Catalysis Today 226 (2014) 192–197

Contents lists available at ScienceDirect

Catalysis Today

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

Acrylic acid synthesis from lactic acid over hydroxyapatite catalysts with various cations and anions

Yumiko Matsuura [a], Ayumu Onda [a,*], Shuhei Ogo [b], Kazumichi Yanagisawa [a]

[a] *Research Laboratory of Hydrothermal Chemistry, Faculty of Science, Kochi University, 2-17-47 Asakurahonmachi, Kochi 780-8073, Japan*
[b] *Department of Applied Chemistry, Waseda University, 3-4-1 Ookubo, Shinjyuku, Tokyo 169-8555, Japan*

ARTICLE INFO

Article history:
Received 17 June 2013
Received in revised form 2 September 2013
Accepted 4 October 2013
Available online 12 November 2013

Keywords:
Hydroxyapatite
Acrylic acid
Lactic acid
Acid–base properties

ABSTRACT

We prepared substituted hydroxyapatite catalysts, such as $Ca_{10}(PO_4)_6(OH)_2$, $Sr_{10}(PO_4)_6(OH)_2$, $Pb_{10}(PO_4)_6(OH)_2$, $Ca_{10}(VO_4)_6(OH)_2$, and $Sr_{10}(VO_4)_6(OH)_2$, and carried out conversions of lactic acid over the prepared catalysts. The hydroxyapatite catalysts had stabilities for the reaction media under flowing gas including lactic acid and water at 623 K. The hydroxyapatite catalysts exhibited markedly higher acrylic acid yields than those of P_2O_5/SiO_2 and MgO catalysts. In the lactic acid conversions, the relatively acidic catalysts, such as P_2O_5/SiO_2, $Ca_{10}(VO_4)_6(OH)_2$ and $Sr_{10}(VO_4)_6(OH)_2$ catalysts, accelerated the formations of acetaldehyde and propionic acid, whereas the relatively basic catalysts, such as MgO and $Pb_{10}(PO_4)_6(OH)_2$ catalysts, gave large amounts of unidentified products. On the other hand, the moderate acid–base catalysts, such as $Ca_{10}(PO_4)_6(OH)_2$ and $Sr_{10}(PO_4)_6(OH)_2$ catalysts, selectively accelerated the dehydration of lactic acid into acrylic acid.

1. Introduction

Acrylic acid is widely used as a principal raw feedstock for functional materials, such as water absorbent polymer. At present, acrylic acid is mainly produced by the two-step partial oxidation of propylene derived from fossil resources in the petrochemical industry. Meanwhile, the lack of petroleum and the global warming have driven researchers to find new processes for acrylic acid production from sustainable raw materials.

Recently, biomass resources have been attracting attention as alternative to fossil resources [1]. Lactic acid is one of a number of commodity chemicals produced from renewable biomass resources [2]. Acrylic acid can be formed by a simple dehydration of lactic acid, through the elimination of one water molecule [3]. Some researchers have reported the dehydration of lactic acid to acrylic acid under supercritical water [4–6] and gas phases at 573–673 K [7–13]. In most of those reports, catalysts with both acid and basic sites, such as modified NaY zeolite catalysts, were used. Miller et al. studied the reaction mechanism of lactic acid into acrylic acid and proposed the formation of sodium lactate is crucial for acrylic acid production [8–10]. Huang et al. reported that $La(NO_3)_3$ supported NaY zeolite catalyst exhibited acrylic acid selectivity of 35–56 mol%, and KNO_3 supported NaY zeolite catalyst exhibited acrylic acid selectivity of 21–41 mol% at 623 K [11,13]. Au et al. [12] reported that alkali phosphates-modified NaY zeolite catalysts exhibited acrylic acid selectivity of 54–59 mol% at 623 K. However, these acrylic acid yields were not sufficient and were limited by side reactions which are shown in Scheme 1 [9].

