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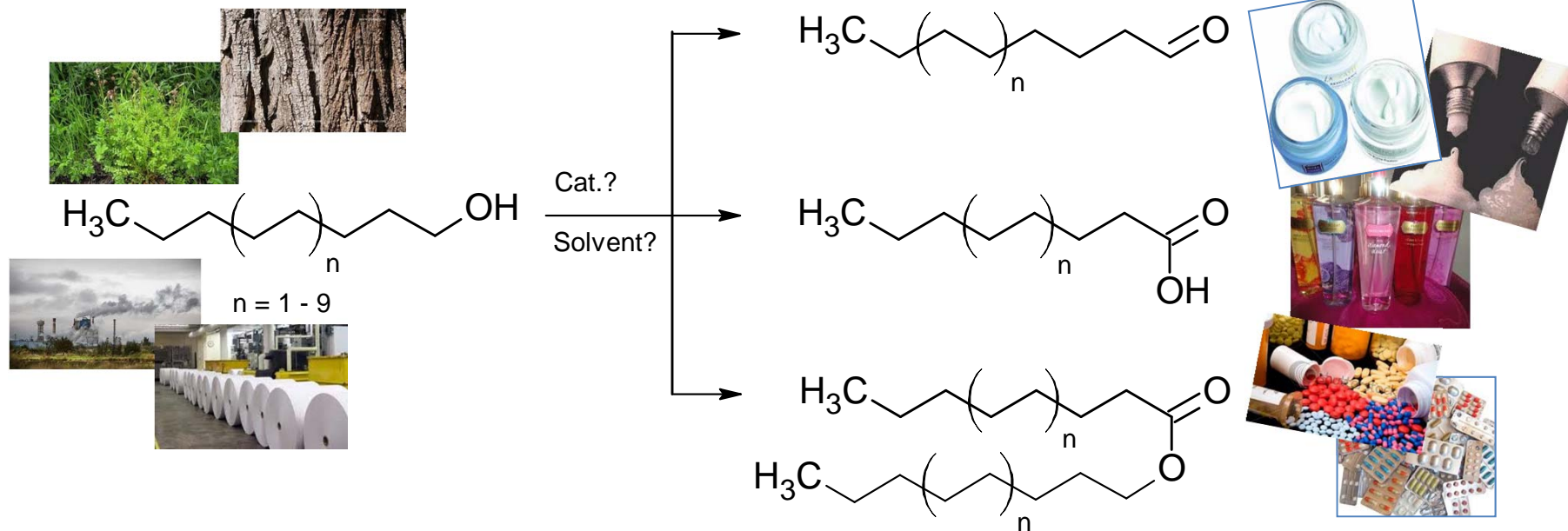
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Green oxidation of fatty alcohols: challenges and opportunities

V. Cortés Corberán*, M.E. González-Pérez, S. Martínez-González, A. Gómez-Avilés

HIGHLIGHTS

Oxidation of fatty alcohols may produce high value aldehydes, acids and esters, but is scarcely studied

Challenges and technological opportunities of this reaction are discussed

State-of-art of selective oxidation of C₈₊ fatty alcohols is critically reviewed to identify trends and features.

Our critical evaluation supports the feasibility of higher fatty alcohols selective oxidation by green processes

Such processes may allow new routes to valued chemicals production from biomass

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Dedicated to Prof. B. Delmon on occasion of his 80th anniversary

Abstracts

Selective oxidation of the so-called fatty alcohols, aliphatic long chain alcohols that are present in vegetable waxes, forestry residues and pulping industry subproducts, could be used to obtain the corresponding aldehydes, acids and esters, widely used in pharmaceutical and cosmetic applications and as emulsifiers. The physico-chemical characteristics of this type of alcohols entail specific challenges for the reaction. This work is aimed to review and evaluate the state-of-art of catalytic selective oxidation of the higher fatty alcohols (C₁₀₊), to assess the feasibility of new “green” processes using biomass for the production of fine chemicals. Due to the scarcity of information available on these reactions, the scope was extended to all C₈₊ primary alkanols, to identify trends and characteristics of the oxidation of longer chain aliphatic alcohols, as well as suitable process conditions.

The critical evaluation of available literature allows to conclude that the oxidation of higher alcohols is feasible using non enzymatic heterogeneous catalysts, either without solvent or with solvents miscible with both polar and nonpolar media (depending on the alcohol chain length), and using clean oxidants such as H₂O₂, molecular oxygen or air. The appropriate selection of the catalytic system and solvent may allow directing the reaction selectively to production of the aldehyde, the acid or the ester. These features would allow the implementation of small-scale processes, well in accordance with the principles of "green chemistry".

Keywords: green chemistry, sustainable chemistry, fatty alcohols, selective oxidation, gold catalysts, oxide catalysts, alcohol oxidation, fatty acid production, long-chain aliphatic aldehydes, wax esters

1. Introduction: motivation and opportunities

The sustained growth of population, as well as the exponential growth of their quality of life, has resulted in increased demand for fuels and chemicals. Currently the main raw material for their production is crude oil. Environmental concerns, together with the need to reduce the society's dependence on oil, and the possibility to diversify resources and their location have boosted the interest in biomass as a source for chemicals production. The industrial application of feedstock from renewable resources requires new processes, that could also be useful for valorizing wastes from some economic sectors (such as forestry, agriculture and the paper industry), by using them as raw materials.

The higher alcohols (monohydric aliphatic alcohols of six or more carbon atoms) with long carbon chains are generally denoted as fatty alcohols, because historically they were mostly derived from fats, oils and waxes [1], though nowadays are also produced by chemical synthesis. Those of natural origin are unbranched. Fatty alcohols are also present in forestry wastes, such as beech or Douglas-fir barks, in tall oil, the third largest subproduct of the Kraft pulping process of wood mainly from coniferous trees [2], and in pulps from several non woody species (flax, hemp, sisal and abaca) by alkaline pulping [3]. Selective oxidation of these alcohols could allow to using them as a new resource for producing desired aldehyde, ketone, ester and fatty acid products that are valuable intermediates for the fine chemical, pharmaceutical [4] and agrochemical sectors. For instance, behenic acid ($C_{22}H_{43}O_2$) is used in cosmetics, hair conditioners and creams, due to its high wettability [5], and lignoceric acid ($C_{24}H_{48}O_2$) is used in pharmaceutical [6,7] and health-care preparations [8] and as additives in foods [9].

At present, natural fats and oils are the main source of fatty acids. They are composed of triglycerides of even numbered carbon fatty acids having a chain length in the diesel oil range, which explains the large effort devoted in the past few years to the conversion of fats into fuels [10]. But now there is a shift from triglycerides toward lignocellulose as raw material for the future development for large-scale production of biofuels. This may increase the availability of some fatty acids (especially, those edible ones) and open opportunities for synthesizing products with a higher added value [11]. It should be noted, however, that: a) the preponderant number of technically available triglycerides consists particularly of C_{16} and C_{18} fatty acids with one or more insaturations [12]; and b) that fatty acids with twenty or more carbon atoms are extremely scarce in nature. New ways to produce them, as well as other acids less available, would be of great applied interest. Many aldehydes and ketones with a lineal, aliphatic carbon chain, found in natural products (essential oils and fruits of plants) or made synthetically, have desirable olfactory properties. Examples of these odoriferous aldehydes include n-valeraldehyde (C_5) (occurring in musk, herbs), n-

octanal (occurring in lemon oil, lemongrass oil), n-nonanal (occurring in mandarin, orris root, Ceylon cinnamon), n-capraldehyde (C₁₀) (occurring in sweet orange, lemongrass, mandarin neroli, coriander), n-dodecanal (occurring in oils of silver fir, lemon and rue), n-tetradecanal (occurring in ocotea, pinus, and Formosan camphor oils), n-hexadecanal and n-octadecanal, as well as those not naturally occurring with odd carbon atom numbers n-heptanal, n-undecanal and n-tridecanal [13]. These odoriferous aldehydes are so potent that they markedly affect the character of a perfume or formulation to which they are incorporated. When prepared synthetically, the purity of the aldehydes or ketones is a controlling factor in their commercial use, as the presence of unpleasant by-odors resulting from by-products formed during the synthesis can make their use in perfume formulations totally unacceptable. Thus, methods of preparing odoriferous aldehydes synthetically that minimize or eliminate objectionable by-products are needed. Selective oxidation of fatty alcohols to the corresponding aldehydes would contribute to this goal.

Wax esters (esters of long-chain fatty acids esterified with long-chain fatty alcohols) have a variety of uses in many industries, as high pressure lubricants, replacing hydraulic oil, and in the pharmaceutical, cosmetic, printing and leather industries. For instance, myristyl myristate (tetradecyl tetradecanoate) is an appreciated emollient used in lotions and creams. Though wax esters are widespread in nature, as common components of the waxy cuticle on aerial surfaces of higher plants [14], but they are usually found in low concentrations. The only known exception among plants is jojoba (*Simmondsia chinensis*) which seeds contain up to 60% of the dry weight of their cotyledons of wax esters composed of very-long-chain (C₂₀, C₂₂, and C₂₄) monounsaturated fatty acids and alcohols [15]. Besides from jojoba oil, wax esters were obtained from spermaceti oil [16], not longer available after the demise of commercial whaling. They also can be found in some deep water fishes, but New Zealand is currently the only country extracting wax esters from fish oil [17].

It seems evident that selective oxidation of fatty alcohols shows potential as one technological option for producing fatty acids with very long chain or odd carbon atoms number, rare aldehydes, and wax esters, which are high value chemicals nowadays scarce.

2. Scope and aim of this review

Selective alcohol oxidation is one of the key transformations in organic synthesis and in industrial practice. By the last turn of century the world-wide annual production of carbonyl compounds was over 10⁷ tonnes and many of these compounds are produced from the oxidation of alcohols [18]. Conventional methods were based in the use of stoichiometric oxidants, mostly noxious transition metal oxides and salts, halogenated compounds or sulfur oxides, which produce great amounts of undesirable subproducts, a nightmare from the environmental point of view. So, it is not surprising

the considerable effort made to comply the principles of green chemistry, by implementing processes based on catalysis and non-toxic oxidants: the number of papers on catalytic selective oxidation of alcohols increased linearly almost tenfold in the last years: from 24 in 1998 to 221 in 2011 [19].

Selective oxidation of alcohols in general have been object of several specific reviews [20-27] and it is also examined inside reviews devoted to some catalytic systems used for it, such as those based on gold [28, 29], ruthenium [30] or heteropolycompounds [31].

However, none of these addresses the specific issues of fatty alcohols oxidation. In fact, most of the published research deals with activated alcohols, such as allylic, benzylic and polyfunctional alcohols, and much less with the aliphatic alcohols (alkanols). More specifically, there are very few papers devoted to selective oxidation of the higher alcohols. The only exception is the oxidation of 1-octanol, usually reported jointly with that of more active alcohols of similar number of carbon atoms for comparison purposes. As a consequence, this information is rather scattered.

This paper is aimed to review and evaluate critically the state-of-art of selective oxidation of the fatty alcohols with the longer carbon chains, and to assess the feasibility of making it by processes in accordance with “green chemistry” principles: economy of atoms, reaction with low toxicity compounds, decreased use of solvents and co-solvents, use of renewable resources, avoiding derivatization, production of biodegradable products and use of catalysis [32].

However, as the information available on the oxidation of those alcohols is very scarce, the scope is extended to all primary alkanols with eight or more carbon atoms (C_{8+}), looking for to identify trends and characteristics of the oxidation of long chain aliphatic alcohols, as well as suitable process conditions. Such processes should overcome the specific challenges caused by the chemical and physical properties of these compounds, quite different from those of activated alcohols, and even from those of short chain aliphatic alcohols.

