



Lactic acid production from aqueous-phase selective oxidation of hydroxyacetone



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ABSTRACT

Lactic acid is an important chemical with a wide range of application in food, pharmaceutical and chemical industries. Its worldwide demand has increased due to the ever-growing market of poly(lactic acid) – PLA. This present contribution aims at studying the catalytic transformation of hydroxyacetone toward lactic acid over heterogeneous systems. Commercial Pt/Al₂O₃ powder catalysts were used and their main features were analyzed as concerning their chemical composition (XRF), crystalline structure (XRD), morphology (TEM) and porosity (N₂ physisorption). Catalytic performance was evaluated in aqueous phase and the results showed that the catalytic activity and selectivity to lactic acid depends on the pH of the reaction medium, being mandatory to operate under strong alkaline conditions. Such reaction conditions promote both the initial oxidation of hydroxyacetone and the intramolecular disproportionation of the obtained aldehyde, which are fundamental steps to lactic acid formation. More importantly, this contribution reports the feasibility of alternatively using heterogeneous catalysts to produce lactic acid with high selectivity (>96%).

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1. Introduction

Lactic acid is an important industrial product with a growing market. It is present in several foods, both as an in situ fermentation product (such as in yogurt, buttermilk and various other foods) or naturally [1]. Lactic acid is non-volatile, odorless and is classified as generally recognized as safe (GRAS) for use as food additive by the Food and Drug Administration (FDA) in USA and other regulatory agencies [2].

Besides the food industry, lactic acid is also used in many other industrial sectors, particularly in textile, pharmaceutical and chemical industries. As for the latter industrial segment, it is used as raw material for the production of esters (lactates), propionic acid and acrylic acid [3–5]. The growing interest in lactic acid, however, is associated with its use in the production of the biodegradable poly (lactic acid) or PLA.

PLA is a high resistant thermoplastic and is considered a green plastic since it can be directly obtained from renewable resources such as corn and sugar beet [6]. It is compostable, presenting a degradation time from 6 months to 2 years [7]. Upon

degradation, only water and CO₂ are produced, which are later absorbed by plants and turned into biomass establishing the carbon cycle. Finally, PLA is also biocompatible, which motivates its use in medicine as sutures (bio-absorbable), systems for controllable release of drugs in the blood stream and orthopedic implants [8].

Lactic acid can be produced by a number of different routes, which may be grouped as biochemical processes (fermentation) [9,10], ordinary chemical synthesis with stoichiometric reagents [11,12] and catalytic reactions based on either homogeneous [13,14] or heterogeneous [15] catalysts. Each process, however, relies on a different feedstock.

The biochemical synthesis corresponds to nearly 90% of the worldwide production and reaches 95% yield on an industrial scale [9,16]; C₆ and C₅ sugars (hexoses and pentoses) are the main substrates used in this case [10] and a wide range of biocatalysts may be applied. Nevertheless, the use of microorganisms requires the mandatory control of the fermentation medium pH, which must be kept between 5 and 7 [9]. Furthermore, a continuous addition of nutrients in the reactor is demanded to maintain the microorganisms activity and thus a profitable industrial run is only accomplished within a few days [11,12].

There are few companies that produce lactic acid by chemical synthesis and mostly the process is based on the hydrolysis of lactonitrile [11,12]. In general terms, lactonitrile is firstly obtained through the addition of hydrocyanic acid to acetaldehyde in the

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presence of a base at atmospheric pressure. After recovering and purification by distillation, lactonitrile is then hydrolyzed to lactic acid using a concentrated solution of hydrochloric acid or sulphuric acid generating lactic acid and the corresponding ammonium salts as by-products. The as-synthesized crude lactic acid is esterified with methanol, generating the methyl lactate, which is recovered, purified and finally hydrolyzed under acidic conditions to produce a pure lactic acid. The sidestream methanol formed upon hydrolysis is recycled to the process unit [1].

Other possible chemical routes to obtain lactic acid consist in the reaction of acetaldehyde with CO and water at high temperatures and pressures, chloropropionic acid hydrolysis and hydrolysis of propylene with nitric acid [11,12]. All these routes require drastic operation conditions and/or are based on harmful and toxic chemicals with potential environmental damage. As expected, they are not economically viable either [11].

Homogeneous catalyzed reactions are also applied and they make use of saccharides (cellulose, sucrose, fructose and glucose) as the main feedstocks and the chemical processes are carried out in aqueous solutions with metal salts [17,18]. The conversion of glycerol to lactic acid with inorganic hydroxides as homogeneous catalysts has also been reported [13,14]. This transformation occurs under hydrothermal conditions, and thus the high pressure and temperature are the main disadvantages.

Alternatively, lactic acid can also be obtained from renewable sources (glucose and glycerol) using heterogeneous catalytic systems [19]. Glycerol is a relevant bio-renewable feedstock due to its ever-growing availability as a consequence of the widespread biodiesel production. Furthermore, it has been shown to be a flexible starting material for many other intermediates. As a matter of fact the use of other organic compounds easily obtained from glycerol may also be a promising alternative as they can allow producing lactic acid under much milder conditions. 1,2-propanediol, dihydroxyacetone and hydroxyacetone or acetol can be listed amongst the most suitable glycerol intermediates [20–25].