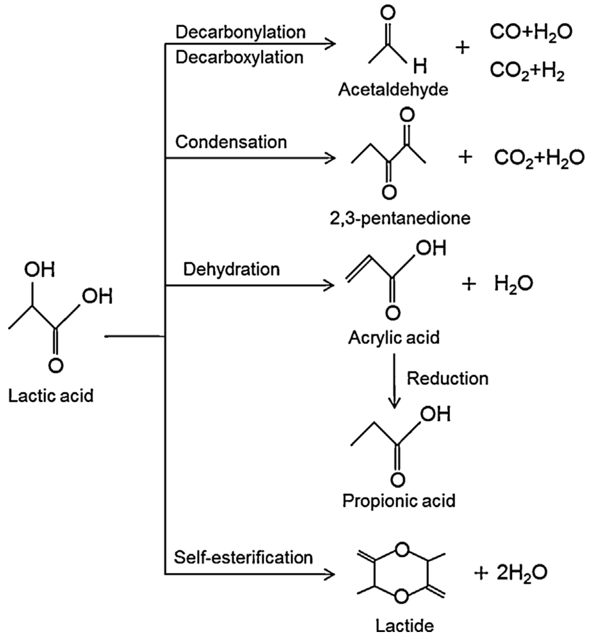
Calcium phosphate (Ca-P) hydroxyapatite has a high thermal stability and affinity for organic compounds. The stoichiometric form of Ca-P hydroxyapatite is $Ca_{10}(PO_4)_6(OH)_2$ with the Ca/P atomic ratio equal to 1.67. Ca-P hydroxyapatite has structural flexibility, and calcium ions and phosphate ions in its structure can be replaced by various kinds of cations and anions [14–16]. We previously reported that the substitution of component ions resulted in a change in the acid–base catalytic properties of Ca-P hydroxyapatite for the conversion of alcohols, such as 2-propanol [17] and ethanol into 1-butanol [18]. Moreover, the acid–base catalytic properties of Ca-P hydroxyapatite differ according to its Ca/P atomic ratio, ranging from 1.5 to 1.67 [19].

Recently, we reported that Ca-P hydroxyapatite catalysts [20] showed a higher acrylic acid yield of 70 C% and selectivity of 86 C% in conversion of lactic acid than those reported for the zeolite catalysts [4–13], and its catalytic activity remained almost unchanged for 60 h of time on stream. Subsequently, Ghantani also reported that a Ca-P hydroxyapatite had a high catalytic selectivity for acrylic acid production from lactic acid [21,22]. In the present study, we aimed to clarify the effects of component ions of apatite compounds on the lactic acid conversion in gas phase. We prepared various hydroxyapatite catalysts, such as $Ca_{10}(PO_4)_6(OH)_2$, $Sr_{10}(PO_4)_6(OH)_2$, $Pb_{10}(PO_4)_6(OH)_2$, $Ca_{10}(VO_4)_6(OH)_2$, and $Sr_{10}(VO_4)_6(OH)_2$, and examined the catalytic

---

* Corresponding author. Tel.: +81 88 844 8353; fax: +81 88 844 8362.
E-mail address: aonda@kochi-u.ac.jp (A. Onda).

0920-5861/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cattod.2013.10.031



Scheme 1. Main conversion pathways of lactic acid in gas phase reactions [9].

properties for the conversion of lactic acid. In addition, we also attempted to evaluate the acid–base properties of the apatite catalysts by the TPD measurements of NH_3 and CO_2 and the 2-propanol conversions under similar reaction conditions to lactic acid conversion and to clarify effects of the acid–base properties on the catalytic properties for lactic acid conversions.

2. Experimental

2.1. Materials and catalysts preparation

All starting materials were reagent grade chemicals (Wako pure chem., Ind., Co.), such as NaOH (>97.0%), H_3PO_4 (85%), P_2O_5 (98%), V_2O_5 (99%), $Ca(NO_3)_2 \cdot 4\ H_2O$ (98.5%), $Sr(NO_3)_2$ (98.0%), and $Pb(NO_3)_2$ (99.5%). MgO (JRC-MGO-4 500A) and silica-gel (CaRiACT G-6) were supplied from the Japan Reference Catalyst and Fuji Silysia Chemical, respectively.

Hydroxyapatite catalysts were prepared by the hydrothermal method that has been described in the earlier synthesis [16,22]. The synthesis procedures of calcium and strontium phosphate hydroxyapatites were as follows: first, an 8 mL of aqueous solution containing calcium nitrate or strontium nitrate (3.33 mmol) was added into a 7 ml of 1 mol L^{-1} sodium hydroxide aqueous solution containing 2.00 mmol of phosphoric acid. The resultant suspension was treated under the hydrothermal condition at 383 K for 14 h with agitation in an autoclave lined with Teflon. After the hydrothermal treatment, the resultant precipitates were washed by the centrifugal separation with distilled water, and then it was dried at 333 K overnight. Lead phosphate hydroxyapatite and calcium and strontium vanadate hydroxyapatites were synthesized by almost the same method as that of calcium phosphate hydroxyapatite. Lead phosphate hydroxyapatite was synthesized using P_2O_5 instead of H_3PO_4, and the vanadate hydroxyapatites were synthesized using 2 mol L^{-1} NaOH aqueous solution and V_2O_5 instead of H_3PO_4. In the preparation, Pb/P, Ca/V, and Sr/V atomic ratios in mixed solution were equal to 1.67.

