



Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Selective synthesis of acetaldehyde from lactic acid on acid zeolites

M.E. Sad, L.F. González Peña, C.L. Padró, C.R. Apesteguía*

Catalysis Science and Engineering Research Group (GICIC), INCAPE (UNL-CONICET) Predio CCT Conicet, Paraje El Pozo, 3000 Santa Fe, Argentina¹

ARTICLE INFO

Article history:

Received 18 December 2016
Received in revised form 7 March 2017
Accepted 16 March 2017
Available online xxx

Keywords:

Lactic acid
Acetaldehyde
Biomass conversion
Acid zeolites
Green chemistry

ABSTRACT

The gas-phase lactic acid conversion to acetaldehyde was studied on zeolites HMCM22, HZSM5 and NaZSM5 in a plug-flow fixed-bed reactor at 583 K. HMCM22 was a strong Brønsted acid zeolite that yielded 39.7% of lactic acid decarbonylation products (acetaldehyde + CO), but formed significant amounts of coke because of lactic acid oligomerization in the narrow sinusoidal channels of the zeolite. HZSM5 exhibited a high density of Brønsted acid sites (Brønsted/Lewis acid sites ratio of 3.1) and promoted at high rates the lactic acid conversion, mainly to decarbonylation products (acetaldehyde + CO yield = 57.0%) and lactic acid oligomers. NaZSM5 contained mainly Lewis acid sites of intermediate strength (Brønsted/Lewis acid sites ratio of 0.4) that promoted the high-selectivity synthesis of acetaldehyde from lactic acid (acetaldehyde + CO yield = 96.0%) by suppressing the competitive lactic acid oligomerization and coke precursor formation.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Acetaldehyde (AD) is widely used to produce valuable chemicals such as acetic acid, acetate esters, α,β -unsaturated aldehydes, pentaerythritol, and pyridine bases [1]. It is commercially obtained through the oxidation of ethylene by the Wacker process in strong acid solutions using PdCl₂-CuCl₂ catalysts or by acetylene hydration promoted by mercury salts [2,3]. This AD production technology involves the use of petroleum-derived raw materials and environmentally harmful catalysts, and thus significant efforts have been made to develop new cleaner and sustainable processes based on biomass-derived feedstocks such as bioethanol [4,5] or lactic acid [6,7].

Lactic acid (LA) is an attractive feedstock for chemical production because of its high reactivity derived from containing two conjugated hydroxyls and one carboxylic group, and can be commercially obtained at low cost by glucose and xylose fermentation [8–10]. Lactic acid has been selected by the U.S. Department of Energy among the 30 best suitable platform molecules for achieving successful biorefinery development [11,12]. The LA conversion network includes the formation of several valuable chemicals and biopolymers, as depicted in Fig. 1. Lactic acid is mainly used for the synthesis of polylactic acid (PLA), a biodegradable polymer

that exhibits performance mechanical properties and thermoplastic processability [13]. Catalytic dehydration of lactic acid leads to acrylic acid (AA) while propanoic acid (PA) and pyruvic acid may be obtained by lactic acid reduction and dehydrogenation, respectively. Lactic acid may also produce 2,3 pentanedione (PD) by condensation, and acetaldehyde either by decarbonylation or decarboxylation (Fig. 1).

Due to both the high reactivity of LA and the many competitive LA conversion pathways, the high-selectivity synthesis of LA-derived products is a challenging task. Many solid catalysts have been investigated for selectively promoting LA conversion reactions of Fig. 1, especially for the synthesis of PLA and AA [14–16]. However, very few papers have studied the selective synthesis of acetaldehyde via lactic acid decarbonylation/decarboxylation. Katryniok et al. [6] investigated the LA conversion on silica-supported heteropolyacids and reported maximum yields of 83% for LA decarbonylation products (AD + CO). Zhai et al. [17] obtained high (AD + CO) yields from LA conversion on metal sulfate catalysts, between 86 and 92%. Nevertheless, heteropolyacids and metal sulfates suffered from a rapid deactivation caused by carbon deposition on the strong surface acid sites. The LA conversion to AD was also studied on aluminum phosphates and magnesium aluminate spinels [7,18]. Although the results in literature showed that the reaction is promoted by acid catalysts, knowledge regarding the effect of the acid site nature and strength on catalyst activity and selectivity is clearly lacking. Surprisingly, zeolites have not been investigated so far for the selective synthesis of AD from LA. We decided then to study the AD synthesis from LA on zeolites HMCM22, HZSM5 and NaZSM5 which exhibit different acid prop-

* Corresponding author.

E-mail addresses: capesteg@fiq.unl.edu.ar, capesteg@gmail.com (C.R. Apesteguía).¹ Website: <http://www.fiq.unl.edu.ar/gicic>.

