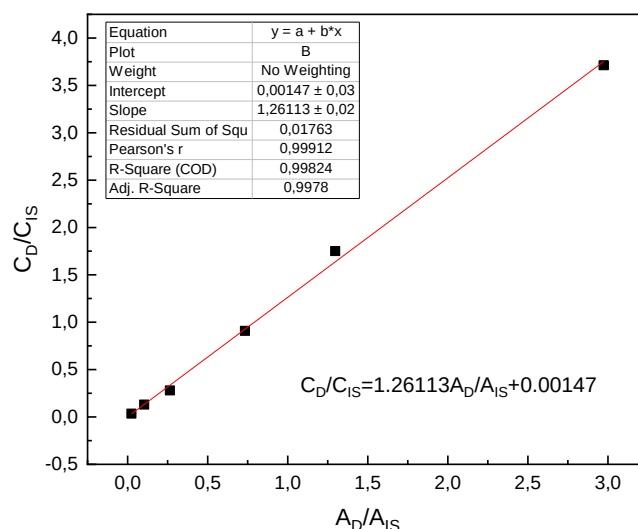


Figure E.6. Calibration curve of 9,10 dihydroxystearic acid

E.3. Partition coefficient calculation

At the end of each catalytic test, it was observed that the carbon balance relative to azelaic acid did not match. For this reason, the possibility that AA remained in the aqueous phase was explored. To measure the concentration of organic compounds the following procedure was applied. First, the organic layer was separated from the aqueous solution by means of a syringe. Then 2 mL of fresh AcOEt was added to the reactor and it was vortexed for 30 seconds. After the separation of the phases, the organic layer was extracted with a syringe and after dilution (0.1/1.5) in AcOEt the sample was analyzed in the GC. Table E3.1. shows an example of AA concentration in different extractions.

Table E3.1. Azelaic acid concentration in different extractions

Organic phase (mg/mL)	Extraction 1 (mg/mL)	Extraction 2 (mg/mL)	Extraction 3 (mg/mL)	Extraction 4 (mg/mL)
2.65	0.35	0.10	0.02	---

It is important to mention that no other components were detected in the aqueous layer after the extractions. This confirms that only AA is capable to form emulsions during the catalytic tests. Table E3.2. compiles the concentrations of AA in both phases from several catalytic tests in order to estimate the partition coefficient through Equation 8.

Table E3.2. Data employed for the calculation of the partition coefficient of Azelaic acid

Test	[AA] Organic (mg/mL)	[AA] Aqueous (mg/mL)	K _{AA}
1	2.15	0.36	0.170
2	1.49	0.27	0.180
3	1.89	0.33	0.176
4	1.91	0.33	0.175
5	2.01	0.35	0.175
6	2.50	0.43	0.171
7	2.80	0.50	0.178
8	2.66	0.45	0.170
9	2.65	0.46	0.174
10	1.65	0.29	0.175
11	1.96	0.34	0.176
12	1.88	0.32	0.169
13	1.78	0.31	0.175
14	2.65	0.46	0.174
15	2.44	0.43	0.176
16	2.56	0.45	0.176
17	2.65	0.47	0.176
18	2.63	0.46	0.174
19	2.74	0.49	0.180
20	2.61	0.46	0.175
Mean Partition Coefficient			0.175
Standard deviation			0.003

Supporting Information Chapter 1

S.1. Granulometric analysis of activated carbon

In this procedure about 100 g of AC was placed at the top of tower of sieves arranged in decreasing order with respect to their opening. After 30 min of shaking and beating the tower of sieves with a Lenoy Samar type LS8011 0.25 kW engine, the mass retained on each sieve was used to construct a semilogarithmic graph of the cumulative amount of material that passed the sieve (expressed in percentage) versus the sieve opening. An example is provided below.

Table S1.1. Data for d_{80} estimation of activated carbon

Sieve opening (mm)	Carbon Mass (g)	Mass retained (%)	Cumulative retained (%)	Cumulative passed (%)
3.36	45.90	44.96	44.96	55.04
2.38	38.10	37.32	82.27	17.73
2.00	12.50	12.24	94.52	5.48
1.41	3.40	3.33	97.85	2.15
1.19	0.20	0.20	98.04	1.96
1.00	1.10	1.08	99.12	0.88
0.71	0.10	0.10	99.22	0.78
< 0.71	0.80	0.78	100.00	0.00

The masses of carbon registered in column 2 are expressed in percentage in column 3. Then the cumulative retained and cumulative passed are calculated and used to plot the graphics shown in Figure 1.1.

S.2. Mass Titration method for PZC determination

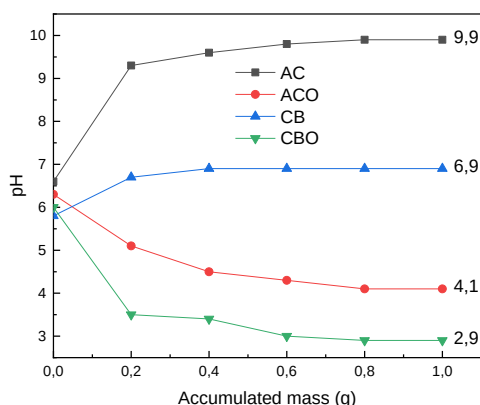


Figure S1.1. PZC of carbon materials by Mass titration method

S.3. Determination of oxygenated groups available for Ru complexation

As stated in the experimental section, the maximum Ru loading on CBO-composite is 2 wt%; therefore, the availability of OH groups for the complexation of Ru ions can be estimated as follows:

$$\frac{m_{\text{Ru}}}{m_{\text{Ru}} + m_{\text{support}}} \times 100\% = 2\% \rightarrow m_{\text{Ru}} = 10.20 \text{ mg Ru} \quad [\text{S1.1}]$$

$$\text{Ru atoms} = 0.0102 \text{ g Ru} \times \frac{1 \text{ atom-g Ru}}{101.07 \text{ g}} \times \frac{6.022 \times 10^{23} \text{ atom Ru}}{1 \text{ atom-g Ru}} = 6.08 \times 10^{19} \text{ Ru atoms} \quad [\text{S1.2}]$$

The amount of phenols in 500 mg of CBO and ACO is 0.22 and 0.40 mmol respectively. Then, the amount of OH groups available for Ru complexation is as follows:

CBO:

$$\text{OH groups} = 0.22 \times 10^{-3} \text{ mol} \times \frac{6.022 \times 10^{23} \text{ molecules}}{1 \text{ mol}} = 1.29 \times 10^{20} \text{ OH groups} \quad [\text{S1.3}]$$

ACO:

$$\text{OH groups} = 0.40 \times 10^{-3} \text{ mol} \times \frac{6.022 \times 10^{23} \text{ molecules}}{1 \text{ mol}} = 2.41 \times 10^{20} \text{ OH groups} \quad [\text{S1.4}]$$

The ratio of phenol groups/Ru atoms for each carbon support is as follows:

$$\text{CBO: } \frac{\text{OH}}{\text{Ru}} = \frac{1.29 \times 10^{20} \text{ groups}}{6.08 \times 10^{19} \text{ atoms}} = 2.1 \quad [\text{S1.5}]$$

$$\text{ACO: } \frac{\text{OH}}{\text{Ru}} = \frac{2.41 \times 10^{20} \text{ groups}}{6.08 \times 10^{19} \text{ atoms}} = 3.9 \quad [\text{S1.5}]$$

Hence, the amount of phenol groups available on CBO and ACO surface is in principle higher than the amount of Ru atoms required to obtain a load of 2 wt%.

S.4. XPS additional spectra

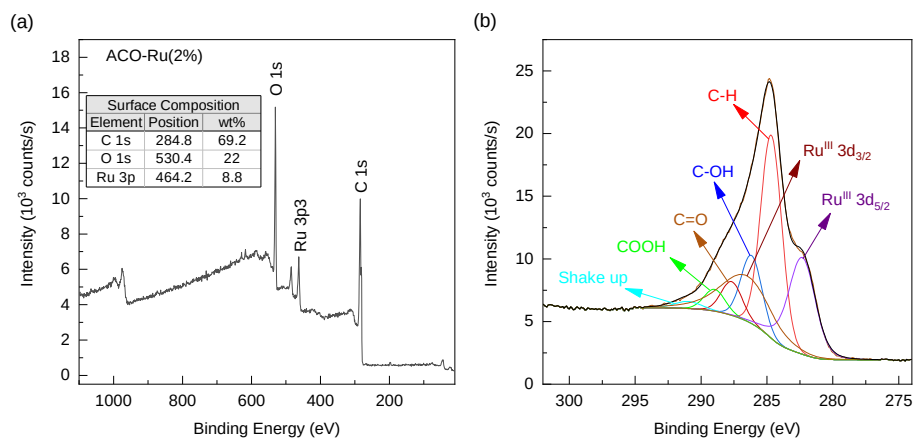


Figure S1.2. a) XPS survey and b) C 1s high resolution spectra of ACO-Ru(2%)