P_2O_5/SiO_2 catalyst was prepared by an impregnation method. The 1.0 g of silica-gel was added into 2 mL of 0.5 mol L^{-1} P_2O_5 aqueous solution. Then, the mixture was stirred on a water bath until dry. The obtained material was further dried at 333 K overnight. All catalysts were pelletized and crushed to a desired size before performing reactions and characterizations.

2.2. Catalysts characterization

The as-prepared powders were characterized by the following techniques. The crystalline phases were identified by powder X-ray diffraction (XRD; Rigaku, Ultima IV) with Cu Kα radiation (40 kV and 20 mA). The bulk elemental composition of each sample was determined by inductively coupled plasma (ICP; Shimadzu, ICPE-9000). The ICP measurement error for A/B (A = Ca, Sr and Pb, B = P and V) atomic ratio was ±0.01. Specific surface area was measured by nitrogen adsorption measurements at 77 K using the BET method (BEL Japan, BELSORP-max). The samples were preheated in flowing Ar at 773 K for 3 h. The basic properties of the samples were evaluated by the temperature-programmed desorption of CO_2 (CO_2-TPD) and NH_3 (NH_3-TPD). The TPD profiles were normalized by specific surface areas. A sample (0.1 g) in a glass U-tube was preheated at 773 K for 1 h in He flow (20 mL/min), and then the catalyst was cooled from 773 K to room temperature. CO_2 or NH_3 (20 kPa) was introduced into the glass tube at room temperature for 30 min. And then, CO_2 and NH_3were evacuated for 30 min. The TPD measurements were done from 298 to 773 K at a heating rate of 5 K/min. The signal was recorded by quadrupolar mass detector (ANELVA, Japan).

2.3. Catalytic activity measurements

The typical catalytic conversions of lactic acid to acrylic acid were carried out at 623 K using 1.0 g of the catalysts in a fixed-bed continuous-flow reactor (8 mm i.d.) under atmospheric pressure. Before catalytic reactions, the pelletized catalysts were pretreated at 773 K for 3 h in Ar flow. A 38 wt.% of lactic acid aqueous solution was introduced into the reactor using micro syringe pump. The initial concentration of lactic acid in Ar flow corresponded to 3.4 mol%. The liquid products were condensed in an ice-water trap and collected for analysis on a GC-FID (Shimadzu GC14B) with a Stabil wax®-DA capillary column (30 m, 0.32 mm i.d.) and an HPLC with a UV detector and a Shodex KC811 column. The gas products were also analyzed by GC-TCD (Shimadzu GC8A) with a Gaskuropack 54 packed column (2 m, 3 mm i.d.). Lactic acid conversion was determined by the HPLC. Acrylic acid yield was determined by both of the HPLC and the GC-FID. The other major products were determined by the GC-FID and GC-TCD. These calculation formula were as follows,Lactic acid conversion (%) = (1 − mol of unreacted lactic acid/mol of introduced lactic acid) × 100Product yield (C%) = (C mol of product/C mol of introduced lactic acid) × 100Product selectivity (C%) = (product yield/lactic acid conversion) × 100$W/F_{\text{lactic acid}}$ (h g_{catalyst} $\text{mol}_{\text{lactica acid}}{}^{-1}$) = catalyst weight (g)/lactic acid(mol h^{-1})

3. Results and discussion

3.1. Characterization of apatite compounds

Fig. 1 shows X-ray diffraction patterns of the prepared calcium, strontium, and lead phosphate hydroxyapatites (Ca-P, Sr-P or Pb-P) and calcium and strontium vanadate hydroxyapatites (Ca-V or Sr-V).These XRD patterns were attributed to each hydroxyapatite phase, such as $Ca_{10}(PO_4)_6(OH)_2$ (PDF#9-0432), $Sr_{10}(PO_4)_6(OH)_2$ (PDF#33-0432), $Pb_{10}(PO_4)_6(OH)_2$ (PDF#8-259), $Ca_{10}(VO_4)_6(OH)_2$ (PDF#1-70-1996), or $Sr_{10}(VO_4)_6(OH)_2$ (PDF#28-1272), without any other phases. Table 1 shows the chemical compositions and specific surface areas of the prepared hydroxyapatite catalysts. The bulk A/B atomic ratios (A = Ca, Sr and Pb, B = P and V) of hydroxyapatite catalysts were close to 1.67, but that of Pb-P hydroxyapatite