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# Selective synthesis of 1-butanol from ethanol over strontium phosphate hydroxyapatite catalysts

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#### ARTICLE INFO

#### ABSTRACT

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Keywords: Strontium phosphate hydroxyapatite Ethanol 1-Butanol We previously reported the ability of strontium hydroxyapatite to catalyze the conversion of ethanol into 1-butanol with higher selectivity than that reported for calcium hydroxyapatite catalysts. In the present study, we investigated the catalytic conversions of ethanol over substituted hydroxyapatites, such as  $Sr_{10}(PO_4)_6(OH)_2$ ,  $Ca_{10}(VO_4)_6(OH)_2$ ,  $Sr_{10}(VO_4)_6(OH)_2$ , and  $Ca_{10}(PO_4)_6(OH)_2$ , and their solid solutions, such as  $Ca_{10-z}Sr_z(PO_4)_6(OH)_2$ ,  $Ca_{10}(PO_4)_{6-x}(VO_4)_{6-x}(OH)_2$ , and  $Sr_{10}(PO_4)_{6-x}(VO_4)_{6-x}(OH)_2$ , were investigated. The strontium phosphate hydroxyapatite [ $Sr_{10}(PO_4)_6(OH)_2$ : Sr-P] exhibited the highest 1-butanol selectivity among the tested catalysts in the region of the ethanol conversions between 1 and 24%. The reaction mechanism of 1-butanol formation over the Sr-P hydroxyapatite catalyst includes the dehydrogenation of ethanol into acetaldehyde, 2-buten-1-ol, and/or butyraldehyde into 1-butanol. The Sr-P hydroxyapatite catalyst showed high selectivity into crotonaldehyde in the addol condensation of acetaldehyde and inhibited the coking in the hydrogen transfer reaction of 2-buten-1-ol into 1-butanol, which might be reasons why the Sr-P hydroxyapatite catalyst showed the high 1-butanol selectivity in the catalyst conversion of ethanol.

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#### 1. Introduction

Calcium phosphate hydroxyapatite [Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>: Ca–P] has a high thermal stability and an affinity for organic compounds. The Ca-P hydroxyapatite is used widely in various fields such as biomaterials, adsorbents, and chromatography [1]. The Ca-P hydroxyapatite has both acidic and basic sites in a crystal lattice, and shows the catalytic properties for the dehydration and dehydrogenation of alcohols [2,3]. Moreover, the Ca-P hydroxyapatite has a high capacity for substitutions of Ca<sup>2+</sup> ions and PO<sub>4</sub><sup>3-</sup> ions by other cations and anions [1,4–7]. It was reported that substitutions of the component ions resulted in a change in the catalytic properties for the conversions of 2-propanol [8] and methanol [9], the Michael reactions [10], and the aldol condensations [10]. In our previous work, it was clarified that the catalytic properties of hydrothermally synthesized substituted hydroxyapatites, such as  $Ca_{10}(PO_4)_6(OH)_2$ ,  $Sr_{10}(PO_4)_6(OH)_2$ ,  $Ca_{10}(VO_4)_6(OH)_2$ , and  $Sr_{10}(VO_4)_6(OH)_2$ , for the conversion of 2-propanol [8]. In the catalytic conversion of 2-propanol, the substitution of Ca-P hydroxyapatite by  $Sr^{2+}$  ions resulted in the increase of the acetone selectivity. In contrast, the substitution of Ca-P hydroxyapatite by VO<sub>4</sub><sup>3-</sup> ions resulted in the increase of the propylene selectivity.

Biomass-derived ethanol is expected to be one of renewable feedstocks. Its conversions into valuable chemicals are expected to replace fossil resources. Recently, the catalytic conversions of ethanol into 1-butanol over various catalysts were reported [11–19]. 1-Butanol is widely used as a solvent and a raw material for chemicals. A liquid phase reaction of ethanol using homogenous catalysts, such as [Ir(acac)(cod)], sodium ethoxide, and 1,7-octadiene, was carried out at 120 °C. The 1-Butanol selectivity and yield were 51 C% and 21 C%, respectively [11]. In contrast, the gas phase reactions using heterogeneous catalysts, such as MgO catalyst [12-14], Mg-Al mixed oxides [15], alkaline cation zeolites [16], and the Ca–P hydroxyapatite catalysts [17–19], were carried out at relatively high reaction temperatures between 300 and 450 °C. Among the reported catalysts, the Ca-P hydroxyapatite catalyst showed the highest 1-butanol selectivity of 76 C% at an ethanol conversion of 15 C%. However, the 1-butanol selectivity of Ca-P hydroxyapatite catalyst was insufficient. As mentioned above, the substitutions of component ions of Ca-P hydroxyapatite resulted in change of their catalytic properties. Therefore, it was expected the developments of highly selective catalyst for 1butanol formation by the various substitutions of component ions of Ca-P hydroxyapatite catalyst.