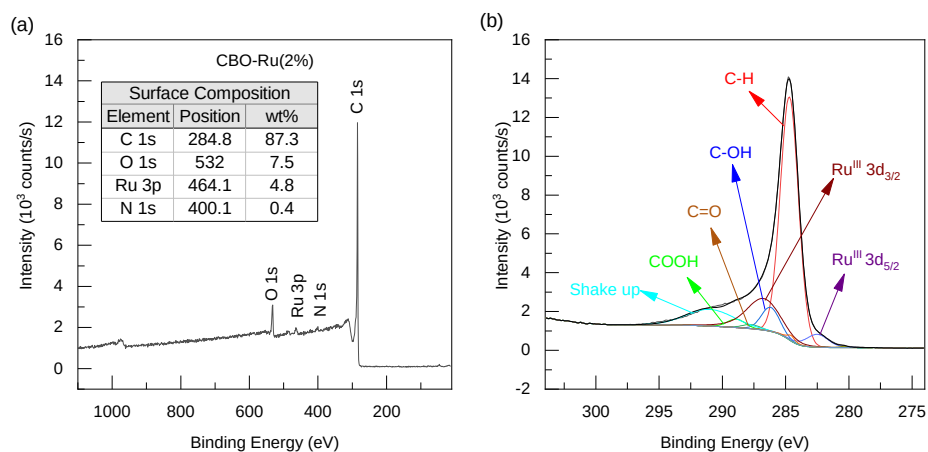


Figure S1.3. a) XPS survey and b) C 1s high resolution spectra of CBO-Ru(2%)

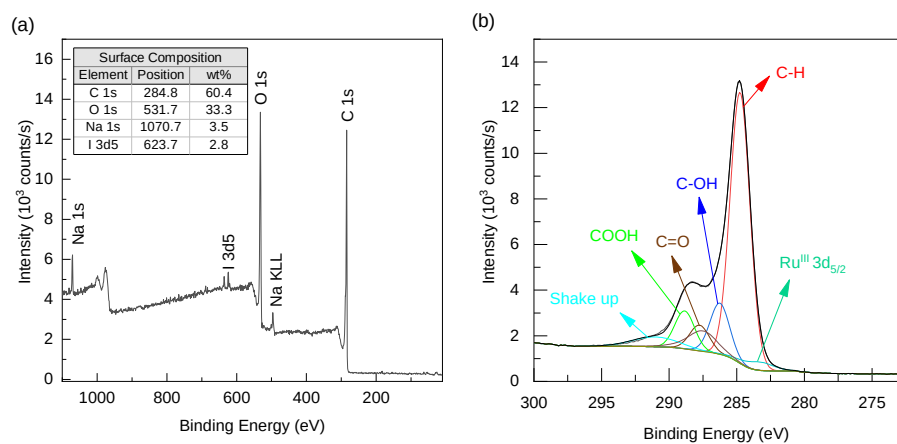


Figure S1.4. a) XPS survey and b) C 1s high resolution spectra of spent ACO-Ru(2%)

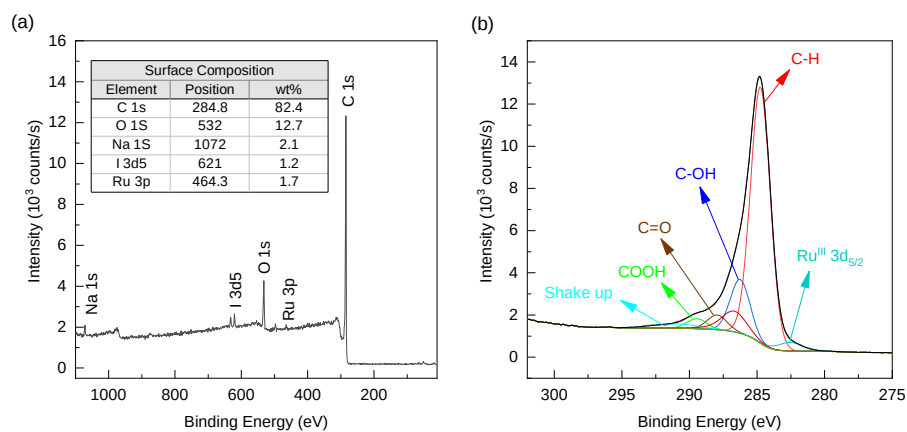


Figure S1.5. a) XPS survey and b) C 1s high resolution spectra of spent CBO-Ru(2%)

S.5. Additional catalytic tests

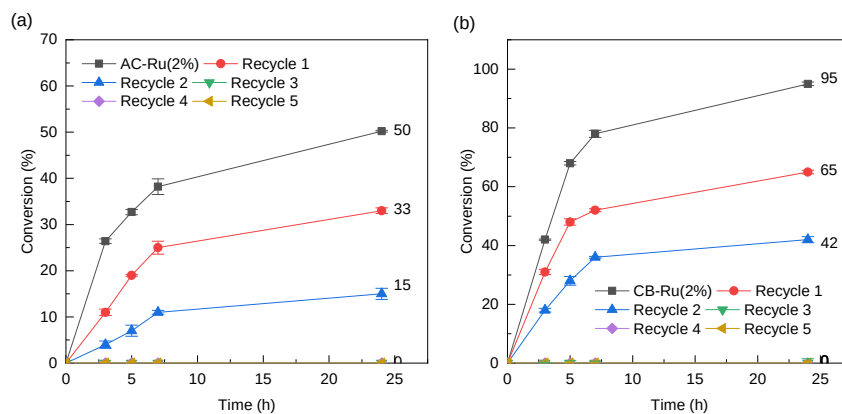


Figure S1.6. Recycling tests of: a) AC-Ru(2%) b) CB-Ru(2%)

Supporting Information Chapter 2

S.1. Deposition of NH₂-bpy on CBO surface

Based on Boehm's titration results displayed in Table S2.1, 1.3 equivalent of NH₂-bpy was selected to ensure a total impregnation of this ligand on CBO surface by means of conventional chlorination and NHS/EDC method.

Table S2.1. Boehm's titration results of carbon black

Support	Phenols (mmol/g)	Lactones (mmol/g)	Carboxylic acids (mmol/g)	Total Acidity (mmol/g)
CB	0.06	0.54	0.04	0.64
CBO	0.43	0.52	1.02	1.97

Since two COOH may interact with 1 molecule of NH₂-bpy (it contains 2 amine groups), the theoretical mass of ligand to be deposited can be estimated as follows:

$$\text{COOH} = 1.02 \text{ mmol/g} \times 4 \text{ g of CBO} = 4.08 \text{ mmol COOH} \quad [\text{S2.1}]$$

$$\text{NH}_2 - \text{bpy} = 4.08 \text{ mmol} \times \frac{1 \text{ mmol NH}_2 - \text{bpy}}{2 \text{ mmol COOH}} \times \frac{186.22 \text{ mg}}{1 \text{ mmol NH}_2 - \text{bpy}} = 379.88 \text{ mg} \quad [\text{S2.2}]$$

$$\text{Theoretical impregnation} = \frac{m_{\text{NH}_2 - \text{bpy}}}{m_{\text{NH}_2 - \text{bpy}} + m_{\text{CBO}}} \times 100\% = 8.5\% \quad [\text{S2.3}]$$

S.2. Deposition of polydopamine on CBO surface

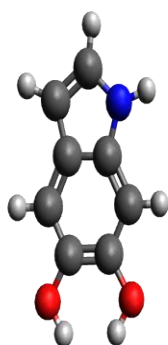
For this purpose, it was considered that the monomer (indole ring structure in Figure S2.1) of the polymer may interact with CBO surface by π -stacking. So, the measures (bond lengths and angles) within indole ring structure were estimated by molecular mechanics theory. Then, its dimensions were used to calculate the amount of monomers that can cover the external surface of CBO = 116 m²/g calculated from the N₂ physisorption isotherms (t-plot method, Table 2.2).

