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Short Communication

Selective conversion of lactic acid into acrylic acid over hydroxyapatite catalysts

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ABSTRACT

Lactic acid conversion into acrylic acid was carried out over Ca-HAP catalysts at 623 K. Stoichiometric Ca-HAP catalyst gave a high acrylic acid yield of about 60 C-%. Furthermore, non-stoichiometric calcium deficient Ca-HAP catalysts containing the specific amounts of sodium ions, which were prepared under hydrothermal conditions, exhibited remarkably high acrylic acid yields of about 80 C-%. In contrast, non-stoichiometric Ca-HAP catalysts with vacancy sites and Ca-HAP catalysts with excess amounts of sodium species showed relatively low acrylic acid yields and high selectivities into acetaldehyde and 2,3-pentanedione.

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 shortage of petroleum and the prevalence of 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 an 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 about the dehydration of lactic acid to acrylic acid under supercritical water [4–6] and gas phase [7–12] at 573–673 K. In most of those reports, catalysts with both acid and basic sites, such as modified NaY zeolite catalysts, were used. However, the acrylic acid yields were not sufficient and were limited by side reactions as shown in Scheme 1 [13].

Calcium phosphate hydroxyapatite (Ca-HAP) catalysts have a high thermal stability and affinity for organic compounds. The stoichiometric form of Ca-HAP catalyst is $Ca_{10}(PO_4)_6(OH)_2$ with the Ca/P atomic ratio equal to 1.67. Ca-HAP catalysts have structural flexibility, and calcium ions and phosphate ions in its structure can be replaced by various kinds of cations and anions [14,15]. The substitution of component ions resulted in a change in the acid–base or bifunctional catalytic properties of Ca-HAP catalysts [16–19]. Moreover, the acid–base catalytic properties of Ca-HAP catalysts differed according to its Ca/P atomic ratio, ranging from 1.5 to 1.67 [20,21].

Recently, we reported that Ca-HAP catalysts showed a higher acrylic acid yield in the conversion of lactic acid and a longer catalyst age than those over the previously reported catalysts [22]. And, Ghantani et al. also reported about the advantages of Ca-HAP catalysts for the acrylic acid production from lactic acid [23]. So, in the present study, we propose that Ca-HAP catalysts with moderate Ca/P atomic ratios and specific amount of sodium ions in their structure show the highly selective conversion of lactic acid into acrylic acid.

2. Experimental

2.1. Catalysis preparation

Ca-$HAP_{\_NaOH}$ catalysts were prepared by a hydrothermal method using sodium hydroxide as an alkaline source. An aqueous solution containing calcium nitrate was added into an aqueous solution containing phosphoric acid and sodium hydroxide, and then, the resultant suspension was treated under hydrothermal conditions at 383 K for 14 h and washed with distilled water. Ca-$HAP_{\_NH3}$ catalysts were prepared by almost the same procedure as the Ca-$HAP_{\_NaOH}$ catalysts, except for using ammonia aqueous solution as an alkali source. NaOH/Ca-HAP $(1.68)_{\_NH3}$ catalyst was prepared by the impregnation method using Ca-HAP $(1.67)_{\_NH3}$. HAP-300 (Taihei Chemical), SiO_2 (CaRiACT G-6, Fuji Silysia) and MgO (JRC-MGO-4 500A, The Catalyst Society of Japan) were also used. All catalysts were pelletized and crushed to the desired size and pretreated at 773 K for 3 h under Ar.

2.2. Characterization

The X-ray powder diffraction (XRD) measurements of the samples were carried out on a Rigaku Ultima IV with Cu Kα radiation at 40 kV and 20 mA. The chemical composition was determined by inductively couple of plasma (ICP) spectroscopy with ICPE-9000 (Shimadzu). ICP

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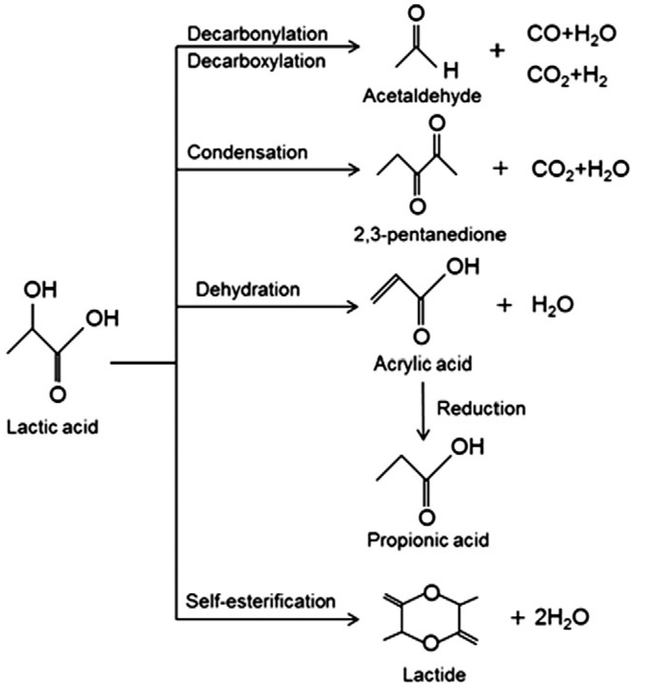

