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Catalytic features of Nb-based nanoscopic inorganic fluorides for an efficient one-pot conversion of cellulose to lactic acid

Marian Verziu^a, Marion Serano^{a,b}, Bogdan Jurca^c, Vasile I. Parvulescu^a,
Simona M. Coman^{a,*}, Gudrun Scholz^d, Erhard Kemnitz^{d,*}

^a Department of Organic Chemistry, Biochemistry and Catalysis, Faculty of Chemistry, University of Bucharest, Regina Elisabeta Blvd., No. 4-12, Bucharest 030016, Romania

^b Chemistry Department, Superior National School of the Engineers in Chemical and Technological Arts, 4 allée Emile Monso – CS 44362, 31030 Toulouse Cedex 4, France

^c Catalysts and Catalytic Processes Center, Department of Organic Chemistry, Biochemistry and Catalysis, Faculty of Chemistry, University of Bucharest, Regina Elisabeta Blvd., No. 4-12, Bucharest 030016, Romania

^d Department of Chemistry, Humboldt-Universität zu Berlin, Brook-Taylor-Straße 2, D12489 Berlin, Germany

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ABSTRACT

A series of niobium-modified fluorides (denoted Nb@MgF₂ and Nb@CaF₂), prepared *via* the fluorolytic sol gel synthesis was investigated for the catalytic one-pot conversion of cellulose to lactic acid. In order to establish the main catalytic features influencing the synthesis of lactic acid, physical-chemical properties – catalytic performance correlations were made and compared with previously reported Sn@MgF₂ and Nb@AlF₃ catalysts. The structure of the catalysts is the result of three important parameters: the ionic radii of the guest-host cations, the fluorolysis rate of each alkoxide species and the concentration of the guest cation. As a function of these parameters samples with different catalytic performances in terms of lactic acid yields are obtained. Nb@CaF₂ sample leads to similar yields to lactic acid by comparison with the previously reported Nb@AlF₃ (15.4% versus 17.0%). In addition, Nb@CaF₂ displays a higher hydrothermal stability.

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1. Introduction

Environmental concerns and depletion of fossil resources have focused the research on the valorization of non edible renewable resources into biochemicals and biofuels. A such renewable resource might be represented by cellulose, the most abundant natural polymer on the earth, its one-pot conversion to important bio-chemicals such as levulinic acid [1–3], lactic acid [4–6], sorbitol [7,8], gamma-valerolactone [9], polyols [10,11], and so on being extremely attractive for many research groups in the nowadays chemistry.

The production of lactic acid became very attractive due to its wide application in food processing and preservation, pharmaceutical and cosmetics industries [12] and more recently, in the synthesis of poly(lactic)acid [13]. Currently, lactic acid is mainly produced by carbohydrates fermentation in the presence

of homo-fermentative bacteria such as *Lactobacillus delbrueckii* or *L. amylophilus* [14]. The major limitations of the process, such as low productivity and multiple purification steps [12] have focused the scientific researches in the development of non-fermentative chemocatalytic systems for the synthesis of lactic acid from renewable raw materials. In this context, one of the most promising methods is the hydrothermal processing of lignocellulosic wastes, under high temperature and pressure conditions [15]. Some reports showed that lactic acid may be formed by this process without the addition of a catalyst but the addition of alkali, such as Ca(OH)₂, can accelerate the reaction rate and the lactic acid can be obtained in higher yields [16,17]. The catalytic performance of Ca(OH)₂ in the production of lactic acid from biomass, under the hydrothermal processing conditions, was highlighted by C. Sánchez et al. [18].

The catalytic decomposition of glucose with sodium hydroxide was also reported by Onda and co-workers [19,20] as an efficient method for the synthesis of the lactic acid. However, to obtain high yield of lactic acid, a large amount of catalyst (noble metal supported on activated carbon) and sodium hydroxide (20 equiv compared to sugar) were required, which made the separation of the sodium lactate quite difficult.

* Corresponding authors.

E-mail addresses: simona.coman@chimie.unibuc.ro (S.M. Coman), erhard.kemnitz@chemie.hu-berlin.de (E. Kemnitz).

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However, the high performances of such homogeneous basic catalysts are accompanied by drawbacks like temperatures up to 300 °C, the use of mineral acids to produce free lactic acid, and the corrosion of equipment [5,17].

The advantages of the use of heterogeneous catalysts upon the homogeneous ones have encouraged the development of some solid materials able to catalyze the one-pot conversion of cellulose to lactic acid. Chambon et al. [21] showed, for instance, that solid Lewis acid catalysts, such as tungstated zirconia and tungstated alumina, exhibited a remarkable promoting effect on the cellulose depolymerisation leading to a 27% lactic acid yield at 190 °C over 24 h, while Liu et al. [22] used a solid base MgO catalyst to achieve similar yields in methanol at 200 °C over 20 h.

Additionally, Sn-Beta zeolite was found to be able to form methyl lactate from glucose in a high yield of 43% at 160 °C [23]. However, the application may be limited due to the long synthesis time of this catalyst.

Another aspect which is worth mentioning in the evaluation of the performance of solid acid catalysts in biomass valorization is their tolerance to water. In this context, niobium compounds, characterized by a high acidity ($\text{Ho} = -8.2$), attracted much attention in last years due to the stability of their acidity in aqueous medium [24]. Due to these characteristics, niobia-based catalysts were investigated by different research groups, in different transformations of biomass derivatives [1,25,26]. In this context, recently we reported the one-pot transformation of cellulose to lactic acid in the presence of a series of niobium-modified aluminum hydroxide fluorides (denoted Nb@AlF₃), prepared *via* the fluorolytic sol gel synthesis [6]. The structure of the new acid catalysts is the result of the dispersion of niobium fluoride in an aluminum fluoride hydroxide matrix. The calcination of the catalysts at a relatively low temperature (350 °C) stabilized this structure, improving both its hydrothermal stability and acidity in aqueous phase reactions. Catalytic performances in terms of lactic acid yields (27.3%) are directly correlated with the niobium content.