3. Fatty alcohols characteristics: the challenges

The first challenge is that chemical reactivity of aliphatic alcohols is much lower than that of benzylic, allylic or functionalized alcohols. For instance, the turnover frequencies (TOF, h^{-1}) of the solvent-free oxidation of different types of C_8 primary alcohols to aldehydes using Au-Pd/TiO₂ catalysts (with oxygen at 160 °C) are: 269,000 for 1-phenylethanol, 86,500 for benzyl alcohol, 10,630 for 3-octanol and just only 2,000 for 1-octanol [33]; this evidences clearly the higher difficulty of oxidizing the non-activated aliphatic alcohols, such as fatty alcohols. Furthermore, TOF for 1-butanol (5,930) was almost threefold that of 1-octanol, which indicates that reactivity decreases with the increase of chain length.

Additional challenges come from some physical properties of primary fatty alcohols, summarized in Table 1. It shows definite trends in physical properties which are of relevance for operative conditions to be used in selective oxidation. Both the melting and the boiling points increase progressively with the increase of the number of carbon atoms. And also hydrophobicity: solubility of fatty alcohols in water decreases exponentially with the chain length increase [34]. In parallel, the viscosity increases with the number of carbon atoms: 8.4, 13.8, 18.8 and 53 cP at 20 °C for the alcohols with 8, 10, 12 and 16 carbon atoms, respectively. These characteristics impose some constraints for the practical reaction conditions.

On one hand, the high boiling points make the operation in the gas phase unpractical and energy costly. On the other, high melting points (and high viscosity of the heavier alcohols) impose progressively higher minimum reaction temperatures (T_R) to operate without solvent, or the use of solvents to operate in the liquid phase. Hydrophobicity of the alcohols with longer chains (and of their oxidation products) conflicts with the use of water as solvent. The limited solubility in water may be overcome by using co-solvents, such as ethers of general formula $R_1O(CH_2CH_2O)_nR_2$ where $n=1-4$ and R_1, R_2 are alkyl radicals of 1-4 carbon atoms. Thus, aerobic oxidation of 1-octanol over a commercial 5% Pt/C catalyst reaches a 77.4 % yield of caprylic acid when dissolved in diglycol dimethyl ether, while in water the yield is just 1% under the same reaction conditions (alcohol / catalyst (A/C) ratio = 4, $T_R = 90$ °C, reaction time (t) = 20 h) [35]. Alternatively, a phase transfer catalyst may be used.

On the opposite sense, the use of organic solvents conflicts with the use of polar and water soluble oxidants, such as hydrogen peroxide, often used as the “clean” oxidant of choice for liquid phase oxidations, and with the limited stability of enzymes in organic media. In general, the higher alcohols are soluble in lower alcohols and methanol, in diethyl ether and petroleum ether. The lower alcohols must be discarded as solvents due to their higher reactivity in the oxidation reaction, which would compete with the desired reaction and cause difficulties with product separation and purification. The use of oxygen or air as oxidants (aerobic oxidation) introduces risks of flammability. This further restricts the selection of the organic solvent, as it must be inert under the reaction conditions, and resistant to peroxide formation and other oxidative processes.

Summarizing, fatty alcohols form the less active type of non activated aliphatic alcohols, whose low reactivity makes its selective oxidation to be the most demanding among those of the diverse types of alcohol structures. This higher difficulty faces limitations of the possible reaction conditions imposed by their physical properties. The combination of these opposite factors is probably the cause of the very little information available on their oxidation.

4. Oxidation of the longer chain (C₁₀₊) fatty alcohols

Despite the number of papers on catalytic selective oxidation of alcohols has rocketed in the last years, research on the oxidation of C₁₀₊ fatty alcohols is so scarce that only some 15 references could be found in literature since 1990 [19]. Not all the alcohols have been tested, and usually only specific combinations alcohol-catalyst are reported. Therefore, they are discussed next according to the type of catalysis and, where possible, in the order of decreasing carbon chain length.

4.1 Enzymatic catalysts

In nature very-long-chain fatty alcohols are oxidized to fatty acids by the sequential action of a fatty alcohol oxidase (FAO) and a fatty aldehyde dehydrogenase (FADH) [36].

At present, the only commercially available enzymes capable of oxidizing aliphatic alcohols up to 16 carbon atoms are the alcohol dehydrogenases produced by *Candida tropicalis* and *Candida lipolytica*. Enzyme E.C.1.1.1.192 (long chain fatty acids alcohol dehydrogenase) is active for the oxidation of hexadecanol to palmitic (hexadecanoic) acid. This oxidoreductase requires the use of stoichiometric cofactor NAD⁺: two moles of NAD⁺ are required per mole of acid produced [37]. Horse liver alcohol dehydrogenase (HLAD) oxidizes docosanol (C₂₂) and tetracosanol (C₂₄), although at lower rates than short chain alkanols. Initial oxidation rates of the C₁₂, C₁₆, C₂₂ and C₂₄ are 30, 17, 21 and 15 %, respectively, of the oxidation rate of octanol [38]. This enzyme is poorly stable at moderate T_R and concentrations of organic solvents. This makes necessary to immobilize them, especially when working with highly hydrophobic substrates such as long-chain fatty alcohols. Immobilization on glyoxyl agarose increases dramatically the stability of HLAD [39], and reduces significantly the activity drop with increasing chain length observed with free HLAD: initial oxidation rates of C₁₂-C₂₄ alcohols are 64-54% of that of octanol. To broaden the T_R range of operation, the production of alcohol dehydrogenases with the capacity of oxidizing long chain aliphatic alcohols able to operate at different temperature ranges (mesophilic, thermophilic and hyperthermophilic strains) has been investigated. Among them, the highest initial rates of oxidation of docosanol (C₂₂) and eicosanol (C₂₀), 196.9 and 218.8 μmol NADH min⁻¹ g of protein⁻¹, respectively, were obtained at room temperature with the enzyme from *C. tropicalis* ATCC20336 (dissolved in phosphate buffer at pH 7.0 with 0.6% diglyme) [40]

The low availability of suitable enzymes, their limited ranges of operation conditions (solvent, pH, temperature, low substrate concentration), the cost of co-enzymes and oxidant, and their low productivity per volume unit may restrict the applicability of these reactions to very small scale operations.

4.2 Homogeneous and combined catalytic systems

Among the numerous reports on oxidation of alcohols with homogeneous catalysts, very few relate to C₁₀₊ fatty alcohols. They are presented next in the order of increasingly cleaner oxidant.

Ruthenium complexes, such as [Ru₃O(OAc)₆(MeOH)₃]⁺OAc⁻, are useful catalysts to oxidize some aliphatic alcohols to the corresponding aldehydes with iodobenzene [41]. Polymer-supported ruthenium complex PS–Phen–Ru (where PS = chloromethyl polystyrene resin, Phen = 1,10-phenanthroline) catalyzes the quantitative oxidation of 1-dodecanol and 1-hexanol to their corresponding aldehydes in 6 and 2 h, respectively (solvent CH₃CN, PhIO/alcohol = 2.5, T_R = 60 °C) [42]. This difference in reaction time needed evidences how reactivity decreases with increasing carbon chain length.

Zirconium alkoxides catalyze the oxidation of nonactivated primary and secondary alcohols with hydroperoxides such as *tert*-butyl hydroperoxide (TBHP) or cumene hydroperoxide (CHP) into the corresponding aldehydes and ketones [43]. Thus, using the combined system Zr(O-*n*-Pr)₄/TBHP/3Å molecular sieves (MS3A, a Brønsted base), 1-dodecanol is oxidized to dodecanal up to a 70% yield before any subproduct could be detected by GC (TBHP/alcohol = 2; A/C = 10, T_R = 20 °C, t = 22 h). However, formation of carboxylic acids was observed under prolonged reaction times, higher T_R and with an excess of TBHP as the oxidant. Thus, oxidation of 1-octanol gives a mixture aldehyde/acid in ratio 4:1 at 60 °C in just 2 h (alcohol conversion C_{OL} >98%), while this ratio is 9:1 when it is obtained at 20 °C in 20 h (C_{OL} = 96%). Authors conclude that good aldehyde yields are obtained by lowering the T_R, decreasing the amount of TBHP or replacing TBHP by CHP, and/or exchanging the more active catalyst Zr(O-*t*-Bu)₄ by Zr(O-*n*-Pr)₄ or silica gel-supported Zr(OR)_x.

But primary aliphatic alcohols can also be oxidized with oxygen, by using palladium catalysts.

Palladium acetate, Pd(OAc)₂, catalyzes the oxidation of octadecanol (in the presence of a catalytic amount of a perfluoroalkylated-pyridine as a ligand) with molecular oxygen in a fluoruous biphasic system (FBS) composed of toluene and perfluorodecalin, reaching 55 % conversion with a selectivity to aldehyde S_{AL} = 100% (alcohol/metal ratio (A/M) = 20, P(O₂) = 1 bar, T_R = 80 °C, t = 6 h) [44].

Over these catalysts 1-dodecanol is similarly converted to the aldehyde (C_{OL} = 92 % with S_{AL} = 83 %; t = 10 h) and 2-dodecanol is oxidized to 2-dodecanone with 90% selectivity (C_{OL} = 100 % at t = 9 h).

The combined system Pd(OAc)₂:pyridine (1:4)/MS3A catalyzes the aerobic oxidation in toluene of a variety of primary and secondary alcohols into the corresponding aldehydes and ketones, with no formation of carboxylic acids or their esters [45]. Thus, with this combined system, octadecanol oxidation reaches C_{OL} = 95% with a S_{AL} = 96%, compared to C_{OL} = 58 % with S_{AL} = 61% in the absence of MS3A (solvent toluene, A/M = 20, P(O₂) = 1 bar, T_R = 80 °C, t = 2 h). The ratio of O₂

uptake to Y_{AL} is ca. 2:3 in the presence of MS3A, and ca. 1:1 in its absence. This suggests the in situ formation of H_2O_2 by the Pd complex and its decomposition by MS3A into water and oxygen. The catalytic cycle proposed includes the formation of a Pd(II)-alcoholate followed by β -elimination of a Pd(II)H species and a carbonyl compound followed by the formation of a Pd(II)OOH species. The combined system also catalyzes dodecanol oxidation ($C_{OL} = 93\%$ with $S_{AL} = 97\%$) under the same conditions with MS3A addition.

These high aldehyde selectivity values and the clean oxidants as air are indeed of interest. However, the drawbacks of the complexity of the catalytic systems and the inherent difficulty of its separation, make these systems not competitive with the heterogeneous alternatives.

4.3. Heterogeneous catalysts

Research on heterogeneous oxidation of primary C_{10+} alkanols is rather less than that of lower alkanols. To our knowledge, the only example of catalytic oxidation of long chain alkanols in the gas phase is the use of gold catalysts (pure gold wire gauze or gold plated copper wire) with low surface area ($\leq 2\text{ m}^2/\text{g}$) [46]. The alkanols with 8, 10, 12 and 14 carbon atoms were oxidized with air at atmospheric pressure to yield the corresponding aldehyde with high S_{AL} over gold plated metal gauze at $T_R = 300\text{--}470\text{ }^\circ\text{C}$, depending on the alcohol boiling point. Under their respective optimal reaction conditions, myristic alcohol (C_{14}) yields 59% aldehyde ($S_{AL} = 85\%$) at $312\text{ }^\circ\text{C}$, dodecanol yields only 41.8% aldehyde ($S_{AL} = 100\%$) at $400\text{ }^\circ\text{C}$, 1-decanol yields 66.8% decanal ($S_{AL} = 97\%$) at $415\text{ }^\circ\text{C}$, and 1-octanol yields 82.8% octanal ($S_{AL} = 91.5\%$) at $340\text{ }^\circ\text{C}$. Operation at $T_R > 400\text{ }^\circ\text{C}$ shortened catalyst life, and it needed to be replaced after 600-700 h on stream.