Scheme 1. Main conversion pathways of lactic acid in the gas phase reaction [13].

measurement error for Ca/P atomic ratio was ±0.015. The BET specific surface areas of the samples were determined by N_2 adsorption using a BELSORP-max instrument. The acid–base properties were evaluated by NH_3-TPD and CO_2-TPD. After the pretreatment at 773 K, the sample was exposed under the gas mixture (20 kPa) of 10% CO_2/He or 10% NH_3/He at 353 K for 0.5 h and evacuated under vacuum at 353 K. Then, the temperature was raised from 353 K to 773 K at a ramp rate of 5 ºC/min. CO_2 (m/e = 44) or NH_3 (m/e = 15) was detected by quadrupole mass spectrometery (ANELVA, M-201QA-TDM). The acid and basic surface densities were estimated from the peak areas of TPD profiles from 360 to 700 K, using the specific surface areas of samples and the pulse calibrations.

2.3. Dehydration of lactic acid

The typical catalytic conversions of lactic acid to acrylic acid were carried in a fixed-bed continuous-flow reactor under atmospheric pressure. Before reaction, the pelletized catalysts (0.2–1.0 g) were pretreated at 773 K for 3 h in Ar flow and cooled to 623 K. 38 wt.% lactic acid aqueous solution (1.2 mL h^{-1}) was introduced into the reactor by a microsyringe pump with 40 mL min^{-1} of Ar gas. The products were condensed in an ice–water trap. The collected liquid products were analyzed on a GC-FID (Shimadzu GC14B) with a Stabilwax-DA column. And, after the dilutions of the collected liquid products with distilled water into 50 mL, they were analyzed using an HPLC (HITACHI LC-2000 with UV detector) with a Shodex KC811 column, and a total organic carbon analyzer (TOC2000, Shimadzu). The gas product of acetaldehyde was determined by on-line GC-TCD (Shimadzu GC8A) with a Gaskuropack 54. CO and CO_2 were non-quantitatively analyzed by on-line GC-TCD. The lactic acid conversion and product yield were calculated based on the following equations:

$$\text{Lactic acid conversion }(\%) = (1\text{–mol of unreacted lactic acid/mol of introduced lactic acid}) \times 100$$

$$\text{Product yield}(\text{C-}\%) = (\text{C mol of product/C mol of introduced lactic acid}) \times 100.$$

The mass balance (C-%) was estimated to be a sum of TOC (C-%) and vaporized acetaldehyde yield (C-%). The reproducibility errors of lactic acid conversions, product yields, and mass balances were less than ±4%.

3. Results and discussion

Fig. 1 shows XRD patterns of the prepared Ca-HAP catalysts and HAP-300. All XRD patterns were assigned to $Ca_{10}(PO_4)_6(OH)_2$ phase (PDF#9-0432) with single phase. Table 1 shows chemical compositions determined by ICP analysis, the Ca/P atomic ratios are also shown in parenthesis in catalyst names and the alkali sources are noted at the tails of the names. The bulk atomic ratios were controlled by Ca/P atomic ratios of mother solutions. In the cases of Ca-HAP$_{\_NaOH}$ catalysts, the Ca/P atomic ratios were 1.55 and 1.61 which were significantly less than

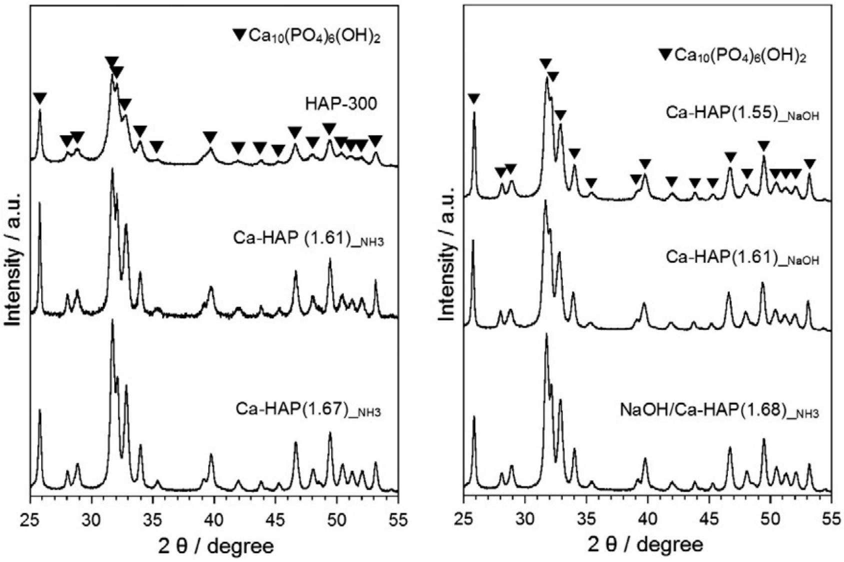

Fig. 1. XRD patterns of (a) HAP-300 and as-synthesized Ca-HAP catalysts using (a) ammonia and (b) NaOH as alkali source.