Dehydration of ethyl lactate over alkaline earth phosphates: Performances, effect of water on reaction pathways and active sites

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ABSTRACT

In this work, alkaline earth phosphates have been prepared by co-precipitation and evaluated in gas phase dehydration of ethyl lactate to acrylic acid and ethyl acrylate. These solids, which were previously shown to be active for the dehydration of lactic acid, appeared more efficient. Indeed, it was shown that the decarbonylation/decarboxylation route leading to acetaldehyde was strongly inhibited compared to conversion of lactic acid and molar selectivity values to dehydration products reaching 87% were obtained. Furthermore, it was shown that the deactivation of the catalysts could strongly be slowed by addition of water vapor to the feed. The reaction pathways have been studied in the presence and absence of water and it was shown that acrylic acid was mainly formed by a simultaneous dehydration/hydrolysis reaction. The characterization of the catalysts surface from the results of XPS, cross polarization NMR, DRIFT and TEM showed the presence of a surface amorphous layer containing POH species. *In situ* DRIFT measurements have revealed that formation of POH groups was favored under water vapor and that these species interacted with reactants or reaction products at the reaction temperature.

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1. Introduction

Acrylic acid (AA) is a platform molecule used as a building block to produce acrylate polymers and plastics [1]. Its production has grown 4%/year between 2006 and 2011 reaching 4.2 Mt in 2011 and was predicted to increase about 5% per year between 2012 and 2017 [2]. AA is currently produced by catalytic oxidation of propylene using a two-step process. However, it is widely affected by the propylene price as it represents only 2% of its global consumption [1]. An alternative route to produce AA is therefore required especially in the context of commitment to environment-friendly catalytic processes. A first possibility that has been studied in our laboratory could be the dehydration of glycerol to acrolein [3–5] with its subsequent oxidation to AA. It could also correspond to a one step dehydration of lactic acid (LA). This important platform molecule, which can be yielded by sugar fermentation [6] but also from lignocelluloses [6] and glycerol dehydrogenation [7] has gained attention in recent years [1]. However, AA is rarely obtained selectively from LA because of easy decarbonylation/decarboxylation leading to acetaldehyde (A) and CO_x [8–10]. High yields of acrylic acid were obtained using modified zeolites [11–16] but they suffered from coking and probable hydrothermal instability.

Other efficient catalysts for LA dehydration are sulphates [17], alkaline earth phosphates [18–21] and hydroxyapatites [22–24]. Recently, we have shown that selective alkaline earth phosphates contained mostly acidic and basic sites with similar weak strength. Furthermore, a correlation between the selectivity value to acrylic acid and the acid–base balance was clearly established [21]. Later, another correlation was reported over hydroxyapatites with a volcano curve in the AA production rate and an optimal acid–base balance of 4 [20]. A similar cooperative acid–base catalysis was suggested and a reaction scheme involving POH and M^{2+} pairs was proposed.

Alkyl lactates are easier to vaporize and less polymerisable than lactic acid. Their ester functions that are less reactive limit decarbonylation/decarboxylation reactions. The interest in use of alkyl lactate instead of lactic acid as reactant to reach higher AA selectivity has been previously illustrated for $Ca_3(PO_4)_2 - Ca_2(P_2O_7)$ (50/50 wt%) mixture [18]. The highest AA molar selectivity was found for ethyl lactate (79%), followed by methyl lactate (75%) and lactic acid (54%). Moreover, the use of alkyl lactates could simplify the separation and purification process and reduce production costs [25] even if it would imply recycling of co-produced alcohols. In that regard, additional molecules of alkyl lactates could be produced by reaction of recycled alcohols with ammonium lac-

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tate obtained by fermentation [26]. Dehydration of methyl lactate to methyl acrylate and acrylic acid over silica supported sodium phosphates was investigated in a fixed-bed continuous flow reactor [25]. The highest molar selectivity to dehydration products (52%) obtained for NaH_2PO_4/SiO_2 catalyst at 380 °C was assumed to be related to the acidity and the amount of POH groups at the end of polyphosphate chains formed during calcination.

In this paper, the catalytic performances of different alkaline earth phosphates in dehydration of ethyl lactate (EL) to ethyl acrylate (EA) and AA were determined and compared to the results obtained for conversion of lactic acid [21]. As ethyl lactate is hydrolysable, different routes depending on the reaction conditions can lead to AA (Fig. 1). Indeed, it can be formed by (i) direct hydrolysis of EA formed by dehydration of EL, (ii) simultaneous dehydration/hydrolysis or (iii) dehydration of LA consecutively to the hydrolysis of EL. Hence, it was essential for further developments to determine which of these pathways was taking place and specific studies have been conducted to answer the question. Furthermore, the influence of the water partial pressure on the catalytic properties and on the reaction mechanisms to dehydration products has been investigated. Finally several characterization techniques like XPS, (^{1}H)–^{31}P NMR, ^{31}P–^{31}P NMR, TEM, DRIFT and in situ DRIFT measurements have been used to identify the active sites and to study the effect of water vapor partial pressure on them.