Heyns and Blazejewicz [47] reported in 1960 the oxidation in the liquid phase of lauryl (C_{12}), myristyl (C_{14}), cetyl (C_{16}), and stearyl (C_{18}) alcohols in their study of the oxidation of a wide range of primary and secondary alcohols with platinum catalysts. Catalyst precursor PtO_2 was pretreated in H_2 before the oxidation. Reaction rates depended on the solvent: the highest ones were obtained in n-heptane, though this solvent allows working only in dilute solutions. Using it and the stoichiometric amount of oxygen, these alcohols were oxidized at $T_R = 60\text{ }^\circ\text{C}$ to the corresponding aldehydes in high yields (Y_{AL}) in short reaction times (t): 77% in 15 min, 91% in 45 min and 77% in 30 min for C_{12} , C_{14} and C_{18} alcohols, respectively. The oxygen amount is key for product selectivity: using the stoichiometric amount, longer reaction times allow to complete the conversion to aldehyde (for instance, oxidation of cetyl alcohol reaches $Y_{AL} = 91\%$ in $t = 7\text{ h}$); but with higher amounts of oxygen, longer reaction times lead to almost quantitative oxidation to the acid. Thus, lauryl alcohol (C_{12}) is oxidized quantitatively to lauric acid ($Y_{AC} = 96\%$) in 2 h with 1 mol O_2 /mol alcohol (compared to $Y_{AL} = 77\%$ in 15 min with 0.5 mol O_2 /mol alcohol).

Since that study, only isolated reports on some alcohols and specific catalytic systems can be found, and they will be revised hereinafter in the decreasing order of chain length.

Bi and coworkers [48] reported the oxidation of octadecanol (C_{18}) and eicosanol (C_{20}) with hydrogen peroxide over quaternary ammonium peroxotungstophosphate catalysts $Q_3[PW_4]$, where PW_4 denotes $\{PO_4[W(O)(O_2)_2]\}^{3-}$, and Q denotes one quaternary ammonium ion: $C_{18}H_{37}(CH_3)_3N^+$ (denoted by authors as 1831), $C_{16}H_{33}(CH_3)_3N^+$ (denoted 1631) or $(C_8H_{17})_3CH_3N^+$ (denoted 3811, commercially known as Aliquat®336) [49]. One limitation of the use of hydrogen peroxide for the solventless oxidation of the hydrophobic higher alcohols is the active oxygen transfer in the biphasic (aqueous/organic) system. These catalysts form a functionalized ionic liquid that efficiently transfers the active oxygen species from the aqueous to the alcoholic organic phase. Catalysts were tested in a discontinuous reactor ($A/C = 200$, $T_R = 70-110\text{ }^\circ\text{C}$, $t = 2-10\text{ h}$), using a H_2O_2 /alcohol ratio = 3, that was found optimal. Alcohol conversion increased with T_R up to $90\text{ }^\circ\text{C}$, but decreased at higher T_R probably due to the faster thermal decomposition of the peroxide. The main product was always the corresponding acid ($S_{AC} = 54-96\%$) reaching $C_{OL} = 49-83\%$ after 6 h of reaction. Both conversion and acid yield (Y_{AC}) depended on the nature of the quaternary ion Q^+ and the mode of H_2O_2 addition. Using the preferred addition procedure (in three portions along the reaction period), catalyst with Q^+ ion 1831 showed the highest S_{AC} (96%) with $Y_{AC} = 57.4\%$. Oxidation of C_{16} , C_{18} and C_{20} primary alcohols over this catalyst under the optimal conditions (no solvent, H_2O_2 /alcohol = 3, $A/C = 200$, $T_R = 90\text{ }^\circ\text{C}$, $t = 6\text{ h}$) showed that both C_{OL} and Y_{AC} increased with increasing carbon atom number while the selectivity was practically the same ($S_{AC} = 96\%$). Using the same catalyst, the oxidation of docosanol (C_{22}) to the acid with slow continuous addition of the peroxide gives $C_{OL} = 81\%$ with $S_{AC} = 55\%$ (no solvent, H_2O_2 /alcohol = 3, $A/C = 100$, $T_R = 90\text{ }^\circ\text{C}$, $t = 6\text{ h}$) [50].

The same group studied the oxidation of eicosanol (C_{20}) over Ti-MCM-41, pure or impregnated with Cu, Cr or $Q_3[PW_4]$ [51]. When using H_2O_2 as oxidant, activity of pure Ti-MCM-41 was quite low, even at the optimal $T_R = 90\text{ }^\circ\text{C}$ ($C_{OL} = 1.5\%$ for $Ti/Si = 100$ and 7% for $Ti/Si = 30$); however, its impregnation with $Q_3[PW_4]$ with Q^+ ion 1381 increases dramatically activity, reaching $Y_{AC} = 46\%$ ($S_{AC} = 94\%$) at the same T_R (no solvent, $A/C = 200$, H_2O_2 /alcohol = 3, $T_R = 90\text{ }^\circ\text{C}$, $t = 5\text{ h}$). On the contrary, when an O_2 flow is used as oxidant, the activity of pure Ti-MCM-41 was much higher, and independent of Ti/Si ratio for $Ti/Si \leq 50$ (no solvent, flow $30\text{ mL min}^{-1} O_2$, $A/C = 100$, $T_R = 130\text{ }^\circ\text{C}$, $t = 5\text{ h}$). The optimal T_R is $150\text{ }^\circ\text{C}$: at higher T_R the acid yield was lower due to the decreased solubility of oxygen in the alcohol. Impregnation with Cu decreases Y_{AC} by 92%, while impregnation with Cr increases it by 50%.

Supported $\text{Co}_3\text{O}_4/\text{SiO}_2$ catalysts, prepared by impregnation, were used for the oxidation of 1-octadecanol to octadecanoic acid with an oxygen flow [52], investigating the effect of catalyst cobalt content and reaction parameters. The best catalyst (5 wt.% Co) gives $C_{\text{OL}} = 25\%$ with $S_{\text{AC}} = 97.5\%$ under optimal reaction conditions (solventless, 30 mL/min O_2 , A/C = 50 w/w, $T_{\text{R}} = 130\text{ }^\circ\text{C}$, $t = 5\text{ h}$). This catalytic performance can be improved by combining Co and Cr oxides [53]. Under the same reaction conditions, supported chromium oxide (5% Cr/SiO₂) is more than twice more active than 5% Co/SiO₂ catalyst but little selective ($S_{\text{AC}} = 24\%$). However, the bicomponent 5% Cr-5% Co/SiO₂ catalyst gives a conversion a 50% higher than that of the single cobalt catalyst while keeping $S_{\text{AC}} = 99.9\%$. Thus, acid yields up to $Y_{\text{AC}} = 52.4\%$ are reached ($t = 8\text{ h}$).

Ruthenium combined with microcrystals of cobalt hydroxide and cerium oxide, Ru-Co(OH)₂-CeO₂, a highly efficient catalyst for the oxidation of several types of alcohols, allows to oxidize octadecanol with molecular oxygen to octadecanoic acid giving $Y_{\text{AC}} = 82\%$ at full conversion (solvent: TFT, A/M = 10, $T_{\text{R}} = 60\text{ }^\circ\text{C}$, $t = 5\text{ h}$) [54]. Tests of 1-octanol oxidation (see Section 5.1) evidenced that the combination of Ru with both Co and Ce is necessary to achieve high Y_{AC} . Ru K-edge XAFS revealed that the Ru⁴⁺ cation exists as a monomeric species on the surface of Co(OH)₂ and CeO₂. Ruthenium oxidation state is also Ru⁴⁺ in $\gamma\text{-Fe}_2\text{O}_3$ containing ruthenium hydroxyapatite (Ru/HAP- $\gamma\text{-Fe}_2\text{O}_3$) that catalyzes the oxidation of 1-dodecanol (C₁₂) almost quantitatively to dodecanoic acid: $Y_{\text{AC}} = 98\%$ (solvent: TFT, A/M = 10, $T_{\text{R}} = 90\text{ }^\circ\text{C}$, $t = 9\text{ h}$) [55]. Similarly, a 10% Ru/C catalyst is able to convert 1-dodecanol to dodecanoic acid under an oxygen atmosphere (A/M = 20, $T_{\text{R}} = 90\text{ }^\circ\text{C}$, $t = 24\text{ h}$) but only in the presence of water: $Y_{\text{AC}} = 59\%$ in a mixed toluene:H₂O = 4:1 solvent, but null when solved in pure toluene [56]. However, when ruthenium is forming a bulk oxide, the main product is aldehyde: oxidation of 1-dodecanol with oxygen over a Ru^{IV}-Co^{III} (1:1.5) binary oxide gives $C_{\text{OL}} = 52\%$ with $S_{\text{AL}} = 83\%$ (solvent: toluene, A/M = 10, 25 mL min⁻¹ O_2 , $T_{\text{R}} = 110\text{ }^\circ\text{C}$, $t = 4\text{ h}$) [57]. Mallat et al. [58] studied the oxidation of 1-dodecanol over a Bi-Pt/Al₂O₃ (Bi/Pt = 0.5) to evidence the correlation between selectivity to aldehydes (S_{AL}) in the oxidation of alcohols and the hydration of aldehydes in aqueous medium (see discussion in Section 5.2). S_{AL} decreased monotonously with increasing conversion ($S_{\text{AL}} \sim 80\%$ at low C_{OL} , but only 33% at $C_{\text{OL}} = 55\%$) due to the carboxylic acid formation (A/C = 27, $T_{\text{R}} = 85\text{ }^\circ\text{C}$). A diluted aqueous solution of LiCO₃ and dodecylbenzene sulfonic acid sodium salt detergent was used as solvent (catalyst : carbonate : detergent ratios = 1:1:1 w/w). Palladium nanoparticles (NPs) in mesocellular foam (MCF) were found to be highly efficient for the oxidation of alcohols by molecular oxygen [59]. Palladium was immobilized through the use of amine ligands on aminopropyl-grafted MCF (AmP-MCF), and showed a narrow particle distribution (1–2 nm). Aerobic oxidation of 1-decanol and 1-dodecanol to their corresponding aldehydes on this

Pd/AmP-MCF catalyst gives $C_{OL} = 93$ and 88 %, respectively, with $S_{AL} = 84$ % (solvent mesitylene, $A/M = 13.3$, $P(\text{air}) = 1$ bar, $T_R = 130$ °C, $t = 8$ h).

Ogibin et al. [60] investigated the use of sodium hypochlorite, one of the cheapest and most readily available oxidizing agents, to oxidize 1-decanol using RuCl_3 in a diphasic system $\text{CCl}_4/\text{aqueous NaOCl}$ solution (1:1 v/v). The chloride converted almost immediately to hydrated ruthenium dioxide (HRD, $\text{RuO}_2 \cdot n\text{H}_2\text{O}$), but the catalyst activity was maintained when recovered after reaction, by filtration and washing. At $T_R = 60\text{-}65^\circ\text{C}$, 1-decanol was rapidly converted to 1-decanal ($C_{OL} = 73\text{-}100$ % in 15-30 min) with high selectivity: $S_{AL} = 96\text{-}80$ %, respectively ($A/M = 50\text{-}100$, $0.1\text{-}0.6$ M aqueous NaOCl, $\text{NaOCl}/\text{alcohol} = 1.5$). Under the optimal conditions for this reaction, also lower (1-hexanol) and higher (1-hexadecanol) alkanols are oxidized to their corresponding aldehydes with a high selectivity ($S_{AL} = 88\text{-}90\%$ at $C_{OL} = 66\text{-}95\%$, respectively).

To avoid the acid formation, (non oxidative) dehydrogenation of tetracosanol (C_{24}) to tetracosanal was investigated over mixed Cu-M ($M = \text{Mg, Ca, Ba}$) oxides [61]. Initial aldehyde formation rate depends linearly on the catalyst basic sites concentration. A maximum $Y_{AL} = 68.2$ % with $S_{AL} = 72.0$ % is reached with Cu-Mg-O catalyst ($t = 10$ min). However, these data are reported for a liquid phase batch reactor operated at 300 °C, which seems strange as the tetracosanol boiling point is 287 °C (Table 1).

