Heterogeneous selective oxidation of fatty alcohols: Oxidation of 1-tetradecanol as a model substrate

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ABSTRACT

Selective oxidation of fatty alcohols, i.e., linear long-chain alkanols, has been scarcely investigated to date, despite its potential application in high value chemical's production. We report for the first time the liquid phase heterogeneous oxidation of 1-tetradecanol, used as a model molecule for fatty alcohols, according to green chemistry principles by using a $Au/CeO_2–Al_2O_3$ catalyst and O_2 as oxidant at normal pressure. High selectivity to tetradecanal (ca. 80%) or to tetradecanoic acid (60–70%) are reached at medium conversion (up to 38%), depending on the reaction conditions used. Comparison with similar tests of 1-octanol oxidation shows that the increase of the carbon chain length decreases the alcohol conversion and the formation of ester, probably due to a greater steric effect.

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1. Introduction

The societal awareness of the limits of the available fossil resources and the environmental impact of their use is driving efforts for the identification and use of alternative renewable resources and sustainable processes. These have boosted the interest in biomass as a source for chemicals production. The sustainability of industrial application of feedstock from biomass requires developing processes for carrying it out in agreement with green chemistry principles [1]. Such new processes could also be useful for minimizing and valorizing wastes from forestry, agriculture and the paper industry, using them as raw materials. For example, fatty alcohols are present in forestry wastes, such as beech or Douglas-fir barks, in tall oil, the third largest sub product of the Kraft pulping process [2], and in pulps from several non woody species (flax, hemp, sisal and abaca) by alkaline pulping. [3]. The term "fatty alcohols" denotes the higher alcohols, i.e., monohydric aliphatic alcohols of six or more carbon atoms, and refers specially to those with long-carbon chain (C_{8+}). Those of natural origin are unbranched.

Aliphatic long-carbon chain aldehydes, acids and esters are widely used in pharmaceutical, fragances and cosmetics applications. Aliphatic linear carbon chain $C_{10}–C_{18}$ aldehydes have desirable olfactory properties and are potent odoriferous components in perfumes [4]. It is of great importance to synthesize them in high-purity because by-products can make their use in perfume formulations totally unacceptable. The fatty acids abundant in nature have even numbers of carbon atoms and are frequently unsaturated [5], and those with C_{20+} are very rare; thus, new synthesis methods are needed to prepare those acids not available in nature (aliphatic, odd carbon atoms number or very long carbon chain). Wax esters (esters of long-chain fatty acids with long-chain fatty alcohols) are widespread in nature, as common components of the waxy cuticle on aerial surfaces of higher plants [6], but they are usually found in low concentrations (except in jojoba seeds). They are widely used 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. All these valuable products (rare aldehydes and fatty acids, wax esters) could be produced by selective oxidation of their corresponding fatty alcohols.

Selective alcohol oxidation is one of the key transformations in organic synthesis and in industrial practice, with a world-wide annual production of carbonyl compounds of 10,000 million t/yr

by the last turn of century [7]. Conventional oxidation processes in industry are based upon the use of stoichiometric oxidants, and are not environmentally friendly. Interest in green sustainable processes for these reactions has rocketed research, with an almost 10-fold increase of papers on the subject from 1998 to 2012 [8], but reports on selective oxidation of fatty alcohols with more than eight carbon atoms (C_{8+}) are really scarce: only 15 references since 1990; noticeably, none on tetradecanol oxidation and none reporting the use of nano gold catalysts [9].

This is probably due to their specific chemical and physical characteristics. Being primary and aliphatic, reactivity of fatty alcohols is the lowest among those of the different alcohol types (in fact, 1-octanol oxidation is frequently tested as for comparative purposes for this reason), and besides, it usually decreases with the increase of carbon chain length. In addition, their hydrophobicity, viscosity and melting and boiling points also increase with carbon chain length, which imposes restrictions in the reaction conditions for the higher alcohols oxidation.

In this paper, we investigate the oxidation of 1-tetradecanol as a model molecule for the higher fatty alcohols. To our knowledge, aerobic oxidation of tetradecanol (myristic alcohol) has been reported only twice. The first one, in the liquid phase, using a PtO_2 catalyst pretreated in hydrogen; the main product was the aldehyde or the acid depending on the amount of oxygen and the reaction time [10]. The other, in the gas phase, catalyzed by gold plated copper wire, that yields 59% aldehyde, with 85% selectivity, at 312 °C [4]. In this work, we seek adherence to green chemistry principles, by using a heterogeneous catalyst, a clean oxidant at a pressure as low as possible, reaction temperatures as moderate as possible, and no addition of base to the solvent.