Thus, the amount of dopamine (DA) required to cover 1 g of CBO can be estimated as follows:

$$\text{DA molecules on CBO} = \frac{110 \text{ m}^2 \times 1 \text{ molec}}{8.34 \times 10^{-20} \text{ m}^2} = 1.39 \times 10^{-21} \text{ molecules DA} \quad [\text{S2.4}]$$

$$\text{Mass}_{\text{DA}} = 1.39 \times 10^{-21} \text{ molec DA} \times \frac{1 \text{ mol DA}}{6.022 \times 10^{23} \text{ molec DA}} \times \frac{153.18 \text{ g DA}}{1 \text{ mol DA}} = 0.35 \text{ g DA} \quad [\text{S2.5}]$$

$$\text{Theoretical impregnation} = \frac{m_{\text{PDA}}}{m_{\text{PDA}} + m_{\text{CBO}}} \times 100\% = 25.9\% \quad [\text{S2.6}]$$



$$\text{Area} = 8.34 \times 10^{-20} \text{ m}^2$$

Figure S2.1. Monomer dimensions estimated by molecular mechanics

S.3. Characterization of functionalized carbon materials

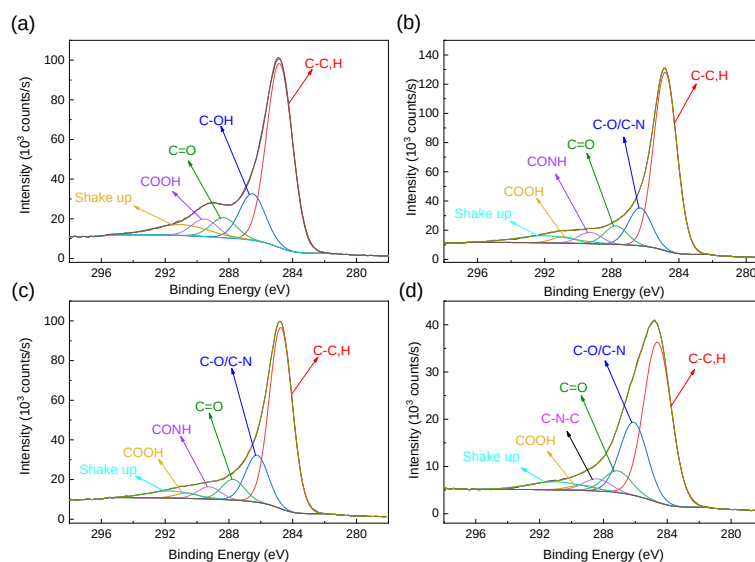


Figure S2.2. C 1s high resolution spectra of: a) CBO; CBP-bpy(NHS/EDC); c) CBO-bpy(SOCl₂) and d) CBO-PDA

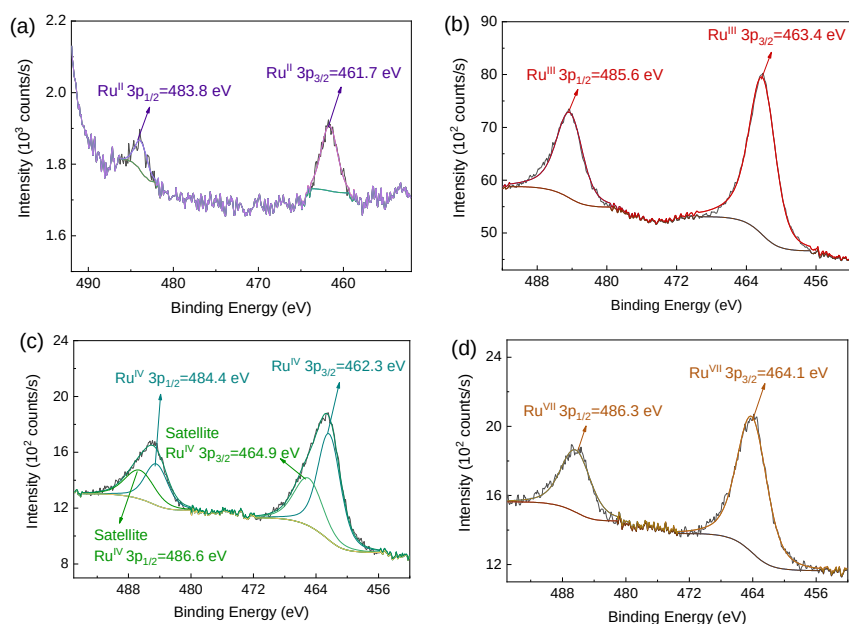


Figure S2.3. a) Ru 3p high resolution spectra of: $[\text{Ru}^{\text{II}}(\text{bpy})_3]\text{Cl}_2$; b) $\text{Ru}^{\text{III}}\text{Cl}_3$; c) $\text{Ru}^{\text{IV}}\text{O}_2$ and d) $\text{KRu}^{\text{VII}}\text{O}_4$

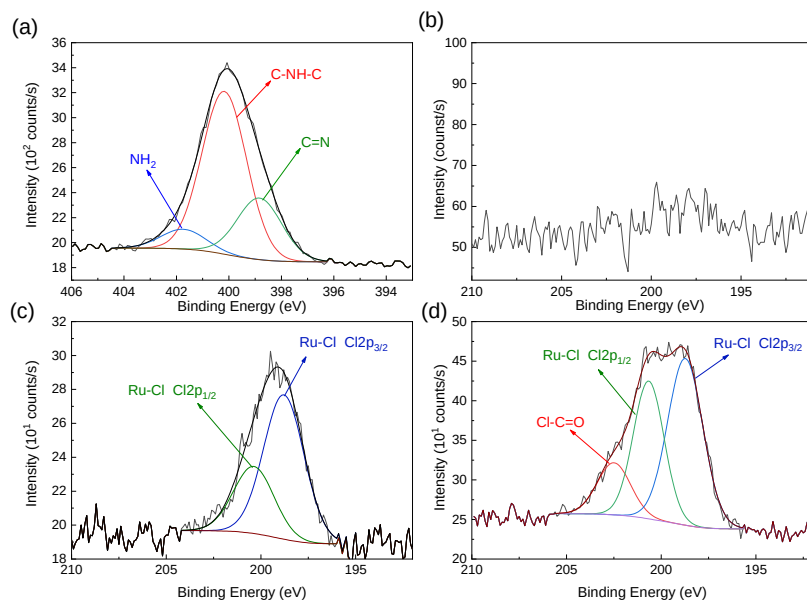


Figure S2.4. a) N 1s high resolution spectra of CBO-PDA; Cl 2p high resolution spectra of: b) CBO-PDA; c) CBP-bpy(NHS/EDC) and d) CBO-bpy(SOCl_2)

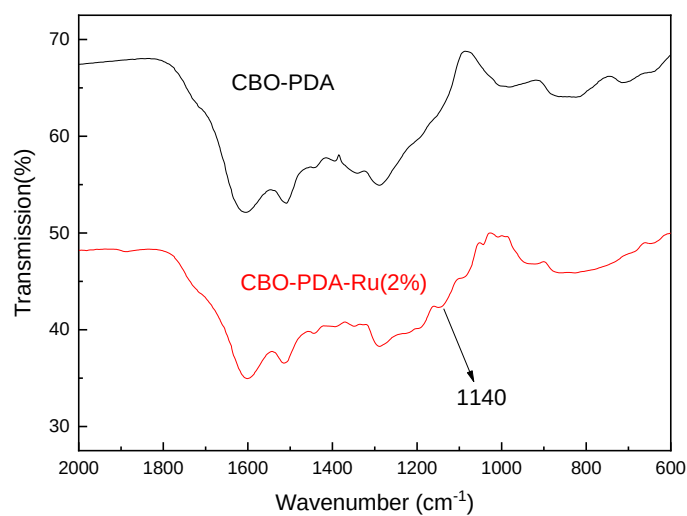


Figure S2.5. FTIR spectra of CBO-PDA and CBO-PDA-Ru(2%)

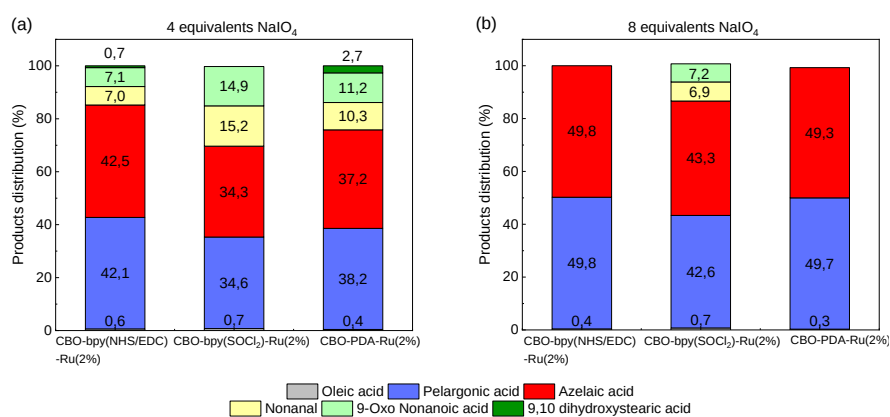


Figure S2.6. Products distribution provided by synthesized catalysts with a) 4 equivalents NaIO₄ and b) 8 equivalents NaIO₄

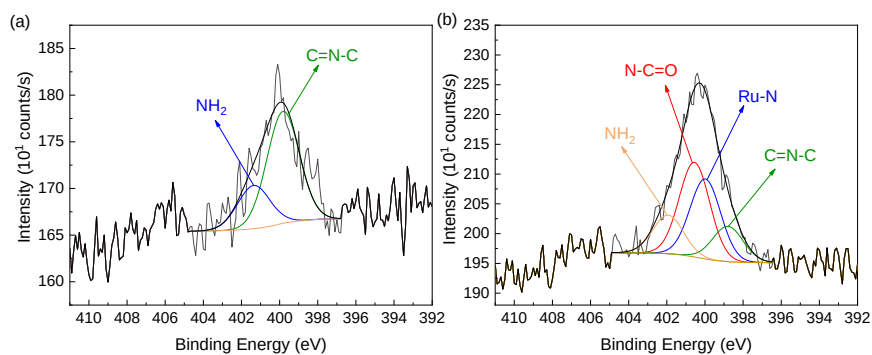


Figure S2.7. N 1s high resolution spectra of a) spent CBP-bpy(NHS/EDC)-Ru(2%) and b) spent CBO-bpy(SOCl₂)-Ru(2%)

Table S2.2. Surface composition (wt%) of spent catalysts (from XPS)

Spent catalysts	C 1s (%)	O 1s (%)	N 1s (%)	Ru 3p (%)	I 3d (%)	Na 1s (%)	Cl 2p (%)
CBO-bpy(NHS/EDC)-Ru(2%)	76.1	16.0	0.3	1.0	1.6	3.0	---
CBO-bpy(SOCl ₂)-Ru(2%)	88.9	6.6	1.2	1.8	---	---	1.5
CBO-PDA-Ru(2%)	75.7	17.2	5.0	2.1	---	---	---

Supporting Information Chapter 3

S.1. NMR characterization of oxidative cleavage products

Oleic acid along with the oxidative cleavage products (pelargonic and azelaic acids) and the identified intermediates are herein characterized by NMR spectroscopy.

