



Gas phase dehydration of lactic acid to acrylic acid over alkaline-earth phosphates catalysts



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ARTICLE INFO

Article history:

Received 15 June 2013

Received in revised form 3 September 2013

Accepted 28 September 2013

Available online 27 October 2013

Keywords:

Lactic acid

Acrylic acid

Gas phase dehydration

Alkaline earth phosphates

Acid–base balance

ABSTRACT

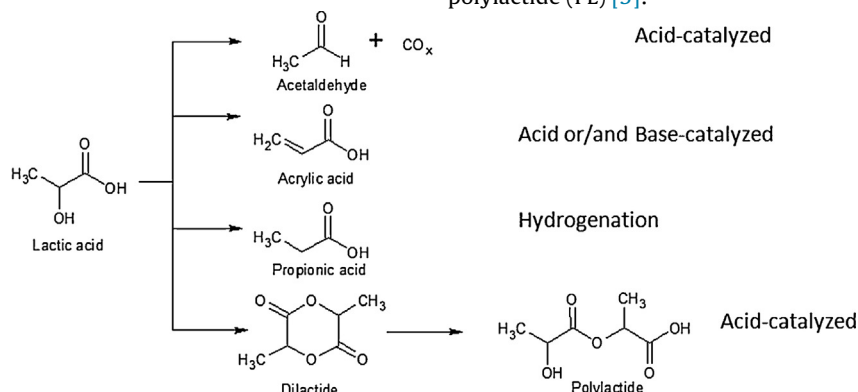
A series of alkaline-earth phosphates were prepared by co-precipitation method using sodium free or sodium containing precursors and evaluated for gas phase dehydration of lactic acid. The catalysts were characterized by BET measurements, X-ray diffraction, chemical analysis, XPS spectroscopy and both NH_3 and CO_2 -TPD. After checking the stability of catalysts under feed, it was shown that selectivity to acrylic acid strongly depended on reaction temperature but not on contact time. At temperature of 380°C , values ranging from 19 to 49% were measured for the different prepared catalysts. The highest value was reached with $\text{Ba}_3(\text{PO}_4)_2$ (55% for C3 products) but selectivities rather close were obtained with different other phosphates suggesting kinetic limitation. Acid–base properties measurements revealed that alkaline-earth phosphates exhibited high proportion of acidic and basic sites with same weak strength. Furthermore, correlation between acrylic selectivity of alkaline earth phosphates and the acid–base balance were clearly established for the first time: selectivity was 50% for balance close to 1 and decreased by factor two increasing this parameter to 2. Finally, FTIR spectra of spent catalysts showed alkaline-earth lactates adsorbed over the catalysts which could be reaction intermediates for dehydration of lactic acid.

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1. Introduction

Acrylic acid (AA) is a platform molecule used as building block to produce polymers and plastics. It is produced at 4.5 Mt/year by selective oxidation of propene, a petrochemical resource whose price is growing up quickly because of increasing demand and rarefaction of petroleum.

With two functional groups, lactic acid (LA) is suitable for numerous applications like food industry, biopolymers such as PLA [1]. LA can be yielded by microbial fermentation processes [2,3] and by glycerol dehydrogenation [4]. As shown in the following scheme, LA can undergo dehydration to achieve AA but also decarbonylation/decarboxylation, condensation, hydrogenation, self-esterification that lead respectively to acetaldehyde (A) and CO_x , 2,3-pentanedione, propionic acid (PA), dilactide (DL) or polylactide (PL) [5]:



Acrylic acid is rarely obtained selectively from LA because of easy decarbonylation leading to acetaldehyde and CO. In the literature, several catalysts consisting chiefly of sulfates and phosphates

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of the group I and II metals, aluminum phosphates treated with an inorganic base, supported phosphates salts have been patented [6–8]. Yields to acrylic acid reaching 68% were obtained using modified zeolithes [9,10] but they suffered from coking and probably hydrothermal instability. Finally, calcium phosphates catalysts were studied. Han et al. [11,12] reported high AA selectivity reaching 75% over composite calcium phosphate in dehydration of methyl lactate. Recently, Ghantani et al. focused on calcium hydroxyapatites for LA dehydration and claimed 60% selectivity to AA [13].

Different studies allowed gathering important information on the reaction mechanism and on the key parameters for high performances. From study of the reaction mechanism over alkali-metal salts, Miller et al. proved that alkali lactate was formed during the reaction and concluded that this formation was key to obtain selectively AA [14–20]. Intramolecular dehydration of LA was proposed to occur under near supercritical water [21,22]. Aida et al. proposed that water must be in interaction with LA to perform dehydration [23]. Finally, Yan et al. who studied the effect of acidic and basic sites on NaY-zeolites modified by alkaline-earth cations, proposed that medium acidic and basic sites contribute to enhance LA dehydration [24].

The motivation of this work was to develop an alternative green route consisting in dehydration of lactic acid (LA). With that purpose, alkaline-earth ortho, pyrophosphates and hydroxyapatites were prepared and evaluated for gas phase dehydration of LA. Reaction parameters such as temperature and contact time were optimized for one catalyst to compare the performances of all the prepared catalysts. NH_3 - and CO_2 -TPD measurements were achieved to search for correlations with the selectivities. In particular, the influence of residual sodium cations on both the acido-base and catalytic properties was investigated.

2. Experimental

2.1. Catalysts preparations

Sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$), sodium hydrogenophosphate (Na_2HPO_4), diammonium hydrogenophosphate ($(\text{NH}_4)_2\text{HPO}_4$), calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), strontium nitrate ($\text{Sr}(\text{NO}_3)_2$), barium nitrate ($\text{Ba}(\text{NO}_3)_2$) were purchased from Aldrich and used as precursors for catalysts preparations. The purity of these salts was 99%. A series of metals orthophosphates (MOP) and metals pyrophosphates (MPP) were prepared by coprecipitation. Since residual Na was detected for some catalysts prepared using sodium containing precursors, they were noted MOP-Na or MPP-Na.