It can be seen that several heterogeneous catalysts have been found efficient for oxidation of some fatty alcohols in the liquid phase; however, the specificity and scattering of available data do not allow to identify clear general trends or forecasts for guiding catalyst selection and reaction conditions optimization. For this reason, the scope is extended to a shorter chain fatty alcohol, 1-octanol, which oxidation is reviewed in the next Section.

5. Oxidation of 1-Octanol:

1-Octanol is very often used as a model molecule, representative of the reactivity of non activated, linear, long-chain, aliphatic primary alcohols, in the evaluation of catalytic properties with the different types of alcohols. This causes that, on one hand, many catalytic systems have been tested for its selective oxidation, and, on the other, this abundant information is scattered and mostly not systematic. The more relevant results in literature, summarized in Table 2, are discussed hereinafter aiming to extract trends that could be extrapolated for the oxidation of fatty alcohols with longer carbon chain lengths.

To show the progress attained towards higher catalytic efficiency, the results, grouped by catalytic system, will be discussed in the order of their ability to operate at increasingly milder conditions (i.e., cleaner oxidant, lower oxidant pressure, lower reaction temperature or shorter reaction time).

5.1. Ru catalysts

Early research of heterogeneous ruthenium catalysts for oxidation of primary alcohols to aldehydes explored efficient oxidants. Sheng [62] patented the use of peracetic acid (AcOOH) to oxidize 1-octanol with $\text{RuCl}_3 \cdot 1.3\text{H}_2\text{O}$ catalyst. Total conversion was reached in 1 h at 82 °C, with $S_{\text{AC}} = 83.4\%$ and $S_{\text{ES}} = 17\%$ (solvent: heptane, A/C = 400 w/w, excess AcOOH). Formation of the ester was inhibited by addition of small amounts of sodium acetate. The solvent heptane was also oxidized to the C_7 acid in minor amounts (ca. 1%).

As mentioned in Section 4.3, hydrated ruthenium dioxide (HRD), formed in situ from RuCl_3 , catalyzes the oxidation of C_6 , C_{10} and C_{16} alkanols with NaOCl [60]. Oxygen can be used as the primary oxidant for alcohols oxidation with HDR [63] and Ru-hydrotalcite [64] but only with activated (i.e., allylic and benzylic) alcohols. Hydrogen peroxide can also be used to oxidize activated alcohols to the corresponding aldehydes or ketones with high selectivity with $[\text{Ru}(\text{terpyridine})(2,6\text{-pyridinedicarboxylate})]$ [65]. However, this catalyst showed no activity for the selective oxidation of primary or secondary alkanols (1- and 2-octanol)

Thus, looking for employing oxygen (or air) as the sole oxidant for non-activated alkanols, Sheldon group [66, 67] combined $\text{RuCl}_2(\text{PPh}_3)_3$ and TEMPO (2,2',6,6'-tetramethylpiperidine N-oxyl) in 1:3 ratio to oxidize 1-octanol yielding 85 % octanal ($S_{\text{AL}} > 99\%$) under a high pressure of pure oxygen (solvent chlorobenzene, A/C = 50, $P(\text{O}_2) = 10$ bar, $T_{\text{R}} = 100$ °C, $t = 7$ h). Similarly, the more active 2-octanol (2- C_8) was oxidized using air instead of pure oxygen yielding 98% octa-2-one (A/C=100, $P(\text{air}) = 10$ bar). However, both ruthenium and TEMPO deactivated slowly during reaction.

Furthermore, the system became little active when supported onto silica or MCM-41 to heterogeneize it [68]. Aerobic oxidation of 1-octanol at a lower pressure was tested in the frame of a study of metal catalysts (see Section 5.3) [69]. A commercial carbon-supported metallic ruthenium catalyst (5 wt.% Ru/C) showed quite low conversion ($C_{\text{OL}} = 7\%$) forming only octanal ($S_{\text{AL}} = 100\%$) (solvent toluene, A/M = 80, $P(\text{air}) = 3$ bar, $T_{\text{R}} = 60$ °C). Catalyst promotion with 1 wt.% Bi increased the activity ($C_{\text{OL}} = 18\%$), keeping the aldehyde selectivity. However, the addition of NaOH (0.5 equiv) into the reaction medium promoted octanal oxidation to octanoic acid ($C_{\text{OL}} = 22\%$, $S_{\text{AC}} = 46\%$). More recently another commercial activated carbon (AC) supported ruthenium catalyst (5 wt.% Ru/AC) was found more active giving $C_{\text{OL}} = 45\%$ to octanal ($S_{\text{AL}} > 99\%$) under similar conditions (10% octanol in toluene; A/M = 100, $P(\text{O}_2) = 3$ bar; $T_{\text{R}} = 85$ °C, $t = 3$ h) [70]. With a slightly higher Ru content, a catalyst supported carbon nanotube (CNT), 5.9 wt.% Ru/CNT, performs the oxidation under atmospheric pressure yielding 24 % of pure octanal (solvent toluene:H₂O = 2 v/v, $P(\text{O}_2) = 1$ bar, $T_{\text{R}} = 85$ °C, $t = 3$ h) [71].

All the same, several ruthenium-based catalysts are highly active for the oxidation of activated and non-activated alcohols to the corresponding carbonyl compounds with only 1 bar of O₂. Ruthenium (III) meso-tetraphenylporphyrin chloride (Ru(TPP)Cl) combined with isobutyraldehyde catalyzes the oxidation of 1-octanol with oxygen bubbling, but mainly to the acid: Y_{AC} = 71 % with C_{OL} = 91% (solvent: TFT, P(O₂) = 1 bar, T_R = 60 °C, t = 1h) [72]. On the contrary, ruthenium on hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂, HAP) catalyst, Ru/HAP (17.1 wt.% Ru) is very selective to carbonyl compounds in the oxidation of many types of alcohols, including primary/secondary alkanols [73]. On this catalyst, oxidation of 1-octanol gives 1-octanal (Y_{AL} = 91%), noticeably without any formation of the carboxylic acid and ester (solvent toluene, O₂ atmosphere, T_R = 60 °C, t = 16 h.). The competitive oxidation of an equimolar mixture of 1-octanol and 4-octanol gives 95% 1-octanal selectively. In the intramolecular competitive oxidation of 1,7-octanediol, the RuHAP catalyst gives chemoselectively 7-hydroxyoctanal in 80% yield. This high chemoselectivity for primary hydroxyl functions was not similar to that of bulk Ru catalysts such as RuO₂ [74], but to that of a monomeric RuCl₂(PPh₃)₃ complex [67], and authors attributed it to monomeric Ru cation species on the RuHAP surface, despite the high Ru content (17.1 wt. %).

Also the Ru(OH)₃/Al₂O₃ system is highly active for the oxidation of activated and non-activated alcohols to the corresponding carbonyl compounds with only 1 bar of O₂. Thus, Ru(OH)₃/γ-Al₂O₃ (1.4 wt.% Ru) catalyzes the oxidation of 2-octanol to 2-octanone in a 91% yield in just 2 h (solvent TFT, A/M = 20, T_R = 83 °C) [75]. Less reactive primary alcohols 1-octanol and 1-decanol were oxidized more slowly to their corresponding aldehydes. Increasing the reaction time did not improve the yield to aldehydes due to their over-oxidation to the carboxylic acids. The addition of a small amount of hydroquinone (1equiv based on Ru) completely suppressed the over-oxidation, which allows obtaining only aldehydes in fairly good yields: 87 % octanal and 71% decanal, respectively, in just 4 h. Identical results for 1- and 2-octanol oxidation were reported when catalyst was prepared with another γ-Al₂O₃ and a slightly higher Ru content (2.1 wt.%) [76]. As with Ru/HAP catalysts, primary alcohols are much faster oxidized than secondary ones in both intra- and intermolecular competitive oxidations. This supports the formation of a Ru-alcoholate as an intermediate and discards free-radical intermediates.

Under similar reaction conditions, but at lower T_R, catalyst Ru-Co(OH)₂-CeO₂ (6.4 wt.% Ru, molar ratio: Ru/Co/Ce = 0.3/2/1) is highly efficient for the oxidation of 2-octanol to octa-2-one (98% yield with 100% selectivity in t = 1.5 h) and the oxidation of 1-octanol to octanoic acid yielding 97 % acid at full conversion, i.e., S_{AC} = 97% (solvent TFT, A/M = 10, P(O₂) = 1 bar, T_R = 60 °C, t = 4 h) [54]. The high S_{AC} is due to the very fast aerobic oxidation of octanal to the acid even at room temperature (Y_{AC} = 93% in 30 min) over this catalyst. Catalyst Ru-Co-Al-CO₃ (without cerium) is slightly less

active for 1-octanol oxidation ($C_{OL} = 90\%$) than the tricomponent catalyst giving both acid and aldehyde in a 2.4:1 molar ratio. The cobaltless Rh/CeO₂ catalysts is rather less active ($C_{OL} = 30\%$, $Y_{AC} = 28\%$) while the support Co(OH)₂-CeO₂ is almost inactive for oxidation ($C_{OL} < 2\%$, $Y_{AC} < 1\%$). These results evidenced that the synergy of the three metals (Ru, Co and Ce) is needed to achieve high yield of the acid.

Partial substitution of Fe for Ru and Cu in ferrite spinel MnFe₂O₄ (MnFe_{1.5}Ru_{0.35}Cu_{0.15}O₄) creates an effective catalyst for aerobic oxidation of alcohols at room temperature without any other additives [77]; however, its oxidation activity is low for primary alcohols such as 1-octanol, which only reaches 51% octanal yield ($S_{AL} = 100\%$) in 7 h using a high amount of catalyst (solvent: toluene, A/M = 2.4, P(air) = 1 bar, T_R = 20 °C). It is worth noting that initial oxidation rates for octanol and benzyl alcohol are 0.8 and 16.2 mmol h⁻¹g⁻¹, respectively.

Perruthenate (RuO₄⁻) anchored to an Amberlyst anion-exchange resin via quaternary ammonium groups catalyzes the oxidation with oxygen of primary alcohols to pure aldehydes [68]: that of 1-octanol gives $Y_{AL} = 91\%$ (solvent toluene, T_R = 85 °C). However, it is unstable, probably due to oxidative degradation of the polystyrene support. To avoid this, similar but recyclable ruthenium catalysts have been prepared by doping organically modified silicas (ormosil) with tetra-*n*-propylammonium perruthenate (Pr₄N⁺ RuO₄⁻, TPAP) by direct encapsulation of TPAP via the sol-gel process [78]. With the best catalyst, prepared using methyltrimethoxysilane (MTMS) as unique material precursor, 1-octanol was oxidized with oxygen to octanal, giving 70% conversion (solvent toluene, A/C = 10, P(O₂) = 1 bar, T_R = 75 °C, t = 7 h). Absence of leached Ru confirmed the heterogeneous nature of the aerobic oxidation.

5.2. Pd catalysts

Baiker group investigated an alternative solution to flammable organic solvents used for water-insoluble alcohols, such octyl alcohols: to carry out the reaction in “supercritical” carbon dioxide (scCO₂; T_c = 30.9 °C, p_c = 73.8 bar) [79]. The tests were carried out in a continuous fixed bed reactor, at 80–140 °C and 75–125 bar, using the oxidation of 1- and 2-octanol as model reactions.

