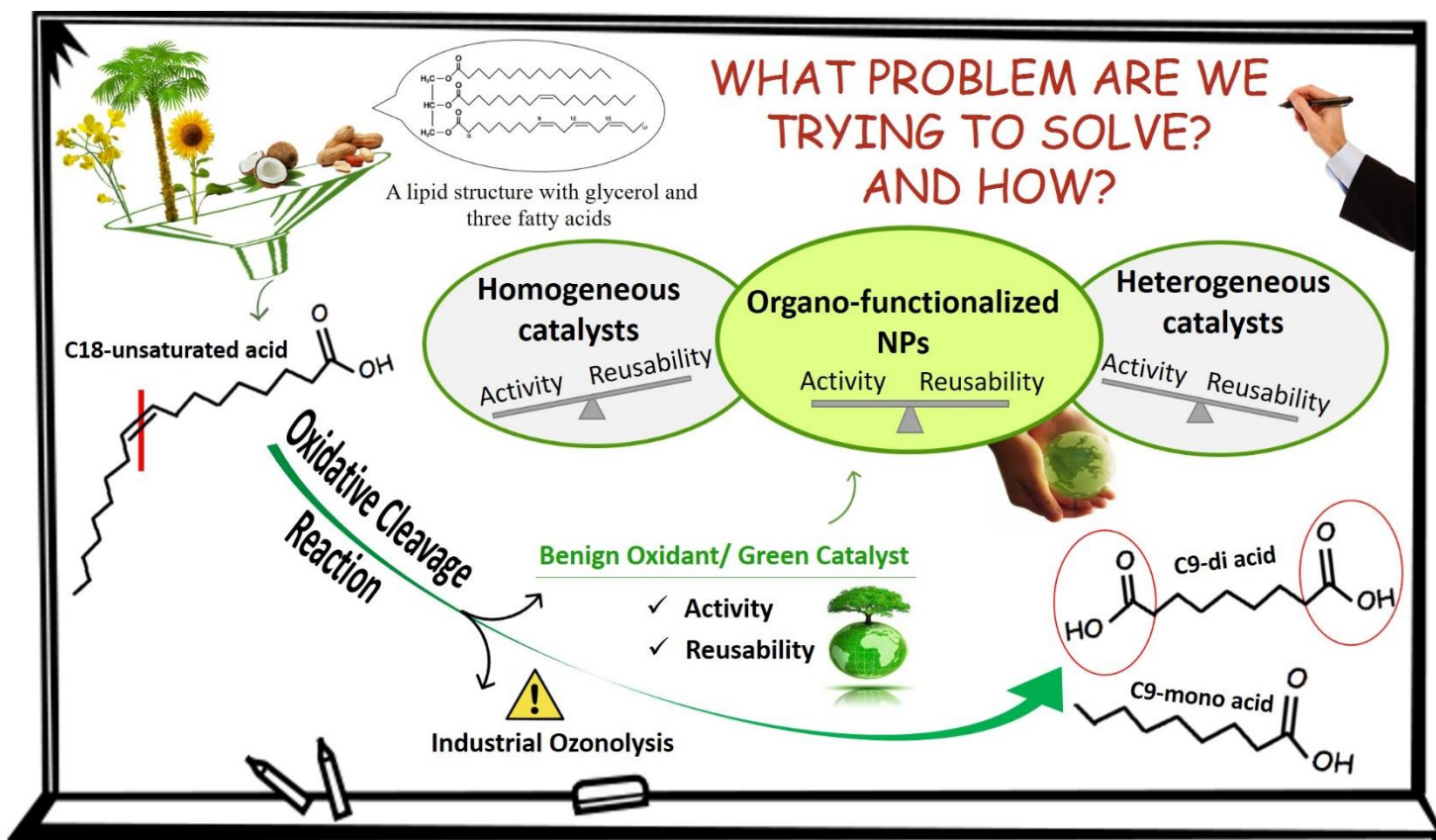


Chapter 1. Introduction



In this chapter, seminal concepts of the oleochemical science and oxidative cleavage of oleic acid are quite succinctly presented to bring up the problem statement, and then, the scope and organization of the thesis are elucidated.

1.1 Problem statement

Nowadays, sustainable development in the field of chemistry has propelled the industry to utilize renewable raw materials, which exploit the synthetic capabilities of nature, instead of petroleum materials. Among all feedstock materials, oils and fats of vegetable and animal origins have attracted considerable attention over the past decades. This attention arises from not only the environmental reasons, but also economic ones. Unsaturated fatty acids (UFAs) with long hydrocarbon chain, which are the constituent of lipids molecules, have several functional sites for chemical modifications in their structures. Accordingly, a variety of products with different properties can be obtained from the reactions of oils and fats.