In the case of liquid phase reactions using Ir complex catalysts, it was reported that 1-butanol formation mechanism was described in Scheme 1 [11]. In this mechanism, 1-butanol was formed from ethanol through four steps, such as STEP 1 of the dehydrogena-

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Scheme 1. The reaction mechanism of 1-butanol formation in liquid phase reaction of ethanol [11].

tion of ethanol, STEP 2 of the aldol condensation of acetaldehyde, and STEP 3 and 4 of the hydrogenations. In the case of gas phase reaction of ethanol, it was also reported that 1-butanol formation mechanism was almost the same as that shown in Scheme 1 [13-15,19]. On the other hand, another reaction mechanism of 1butanol formation in the gas phase reactions was proposed by other researchers [12,16]. They reported that 1-butanol was formed from ethanol but it was not formed from acetaldehyde and crotonaldehvde, which were intermediates of the mechanism that shown in Scheme 1, in the gas phase reaction using the zeolite catalysts [16]. From these results, it was proposed that the acetaldehyde and crotonaldehyde were by-products and 1-butanol was formed through the direct bimolecular condensation of ethanol in the gas phase reaction. Thus, because these two reaction mechanisms of 1-butanol formation from ethanol were proposed, the reaction mechanism of the conversion of ethanol into 1-butanol in the gas phase reaction was not clear.

We previously reported the ability of strontium hydroxyapatite to catalyze the conversion of ethanol into 1-butanol with higher selectivity than those over calcium hydroxyapatite catalysts [20]. In the present work, we aimed at highly selective conversion of ethanol into 1-butanol in the gas phase reaction. We prepared the substituted hydroxyapatite catalysts, such as Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>, Sr<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>, Ca<sub>10</sub>(VO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>, and Sr<sub>10</sub>(VO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>, and their solid solution catalysts, such as Ca<sub>10-y</sub>Sr<sub>y</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>, ca<sub>10</sub>(PO<sub>4</sub>)<sub>6-x</sub>(VO<sub>4</sub>)<sub>6-x</sub>(OH)<sub>2</sub>, and Sr<sub>10</sub>(PO<sub>4</sub>)<sub>6-x</sub>(VO<sub>4</sub>)<sub>6-x</sub>(OH)<sub>2</sub>, and examined the conversions of ethanol over the prepared catalysts. In addition, we also attempted to clarify the reaction mechanism of 1-butanol formation and the effects of component ions of hydroxyapatite catalysts on the product selectivities.

#### 2. Methods

#### 2.1. Catalyst preparations

All starting materials were reagent grade chemicals (Wako Pure Chem., Ind., Co.), such as NaOH ( $\geq$ 97.0%), P<sub>2</sub>O<sub>5</sub> ( $\geq$ 98.0%), V<sub>2</sub>O<sub>5</sub> ( $\geq$ 99.0%), Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O ( $\geq$ 98.5%), and Sr(NO<sub>3</sub>)<sub>2</sub> ( $\geq$ 98.0%). The substituted hydroxyapatites and their solid solutions were prepared by the hydrothermal methods described in detail [6–8]. Firstly, solution A containing strontium nitrate and/or calcium nitrate (total 3.34 mmol) in 8 ml of distilled water was added into solution B containing P<sub>2</sub>O<sub>5</sub> and/or V<sub>2</sub>O<sub>5</sub> (total 1 mmol) in 7 ml of

distilled water with NaOH, so that (Ca+Sr)/(P+V) molar ratios in the mixed solution were 1.67. The amounts of added NaOH were 14 and 7 mmol in the case of the preparation of hydroxyapatites with and without vanadate, respectively [8]. The resultant suspension was treated under the hydrothermal condition at 110 °C 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 60 °C for 5 h.