Preliminary screening of various supported Pt, Ru, and Pd catalysts revealed that 0.5 wt% Pd/Al₂O₃ showed the best activity combined with good stability. Oxidation of 2-octanol yielded almost exclusively 2-octanone (>99.5% selectivity) (alcohol/O₂ = 2, W/F = 1 g h mol⁻¹, T_R = 120 °C, total pressure 95 bar). However, oxidation of 1-octanol resulted in a mixture of 1-octanal, octanoic acid, and octyl octanoate as major products, behavior similar to that observed in the Pt-catalyzed aerobic oxidation of 1-dodecanol in water (see Section 4.3). At constant T_R, both C_{OL} and S_{AL} increased with the increase of pressure, while for a given pressure C_{OL} increased and S_{AL} decreased with the

increase of T_R . This results in a limited practical potential of the catalyst (Pd/alumina) and solvent ($scCO_2$) for the selective oxidation of 1-octanol. The initial selectivity to aldehyde is high ($S_{AL} = 73\%$ at $C_{OL} = 3.3\%$) but decreases with increasing conversion. This is due to rapid hydration of the aldehyde, followed by dehydrogenation of the geminal diol to the carboxylic acid (Scheme 1).

Apparently, the presence of co-product water on the metal surface is sufficient for the rapid hydration of aldehyde; and besides, water is regenerated after dehydrogenation to acid, and esterification of the reactant alcohol, that feeds back the process.

This scheme is coherent with the effect of solvent on the 1-octanol oxidation with several activated carbon supported Pd catalysts (0.3-10.5 wt. % Pd/AC) under mild conditions (0.3M alcohol solution, $A/M = 500$, $P(O_2) = 1.5$ bar, $T_R = 60$ °C, $t = 8$ h) [80]. Using toluene as solvent, their catalytic performance was similar and very poor ($C_{OL} = 2-3\%$), giving octanal as main product ($S_{AL} = 97\%$) and ester as only subproduct. In contrast, and despite the formation of a triphasic system, their activity in water was much higher ($C_{OL} = 34-38\%$) but giving an unselective mixture of the aldehyde ($S_{AL} = 30-33\%$), the acid ($S_{AC} = 21-26\%$) and octyl octanoate (ester selectivity, $S_{ES} = 44-46\%$). Addition of a base (1 equiv. NaOH) to the aqueous solution makes octanoic acid and octyl octanoate to become the main products: $S_{AC} = 60\%$ and $S_{ES} = 31\%$ at 90% conversion [81]. Similarly, Pd NPs dispersed in amphiphilic polystyrene-poly(ethylene glycol) (PS-PEG) resin, Pd/ARP, catalyze the aerobic oxidation of 1-octanol to octanoic acid ($Y_{AC} = 90\%$) in a 0.2M K_2CO_3 aqueous solution ($A/M = 5$, $P(\text{air}) = 1$ bar, $T_R = 100$ °C, $t = 40$ h)[82]. This positive effect of base addition on catalytic activity using water as solvent will be discussed in Section 5.4.

Nevertheless, palladium as monomeric species or in nanoparticles (NPs) may catalyze efficiently the aerobic oxidation of 1-octanol to octanal in organic solvents. Highly stable monomeric Pd(II) species can be prepared by interlayer intercalation in anion-exchangeable hydroxy double salt, such as the Ni-Zn mixed basic salt (NiZn), that has a typical chemical composition of $Ni_{1-x}Zn_{2x}(OAc)_{2x}(OH)_2 \cdot nH_2O$ ($0.15 < x < 0.25$). Thus, catalyst Pd/NiZn ($x = 0.02$) gives complete octanol conversion with $S_{AL} > 99\%$ (solvent TFT, $A/C = 50$, air flow: 20 mL min^{-1} , $P(\text{air}) = 1$ bar, $T_R = 100$ °C, $t = 24$ h) [83]. Catalyst Pd/AmP-MCF, containing Pd NPs in a mesocellular foam (see Section 4.3), also catalyzes the aerobic oxidation of 1-octanol to octanal with $C_{OL} = 98\%$ and $Y_{AL} = 77\%$; this C_{OL} is slightly higher but Y_{AL} is similar to those observed with C_{10} and C_{12} alkanols under the same conditions ($A/M = 13.3$, $P(\text{air}) = 1$ bar, $t = 8$ h), though using p-xylene instead of mesitylene as solvent [59]. Performance of Pd NPs can be modulated by manganese oxide. The catalytic activity of Pd NPs homogeneously dispersed onto manganese oxide-multi-walled carbon nanotube composite (MnO_x/CNT) in solvent-free benzyl alcohol oxidation was correlated with MnO_x loading [84]. Though its initial TOF is 1/11 of that for benzyl alcohol, 1-octanol is also converted selectively to

octanal ($C_{OL} = Y_{AL} = 19.9\%$) on Pd/2.5MnO_x/CNT catalyst with oxygen flow (no solvent, 20 mL min⁻¹ O₂, A/C = 1.3 w/w, T_R = 160 °C, t = 6 h). The strong metal support interaction (SMSI) preserved remarkably the catalyst stability against deactivation.

5.3. Pt catalysts

Oxidation of alcohols with molecular oxygen on platinum is one of earliest examples of heterogeneous oxidations as it was first reported by Döbereiner in 1845 [85]. Early works report the use of metallic platinum, obtained by *in situ* reduction of a PtO₂ suspension, to catalyze 1-octanol oxidation in ethylacetate under static oxygen atmosphere to give 21% yield octanal at room temperature (solvent ethyl acetate, A/C = 4; t = 20 h) [86]. Platinum on various supports was tested and compared in the oxidation of a wide range of alcohol types by Heyns and coworkers [47] (see Section 4.3). Oxidation of 2-octanol on PtO₂ catalyst at room temperature produced 80 % octa-2-one but very slowly (solvent heptane, T_R = 20 °C, t = 96 h). Oxidation of 1-octanol was not reported but, interestingly, that of 1-heptanol was much faster: 26 % heptanal yield in just 1 h at T_R = 60 °C, However, it consumed 135% of the stoichiometric oxygen amount for this, a clear indication of the further oxidation of the aldehyde to the acid.

Similarly to their Pd homologues (see Section 5.2), activity of carbon supported Pt catalysts (0.4-5 wt.% Pt/C) under mild conditions (0.3M alcohol solution, A/M = 500, 60 °C, P(O₂) = 1.5 bar, t = 8 h) is highly dependent on the solvent used: very poor when toluene was used as solvent ($C_{OL} = 6-8\%$), and more active ($C_{OL} = 29-32\%$) but producing complex mixtures of aldehyde, acid and ester when water was the solvent [80].

A higher activity using toluene as solvent is obtained by depositing Pt onto alumina (5 wt.% Pt/Al₂O₃) instead of carbon: $C_{OL} = 29\%$ with no acid formation ($S_{AL} = 100\%$) (A/M = 80, P(air) = 3 bar; T_R = 60 °C, t = 6 h) [69]. Addition of aqueous NaOH inhibits the activity of Pt/Al₂O₃ but not that of Pt/C. This effect can be attributed to the presence of water strongly adsorbed onto the hydrophilic Al₂O₃ surface, and it is the opposite to that observed with gold catalysts (section 5.4). Activity of Pt/Al₂O₃ is significantly promoted by the addition of Bi (0.3-1 wt.%): $C_{OL} = 53\%$, but it also favours acid formation ($S_{AC} = 14\%$, $S_{AL} = 86\%$). Treatment of Pt-Bi/Al₂O₃ catalyst under H₂ further improves its activity ($C_{OL} = 66\%$), without changing the selectivity pattern ($S_{AC} = 13\%$, $S_{AL} = 87\%$). The H₂-treated Pt-Bi/Al₂O₃ catalyst is more selective to aldehyde than Pt-Bi/C. Bi addition also strongly promotes activity of Pt/C catalysts: Bi-Pt/C reaches total conversion in just 3.5 h (with $S_{AC} = 65\%$), compared to $C_{OL} = 29\%$ in 8 h for Pt/C (A/M = 80, P(air) = 3 bar; T_R = 60 °C). On the contrary, partial substitution of Pt by Ru in Pt-Ru/C catalysts has only detrimental effect. The significant promotional effects of Bi were first reported in the 1970s [20]. The possibility that Bi

suppresses catalyst poisoning from by-product formation or that it protects platinum from over-oxidation by acting as a co-catalyst would fit with the effects observed.

Production of octanoic acid using the promoted 5%Pt-1% Bi/C catalyst can be optimized by running the oxidation in a 50% 1-octanol/50% water system: a 96 % conversion with $S_{AC} = 97\%$ is reached ($A/M = 80$, $P(\text{air}) = 3$ bar; $T_R = 60$ °C, $t = 24$ h; $A/M = 700$) [69]. Octanoic acid may also be produced efficiently using Pt NPs. Amphiphilic polystyrene-poly(ethylene glycol) (PS-PEG) resin-dispersion of Pt nanoparticles (ARP-Pt) is more active than its Pd homologue (see Section 5.2) and catalyzes the aerobic oxidation of 1-octanol in water under atmospheric pressure yielding 95 % octanoic acid (0.2 M K_2CO_3 aqueous solution, $A/M = 10$, $P(\text{air}) = 1$ bar, $T_R = 100$ °C, $t = 36$ h)[87].

5.4. Au catalysts

As shown in Section 4.3, bulk gold (pure gold wire gauze or gold plated copper) catalyzes the gas phase aerobic oxidation of 1-octanol yielding 82.8 % aldehyde ($S_{AL} = 91.5$ %) at 340 °C [46]. Bulk Au (foil) also catalyzes the liquid-phase oxidation of π -activated alcohols, such as benzyl alcohol, into the corresponding aldehydes or ketones by O_2 , but not that of 1-octanol [88]. In comparison, the so-called nanosized gold catalysts may operate this reaction in conditions as mild as 60-100 °C and moderate to low oxygen pressures.

The surprisingly high activity of gold nanoparticles (Au NPs) has caused that nanosized gold based catalysts are among the most investigated systems for the aerobic green oxidation of all types of alcohols in the liquid phase [21, 23-24, 26-27]. To our knowledge, the only exception are, precisely, the fatty alcohols with more than 8 carbon atoms, unlike 1-octanol (and the other shorter alkanols), whose oxidation with gold catalysts have been often reported. This question will be discussed in Section 6.

The Prati group reported that gold supported on active carbon (1% wt. Au/AC catalyst) is inactive to oxidize 1-octanol, using either toluene or water as solvent, at reaction conditions (0.3 M alcohol; $A/M = 500$; $P(O_2) = 1.5$ bar; $T_R = 60$ °C; 8 h) at which their Pd or Pt homologues show moderate activity using water as solvent [80]. However, the addition of a strong base (1 equiv. NaOH) to water increases significantly the activity of Au/AC and sodium octanoate becomes the main product ($S_{AC} = 87\%$ at $C_{OL} = 20\%$) [81]. When water is used as solvent in absence of a base, two different factors play a detrimental effect on catalytic activity: (1) a four-phase system that limits the contact between active sites and reactants; (2) a deactivating effect due to the formation of carboxylic acid instead of aldehyde [89]. One could think that the role of the base is to inhibit this latter deactivation by the acid. However, a recent mechanism study with labeling experiments with $^{18}O_2$ and $H_2^{18}O$ has demonstrated that oxygen atoms originating from hydroxide ions instead of molecular oxygen are

incorporated into the alcohol during the oxidation reaction over supported gold catalysts [90]. Thus high-pH conditions will improve activity by increasing the availability of hydroxide ions, while molecular oxygen is proposed to participate in the catalytic cycle not by dissociation to atomic oxygen but by regenerating hydroxide ions formed via the catalytic decomposition of a peroxide intermediate [90]. This effect shows that Au is a distinctly different catalyst to supported Pt-group metals. In contrast to Pt-group metals, Au cannot catalyze alcohol dehydrogenation in the absence of a strong base. But oxidation of aldehydes to carboxylic acids is an oxygen insertion reaction, and this step runs smoothly on Au, even in organic media. [91].