In polymer industry, dicarboxylic acids are precious materials to make building blocks for polymers. These acids can be produced from UFAs via oxidation process. At present, azelaic acid (C₉, dicarboxylic acid) as a very industrially important chemical is produced in large scale via ozonolysis of oleic acid (C₁₈:1, the most widely distributed and abundant UFA). Pelargonic acid (C₉, monocarboxylic acid) is obtained as a co-product but also a valuable chemical [1]. These types of saturated acids that have short and odd hydrocarbon chains are rare in natural resources [2]. On the other hand, they are very attractive initial materials for the development of numerous bio-based products [3,4]. For instance, azelaic acid converts into different esters for the preparation of polymers (Nylon 6:9), plasticizers, adhesives, solvents, biodegradable lubricants, corrosion inhibitors, and anti-acneic agent for cosmetics [2,3]. Pelargonic acid is an intermediate in the production of lubricants, plasticizers, perfumes, herbicides, fungicides, resins [3,5].

A variety of non-eco-friendly problems associated with use of ozone, however, is not in line with the principles of sustainable chemistry, and therefore, developing an industrial alternative to the hazardous ozonolysis of oleic acid would be a great breakthrough in industry. This alternative process requires a highly efficient catalyst/oxidant system. Combination of hydrogen peroxide with transition metal compounds would be a promising candidate, since such systems have shown high oxidizing ability, particularly in homogeneous form in lab scale. Large scale applications of the homogeneous catalysts, however, have been always a controversial challenge to the industry, due to the lack of recyclability. On the other hand, catalytic activity of the heterogeneous catalysts, with high recyclability, in liquid phase reactions of lipids, roughly speaking, is not comparable to that of homogeneous ones, which

has been often ascribed to the poor reactant/catalyst contact. To address this matter, this research project was planned about five years ago.

1.2 Scope of the research

The primary goal of this research project is to propose a new alternative process for the hazardous ozonolysis of UFAs via developing a highly efficient catalyst for the liquid phase oxidative cleavage of oleic acid with hydrogen peroxide. Use of the green and safe H₂O₂ as oxidant produces only water as a waste product. Given the outlook of this research toward the large-scale applications and based on what the industrial partner of the project, Oleotek Inc., desired, the economic aspects of the process were highly considered. In doing so, our interest was focused on development of a catalysts that possesses efficient and facile recyclability as well as low-cost preparation, in addition to the excellent activity. Therefore, we have tried a variety of synthetic approaches with different precursors, but we ignored those approaches and materials that not only were costly, but also, held often the lab-scale fascination. In this thesis, we have tried to present our most important findings with the utmost conciseness consistent with clarity. Since the subject and field of this research were completely new in our group, we have pioneered a number of methodologies, particularly regarding the analysis of fatty acids with GC-MS. Such seminal works, along with designing the equipment and experimental setup, although were laborious, have not been reported in this thesis. Otherwise, the thesis would be too lengthy and tedious for the readership.

In order to follow a systematic research path for this PhD project, first, all the reported works in literature on different catalyst/oxidant systems for oxidation of UFAs and their derivatives were reviewed. This comprehensive study not only elucidated the plan of our further works, but also resulted in publishing a review paper. We found that among all the used transition metals as catalytic core in such reactions (Os, Co, Ru, Cr, Au, Mn, Fe, Mo, and W), tungsten has attracted a great deal of attention. Homogeneous tungsten-based catalysts have exhibited high potentials in oxidation of UFAs, however with generally low recovery efficiency. Then, our focus was placed, chiefly, on tungsten-based heterogeneous catalysts. Additionally, molybdenum as a metal inherently close to tungsten, which has occasionally shown even better catalytic activity, was our secondary interest.

In order to overcome the reported drawbacks of conventional solid catalysts in the reactions of oils and fats (e.g. low catalyst/reactant contact and pore diffusion limitations), we examine different strategies in the following chapters including:

- Increasing the catalyst's surface area via incorporation of the active sites in a mesostructured support to reach a higher dimensionality of the interaction between the organic reactant and the catalyst's surface (Chapter 4).
- Preparation of nanocatalysts to increase the dispersion of the solid catalysts in the reaction medium (Chapters 4, 5, and 7)
- Exploiting organo-functionalization of the solid catalyst's surface with different organic moieties, to enhance the compatibility of the hybrid organic-inorganic catalyst in the reaction (Chapters 5, 6, and 7).
- Employing the fascinating solid acid catalyst, polyoxotungstates, which their lack in the reported works on oxidation of UFAs is curious (Chapter 6).
- Evaluation of molybdenum oxide catalysts in the reaction (Chapter 7)