#### 2.2. Characterizations

The as-prepared powders without calcination were characterized by following techniques. Crystalline phase was identified by the powder X-ray diffraction (XRD; Rigaku Ultima IV) with Cu K $\alpha$  radiation (40 kV and 20 mA). The specific surface areas were measured by nitrogen physisorption using the BET method (Yuasaionics NOVA-1200). The elemental compositions were determined by the ICP analysis (SII SPS 7000A).

#### 2.3. Catalytic reactions

The catalytic conversions of ethanol were carried out at 300 °C using 0.5-4.0 g of catalysts in a fixed-bed continuous-flow glass reactor (8 mm i.d.) under atmospheric pressure. The catalyst powders were pelletized and crushed to the desired size  $(250-500 \,\mu m)$ . Before catalytic reactions, the as-prepared catalysts were pretreated at 550 °C for 3 h in Ar flow. Ethanol was introduced into the reactor using micro syringe pump. An initial concentration of ethanol in Ar was 16.1 mol%.  $W/F_{ethanol}$  was changed between 6.5 and  $778 h g_{catalyst} mol_{ethanol}^{-1}$  by controlling both of ethanol flow rate and catalyst weight. The typical W/F<sub>ethanol</sub>, catalyst weight, ethanol flow, and Ar flow were  $130 h g_{catalyst} mol_{ethanol}^{-1}$ , 2.0 g,  $15.4 \text{ mmol } h^{-1}$ , and  $1.81 h^{-1}$ . The reaction products were condensed in an ice-water trap and collected for analysis on a GC-FID (Shimadzu GC14B) and a GC-MS (Hewlett-Packard HP5890/HP5972) with a DB-WAX capillary column (60 m, 0.25 mm i.d.). The gas products were also analyzed by the GC-FID and a GC-TCD (Shimadzu GC8A) with an Active Carbon 60/80 packed column (3 m, 3 mm i.d.). The ethanol conversions, product yields, product selectivities,  $W/F_{ethanol}$ , and specific reaction rate were calculated based on the following equations which were also used in previous reports [17–19]:

 $E \text{thanol conversion}(C\%) = \frac{1 - C \text{ mol of unreacted ethanol}}{C \text{ mol of the liquid and gas products and unreacted ethanol}} \times 100$   $P \text{roduct yield}(C\%) = \frac{C \text{ mol of product}}{C \text{ mol of the liquid and gas products and unreacted ethanol}} \times 100$ 

Product selectivity (C%) =  $\frac{\text{product yield}}{\text{ethanol conversion}} \times 100$ 

$$\frac{W}{F_{\text{ethanol}}}(\text{h g}_{\text{catalyst}} \text{mol}_{\text{ethanol}}^{-1}) = \frac{\text{catalyst weight}(g)}{\text{ethanol flow rate}(\text{mol h}^{-1})}$$



Fig. 1. XRD patterns of the (a) Ca-P, (b) Sr-P, (c) Ca-V, and (d) Sr-V hydroxyapatites.

Specific reaction rate(mol  $s^{-1} m^{-2}$ )

 $\frac{(\text{ethanol conversion}/100)}{(\text{specific surface area of catalyst} \times W/F_{\text{ethanol}} \times 3600)}$ 

The mass balance was calculated as the ratio of the weight of collected liquid against the weight of introduced ethanol. The mass balance in the ethanol conversion over the Sr–P hydroxyapatite catalyst was  $100 \pm 1\%$ , while those over the other hydroxyapatite catalysts were  $95 \pm 5\%$ .

The catalytic conversion of acetaldehyde was carried out at 300 °C using 0.6–1.0g of catalyst. An initial concentration of acetaldehyde in Ar was 0.037 mol% (saturated vapor pressure of acetaldehyde at -78 °C). The values of conversions, product yields, and product selectivities calculated based on the equations for the catalytic conversion of ethanol.