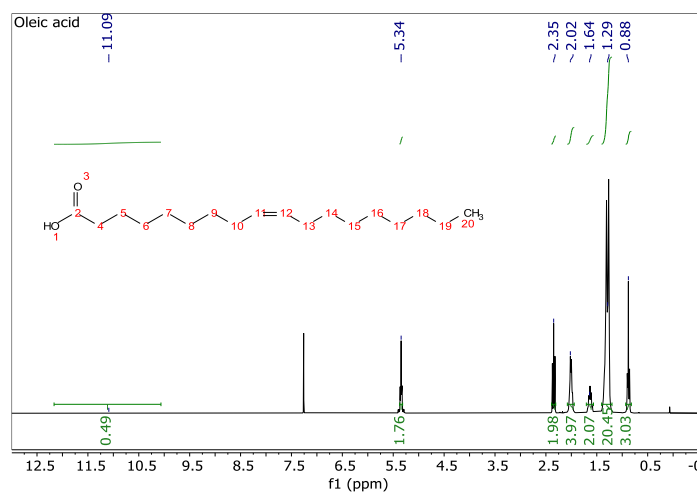


Figure S3.1. Oleic acid ^1H spectrum

Oleic acid NMR ^1H (CDCl_3): $\delta = 0.88$ (t, 3H, CH_3), 1.29 (m, 20H, CH_2), 1.64 (m, 2H, CH_2), 2.02 (d, 4H, CH_2), 2.35 (t, 2H, CH_2), 5.34 (dt, 2H, CH of carbon-carbon double bond), 11.0 (s, 1H, COOH) ppm.

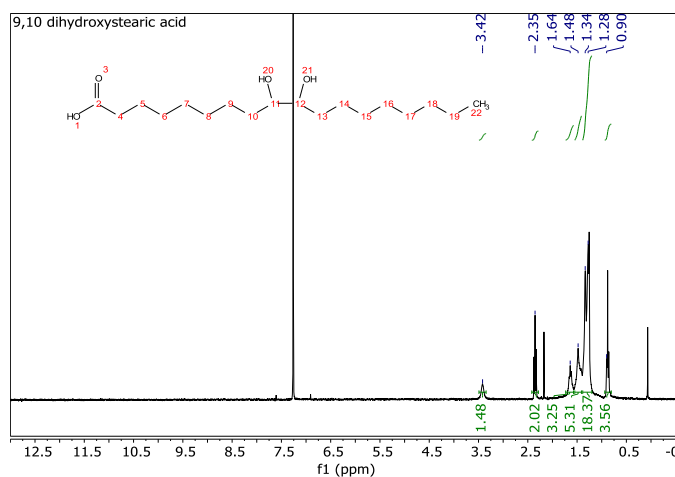


Figure S3.2. 9,10 dihydroxystearic acid ^1H spectrum

9,10-dihydroxystearic acid NMR ^1H (CDCl_3): δ = 0.90 (t, 3H, CH_3), 1.28 (m, 18H, CH_2), 1.34 (m, 5H, CH_2), 1.48 (m, 4H, CH_2), 1.64 (m, 2H, CH_2), 2.29 (t, 2H, CH_2), 3.42 (d, 2H, OH of diol) ppm.

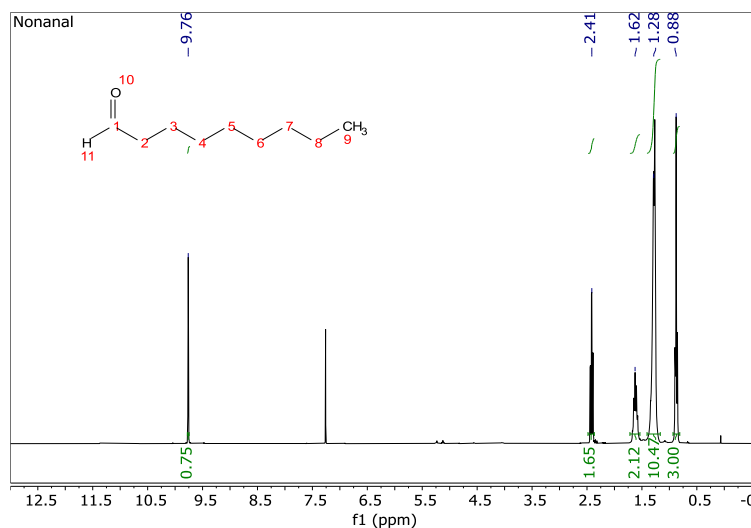


Figure S3.3. 9,10 dihydroxystearic acid ^1H spectrum

Nonanal NMR ^1H (CDCl_3): δ = 0.88 (t, 3H, CH_3), 1.28 (m, 10H, CH_2), 1.62 (m, 2H, CH_2), 2.41 (td, 2H, CH_2), 9.76 (t, 1H, CHO) ppm.

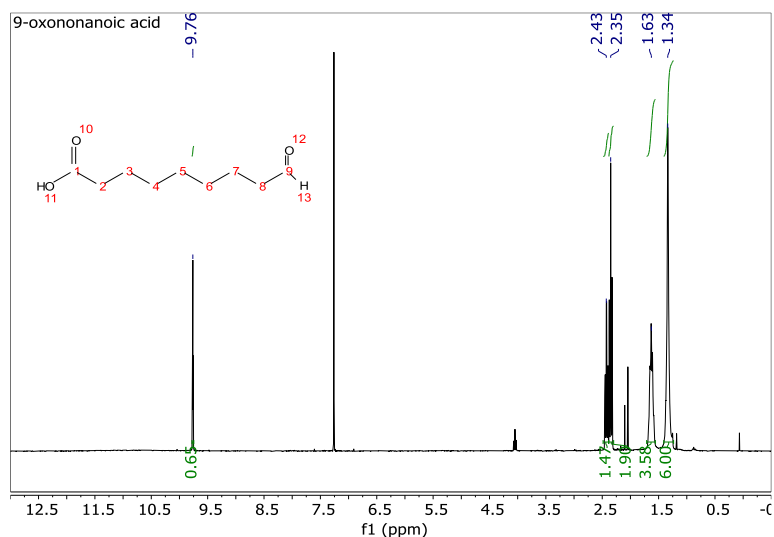


Figure S3.4. 9-oxo nonanoic acid ^1H spectrum

9-oxo nonanoic acid NMR ^1H (CDCl_3): δ = 1.34 (M, 6H, CH_2), 1.63 (m, 4H, CH_2), 2.35 (t, 2H, CH_2), 2.43 (t, 2H, CH_2), 9.76 (t, 1H, CHO) ppm.

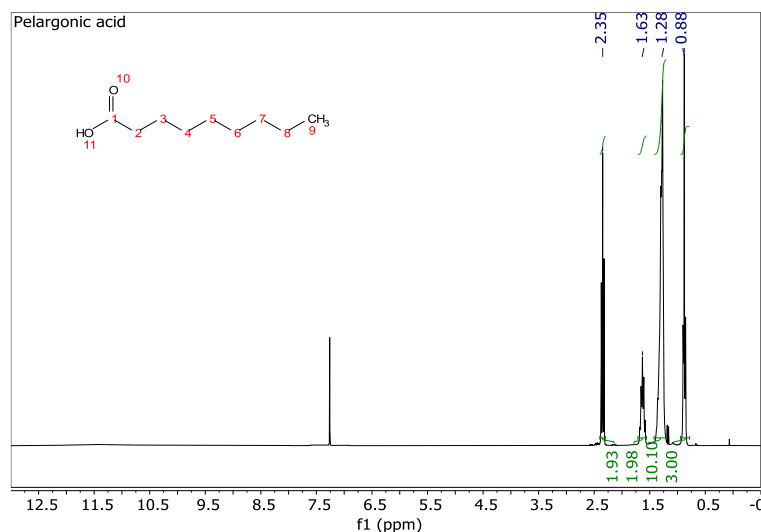


Figure S3.5. Pelargonic acid ^1H spectrum

Pelargonic acid NMR ^1H (CDCl_3): δ = 0.88 (t, 3H, CH_3), 1.28 (m, 10H, CH_2), 1.63 (m, 2H, CH_2), 2.35 (t, 2H, CH_2) ppm.