We report here for the first time the selective oxidation of 1-tetradecanol over a nano sized Au catalyst, using oxygen at atmospheric pressure as oxidant and base-free alkanes as solvents. The catalyst, supported on ceria-alumina, was selected because of its high efficiency for the oxidation of 1-octanol found in a parallel study [11]. The effect of various reaction parameters (reaction temperature, run time, solvent) on catalytic performance has been investigated. Additionally, 1-octanol oxidation has been tested to study the effect of the alcohol carbon chain on the oxidation of fatty alcohols. The results of this preliminary study prove the feasibility of the reaction under these moderate reaction conditions and show the complexity of the dependence of selectivity on the reaction parameters.

2. Experimental

2.1. Materials

Tetrachloroauric acid, $HAuCl_4$ (Alfa Aesar) and a commercial CeO_2–Al_2O_3 support (Puralox® 20, Sasol) were used for catalyst preparation. Oxygen (99,999%, Air Liquide), 1-tetradecanol (97%, Sigma-Aldrich) and 1-octanol (Chromasolv® for HPLC, ≥99%, Sigma-Aldrich) were used as reactants as received without any further purification. Heptane (99% grade HPLC, Scharlau) and n-decane (≥97%, Sigma-Aldrich) were used as solvents.

2.2. Catalyst preparation

Gold was deposited by the direct anionic exchange method, assisted by NH_3. An aqueous solution of $HAuCl_4$ containing the desired gold loading (2 wt.% nominal amount) was heated at 70 °C and put into contact with the support for 20 min. Then the ammonia solution was added and kept for another 20 min. The obtained solid was filtered, dried in oven at 100 °C overnight and calcined in air at
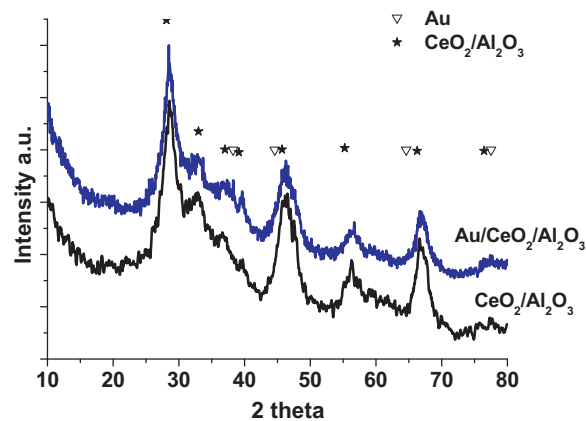

Fig. 1. X-ray diffractograms of the catalyst and the support.

300 °C for 4 h. A detailed description of the synthesis procedure is reported elsewhere [12].

2.3. Catalyst characterization

The catalyst chemical composition was determined by X-ray microfluorescence spectrometry (XRMF) in an EDAX Eagle III spectrophotometer with a rhodium source of radiation. X-ray diffraction (XRD) analysis was performed on an X'Pert Pro PANalytical instrument. Diffractograms were recorded using Cu $K\alpha$ radiation (40 mA, 45 kV) over a 2Θ-range of 10 to 80° with a position-sensitive detector using a step size of 0.05° and a step time of 240 s.

2.4. Catalytic oxidation tests

Tests were conducted under atmospheric pressure at 80–120 °C in a four-necked round bottom flask equipped with reflux condenser, oxygen feed, thermometer and a septum cap. In a typical test, catalyst was added (in a substrate/metal ratio (A/M) = 100–500 mol/mol) to 20 mL of 1-tetradecanol solution (0.1 M) in n-heptane or n-decane, with no base addition. The suspension was stirred and heated to the selected reaction temperature (T_R). Once reached it, run time started when oxygen was bubbled through it with a flow rate of 30 mL/min, under near atmospheric pressure (P = 100 kPa), and the test was run for 6 h. Reaction monitoring was done by analyzing small aliquots of the reaction mixture taken at various intervals. Aliquots were syringe filtered (pore 0.45 μm), and were analyzed by GC in a Varian 450 GC, using a capillary DB wax column (15 m × 0.548 mm), He as the carrier gas and a FID detector. In all measurements the carbon balance was within 100 ± 3%. For comparative purposes, some similar tests were conducted under the same conditions using 1-octanol instead of 1-tetradecanol.

3. Results and discussion

The catalyst chemical composition, determined by XRMF, was: 2.0 wt.% Au, 77.7 wt.% Al_2O_3, 20.3 wt.% CeO_2. Its BET specific surface area was 165 m^2/g. The XRD pattern (Fig. 1) shows only diffraction lines corresponding to the cubic CeO_2 fluorite type structure (JCPDS# 00-004-0593) and to the γ-Al_2O_3 phase (JCPDS# 00-048-0367). No diffraction corresponding to metallic gold was detected. It should be mentioned, that the diffractions of the γ-Al_2O_3 phase overlaps the main diffraction peak of Au at $2\theta = 38°$; however, there are no traces for gold diffractions at higher 2θ angles where no alumina contribution is found. The absence of Au diffraction