The catalytic conversions of crotonaldehyde, 2-buten-1-ol, and butyraldehyde with 2-propanol were carried out at 300 °C using 0.2–1.0g of catalysts. The mixture of substrates, such as croton-aldehyde, 2-buten-1-ol, and butyraldehyde, and 2-propanol were introduced into the reactor using micro syringe pump. The initial concentration of the substrates in Ar were 0.1 mol%, and that of 2-propanol was 12.6 mol%. The values of conversions, product yields, and product selectivities were calculated based on the following equations:

$$Conversions(mol\%) = \frac{1 - mol of unreacted substrates}{mol of introduced substrates} \times 100$$

$$Product yield (mol\%) = \frac{mol of product}{mol of introduced substrates} \times 100$$

$$Product selectivity(mol\%) = \frac{product yield}{conversions} \times 100$$

#### 3. Results and discussion

#### 3.1. Hydrothermal synthesis of substituted hydroxyapatites

We have reported that the well-crystalline substituted hydroxyapatite powders were prepared by the hydrothermal method [8].

#### Table 1

Catalytic conversions of ethanol over the Ca-P, Sr-P, Ca-V and Sr-V hydroxyapatite catalysts.<sup>a</sup>

Catalyst	Ca-P	Sr-P	Ca-V	Sr–V
M/Z molar ratio	1.69	1.68	1.73	1.69
Specific surface area (m <sup>2</sup> g <sup>-1</sup> )	58.7	26.2	26.0	15.3
Conversion (C%)	7.1	7.6	6.6	5.8
Specific reaction rate (mol s <sup>-1</sup> m <sup>-2</sup> ) $\times$ 10 <sup>-9</sup>	6.9	6.2	19.6	1.4
$W/F_{ethanol}$ (hg <sub>catalyst</sub> mol <sub>ethanol</sub> <sup>-1</sup> )	49	130	39	778
Selectivity (C%)				
$C_1$ (CO, CO <sub>2</sub> , CH <sub>4</sub> )	0.0	0.0	0.0	0.0
CH <sub>2</sub> =CH <sub>2</sub>	0.0	0.0	46.2	53.5
C <sub>4+</sub> -olefins	0.1	0.0	23.9	1.7
C <sub>4</sub> H <sub>7</sub> OC <sub>4</sub> H <sub>5</sub>	1.9	1.1	2.1	0.7
CH <sub>3</sub> CHO	0.1	0.3	2.8	28.4
CH <sub>3</sub> CH=CHCHO	0.0	0.0	0.0	0.4
C <sub>3</sub> H <sub>7</sub> CHO	0.3	0.0	0.1	1.2
CH <sub>3</sub> CH=CHCH <sub>2</sub> OH	7.5	4.3	1.2	0.2
1-C <sub>4</sub> H <sub>9</sub> OH	74.5	81.2	21.9	8.1
$C_2H_5CH(C_2H_5)CH_2OH$	5.9	7.5	0.2	0.3
1-C <sub>6</sub> H <sub>13</sub> OH	4.6	3.0	0.4	0.6
$C_4H_9CH(C_2H_5)CH_2OH$	1.0	0.4	0.0	0.2
1-C <sub>8</sub> H <sub>17</sub> OH	0.5	0.1	0.0	0.1
C <sub>6+</sub> -unsaturated alcohols	3.1	1.7	0.5	0.9
Others	0.6	0.5	0.8	3.6

 $^a$  Catalyst 2.0 g, reaction temperature 300  $^\circ\text{C}$  , time on stream 3 h, ethanol 16.1 mol% (Ar balanced).

Fig. 1 shows X-ray diffraction patterns of the Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>,  $Sr_{10}(PO_4)_6(OH)_2$ ,  $Ca_{10}(VO_4)_6(OH)_2$ , and  $Sr_{10}(VO_4)_6(OH)_2$ , which are referred to as Ca-P, Sr-P, Ca-V, and Sr-V. These XRD patterns were attributed to each hydroxyapatite with a single phase. The chemical compositions and specific surface areas of the substituted hydroxyapatites are summarized in Table 1. The M/Z (M=Ca and Sr; Z=P and V) molar ratios of Ca-P, Sr-P, and Sr-V hydroxyapatites were close to 1.67 which is a stoichiometric ratio of hydroxyapatite, but that of Ca–V hydroxyapatite was 1.73. The measurement errors of M/Z molar ratios were  $\pm 0.01$ . The relatively high Ca/V molar ratio might be attributed to the partial substitution of vanadate by carbonate. The specific surface areas of the as-prepared hydroxyapatite powders decreased in the following order; Ca–P  $(58.7 \text{ m}^2 \text{ g}^{-1}) \ge \text{Sr}-P (26.2 \text{ m}^2 \text{ g}^{-1}) \ge \text{Ca}-\text{V}$  $(26.0 \text{ m}^2 \text{ g}^{-1}) \ge \text{Sr-V} (15.3 \text{ m}^2 \text{ g}^{-1})$ , where as the average particle sizes decreased in the following order;  $Sr-V(237 \text{ nm}) \ge Ca-V$  $(66.9 \text{ nm}) \ge \text{Sr}-P (44.7 \text{ nm}) \ge \text{Ca}-P (25.2 \text{ nm})$ . The specific surface areas depended on the average particle sizes.