Using organic solvents Au/AC catalysts are still inactive at 80 °C under 3 bar oxygen [70], but gold catalysts supported on metal oxides are active and selective for octanal production ($S_{AL} = 99\%$) using O_2 flow at 1 bar pressure. Thus, Au/ γ - Ga_2O_3 gives $Y_{AL} = 45\%$ (solvent mesitylene, $T_R = 90$ °C, $t = 2.5$ h) [92], 1 wt.% Au/ $Ga_3Al_3O_9$ gives $Y_{AL} = 23\%$ and Au supported on MIL-101 (a Cr- containing metal organic framework (MOF), $Cr_3(F,OH)O[(O_2C)-C_6H_4-(CO_2)]_3$) gives $Y_{AL} = 38\%$ (solvent toluene $T_R = 80$ °C, $t = 3$ h) [93], while 6 wt.% Au/ SiO_2 gives $C_{OL} = 40\%$, but in this case octanal is not the main product ($S_{AL} = 17\%$) [94].

In the absence of solvent, gold supported on carbon, silica or titania is inactive for 1-octanol oxidation, while supported on CeO_2 or Fe_2O_3 shows little activity ($C_{OL} \leq 1.5\%$) giving octanal and the ester under 2 bar O_2 ($T_R = 100$ °C, $t = 3$ h) [95]. Interestingly, 5 wt% Au/ Fe_2O_3 gave very high selectivity to the ester (S_{ES}), octyl octanoate. By contrast, the solventless oxidation of 3-phenyl-1-propanol with the combination of Au NPs (2–5 nm) and nanocrystalline ceria (~5 nm), 1.54 wt.% Au/ CeO_2 , proceeds almost quantitatively to the corresponding ester ($C_{OL} > 99\%$, $S_{ES} = 88\%$) under much lower pressure, O_2 flow at $P(O_2) = 1$ bar ($A/C = 633$, $T_R = 120$ °C, $t = 7$ h) [96]. This may be indicative of the lower activity of primary alkanols over gold catalysts. A similar behavior was found with gold (5 wt.%) supported on β - MnO_2 nanorods: 20 % conversion, being the ester the main product ($S_{ES} = 88\%$), and octanal the only other product ($P(O_2) = 3$ bar, $T_R = 120$ °C, $t = 8$ h) [97]. The use of bases for alcohol oxidation requires the further neutralization of the formed carboxylates with strong acids, which generates big amounts of waste inorganic salts. This justifies the need of catalyzing base-free oxidation of alcohols to acid and esters for green processes. The Prati group was first to report the base-free oxidation of 1-octanol with O_2 over Au NPs supported on nanometer-sized NiO, to give octanoic acid with moderate conversion but low S_{AC} (31%) [98]. Recently, Haruta and coworkers reported an extensive, specific study of base-free oxidation of 1-octanol (in water) over Au NPs with moderate pressure of O_2 [99]. Screening of Au NPs supported on a variety of metal oxides (Al_2O_3 , TiO_2 , MnO_2 , Fe_2O_3 , Co_3O_4 , NiO, ZnO, ZrO_2 and CeO_2) evidenced that their

activity and the resulting product distribution depend strongly on the nature of the support, with C_{OL} as different as 12 and 90 %, while selectivity to the main products, octanoic acid and the ester, varied broadly. These results contrast with previous reports that indicate that Au catalysts yield aldehydes in the absence on a base. The only exception was Au/ Co_3O_4 , which mainly produced octanal.

Au/ CeO_2 showed the highest selectivity to octyl octanoate ($S_{ES} = 91\%$) at moderate conversion ($C_{OL} = 23\%$), while Au/NiO exhibited the highest catalytic activity ($C_{OL} = 90\%$) and selectivity to octanoic acid ($S_{AC} = 68\%$), under the same conditions (2.3 M octanol in water, A/M = 1000, $P(O_2) = 5$ bar, $T_R = 100$ °C, 18 h). Nature of the solvent also influences markedly the catalytic performance of Au/NiO: it is almost inactive in 1,4-dioxane and acetonitrile, relatively active in toluene (giving ester as main product), more active but unselective ($S_{AC} = 36\%$, $S_{ES} = 36\%$) in absence of solvent, and with the highest activity in water, mostly to acid ($S_{AC} = 66\%$, $S_{ES} = 20\%$). Addition of organic solvent to water allows to reach almost quantitative transformation to octanoic acid ($C_{OL} > 99\%$ with $S_{AC} = 97\%$) using water:dioxane 1:3 v/v under optimized conditions (0.9 M octanol in water; A/M = 33; $P(O_2) = 5$ bar; $T_R = 100$ °C, $t = 48$ h).

With Au/ CeO_2 catalyst the ester production was maximized by optimizing reaction conditions: $S_{ES} \sim 79-82\%$ were obtained at $C_{OL} = 66-80\%$ in $t = 6-12$ h, respectively (0.3 M octanol in water, A/M = 33; $P(O_2) = 5$ bar, $T_R = 80$ °C). The distinctive selectivity trends of Au/NiO (mostly to acid) and Au/ CeO_2 (mostly to the ester) are not due to a different esterification efficiency, because the esterification of equimolecular mixtures of 1-octanol and octanoic acid give similar results over both catalysts. So, to explain the selectivity differences the authors propose that two reaction pathways can lead to ester formation: one similar to that proposed for Pd catalysts (Scheme 1), that will be favoured by Au/NiO catalyst; and a second one, where the initially formed octanal is acetalized with 1-octanol to give the hemiacetal, which consecutive oxidation produces directly the ester (Scheme 2), pathway favoured by Au/ CeO_2 catalyst.

All these results were obtained under moderate pressure of oxygen (5 bar). Recent studies in our laboratory have found that 1-octanol can be oxidized with flowing oxygen at normal pressure and in the absence of a base, using heptane as solvent. Thus, using a Au/ CeO_2 - Al_2O_3 catalyst, conversions up to 62% were achieved at 80 °C in 6 h being octanal ($S_{AL} = 50-70\%$) and octyl octanoate ($S_{ES} = 30-45\%$) the main products (A/C = 100, 30 mL/min O_2 ; $P(O_2) = 1$ bar) [100].

5.5. Bimetallic Au catalysts

Catalytic efficacy of gold can be greatly enhanced by alloying it with a second metal. Though Au/AC catalyst is inactive for oxidizing 1-octanol in toluene (Section 5.4), its physical mixture in Au/Ru ratio = 0.1 with the active Ru/AC catalyst increases its activity keeping the high selectivity to

aldehyde ($Y_{AL} > 99\%$) typical of Ru catalysts (10% v/v octanol, A/M = 100, $P(O_2) = 3$ bar, $T_R = 80$ °C, $t = 3$ h; see Section 5.1) [70]. This is quite unexpected as the presence of Au in carbon supported bimetallic core-shell (Au@Ru)/AC or impregnation of Au/AC catalysts with Ru almost completely suppress the activity of ruthenium. The increased activity is ascribed to the migration of Au atoms to form a more reactive alloy. The activity of the bimetallic catalysts strongly depends on the structure of nanoparticles, and it is increased when alloyed Ru/Au NPs are present, as in the case of Au@(Ru/AC). This catalyst, prepared by depositing Au NPs on the Ru/AC catalyst, shows the highest activity ($Y_{AL} = 66\%$) [70].

It is noteworthy that combining Au with Pt has a negative synergistic effect [80]. On the contrary, alloying Au with Pd has a positive synergic effect, both in toluene and in water, with no significant change in product distribution (a roughly equimolecular mixture of aldehyde, acid and ester) [80]. Thus, octanol conversion in water over 0.73% Au-0.27% Pd/AC was 45 %, compared to 34 % on 1% Pd/AC or nil on 1% Au/AC (0.3 M octanol, A/M = 500; $P(O_2) = 1.5$ bar, $T_R = 60$ °C, $t = 8$ h). The synergistic effect is present in a broad range of the Au–Pd ratio, being maximum for Au₈₀–Pd₂₀ composition [81]. In particular the bimetallic catalysts where the TEM evidenced uniform alloyed bimetallic particles (Au: Pd ratio = 90:10, 80:20, 60:40) showed a higher activity with respect to Au₂₀–Pd₈₀ where the structure is inhomogeneous. Addition of NaOH increases significantly the activity of gold containing catalysts, making gold-rich compositions to be the most active catalysts in water. Thus, with Au₉₀–Pd₁₀/AC catalyst, conversion reached 20% in the absence of base, and 90 % (with $S_{AC} = 72\%$) when 1 equiv. of NaOH was added (0.3 M octanol, A/M = 500; $P(O_2) = 1.5$ bar, $T_R = 60$ °C, 8 h) [81]. Nevertheless, in the absence of base, bimetallic Au-Pd (1 wt.% of each metal, NP average size 3.4 nm) supported on layered double hydroxide (LDH) oxidizes 1-octanol nearly quantitatively into octanoic acid ($C_{OL} = 96\%$, $S_{AC} > 97\%$) in water under O_2 atmosphere (0.33 M octanol; A/M = 67; $P(O_2) = 2$ bar, $T_R = 100$ °C; $t = 6$ h) [101].

A strong synergistic effect between Au and Cu is also found in Au–Cu alloy NPs catalyst for the selective oxidation of structurally diverse alcohols, including less reactive primary alkanols, to aldehydes [94]. Compared to the monometallic Au/SiO₂, Au-Cu/SiO₂ (Au/Cu = 1) catalyst showed increased conversion ($C_{OL} = 47\%$ vs. 40%) and much higher selectivity: $S_{AL} = 73\%$ vs. 17% (1 M octanol in toluene; A/M = 8.6 w/w; 20 mL/min O_2 ; $T_R = 80$ °C; $t = 4$ h).

5.6. Other catalytic systems

A few more systems have been tested for 1-octanol oxidation with clean oxidants. Non activated alcohols, such as 1-octanol, are difficult to be oxidized by N-hydroxyphthalimide (NHPI). But the combined catalytic system NHPI with Co(acac)₃ (0.05 equiv, to NHPI) catalyzes efficiently the

oxidation of 1-octanol to octanoic acid: while it takes 20 h to get a $Y_{AC} = 71\%$ ($C_{OL} = 75\%$) with NHPI, while an almost quantitative yield ($Y_{AC} = 90\%$, $S_{AC} = 95\%$) is achieved in just 5 h with NHPI/Co(acac)₃ (solvent acetonitrile, 10 mol % NHPI, $P(O_2) = 1$ bar, $T_R = 75$ °C) [102]. To allow the recyclability of the homogeneous complex, NHPI has been combined with a supported Co(II) catalyst instead of homogeneous Co(II) counterparts. This supported cobalt catalyst is made by direct grafting of mesoporous silica by a silica precursor-Schiff base Co(II) complex [103]. Aerobic oxidation of 1-octanol with this system yields 87 % octanal ($S_{AL} = 95.6\%$) and 4 % octanoic acid ($S_{AC} = 4.4\%$) (alcohol: NHPI: Co catalyst in 1:0.1:0.0025 ratios, $T_R = 65$ °C).

Several combined systems using TEMPO as cocatalyst have been reported for this reaction. Copper complex [CuBr₂(2,2'-bipyridine)] catalyses selectively the very mild aerobic oxidation of primary alcohols to aldehydes with dioxygen with TEMPO and a base (*t*-BuOK) as cocatalysts: 1-octanol conversion reaches 61% ($S_{AL} > 99\%$) at room temperature or $C_{OL} = 95\%$ at $T_R = 40$ °C 2-octanol (solvent acetonitrile:water (2 : 1), $t = 24$ h) [104]. The system is inactive for octan-2-one formation from 2-octanol. It is worth noting that copper is the active component of most efficient catalysts for the gas phase anaerobic dehydrogenation of 1-octanol [79]: the highest octanal yields (up to $Y_{AL} = 98\%$) were achieved by CuO at 250-300 °C [105]. TEMPO as co-catalyst significantly enhanced the catalytic properties of H₅PV₂Mo₁₀O₄₀: its addition (TEMPO/catalyst = 3) increases 1-octanol conversion to octanal from 0.2 % to 98.4 % (solvent acetone, A/C = 100, $P(O_2) = 2$ bar, $T_R = 100$ °C, $t = 18$ h) [106]. This system also oxidizes secondary octanols to their corresponding ketones.