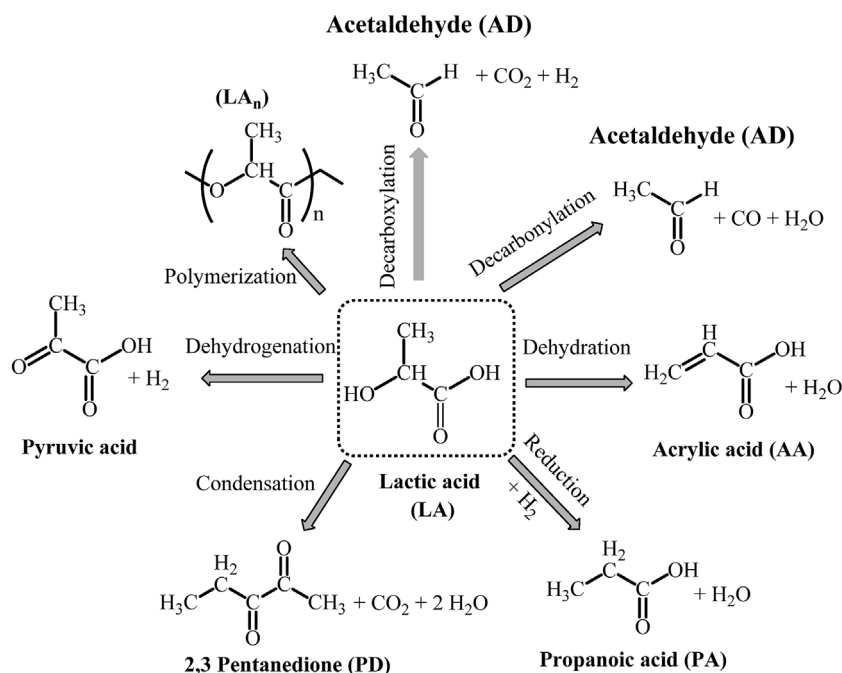


Fig. 1. Lactic acid conversion reactions.

erties. Results are presented in this work and show that the zeolite activity, selectivity and stability for the AD synthesis greatly depend on its acid (acid sites nature and strength) and physical (pore size) properties. In particular, we show here that zeolite NaZSM5 promotes very efficiently the selective synthesis of AD from LA, yielding 96% of LA decarboxylation products (AD + CO) at 583 K.

2. Experimental

2.1. Catalyst preparation

Commercial zeolite NaZSM5 (Zeocat Pentasil PZ-2/25) was calcined at 723 K in dry air flow (60 cm³/min) for 2 h before use. Zeolite HZSM5 was obtained by exchanging commercial NaZSM5 three times with a 1 M ammonium chloride solution (Merck, 99.8%) at 353 K. Zeolite HMCM22 was synthesized according to [19], by using sodium aluminate (Alfa Aesar, Technical Grade), silica (Aerosil Degussa 380), sodium hydroxide (Merck, >99%), hexamethylenimine (Aldrich, 99%) and deionized water as reagents. The molar composition of the synthesis gel was SiO₂/Al₂O₃ = 30, OH/SiO₂ = 0.18, hexamethylenimine/SiO₂ = 0.35 and H₂O/SiO₂ = 45. The gel was transferred to a teflon lined stainless steel autoclave, rotated at 50 rpm, and heated to 423 K in an oven for 7–10 days. After crystallization, the solid was washed with deionized water, centrifugated, dried at 373 K, and finally heated in air at 773 K for 15 h.

2.2. Catalyst characterization

Surface areas (S_{BET}) were measured by N₂ physisorption at 77 K in an Autosorb Quantochrome Instrument 1-C sorptometer. Micropore volumes were determined by *t*-plot [20] methods, using the Harkins–Jura equation [21]. Before adsorption, the samples were treated at 623 K under vacuum for 8 h. Elemental compositions were measured using atomic absorption spectroscopy.

The nature, density and strength of surface acid sites of the samples were determined by infrared spectroscopy (IR) in a Shimadzu FTIR Prestige-21 spectrophotometer using pyridine as probe molecule, as detailed elsewhere [22]. Samples were ground to a

fine powder and pressed into wafers (20–30 mg). The discs were mounted in a quartz sample holder and transferred to an inverted T-shaped Pyrex cell equipped with CaF₂ windows. Samples were initially outgassed in vacuum at 723 K during 2 h and then a background spectrum was recorded after being cooled down to room temperature. Spectra were recorded at room temperature, after admission of pyridine, and sequential evacuation at 423, 573, and 723 K. Spectra were obtained by subtracting the background spectrum recorded previously.

The nuclear magnetic resonance (NMR) spectra for ²⁷Al were recorded at room temperature on a Bruker Avance II 300 spectrometer operating at 78.2 MHz. The sample was spun at the magic angle at a rate of 5 kHz. The ²⁷Al spectrum was recorded using direct polarization with pulses of 1 μs with a repetition time of 2 s. Aluminum chemical shifts are referenced to a 1 M aqueous solution of Al(NO₃)₃.

Coke formed on the catalysts during reaction was measured by temperature-programmed oxidation (TPO). Samples (20–50 mg) were heated at 10 K/min in a 2% O₂/N₂ stream from room temperature to 1073 K. The evolved CO₂ was converted into methane by means of a methanation catalyst (Ni/kieselghur) at 673 K and monitored using a flame ionization detector.

2.3. Catalyst testing

The gas-phase conversion of a 35% wt. aqueous solution of lactic acid (Sigma-Aldrich, 85% aqueous solution) was carried out in a fixed-bed flow reactor at 583 K and 101.3 kPa in continuous flow of nitrogen. Samples (particles with 0.35–0.42 mm diameter) were pretreated in-situ in air at 723 K for 2 h before reaction. In a standard catalytic run, the lactic acid solution was fed at 2 ml/h using a syringe pump and vaporized in nitrogen flow (75 ml/min) at 453 K. Catalytic experiments were performed at different contact times (W/F_{LA}^0), between 3.2 and 19.3 g h/mol. The effluent gases from the reactor were passed through a cooled ice/NaCl trap to ensure condensation of acetaldehyde, one of the most volatile reaction products. Liquid products were collected every 30 min and analyzed using a gas chromatograph Agilent 6850 equipped with a flame ionization detector (FID) and a 30-m HP5 capillary

Download English Version:

<https://daneshyari.com/en/article/6504778>

Download Persian Version:

<https://daneshyari.com/article/6504778>

[Daneshyari.com](https://daneshyari.com)