Fig. 2. XRD patterns of Sr–P hydroxyapatites with and without calcination at 550  $^\circ\text{C}$  for 3 h.

Fig. 2 shows XRD patterns of Sr–P hydroxyapatite with and without calcination at 550 °C for 3 h. The XRD patterns of the calcined Sr–P hydroxyapatite were almost the same as that of as-prepared Sr–P hydroxyapatite. The surface area of the calcined Sr–P hydroxyapatite was 23.1 m<sup>2</sup> g<sup>-1</sup>, which was about 10% less than that of as-prepared Sr–P hydroxyapatite.

Fig. 3 shows XRD patterns and specific surface areas of hydroxyapatite solid solutions, such as  $Ca_{10-y}Sr_y(PO_4)_6(OH)_2$ ,  $Ca_{10}(PO_4)_{6-x}(VO_4)_x(OH)_2$  and  $Sr_{10}(PO_4)_{6-x}(VO_4)_x(OH)_2$ , with various Sr/(Ca+Sr) or V/(P+V) molar ratios. These XRD patterns were attributed to apatite structures with single phase. In the case of the  $Ca_{10-y}Sr_y(PO_4)_6(OH)_2$  (Fig. 3a), the diffraction peaks continuously shifted toward a lower angle with increasing the Sr/(Ca+Sr) molar ratio, which indicated the homogeneously substitution of smaller calcium ions by larger strontium ions. The surface areas of the  $Ca_{10-y}Sr_y(PO_4)_6(OH)_2$  continuously decreased from 58.7 to  $26.2 \text{ m}^2 \text{ g}^{-1}$  with increasing of the Sr/(Sr+Ca) molar ratio. In the case of the  $Ca_{10}(PO_4)_{6-x}(VO_4)_x(OH)_2$  and  $Sr_{10}(PO_4)_{6-x}(VO_4)_x(OH)_2$  (Fig. 3b and c), the diffraction peaks continuously shifted toward a lower angle with increasing the V/(P+V) molar ratio, which indicated the homogeneously substitution of smaller  $PO_4^{3-}$  ions by larger  $VO_4^{3-}$  ions. The surface areas of the  $Ca_{10}(PO_4)_{6-x}(VO_4)_x(OH)_2$  and  $Sr_{10}(PO_4)_{6-x}(VO_4)_x(OH)_2$  and  $Sr_{10}(PO_4)_{6-x}(VO_4)_x(OH)_2$  changed

from 67.7 to 26.0  $m^2\,g^{-1}$  and from 28.4 to 15.3  $m^2\,g^{-1}$  with changing of the V/(P+V) molar ratio.

## 3.2. Catalytic conversions of ethanol over substituted hydroxyapatite catalysts

The catalytic conversions of ethanol were carried out at 300 °C over the Ca-P, Sr-P, Ca-V, and Sr-V hydroxyapatite catalysts. Table 1 shows the catalytic activities and product selectivities. The Ca-V hydroxyapatite catalyst exhibited higher specific reaction rate of  $19.6 \times 10^{-9} \text{ mol s}^{-1} \text{ m}^{-2}$  than those of Ca-P  $(6.9 \times 10^{-9} \text{ mol s}^{-1} \text{ m}^{-2})$ , Sr–P  $(6.2 \times 10^{-9} \text{ mol s}^{-1} \text{ m}^{-2})$ , and Sr–V  $(1.4 \times 10^{-9} \text{ mol s}^{-1} \text{ m}^{-2})$ . The product selectivities also markedly depended on the kinds of component ions of the hydroxyapatite catalysts. The Sr-P hydroxyapatite catalyst exhibited the highest 1-butanol selectivity at 81.2 C%, followed by Ca-P at 74.5 C%, Ca-V at 21.9 C%, and Sr–V at 8.1 C%. The substituted hydroxyapatite catalysts were classified into the following two groups based on the product distributions in the conversions of ethanol. 1-Butanol was the major product and 2-buten-1-ol and C<sub>6</sub> and C<sub>8</sub>-alcohols were formed as the minor products over the Sr-P and Ca-P hydroxyapatite catalysts. The 1-butanol selectivity of Sr-P hydroxyapatite catalyst was higher than that of Ca-P hydroxyapatite catalyst