Strontium (II) added Co₂AlO₄ spinels catalyze the oxidation of alcohols selectively to aldehydes using different oxygen donors such as H₂O₂, TBHO or NaOCl. Oxidation of 1-octanol with TBHP over Co_{0.7}Sr_{0.3}AlO₄ yields 72% octanal ($S_{AL} = 100\%$) but requires a rather high catalyst (solvent acetonitrile, TBHP/alcohol = 1, A/C = 2.6 w/w, $T_R = 80$ °C, $t = 5$ h) [106].

Research of benzyl alcohol oxidation revealed a collaborative effect between ceria nanoparticles and silver-impregnated silica (10 wt.% Ag/SiO₂) in a 1:2 physical mixture [108]. This mixture catalyzes 1-octanol oxidation selectively to octanal ($S_{AL} = 90\%$) in oxygen atmosphere in short reaction time: $C_{OL} = 29\%$ in 45 min (in reflux of xylene, A/M = 43, $T_R = 139$ °C); however, longer reaction times decreased the selectivity considerably.

6. Concluding remarks and outlooks

Despite the scarce specific information found on the catalytic oxidation of alkanols with ten or more carbon atoms, the study of oxidation of aliphatic alcohols with long enough carbon chain (C₈-C₂₀) allows extracting trends and deducing the conditions under which the higher fatty alcohol oxidation could be operational. The features and trends observed are summarized next.

Aliphatic alcohols are less reactive type of alcohols, and their reactivity decreases with the increase of the carbon chain length [38, 45-47, 59, 60], with very few exceptions [48]. However, these differences tend to decrease as the number of carbons increases, and become unimportant for alcohols with more than 16 carbon atoms (C_{16+}). Physical properties of the higher alcohols (boiling point, solubility) imply the need for the liquid phase reaction. Kinetics of these reactions is very slow, so they are carried out in batch type reactor (or semi-batch). Reaction temperatures are usually quite moderate (60-130 °C) and seem to have been selected more based on the physical properties of the alcohol and solvent employed, more than on looking for the optimization of reaction rate.

The catalytic oxidation of fatty alcohols can be conducted without solvent, but this restricts the temperature range and the flexibility in the control of selectivity. Selection of the solvent is not a trivial matter: besides setting limits for the reaction temperature range, the solvent may influence catalytic activity or even (in the case of water) take part in the reaction [79, 90]. The ideal solvent should be soluble in both aqueous and organic media, such as long-chain polyether (ether, diglyme, and derivatives thereof). However, in practice, this type is very little used, excepting for enzymatic applications. Due to the hydrophobicity of the fatty alcohols, the use of water as a solvent brings about the transfer limitations inherent to multiphasic system; nevertheless, phase transfer catalysts have received limited attention for these oxidation reactions. In most cases it is the combination of catalyst and solvent what determines the catalytic performance, i.e., activity and products selectivity. Thus, the selection of the appropriate solvent depends on the catalytic system and the product desired.

The selection of oxidant depends on the catalyst used, and many catalytic systems allow the use of clean oxidants (H_2O_2 , O_2 , air). Noticeably few papers deal with the use of H_2O_2 for these reactions. This is probably due to two factors: the fast thermal decomposition of the peroxide at the usual reaction temperatures; and the limitation of the active oxygen transfer in the biphasic (aqueous/organic) system when H_2O_2 is used with organic solvents or in solventless hydrophobic higher alcohols. When various oxidants have been tested on the same catalyst, the best results are obtained with the oxidant more soluble in the liquid phase [51, 69]. In the aerobic oxidations a wide range of moderate pressures has been explored (1-5 bar), but several catalytic systems may operate at atmospheric pressure of air or molecular oxygen (Table 1).

The chemical nature of the heterogeneous catalysts investigated is all sorts: mostly noble metals, supported on inert or reducible oxides; but also bulk, mesoporous or inert oxides supported metal oxides, heteropoly compounds, and polymer anchored complexes. No clear relationship has been found between the type of catalyst (metal, oxide...) and the selectivity of the process.

In fact, the selectivity issue is quite complex. Besides kinetic parameters (pressure, temperature, reaction time and degree of conversion), the main factors determining product distribution are catalyst nature (active component and support), solvent, and base added or its absence. In practice, optimal selectivity to one of the three products of interest (aldehyde, acid, ester) results from the right combination of catalyst composition and solvent. One should expect that formation of these three products follow the consecutive reaction pathway shown in Scheme 1. However, on some catalytic systems, the ester could be formed by a second route that by-passes the formation of acid (Scheme 2). The prevalence of each of these two routes depends on the catalyst properties (water affinity, oxidizing power). From the practical point of view, these possibilities add flexibility to design a process to obtain either wax esters without acidic subproducts or fatty acids without ester formation.

Based on these trends, we can conclude that: i) oxidation of long-chain fatty alcohols to their corresponding aldehydes, carboxylic acids and esters can be carried out by heterogeneous non-enzymatic catalysts using clean oxidants, such as hydrogen peroxide, molecular oxygen or air; ii) the process can be conducted in liquid phase at moderate temperatures (90-130 °C) either without solvent or using one, usually organic or water; iii) the process can be done under moderate or even normal pressure when using gaseous oxidants (air or oxygen); iv) though the addition of a base can strongly modify the activity and selectivity, this increases the environmental impact of the process, and some catalysts may avoid the need of its use; v) the selection of the catalyst and, to a lesser extent, the solvent must be based on the desired major product; and vi) under appropriate operating conditions, there are catalysts potentially capable of achieving selectivity values approaching 100% to either the aldehyde, the acid or even the ester.

All these features are in accordance to the principles of "green chemistry" and point to feasibility of performing these oxidation processes on a small scale plant, which could be installed in proximity to the source of the feedstock. The investigation to select and optimize the catalyst, the oxidant, and other operating conditions for oxidation of the higher fatty alcohols will constitute a base for developing new processes for obtaining high value aldehydes, acids and esters from natural resources presently unused.

Acronyms used

AC: active carbon

A/C: Substrate to catalyst ratio expressed as alcohol-to-catalyst molar ratio (unless indicated otherwise).

A/M: Substrate to catalyst ratio expressed as alcohol-to-metal molar ratio (unless indicated otherwise).

C_{OL}: alcohol conversion, mol %.

NP: nano particle

P (*x*): total pressure of oxidant *x*, bar.

S_{*i*}: selectivity to product *i* (subscripts: AC, carboxylic acid; AL, aldehyde; ES: ester), mol %.

t: reaction time, h.

TFT: trifluorotoluene

T_R: reaction temperature, °C.

Y_{*i*}: yield to product *i* (subscripts: AC, carboxylic acid; AL, aldehyde; ES: ester), mol %.

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Table 1. Some relevant properties of the higher alcohols

Formula	Common name	IUPAC name	CAS registry number	MW (g/mol)	m.p. (°C)	b.p. (°C)	Solubility ^a					
							H ₂ O	EtOH	Eth	Ace	Bz	Chl
C ₈ H ₁₈ O	capryl alcohol	octanol	111-87-5	130.2	-14.8	195.2	i	msc	msc			
C ₁₀ H ₂₂ O	capric alcohol	decanol	112-30-1	158.3	6.9	231.1	i	msc	msc	msc	msc	msc
C ₁₂ H ₂₆ O	lauryl alcohol	dodecanol	112-53-8	183.3	23.9	260	i	s	s		s	
C ₁₄ H ₃₀ O	myristyl alcohol	tetradecanol	112-72-1	214.4	38.2	287	i	vs	vs	vs	vs	vs
C ₁₆ H ₃₄ O	cetyl alcohol, palmityl alcohol	hexadecanol	36653-82-4	242.4	49.2	312	i	sl	vs	s	vs	vs
C ₁₈ H ₃₆ O	stearyl alcohol	octadecanol	112-92-5	270.5	57.9	335	i	s	s	sl	sl	
C ₂₀ H ₄₂ O	arachidyl alcohol	eicosanol	629-96-9	298.6	65.4	356	i	sl		vs	s	sl
C ₂₂ H ₄₆ O	behenyl alcohol	dodecosanol	661-19-8	326.6	75.5		i	vs	sl			s
C ₂₄ H ₅₀ O	lignoceryl alcohol	tetracosanol	506-51-4	354.7	77.0							
C ₂₆ H ₅₄ O	ceryl alcohol	hexacosanol	506-52-5	382.7	80.0		i	s	s			

^a i: insoluble; msc: miscible; s: soluble; sl: slightly soluble; vs: very soluble; Eth: ether; Ace, acetone; Bz, benzene; Chl, chloroform

Table 2. Selective oxidation of 1-octanol with clean oxidants.

Catalysts ^a	Oxidant	P (bar)	T (°C)	Solvent	Time (h)	Conv. ^b (%)	Selectivity ^c (%)			Ref.
							Aldehyde	Acid	Ester	
RuCl ₂ (PPh ₃) ₃ +TEMPO (2:5)	O ₂	10	100	PhCl	7	85	>99			[66]
RuCl ₂ (PPh ₃) ₃ +TEMPO (1:3)	O ₂	10	100	PhCl	7	85	>99			[67]
Ru(5)/C	Air	3	60	toluene	8	7	100			[69]
Ru(5)Bi(1)/C	Air	3	60	toluene	8	18	100			[69]
Ru(5)/AC	O ₂	3	80	toluene	3	45	>99			[70]
Ru(5.9)/CNTs	O ₂	1	85	toluene/H ₂ O	3	24	100			[71]
Ru(TPP)Cl	O ₂	1	60	TFT	1	93		76		[72]
Ru(17.1)/HAP	O ₂	1	60	toluene	16	95	94			[73]
Ru(6.4)-Co(OH) ₂ -CeO ₂	O ₂	1	60	TFT	4	100	1	97		[54]
Ru/CeO ₂	O ₂	1	60	TFT	4	30	-	93		[54]
Ru-Co-Al-CO ₃	O ₂	1	60	TFT	4	90	29	70		[54]
Ru-Mg-Al-CO ₃	O ₂	1	60	TFT	4	16	94	-		[54]
Ru-Mg-Ce-CO ₃	O ₂	1	60	TFT	4	58	83	2		[54]
Ru(1)Pt(4)/C	Air	3	60	toluene	8	27	86	14		[69]
Ru(2.5)Pt(2.5)/C	Air	3	60	toluene	8	16	100	0		[69]
Ru(4)Pt(1)/C	Air	3	60	toluene	6	13	100	0		[69]
Ru(OH) ₃ /Al ₂ O ₃ + hydroquinone	O ₂	1	83	TFT	4		(Y) 85			[75]
Ru(OH) ₃ /Al ₂ O ₃	O ₂	1	83	TFT	4	87	98			[76]
RuO ₄ -/Amberlyst	O ₂		85	toluene		91	100			[68]
Pr ₄ N ⁺ RuO ₄ ⁻ /ormosil (SiO ₂)	O ₂	1	75	toluene		70	100			[78]
MnFe _{1.5} Ru _{0.35} Cu _{0.15} O ₄	O ₂	1	20	toluene	7	51	100			[77]
Pd(0.5)/Al ₂ O ₃ ^d	O ₂	6.6	80	scCO ₂		3.3	73	n.d.	n.d.	[79]
Pd(0.5)/Al ₂ O ₃ ^d	O ₂	6.6	140	scCO ₂		10.5	38	> 38	n.d.	[79]
Pd(0.3)/C	O ₂	1.5	60	H ₂ O	8	38	33	21		[79]
Pd(0.3)/C	O ₂	1.5	60	toluene	8	3	97	0		[79]
Pd(1)/C	O ₂	1.5	60	H ₂ O	8	34	30	24		[79]
Pd(1)/C	O ₂	1.5	60	toluene	8	2	97	0		[79]
Pd(1)/AC	O ₂	1.5	60	H ₂ O		20	45	29		[81]
Pd(1)/AC	O ₂	1.5	60	H ₂ O + NaOH		90	90	60		[81]
Pd(5)/C (Engelhard)	O ₂	1.5	60	H ₂ O	8	35	30	26		[79]