Hydroxyacetone stands out as a key chemical for producing lactic acid since it is not only obtained from glycerol [24,26] but also from a wide variety of biomass-derived compounds [27,28]. Nevertheless, it has surprisingly been neglected and specific systematic studies on hydroxyacetone transformation to lactic acid are rarely found. It is quite clear though that studying its transformation may also provide a better understanding of lactic acid formation from other oxidative routes. As a matter of fact hydroxyacetone invariably appears as a major intermediate in all processes, whether using a ketone or glycols as starting materials.

The objective of this contribution is thus to assess the selective aqueous-phase transformation of hydroxyacetone to lactic acid over a heterogeneous catalyst under mild conditions.

2. Experimental section

2.1. Materials

Hydroxyacetone (Sigma–Aldrich 90%), D,L-lactic acid (Fluka 90%), pyruvic acid (Sigma–Aldrich 98%), pyruvic aldehyde (SAFC, 40% in water), sulphuric acid (Merck, 95–97%) and NaOH (Vetec, PA) were the chemicals used in this work. 1 wt% and 5 wt% platinum-supported on Al₂O₃ commercial powders (Sigma–Aldrich) were used as oxidation catalysts and they were labeled 1Pt/Al₂O₃ and 5Pt/Al₂O₃, respectively.

2.2. Characterization of fresh catalysts

Crystalline phases were identified by X-ray powder diffraction (XRD) that was performed in a Rigaku Miniflex diffractometer

using CuK α radiation (1.5406 Å), operating at 30 kV and 15 mA. The diffraction patterns were obtained in the range 2–90° by increasing 2θ with 0.01 steps.

Surface area, pore volume and average pore diameter were determined from N₂ physisorption at –196 °C according to BET and BJH methods. Analyzes were conducted on an ASAP 2020 apparatus from Micromeritics. Prior to analyzes the samples were treated at 300 °C under vacuum.

Chemical composition of the commercial catalysts was determined by X-ray fluorescence (XRF) in a S8 Tiger spectrometer from Bruker. Powder samples were analyzed without any previous treatment.

The morphology of the catalysts was identified by transmission electron microscopy (TEM) that was conducted on a Tecnai 20 FEI microscope operating at 200 kV. The powder samples were firstly ultrasonically dispersed in 2-propanol and then deposited on a carbon-coated copper grid for TEM examination.

2.3. Catalyst evaluation and analytical method

The catalytic tests were carried out in liquid phase in a glass semi-batch reactor heated in an oil bath. Before the reaction, the catalyst was reduced at 350 °C for 1 h under pure H₂ flow at 50 mL/min. The reactions were performed at 40 °C and atmospheric pressure, using 250 mL of an aqueous solution of hydroxyacetone at 0.20 mol/L as starting material. A constant flow of synthetic air (30 mL/min) was bubbled into the reaction medium throughout the experiment and it was stirred at 1000 rpm to guarantee that the reactor content was powerfully mixed, to favor gas diffusion and to ensure kinetic control. Different alkaline conditions were provided by continuous addition of a NaOH solution into the reactor through an addition vessel attached to a reactor mouth. The pH measurement was possible through a pH probe placed into the reactor throughout the experiments. Unless indicated otherwise, all catalytic runs were monitored for 6 h and liquid aliquots (1 mL) were taken at every 30 min to determine hydroxyacetone conversion and products formation. The samples were analyzed by HPLC in a Waters Alliance equipment coupled to a photodiode array detector (PDA) and a refractive index detector (RID) operating at 50 °C. A Biorad Aminex HPX-87H ion exchange column was used at 65 °C to separate all products; the analyzes were performed in isocratic elution mode (0.7 mL/min), using a H₂SO₄ aqueous solution at 0.005 mol/L as mobile phase.

Initial reaction rates (rates at the zero conversion limit) were determined by calculating the initial slope (dC/dt) from the time-resolved profiles of hydroxyacetone concentration.

2.4. Characterization of used catalysts

The catalysts were recovered after liquid-phase reaction and characterized as concerning the most critical points – porosity, metal leaching and dispersion. BET surface area was determined by N₂ physisorption at –196 °C in a Micromeritics ASAP 2020 apparatus. Platinum loading was assessed by X-ray fluorescence spectrometry (XRF) in a S8 Tiger spectrometer from Bruker while its dispersion was estimated by hydrogen chemisorption at 35 °C in Micromeritics AutoChem 2920 equipment. Platinum dispersion was calculated by assuming a stoichiometry (H:Pt) of 1:1. Complementarily, after filtration to separate the solid catalysts, the liquid phase was also analyzed by atomic absorption spectroscopy (AAS) in a Varian 280FS equipment.

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