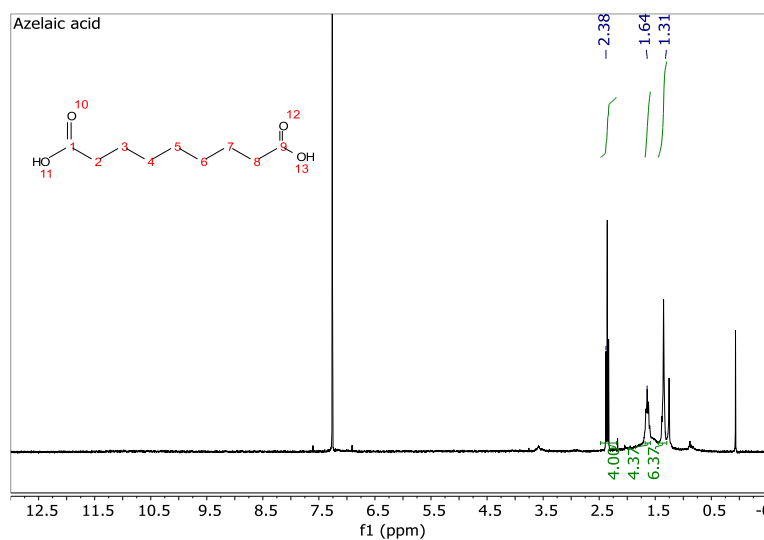


Figure S3.6. Azelaic acid ^1H spectrum

Azelaic acid NMR ^1H (CDCl_3): δ = 1.21-1.31 (M, 6H, CH_2), 1.64 (m, 4H, CH_2), 2.38 (t, 4H, CH_2) ppm.

S.2. NaIO₄ consumption

Aqueous solutions of NaIO₄ were prepared with concentrations below 1×10^{-4} mol/L. The maximum absorbance was detected at 222 nm, and the calibration curve was constructed by relating the different absorbance values obtained with the known concentration values.

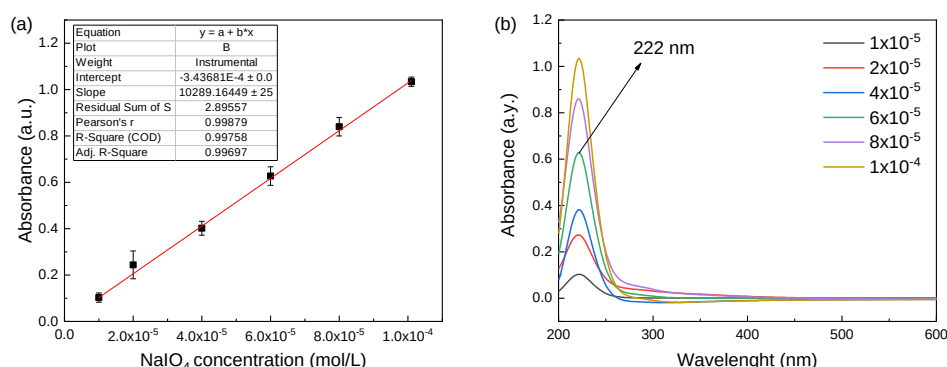


Figure S3.7. a) calibration curve for NaIO₄ consumption; b) absorbance of different NaIO₄ solutions at $\lambda_{\max}=222$ nm

S.3. Characterization of CBO-PDA-Ru catalyst

Boehm's Titration results are summarized in Table S3.1. Carboxylic acids are the most abundant superficial groups on oxidized carbon black which is in concordance with the FTIR peaks shown in Figure 1.2 (p. 69). After the oxidation treatment with HNO₃, the amount of phenol groups increased from 0.06 to 0.43 mmol/g while after the deposition of PDA this amount increased to 0.66 mmol/g. These results confirm that the polymer provided extra hydroxyls functionalities on CBO surface.

Table S3.1. Boehm's Titration Results.

Sample	Phenols (mmol/g)	Lactones (mmol/g)	Carboxylic (mmol/g)	Total Acidity (mmol/g)
CB	0.06	0.54	0.04	0.64
CBO	0.43	0.52	1.02	1.97
CBO-PDA	0.66	0.57	0.00	1.23

As stated in the experimental section, the maximum Ru loading on CBO-PDA composite is 4%; therefore, the availability of OH groups for the complexation of Ru ions can be estimated as follows:

$$\frac{m_{\text{Ru}}}{m_{\text{Ru}} + m_{\text{support}}} = 4\% \rightarrow m_{\text{Ru}} = 20.8 \text{ mg Ru} \quad [\text{S3.1}]$$

$$\text{Ru atoms} = 0.0208 \text{ g Ru} \times \frac{1 \text{ atom-g Ru}}{101.07 \text{ g}} \times \frac{6.022 \times 10^{23} \text{ atom Ru}}{1 \text{ atom-g Ru}} = 1.24 \times 10^{20} \text{ Ru atoms} \quad [\text{S3.2}]$$

The amount of phenols in 500 mg of support is 0.33 mmol. Then, the amount of OH groups available for Ru complexation is as follows:

$$\text{OH groups} = 0.33 \times 10^{-3} \text{ mol} \times \frac{6.022 \times 10^{23} \text{ molecules}}{1 \text{ mol}} = 1.99 \times 10^{20} \text{ OH groups} \quad [\text{S3.3}]$$

The ratio of phenol groups/Ru atom then resulted to be:

$$\frac{\text{OH}}{\text{Ru}} = \frac{1.99 \times 10^{20} \text{ groups}}{1.24 \times 10^{20} \text{ atoms}} = 1.6 \quad [\text{S3.4}]$$

Hence, the amount of phenol groups available on CBO-PDA surface is in principle higher than the amount of Ru atoms required to obtain a load of 4 wt%, and more than enough to chelate Ru atoms corresponding to Ru loads of 1 wt% and 2 wt%.

Nitrogen physisorption analyses were carried out to determine the textural properties of carbon black catalysts after PDA and Ru deposition (Table S3.2). All carbonaceous composites showed a *quasi*-type 2 isotherm with a narrow hysteresis loop H3 which is characteristic of materials displaying big mesopores (Figure S3.7).

Table S3.2. Textural properties of carbon black composites

Sample	BET surface area (m ² /g)	External area (m ² /g)	Pore Volume (cm ³ /g)	Mean pore diameter (nm)
CB	154	116	0.58	24.3
CBO	149	116	0.53	22.9
CBO-PDA	80	78	0.38	34.2
CBO-PDA-Ru(1%)	81	57	0.31	16.7
CBO-PDA-Ru(2%)	81	62	0.30	16.7
CBO-PDA-Ru(4%)	82	70	0.33	16.5

These should be understood as pores located in between the carbon black nodules forming the observed aggregates, the nodules themselves not being porous. In the case of the CBO-PDA composite, the specific surface area diminished as compared to CBO from 154 to 80 m²/g. Comparatively, CBO

specific surface area and pore volume only slightly varied after Ru impregnation.

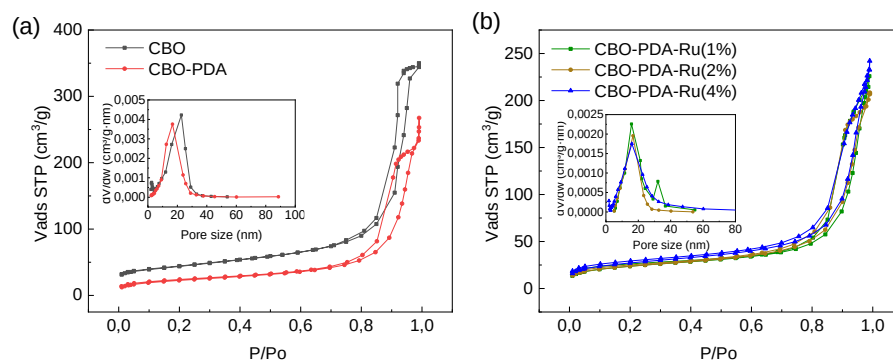


Figure S3.8. N₂ physisorption isotherms of a) CBO and CBO-PDA; b) CBO-PDA-Ru(1%), CBO-PDA-Ru(2%) and CBO-PDA-Ru (4%).