Based on this state of the art, in this study we explored novel heterogeneous Nb-doped nanoscopic inorganic fluorides (denoted Nb@MF₂, where M = Mg, Ca) catalytic systems in one-pot conversion of cellulose to lactic acid. The catalytic results are discussed in comparison with those obtained in the presence of the previously developed and reported Sn@MgF₂ [27] and Nb@AlF₃ [6] catalysts. Catalytic properties – catalytic performances correlation has allowed us to establish the most important catalytic features needed for the development of highly active and selective inorganic fluorides based catalysts for the one-pot transformation of cellulose to lactic acid.

2. Experimental section

2.1. Catalyst preparation

Nanosopic Nb-doped hydroxylated magnesium or calcium fluoride with 25 mol% Nb were prepared through the fluorolytic sol-gel-route, as follows: to an ethanolic solution of $\text{M}(\text{O}^i\text{Pr})_3$ (M = Ca or Mg) and 25 mol% Nb(OEt)₅, in a molar ratio M/Nb = 3/1, an anhydrous hydrogen fluoride (HF) in ethanol solution was stoichiometrically added to the overall metal equivalents. Since the niobium precursor was in the oxidation state 5+, two equivalents of HF for each M²⁺, and 5 equivalents HF for each Nb⁵⁺ were used. The overall final concentration of the finally obtained ternary metal fluoride sols was 0.4 molar related to the sum of n_M and n_{Nb} irrespective of their oxidation state. After stirring this sol overnight, the solvent was removed in vacuum at 80 °C. Parts of magnesium based catalysts were forward calcined in air at 350, 550 and 700 °C, respectively (5 K/min, 24 h), while calcium based catalysts

were calcined at 350 and 600 °C, respectively. *Note*: the calcination temperatures were chosen based on TG-DTA analysis. The obtained samples were denoted 25Nb@MF₂-y, with M = Mg or Ca and y = calcination temperature (e.g., 350, 550, 600 or 700 °C). For comparison, nanoscopic Nb-containing aluminum fluoride, with 25 mol% Nb (denoted as 25Nb@AlF₃), which was proven to be the most active and selective catalyst for the one-pot synthesis of lactic acid from cellulose was also prepared for comparison, following a previously reported procedure [6].

2.2. Catalyst characterization

The obtained catalysts were exhaustively characterized using different techniques as powder X-ray diffraction (XRD), N₂ adsorption/desorption isotherms at -196 °C, differential thermal analysis and thermogravimetric analysis (TG-DTA), ¹⁹F MAS NMR, ICP-OES, NH₃-TPD and infrared photoacoustic spectroscopy of chemisorbed pyridine (Py-IR).

Powder X-ray diffraction (XRD) patterns were recorded on a Shimadzu XRD-7000 diffractometer using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$, 40 kV, 40 mA) at a step of 0.2° and a scanning speed of 2° min⁻¹ in the 5–90° 2 θ range.

N₂ adsorption/desorption isotherms at -196 °C were recorded with a Micromeritics 2010 apparatus after degassing the samples at 150 °C for 12 h.

Differential thermal analysis in combination with thermogravimetric analysis was carried out using a TG-DTA analyzer (Shimadzu DTG-60 Simultaneous DTA-TG Apparatus) on 4–6 mg samples under air atmosphere with a rate flow of 20 mL min⁻¹ at a heating rate of 5 K/min until 800 °C and using alpha-alumina as reference.

¹⁹F MAS NMR spectra were recorded on a Bruker Avance 400 spectrometer in a 2.5 mm MAS probe with 2.5 mm rotors made of ZrO₂. A rotation frequency of 20 kHz was applied. The ¹⁹F MAS NMR spectra were recorded with a $\pi/2$ pulse duration of 3.3 μs , a spectrum width of 400 kHz, a recycle delay of 5 s, and accumulation numbers between 64 and 512. The isotropic chemical shifts δ_{iso} of ¹⁹F resonances are given relative to CFCl₃ standard using α -AlF₃ as secondary standard (δ_{19F} : -172.6 ppm). Existent background signals of ¹⁹F were suppressed with the application of a phase-cycled depth pulse sequence according to Cory and Ritchey [28].

The contents of niobium, calcium and magnesium were determined by ICP-OES (Agilent Technologies, 700 Series) after calibrating the instrument with standard solutions. The amount of fluoride in the samples was determined by the Seel Method, under the same conditions as described previously [29].

The temperature programmed desorption profiles of ammonia (NH₃-TPD) were recorded with a Perkin Elmer FTIR-System 2000 at 930 cm⁻¹. The preheated (200 °C) solid was loaded with ammonia at 120 °C. After purging with nitrogen (10 mL min⁻¹), the temperature was raised by 10 K/min until reaching 500 °C while the desorbed ammonia was recorded.

For the determination of the nature of acid sites (Lewis/Bronsted) on the catalysts surfaces the infrared photoacoustic spectroscopy of chemisorbed pyridine was employed. The whole procedure was carried out under the same conditions as described previously [6]: 30 μL of liquid pyridine was injected into a vaporizer (located on the inlet of the reactor, permanent nitrogen flow) and passed to the solid sample pressed into a self-supporting pellet (2 cm², 70 mg, pressure of 1.5 tons) at 150 °C in a flow system. The excess of gaseous and physisorbed pyridine was removed by purging with dried nitrogen. After cooling to room temperature the sample was transferred into a MTECH photoacoustic cell coupled with a FTIR spectrometer.

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