2. Experimental part

2.1. Catalysts preparations

Alkaline earth orthophosphates (MOP), pyrophosphates (MPP) and hydroxyapatites (MPOH) were synthesized by co-precipitation of phosphorus and M metal salts according to protocols previously described [21]. Several solids were obtained from sodium containing precursors ($Na_4P_2O_7$, Na_2HPO_4) and residual Na was detected [21]. This was specified in their labeling: for instance, calcium pyrophosphate containing residual Na was noted CaPP-Na instead of CaPP for the free Na compound.

2.2. Catalysts characterization

X-ray photoelectron experiments were carried out in a Kratos Axis Ultra DLD spectrometer. The base pressure in the analysis chamber was lower than 5×10^{-8} Pa. The spectra were recorded using the Al Kα X-ray radiation (1486.6 eV), with pass energy of 20 eV and spot size aperture of $300 \times 700\,\mu m$. As the samples were insulating, charge neutralizer was used and the binding energies were calibrated using the C 1 s band at 284.6 eV. The O 1 s level was decomposed into individual components after Shirley background subtraction using symmetric line-shape with a Gaussian/Lorentzian product form (GL30). The full width at half maximum values were fixed at 1.4 eV ± 0.1 eV for the O 1 s major component and 1.75 eV ± 0.15 eV for the O 1 s minor component.

(^{1}H)–^{31}P CP MAS NMR experiments were carried out at 9.4 Tesla on a Bruker DSX400 spectrometer operating at 162.0 MHz. Samples were spun at 10 KHz on a 4 mm triple HXY probe. The spectra were recorded at 10 KHz spinning frequency with a contact time (^{1}H)–^{31}P of 2 ms over a spectral range of 300 ppm. Recycle delays were set to 40 s and 512 scans were achieved. All ^{31}P chemical shifts were referenced to H_3PO_4 85% (0 ppm). Double quantum ^{31}P NMR experiments were carried out at 11.4T, an RF field of 105 KHz, a recycle delay of 60 s on a Bruker AVANCE III spectrometer operating at a Larmor frequency of 202.4 MHz. Samples were spun at 15 KHz in a commercial 2.5 mm MAS probe at room temperature and chemical shifts were referenced to H_3PO_4 in aqueous solution (85 wt%). The compensated C7 (Post-C7) pulse sequence was applied to get through space single quantum–double quantum correlations experiments [27]. Double quantum excitation and recovery time were set to 380 µs. Quadrature detection in the f1 dimension was achieved by the hypercomplex approach. For each t1 increment, 16 transients were accumulated and a total of 128 increments were collected to yield a 2D DQ spectrum. DQ experiments were optimized on a $Zn_2P_2O_7$ reference.

TEM images were achieved with a JEOL 2010 microscope. The acceleration voltage was 200 kV with LaB$_6$ emission current and the point resolution was 0.19 nm. Before measurements, a dispersion of catalyst crushed in ethanol was deposited on standard holey carbon-covered copper TEM grids. In situ DRIFT spectra were achieved with a Nicolet 6700 FTIR spectrometer (Thermo Scientific) equipped with Praying Mantis^{TM} High Temperature Reaction Chamber (Harrick, model HVC-DRP-4). The CaF_2 windows used for the experiments were heated at 70–80 °C with external water system to avoid condensation. TGA/DTA measurements of used catalysts were achieved under air flow up to 800 °C with a SETARAM TG12 apparatus to characterize the organic matter deposited over catalysts during reaction. NH_3 and CO_2-TPD measurements were achieved using a protocol previously described [21].

2.3. Catalytic testing

Gas phase dehydration of ethyl lactate (EL) or lactic acid (LA) was conducted in a fixed bed reactor at atmospheric pressure. Pure or 20% by weight aqueous solution of reactant was fed using a 307HPLC pump (Gilson) vaporized at 160–170 °C with an in house system and diluted with N_2 before entering the reactor. The vaporization temperature was previously determined from liquid vapor equilibrium simulated by the ProSIM software. Before addition of the vaporized solution, the reactor was heated at the reaction temperature under N_2. After trapping at −20 °C for testing with pure EL and −4 °C for testing with aqueous solution of reactant, the condensed products (mainly ethyl acrylate (EA), acrylic acid (AA), acetaldehyde (A), propionic acid (PA), lactic acid (LA)) were 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 on line with the same chromatograph but using sampling valve, Carboxen1000 column and TCD detector.

The conversion value was varied by changing the contact time defined by:

$$\text{Contact time} = \frac{\text{Volume of catalyst}}{\text{Total gas flow rate}} = D(N_2) + 24055$$
$$\times \left(\frac{d(R)}{M(R)} + \frac{d(H_2O)}{18} \right)$$

where, $D(N_2)$ corresponds to the nitrogen volume flow rate at room temperature, $d(R)$ and $d(H_2O)$ to the mass flow rates of liquid reactant and H_2O, respectively and $M(R)$ to the molar mass of reactant.

The formulas used to calculate the conversions, carbon selectivity sets and the products carbon balances were the following:

$$\text{Conversion (\%)} = \frac{\text{moles of reactant fed} - \text{moles of reactant trapped}}{\text{moles of reactant fed}} \times 100$$

$$\text{Carbon selectivity (\%)} = K \times \frac{\text{moles of product}}{\text{moles of reactant converted}} \times 100 \text{ with}$$

$$K = \frac{\text{number of carbons in product}}{\text{number of carbons in reactant}}$$