S.4. Polydopamine characterization

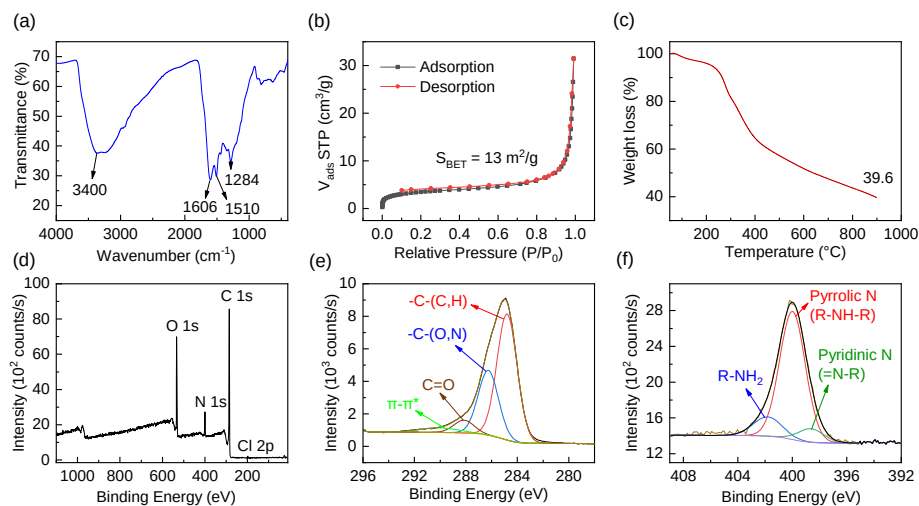


Figure S3.9. Characterization of pure PDA a) FTIR; b) N₂ adsorption-desorption isotherms; c) Thermogram; d) XPS survey; e) C 1s and f) N 1s deconvolution spectra

S.5. GC identification of oxidative cleavage products

It was possible to detect peaks that did not match with the those corresponding to oleic acid or to the reaction products. Besides, since the conversion was not complete, the presence of intermediates became a possibility. The reaction mechanism illustrated in Scheme 10 (p.19), shows that a diol and aldehydes can be formed during the oxidative cleavage of UFAs.

Therefore, 9,10-dihydroxystearic acid (the corresponding diol of oleic acid), nonanal (aldehyde of PA) and 9-oxononanoic acid (aldehyde of AA) were analyzed by GC. The peaks arrived exactly at the same times as the unidentified peaks in the chromatograms of the catalytic tests. Figure S3.9 illustrates the chromatogram with the peaks of all products involved in this reaction.

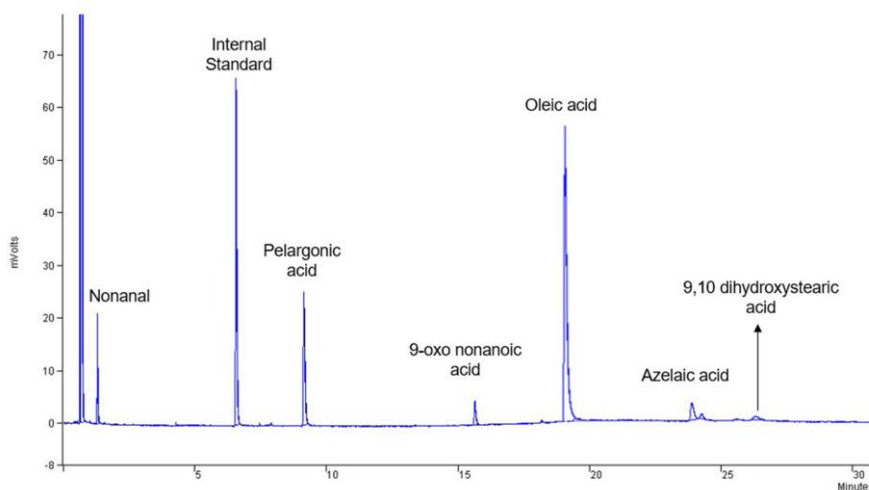


Figure S3.10. Chromatogram of all products involved in the oxidative cleavage of oleic acid with CBO-PDA-Ru(2%).

Supporting Information Chapter 4

S.1. Deposition of polydopamine on calcined carbon particles surface

For this purpose, it was considered that the monomer (indole ring structure in Figure S2.1) of the polymer may interact with calcined carbon nanoparticles (CCNs) surface by π -stacking interaction. The measures of this monomer (bond lengths and angles) were estimated by molecular mechanics approach. Then, its dimensions were used to calculate the amount of monomers that can cover the external surface area of CCN = 37 m²/g calculated from the N₂ physisorption isotherms (t-plot method, Table 4.2). Thus, the amount of dopamine (DA) required to cover 1 g of CCN can be estimated as follows:

$$\text{DA molecules on CCN} = \frac{37 \text{ m}^2 \times 1 \text{ molec}}{8.34 \times 10^{-20} \text{ m}^2} = 4.44 \times 10^{-20} \text{ molecules DA} \quad [\text{S4.1}]$$

$$\text{Mass}_{\text{DA}} = 4.44 \times 10^{-20} \text{ molec DA} \times \frac{1 \text{ mol DA}}{6.022 \times 10^{23} \text{ molec DA}} \times \frac{153.18 \text{ g DA}}{1 \text{ mol DA}} = 0.11 \text{ g DA} \quad [\text{S4.2}]$$

$$\text{Theoretical impregnation} = \frac{m_{\text{PDA}}}{m_{\text{PDA}} + m_{\text{CBO}}} \times 100\% = 10.1\% \quad [\text{S4.3}]$$

Table S4.1. PDA deposition performance in CCN surface

Functionalized Carbon	Theoretical content of PDA/bpy (%)	Experimental content of PDA/bpy (%)	Deposition yield (%)
CCN-PDA	10.1	5.7	56

S.2. Supplementary characterization of carbon nanoparticles

Superficial composition of the synthesized carbon supports was obtained by XPS spectroscopy. Table S4.2 shows that oxygen content diminished after the calcination treatment of carbon nanoparticles.

Table S4.2. Surface composition (wt%) of synthesized carbon materials from (XPS)

Carbon support	C 1s	O 1s	N 1s
CN	73.75	26.25	---
CCN	77.78	22.22	---
CCN-PDA	66.03	31.81	8.16

Nevertheless, after the deposition of PDA, the oxygen content increased as a result of extra catechol provided by the polymer.

After the impregnation of Ru on CN and CCN, the deconvolution of O 1s and Ru 3p peaks were performed to estimate the chemical environment of Ru and its oxidation state respectively.

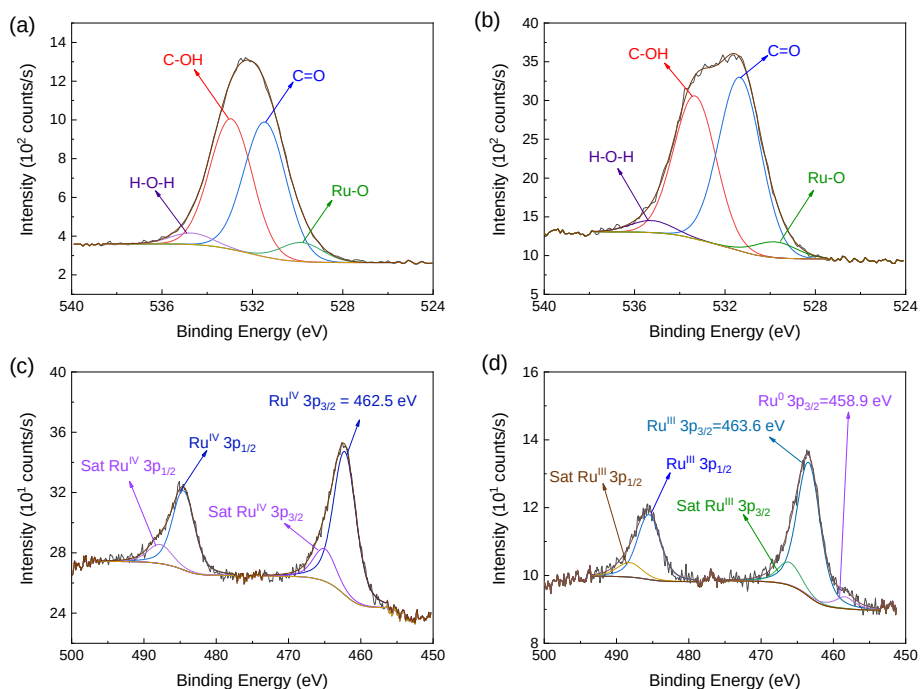


Figure S4.1. a) O 1s high resolution spectrum from CN-Ru(2%); b) O 1s high resolution spectrum from CCN-Ru(2%); c) Ru 3p high resolution spectrum from CN-Ru(2%) and d) c) Ru 3p high resolution spectrum from CCN-Ru(2%)

S.3. Catalytic tests

The presence of intermediates during the catalytic tests with the synthesized carbon catalysts was detected and quantified by gas chromatography as shown in Figure S4.2.

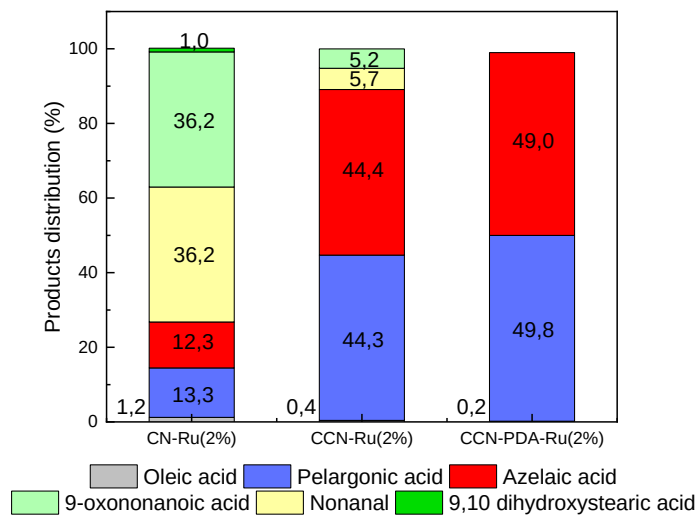


Figure S4.2. Products distribution after 24 h of performing the oxidative cleavage of oleic acid with 8 equivalents of NaIO_4

S.4. Influence of NMO

N-Methylmorpholine N-oxide (NMO) can re-oxidize $\text{H}_2\text{Ru(VI)O}_4$ into Ru(VIII)O_4 during the oxidative cleavage of UFAs as depicted in Figure S4.3.