In a typical preparation of MOP catalyst, a solution of $(\text{NH}_4)_2\text{HPO}_4$ or Na_2HPO_4 at 0.2 mol L^{-1} was prepared. The pH of the solution was then adjusted to 9 adding NH_4OH (32%vol) or NaOH (0.5 M). Another solution of metal nitrate at 0.3 mol L^{-1} was added drop wise to the first solution maintaining constant the pH and stirring for 1 h.

To prepare MPP catalysts, $\text{Na}_4\text{P}_2\text{O}_7$ or $(\text{NH}_4)_2\text{HPO}_4$ were used as phosphorus precursor. In the first case, a solution of metal nitrate at 0.3 mol L^{-1} was added drop wise to a solution of $\text{Na}_4\text{P}_2\text{O}_7$ at 0.15 mol L^{-1} and the mixture was stirred for 1 h. Alternatively, a solution of $(\text{NH}_4)_2\text{HPO}_4$ at 0.5 mol L^{-1} was prepared and the pH was adjusted to 10 using NH_4OH (32%vol) before adding drop wise a solution of metal nitrate at 0.5 mol L^{-1} while maintaining constant the pH and stirring for 1 h. Finally, CaPP and SrPP were obtained by precipitating $(\text{NH}_4)_2\text{HPO}_4$ (0.2 M) and $\text{M}(\text{NO}_3)_2$ (0.3 M) in formamide for 48 h. The low solubility of precursors in this solvent is assumed to slow down precipitate formation.

For all the preparations, the precipitates were filtrated off, washed with deionized water, dried at 100°C and calcined

for 6 h under air-flow at a temperature determined from TGA measurement. As sodium-free and sodium containing calcium and strontium hydroxyapatites were obtained using the MOP or MPP protocols, they were respectively labeled MPOH and MPOH-Na.

2.2. Catalysts characterization

TGA/DTA measurements of dried precipitates and used catalysts were achieved under air flow up to 800°C with a SETARAM TGA12 apparatus to determine respectively the calcination temperature and to characterize the organic matter deposited during reaction. Elementary analyses were obtained from ICP-OES spectra (ACTIVA/Jobin Yvon) after acidic dissolutions. The BET Specific Surface Areas (S_{BET}) were measured by nitrogen physisorption at -196°C using a Micromeritics ASAP 2020 instrument and applying the BET method. The samples were previously outgassed under vacuum of 10^{-3} Pa for 3 h at 300°C .

Powder X-ray diffraction patterns were achieved on a Bruker D8 Advance A25 diffractometer equipped with a Ni filter ($\text{Cu K}\alpha$ radiation: 0.154184 nm) and a one-dimensional multistrip detector (Lynxeye, 192 channels on 2.95°). The International Center for Diffraction Data (ICDD) library was used for phase identification and BRUKER TOPAS P program for quantification of the phases identified. FTIR spectra of self-supporting disks of powder dispersed in KBr were recorded at room temperature with a Vector 22 (Bruker) spectrometer. X-ray photoelectron experiments were carried out in a Kratos Axis Ultra DLD spectrometer. The spectra of the P 2p, C 1s, O 1s, Na 1s, Sr 3d, Sr 3p, Ba 3d, Ca 2p levels were recorded using the Al $\text{K}\alpha$ X-ray radiation (1486.6 eV), with pass energy of 20 eV and spot size aperture of $300 \times 700 \mu\text{m}$. The binding energies were calibrated using the C 1s band at 284.6 eV .

Acid and base properties have been determined by TPD of NH_3 and CO_2 respectively. The measurements were achieved with BELCAT-M apparatus (BEL JAPAN, INC.). 100–200 mg of catalysts were pretreated at the calcination temperature for 1 h under He flow (50 mL min^{-1} , NTP). After cooling down to 100°C , NH_3 and CO_2 were adsorbed by flowing the catalysts under 5% NH_3 -He or 5% CO_2 -He gas mixture for 30 min (30 mL min^{-1} , NTP) followed by He treatment at 100°C for 15 min to remove physisorbed molecules. The catalysts were then heated under He flow (50 mL min^{-1} , NTP) up to the calcination temperature with heating rate of 8°C min^{-1} . The acid and basic surface densities were calculated integrating the peaks areas from 100 to 450°C , using pulse calibrations and surface areas values.

2.3. Catalytic testing

Dehydration of lactic acid was conducted in a fixed bed reactor (inner diameter 14 mm) operating at atmospheric pressure. A 20 weight% aqueous solution of lactic acid was fed using 307 HPLC pump (Gilson), vaporized at 170°C with home-made system and diluted with N_2 . The vaporization temperature was determined from liquid vapor equilibrium simulated by the ProSim plus software (ProSim S.A.). The feed composition was LA/ H_2O / N_2 : 3/66/31. Before addition of the vaporized LA solution, the reactor was heated at the reaction temperature under N_2 . The contact time was varied from 0.1 to 4.1 s (GHSV from 36,000 to 880 h^{-1}). Condensable molecules were collected in a cold trap at -4°C and analyzed off-line with a GC-2014 chromatograph (Shimadzu) equipped with AOC-20i auto injector, ZB-WAXplus (30 m, 0.32 mm) column and FID detector, while gas products, mainly CO, CO_2 and N_2 were analyzed online with the same chromatograph but using sampling valve, Carboxen 1000 column and TCD detector. The formulas used to calculate the conversions, products selectivity sets and carbon

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