Pd(5)/C (Engelhard)	O ₂	1.5	60	toluene	8	3	98	0		[79]
Pd(8.25)/AmP-MCF	Air	1	130	p-xylene	8	98	77			[59]
Pd(1)/MnO _x (2.5)/CNT	O ₂	1	160		6	19.9	100			[84]
Pd/NiO	O ₂	5	100	H ₂ O	18	4	50	0	0	[99]
Pd/ARP resin	O ₂		100	H ₂ O	40		(Y) 90	-		[82]
Pd(0.2)/NiZn acetate	O ₂	1	80	TFT	24	>99	>99			[83]
Pt	O ₂	1	20	ethyl acetate	20		(Y) 21			[86]
Pt(5)/C	Air	3	60	toluene	8	29	86	14		[69]
Pt(5)Bi(1)/C	Air	3	60	toluene	0.5	89	85	15		[69]
Pt(5)Bi(1)/C	Air	3	60	toluene	3.5	100	35	65		[69]
Pt(5)Bi(1)/C	Air	3	60	toluene	8	60	81	19		[69]
Pt(5)Bi(2.5)/C	Air	3	60	toluene	6	46	97	3		[69]
Pt(5)Bi(5)/C	Air	3	60	toluene	6	46	96	4		[69]
Pt(5)Bi(1)/C	H ₂ O ₂		60	toluene	0.5	76	89	11		[69]
Pt(5)Bi(1)/C	H ₂ O ₂		60	toluene	3.5	100	38	62		[69]
Pt(5)Bi(1)/C	Air	3	60	H ₂ O	24	96	2	97	1	[69]
Pt(0.4)/AC	O ₂	1.5	60	H ₂ O	8	29	30	27		[80]
Pt(0.4)/AC	O ₂	1.5	60	toluene	8	6	98	0		[80]
Pt(1)/AC	O ₂	1.5	60	toluene	22	6	98	0		[80]
Pt(1)/AC	O ₂	1.5	60	H ₂ O	8	32	31	25		[80]
Pt(5)/C Degussa	O ₂	1.5	60	H ₂ O	8	31	35	34		[80]
Pt(5)/C Degussa	O ₂	1.5	60	toluene	8	8	100	0		[80]
Pt(5)/Al ₂ O ₃ -1	Air	3	60	toluene	6	29	100			[69]
Pt(5)/Al ₂ O ₃ -1	Air	3	60	toluene	8	34	94	6		[69]
Pt(5)/Al ₂ O ₃ -2	Air	3	60	toluene	6	27	100			[69]
Pt(5)/Al ₂ O ₃ -2	Air	3	60	toluene	8	21	100			[69]
Pt(5)Bi(0.25)/Al ₂ O ₃ -1	Air	3	60	toluene	8	53	86	14		[69]
Pt(5)Bi(1)/Al ₂ O ₃ -1	Air	3	60	toluene	8	53	88	12		[69]
Pt(5)Bi(1)/Al ₂ O ₃ -1 (H ₂ -tr.)	Air	3	60	toluene	8	66	87	13		[69]
Pt(10) in ARP-Pt[a]	O ₂		100	H ₂ O	36		(Y) 95			[87]
Au	Air	1	340		-	-	90	92		[47]
Au/AC	O ₂	3	80	Toluene	3	-	-			[70]
Au(1)/AC	O ₂	1.5	60	H ₂ O	8	20	-	-		[81]
Au(1)/AC	O ₂	1.5	60	H ₂ O + NaOH	8	90	-	87		[81]

Au(5)/Fe ₂ O ₃	O ₂	2	100	no solvent	3	2,1	49		51	[95]
Au(5)/MnO ₂ -nanorods	O ₂	3	120	no solvent	8	20	12		88	[97]
Au(2.5)/g-Ga ₂ O ₃	O ₂	1	90	mesitylene	2.5	45	99			[92]
Au(1)/Ga ₃ Al ₃ O ₉	O ₂	1	80	toluene	3	23	99			[93]
Au(0.5)/ MIL-101	O ₂	1	80	toluene	3	38	> 99			[93]
Au/Al ₂ O ₃	O ₂	5	100	H ₂ O	18	54	2	26	63	[99]
Au/CeO ₂	O ₂	5	100	H ₂ O	18	23	9	0	91	[99]
Au/CeO ₂ ^e	O ₂	5	80	H ₂ O	12	84	1	8	79	[99]
Au/Co ₃ O ₄	O ₂	5	100	H ₂ O	18	12	33	<1	<1	[99]
Au/Fe ₂ O ₃	O ₂	5	100	H ₂ O	18	57	4	14	26	[99]
Au/MnO ₂	O ₂	5	100	H ₂ O	18	33	6	12	30	[99]
Au/NiO	O ₂	5	100	H ₂ O	18	90	0	68	28	[99]
Au/TiO ₂	O ₂	5	100	H ₂ O	18	34	3	41	56	[99]
Au/ZnO	O ₂	5	100	H ₂ O	18	30	7	7	57	[99]
Au/ZrO ₂	O ₂	5	100	H ₂ O	18	52	2	30	68	[99]
Au/NiO	O ₂	5	100	toluene	18	29	34	0	59	[99]
Au/NiO	O ₂	5	100	1,4-dioxane	18	5	60	0	0	[99]
Au/NiO	O ₂	5	100	MeCN	18	5	0	0	0	[99]
Au/NiO	O ₂	5	100	solvent-free	18	44	9	36	36	[99]
Au/NiO	O ₂	5	100	H ₂ O	18	83	0	66	20	[99]
Au/NiO	O ₂	5	100	H ₂ O/toluene	18	31	29	74	26	[99]
Au/NiO	O ₂	5	100	H ₂ O/MeCN	18	19	16	37	42	[99]
Au/NiO	O ₂	5	100	H ₂ O/dioxane	18	22	23	55	5	[99]
Au/NiO ^f	O ₂	5	100	H ₂ O/dioxane	18	95	0	98	2	[99]
Au/NiO ^f	O ₂	5	100	H ₂ O/dioxane	48	>99	0	97	2	[99]
Au(6)/SiO ₂	O ₂	1	80	Toluene	4	40	17			[101]
Au(3)Cu(3)/SiO ₂	O ₂	1	80	Toluene	4	47	73			[101]
Au/C + Ru/AC	O ₂	3	80	Toluene	3	50	>99			[70]
Au@(Ru/AC)	O ₂	3	80	Toluene	3	66	>99			[70]
Ru@(Au/AC)	O ₂	3	80	Toluene	3	2	>99			[70]
Ru@Au/AC	O ₂	3	80	Toluene	3	6	>99			[70]
Au(2.5)Pd(2.5)/TiO ₂	O ₂	1	60	No solvent			>96			[33]
Au(0.6)Pd(0.4)/C	O ₂	1.5	60	H ₂ O	8	28	28	31		[80]
Au(0.6)Pd(0.4)/C	O ₂	1.5	60	toluene	8	2	94	0		[80]

Au(0.73)Pd(0.27)/C	O ₂	1.5	60	H ₂ O	8	45	29	34	[80]
Au(0.73)Pd(0.27)/C	O ₂	1.5	60	toluene	8	6	70	12	[80]
Pd ₁₀ @Au ₉₀ (1)/AC	O ₂	1.5	60	H ₂ O		20	43	33	[81]
Pd ₁₀ @Au ₉₀ (1)/AC	O ₂	1.5	60	H ₂ O + NaOH		90	-	82	[81]
Pd ₂₀ @Au ₈₀ (1)/AC	O ₂	1.5	60	H ₂ O		20	44	30	[81]
Pd ₂₀ @Au ₈₀ (1)/AC	O ₂	1.5	60	H ₂ O + NaOH		90	5	72	[81]
Pd ₄₀ @Au ₆₀ (1)/AC	O ₂	1.5	60	H ₂ O		20	45	30	[81]
Pd ₄₀ @Au ₆₀ (1)/AC	O ₂	1.5	60	H ₂ O + NaOH		90	7	68	[81]
Pd ₈₀ @Au ₂₀ (1)/AC	O ₂	1.5	60	H ₂ O		20	45	29	[81]
Pd ₈₀ @Au ₂₀ (1)/AC	O ₂	1.5	60	H ₂ O + NaOH		90	8	64	[81]
Pd(1)Au(1)/LDH	O ₂	1	100	H ₂ O	6	96		> 97	[101]
Cu/MgO	-		300		-	59	99		[79]
CuO	-		300		-		(Y) 98		[79]
Cu-Zn-Bi	-		450		-	99	95		[79]
Co(OH) ₂ -CeO ₂	O ₂		60	TFT	4	< 2	< 50	-	[54]
NHPI + Co(acac) ₃ (20:1)	O ₂	1	75	Acetonitrile	5	90		95	[102]
NHPI	O ₂	1	75	Acetonitrile	20	75		95	[102]
NHPI + Co(II)-SiO ₂	O ₂	1	65	Acetonitrile	40		(Y) 4	(Y) 87	[103]
CoSA4-900	TBHP		80	Acetonitrile	5	72	100		[106]
Zr(n-PrO) ₄	TBHP		60	toluene	2	>98	80	20	[43]
Zr(n-PrO) ₄	TBHP		20	toluene	20	96	90	10	[43]
Ag(10)/SiO ₂ + CeO ₂	O ₂	1	140	Xylene	0.75	29	90		[108]
H ₃ PV ₂ Mo ₁₀ O ₄₀	O ₂	2	100	Acetone	18	0.2	100		[106]
H ₃ PV ₂ Mo ₁₀ O ₄₀ + TEMPO	O ₂	2	100	Acetone	18	98.4	100		[106]

^a Figures in brackets indicate the metal load in wt.%

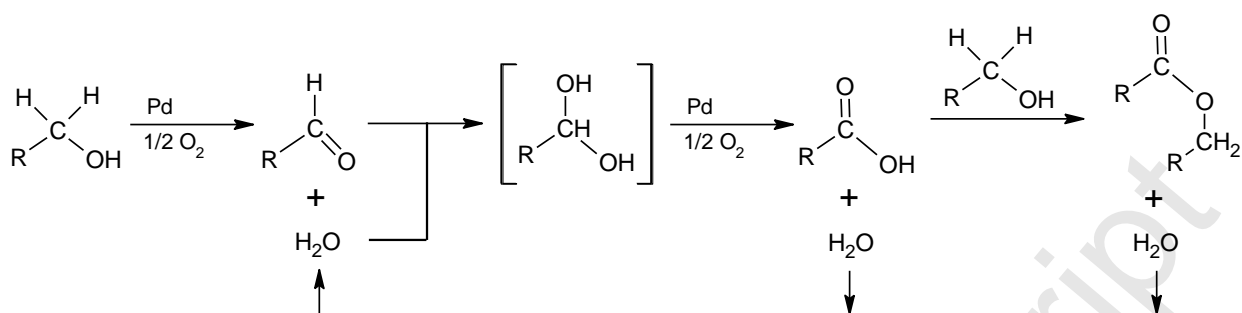
^b Alcohol conversion

^c (Y) data of yield instead of selectivity are given

^d Total pressure 110 bar, 6 mol% O₂; scCO₂ : supercritical CO₂

^e Under reaction conditions optimized for ester formation

^f Under reaction conditions optimized for acid formation

Scheme 1. Formation of acid and ester byproducts during oxidation of 1-octanol. Adapted from [79].**Scheme 2.** Formation of ester via hemiacetal during oxidation of 1-octanol. Adapted from [99].