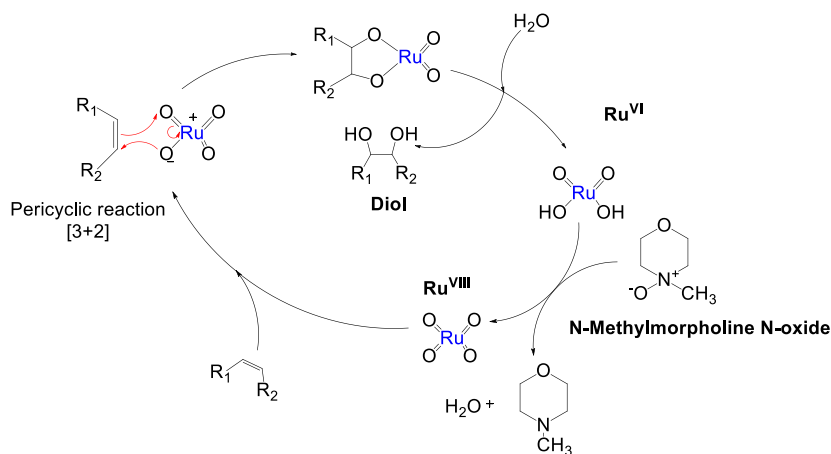


Figure S4.3. Re-oxidation of $\text{H}_2\text{Ru(VI)O}_4$ by NMO in oxidative cleavage reaction (inspired from [365])

To verify the possibility of oxidizing Ru^{III} -catecholate into $\text{Ru}^{\text{VIII}}\text{O}_4$, RuCl_3 solution was put in contact with 8 equivalents of NMO as well as 8 equivalents NaIO_4 separately. Figure S4.4a demonstrates that NaIO_4 can transform a Ru^{III} species into $\text{Ru}^{\text{VIII}}\text{O}_4$ which is responsible for triggering the oxidative cleavage of oleic acid. On the other hand, NMO was not strong enough to perform the same oxidation.

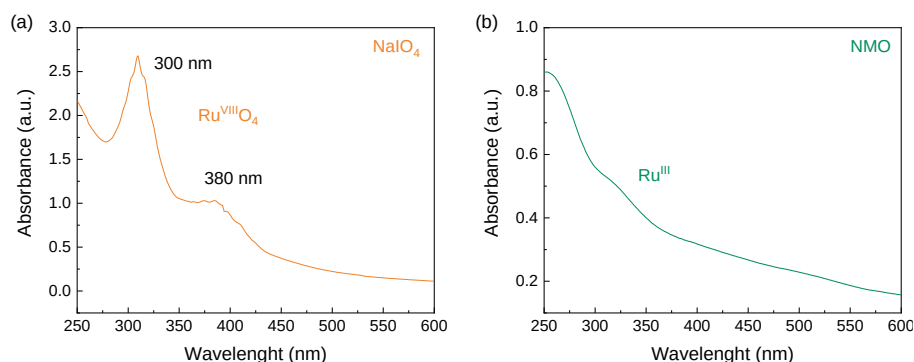


Figure S4.4. UV-Visible spectra of RuCl_3 oxidation by a) 8 equivalents of NaIO_4 and b) 8 equivalents of NMO

The possibility of aldehydes oxidation by NMO was explored by nonanal transformation into pelargonic acid. Figure S4.5 shows that NMO was not able to oxidize aldehydes either. Therefore, this amine oxide is only useful in the re-oxidation of $\text{H}_2\text{Ru}^{\text{VI}}\text{O}_4$ as stated in Figure S4.3.

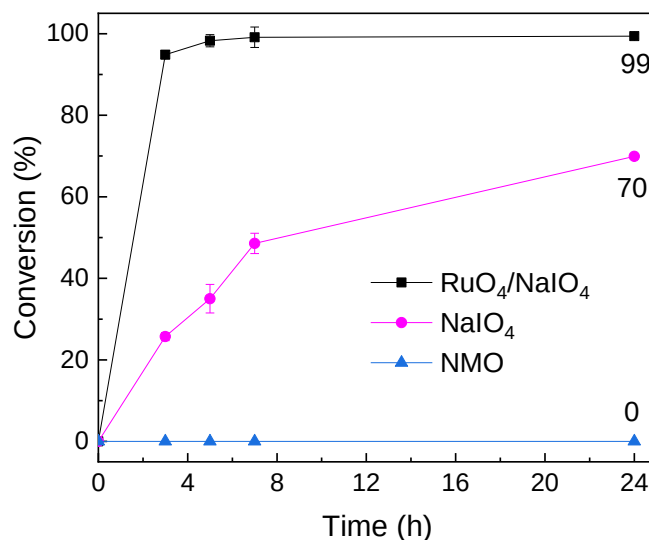


Figure S4.5. Nonanal oxidation by $\text{Ru}^{\text{VIII}}\text{O}_4$, NaIO_4 and NMO

Supporting Information Chapter 5

S.1. Calibration curves

Figures S5.1 to S5.3 shows the calibration curves of methyl oleate (MO), methyl linoleate (ML) and mono methyl azelate (MA) respectively. These curves were employed to quantify the concentration of each compound throughout the catalytic tests.