1.3 Organization of the thesis

This short introduction chapter is followed by Chapter 2, which contains our theoretical studies on the subject. In this chapter, first the fundamentals of oils and fats as renewable raw materials and their applications in oleochemical industries, with an emphasis on the target application, are presented (section 2.1). Then, the basic concepts and seminal studies of UFAs and their reactions, which have been widely reviewed [6-9], with an emphasis on oxidation will be shortly summarized (section 2.2) in order to approach to the main topic. The recent works regarding use of different catalyst/oxidant systems in the oxidative cleavage of UFAs and their derivatives will be then discussed (section 2.3). Herein, we divided the reported catalytic systems into three classes: homogenous, heterogeneous, and semi-heterogeneous (NP-based) catalysts. Important features such as catalytic activity and recoverability with specific respect to commercializing viewpoint are discussed in a critical fashion for each class to be able to reasonably plan future works. The unique and interesting properties of NPs propose them as the frontier of homogeneous and heterogeneous catalysts that can

simultaneously exploit the best features of both. These properties along with the recent breakthroughs which would interestingly increase the performance of NP-based catalysts in the biphasic oxidative cleavage reaction of UFAs, are also reviewed. Finally, in section 2.4, we thoroughly discuss heterogeneous catalysis by tungsten-based polyoxometalates, after brief introductions on (i) the interesting inherent properties of tungsten (section 2.4.1), and (ii) the fundamentals of POMs (section 2.4.2). We have tried to review all the recent works on solid polyoxotungstate catalysts and their applications in liquid phase organic reactions. We have divided the reported works into four groups, based on the heterogenization strategy that they used to solidify the inherently homogeneous POTs (sections 2.4.3.1-4). Also, the target organic reaction, although it includes a variety of reactions, has been classified into two major classes, oxidation reaction and acid catalysis reactions, to gain a better outcome.

In Chapter 3, the characterization techniques employed throughout our works are explained (section 3.1), however with the utmost conciseness, since details of these methods are not only beyond the scope of this thesis, but also available in many books. We have succinctly reviewed the fundamentals of each method along with bolding the information that we acquired from them. Then, we will explain, in details, the quantitative analysis of the reaction products with GC-MS, along with the sample preparation prior to injection and calculation procedure of the reaction efficiency (section 3.2).

In Chapter 4, we report a solvothermal synthesis method for preparation of high surface area mesoporous WO_3 supported on γ -alumina with narrow particle size distribution using glucose as template. This chapter chiefly concentrates on increasing the catalyst surface area via incorporation of the active sites in the mesostructured support, followed by examination of this increase in the catalytic activity of the prepared catalysts by changing the ratio of $\text{WO}_3/\text{Al}_2\text{O}_3$.

In Chapter 5, we present syntheses of different structures of tungsten oxide like $[(\text{WO}_2)\text{O}_2\cdot\text{H}_2\text{O}]$, WO_3 , $\text{WO}_3\cdot 0.33\text{H}_2\text{O}$, and $\text{WO}_3\cdot\text{H}_2\text{O}$ via a straightforward and green method based on oxidative dissolution of bare W powder in H_2O_2 . Moreover, organo-functionalization of the nanocatalysts surfaces by CTAB is reported. The key features of this approach are using cheap W powder as precursor, avoiding use of time- and energy-consuming operations in the synthetic procedure such as thermal treatment in autoclave and purification, as well as avoiding use of organic solvents, metal salts, and/or coordination compounds. Optimization of the organic moiety amount on the surface of catalyst is, also, discussed.

In chapter 6, we introduce a novel, one-pot, and green synthesis method, complying with the principles of “Chimie Douce”, for preparation of hybrid organic-inorganic POTs, starting with tungsten powder as precursor, by contrast to the prior methods that often use phosphotungstic or tungstic acid. Two novel hybrid organic-inorganic Keggin compounds are introduced in this chapter: $\text{TPA}_x[\text{H}_{8-x}\text{W}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}$ and $\text{TBA}_x[\text{H}_{8-x}\text{W}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}$ (TPA: tetrapropylammonium and TBA: tetrabutylammonium). Furthermore, a pioneer application for solid POT catalysts in the oxidative cleavage of oleic acid is reported in this chapter.

Chapter 7, includes the results of our works on molybdenum oxide catalysts, synthesized via almost the same synthesis approach as Chapter 5. Organo-functionalization by two quaternary ammonium cations with different lengths, CTAB and TMA (tetramethylammonium), and effects of concentration of these organic surfactants on physicochemical properties and catalytic activities of the products are also reported.

In Chapter 8, we highlight the major conclusions derived from the works in this research. Suggestions to foster the future works are also succinctly presented.