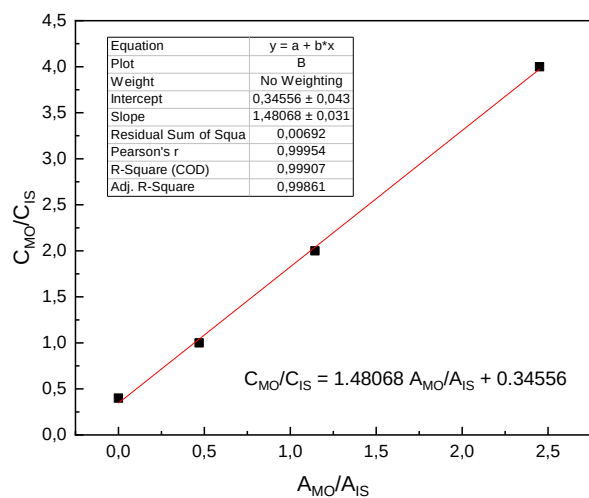


Figure S5.1. Calibration curve of methyl oleate

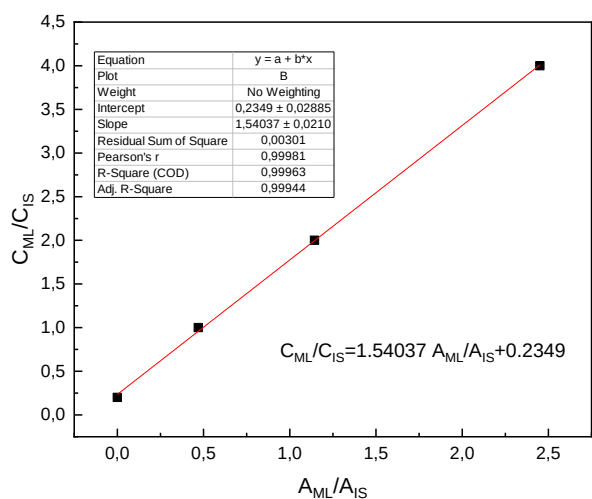


Figure S5.2. Calibration curve of methyl linoleate

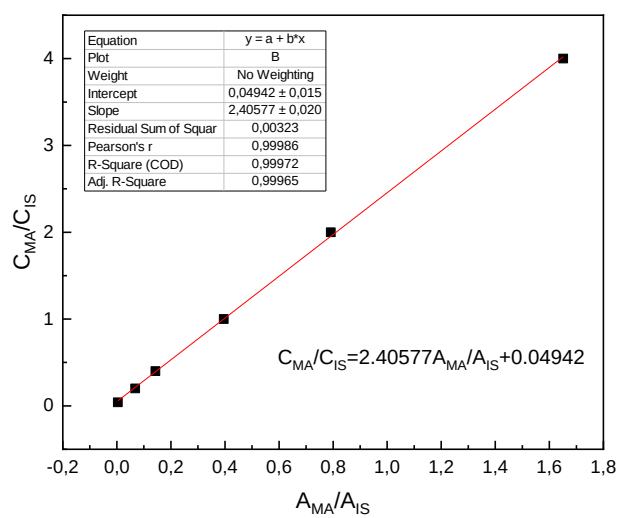


Figure S5.3. Calibration curve of methyl azelate

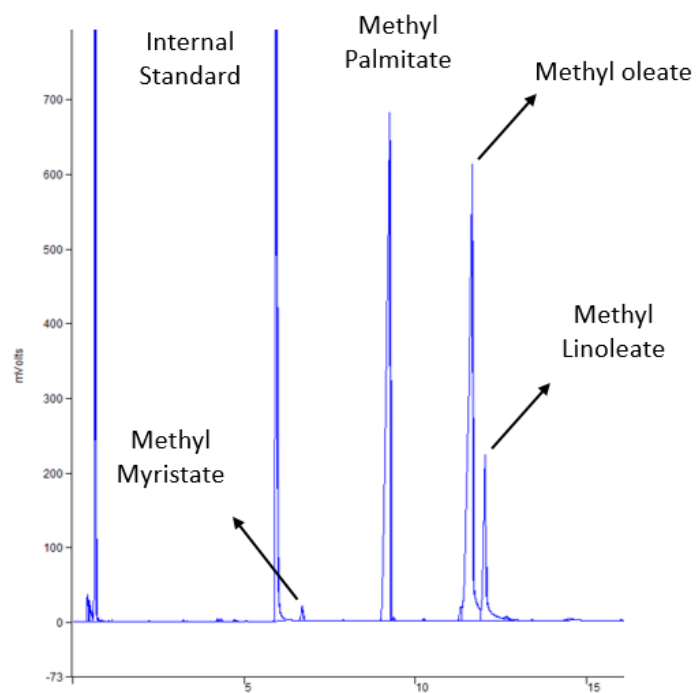


Figure S5.4. Chromatogram of main FAs within Ecuadorian palm oil

S.2. Conversion, yield and selectivity calculation

Conversion was estimated through the ratio between all UFAs (oleic+ linoleic acids) reacted and UFAs fed to the reactor at the beginning of the reaction as exposed in Equation S5.1:

$$\chi = \frac{n_0 - n_t}{n_0} \times 100\% \quad [\text{S5.1}]$$

where n_0 correspond to the initial moles of UFAs and n_t refers to the moles UFAs at a given reaction time. Yield is defined as the ratio of moles of pelargonic (PA) and methyl azelate (MA) produced and the theoretical amount of these products that could have been produced. It is important to mention that PA is only produced from oleic acid (OA) while MA is produced from both UFAs. Therefore, yields are calculated as follows:

$$Y_{\text{PA}} = \frac{n_{\text{PA}}}{n_{\text{UFAs}} \times 1 \text{ mol PA}/1 \text{ mol UFAs}} \times 100\% \quad [\text{S5.2}]$$

$$Y_{\text{MA}} = \frac{n_{\text{MA}}}{n_{\text{UFAs}} \times 1 \text{ mol MA}/1 \text{ mol UFAs}} \times 100\% \quad [\text{S5.3}]$$

where n_{UFAs} is the initial moles of methyl oleate and methyl linoleate while n_{PA} and n_{MA} are the produced moles of pelargonic and methyl azelate respectively. Finally, selectivity refers to the moles of PA and MA produced versus the moles of UFAs reacted. Therefore, selectivity can be calculated by incorporating conversion to the above-mentioned equations:

$$S_{\text{PA}} = \frac{n_{\text{PA}}}{n_{\text{UFAs}} \times \chi \times 1 \text{ mol PA}/1 \text{ mol UFAs}} \times 100\% \quad [\text{S5.4}]$$

$$S_{\text{MA}} = \frac{n_{\text{MA}}}{n_{\text{UFAs}} \times \chi \times 1 \text{ mol MA}/1 \text{ mol UFAs}} \times 100\% \quad [\text{S5.5}]$$

S.3. Catalytic tests

Products distribution in Figure S5.5 shows a surplus of 6% in methyl azelate production since this compound comes from the oxidative cleavage of methyl oleate and methyl linoleate in palm oil.

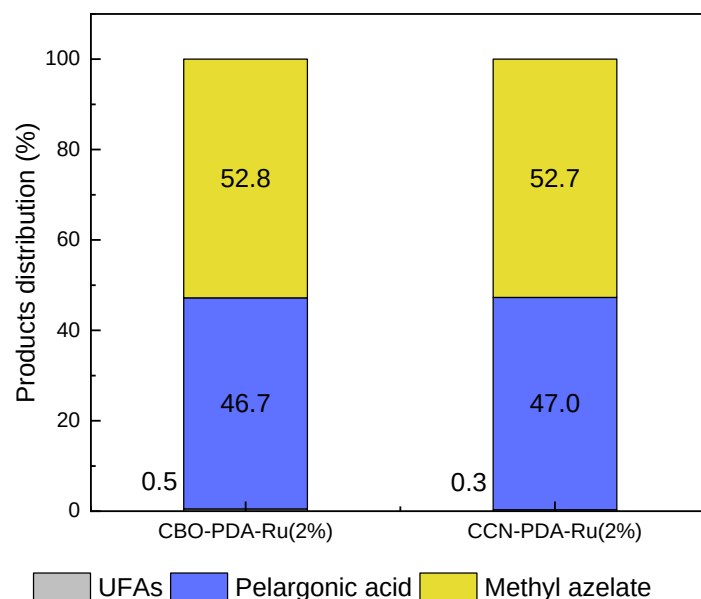


Figure S5.5. Products distribution after 24 h of performing the oxidative cleavage of oleic acid with 8 equivalents of NaIO_4

UV-Visible monitoring tests were carried out to verify the presence of Ru species in the reaction medium. The spectra in Figure S5.6. show bands at 309 and 385 nm which are attributed to $\text{Ru}^{\text{VIII}}\text{O}_4$ while the bands at 385 nm and 470 nm are ascribed to the reduced species $\text{H}_2\text{Ru}^{\text{VI}}\text{O}_4$. The latter Ru species is reoxidized into $\text{Ru}^{\text{VIII}}\text{O}_4$ by means of the oxidizing agents (e.g. NaIO_4 or NMO). After 24 h of agitation, both Ru species disappear from the organic phase suggesting that PDA functional groups on CBO and CCN surface should have re-adsorbed Ru from the reaction medium.

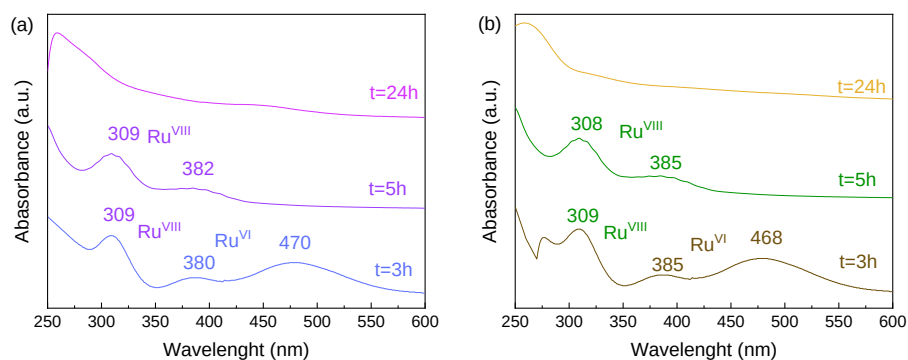


Figure S5.6. UV-Visible monitoring of the organic phase during oxidative cleavage of palm oil with a) CBO-PDA-Ru(2%) and b) CCN-PDA-Ru(2%)

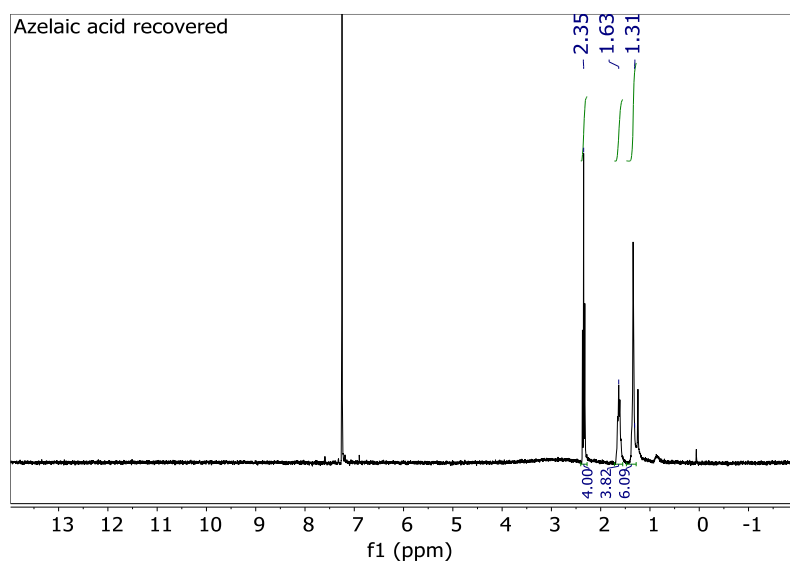


Figure S5.7. ^1H spectrum of azelaic acid isolated from palm oil after oxidative cleavage

Azelaic acid NMR ^1H (CDCl_3): δ = 1.17-1.31 (M, 6H, CH_2), 1.63 (m, 4H, CH_2), 2.35 (t, 4H, CH_2) ppm.