**Fig. 3.** XRD patterns of the (a)  $Ca_{10-y}Sr_y(PO_4)_6(OH)_2$ , (b)  $Ca_{10}(PO_4)_{6-x}(VO_4)_x(OH)_2$ , and (c)  $Sr_{10}(PO_4)_{6-x}(VO_4)_x(OH)_2$  hydroxyapatite solid solutions.



**Fig. 4.** XRD patterns of the (a) Ca–P, (b) Sr–P, (c) Ca–V, and (d) Sr–V hydroxyapatites after the catalytic conversion of ethanol.

while the C<sub>4</sub> and C<sub>6+</sub>-unsaturated alcohols selectivities of Sr–P hydroxyapatite catalyst were lower than those of Ca–P hydroxyapatite catalyst. On the other hand, ethylene was the major product and 1-butanol, acetaldehyde, and C<sub>4+</sub>-olefins were formed as the minor products over the Ca–V and Sr–V hydroxyapatite catalysts. It was reported that the hydroxyapatite catalysts with lower M/Z molar ratio exhibited the dehydration catalysis for the alcohol conversions [3]. Although the M/Z molar ratio of the Ca–V hydroxyapatite catalyst was higher than those of other catalysts, the Ca–V hydroxyapatite catalyst showed high dehydration selectivity into ethylene. Probably, the Ca–V hydroxyapatite catalyst with the Ca/V molar ratio of 1.67 might exhibit higher ethylene selectivity than that shown in Table 1.

Fig. 4 shows XRD patterns of the Ca–P, Sr–P, Ca–V, and Sr–V hydroxyapatite catalysts after the catalytic conversions. All hydroxyapatite catalysts retained each hydroxyapatite structure, except for the Sr–V hydroxyapatite catalyst. The Sr–V hydroxyapatite catalyst partially decomposed into Sr<sub>3</sub>(VO<sub>4</sub>)<sub>2</sub>, which might be the cause of the low catalytic activity of the Sr–V hydroxyapatite catalyst. The thermal gravimetric analysis showed that the Sr–V hydroxyapatite was stable until 1000 °C in air [8]. These results indicated that ethanol might contribute to the decomposition of the Sr–V hydroxyapatite.

Fig. 5 shows changes in the 1-butanol selectivity against the ethanol conversion over the Ca–P, Sr–P, Ca–V, and Sr–V hydroxyapatite catalysts. The Sr–P hydroxyapatite catalyst exhibited the highest 1-butanol selectivity among the prepared catalysts in the region of the ethanol conversions between 1 and 24%. The maximum 1-butanol selectivities of Sr–P, Ca–P, Ca–V, and Sr–V hydroxyapatite catalysts were 81.5 C%, 75.3 C%, 30.6 C%, and 8.1 C%, respectively. The 1-butanol selectivities of Sr–P and Ca–P hydroxyapatite catalysts increased with the increase in the ethanol conversions up to 5 C%, and then, it decreased very gradually with increasing of the ethanol conversions. On the other hand, the 1-butanol selectivities of the Ca–V and Sr–V hydroxyapatite catalysts slightly increased with increasing of the ethanol conversions but the selectivities were lower than 30 C%.

As mentioned above, the catalytic activities and product selectivities depended on the component ions of hydroxyapatite catalysts in the ethanol conversion. Then, it was expected that the



**Fig. 5.** Changes in the 1-butanol selectivities against the ethanol conversions over the Ca–P, Sr–P, Ca–V, and Sr–V hydroxyapatite catalysts. *Reaction condition*: catalyst 0.5–4.0 g, reaction temperature 300 °C, time on stream 3 h, ethanol 16.1 mol% (Ar balanced).

catalytic activity and/or the 1-butanol selectivity in the ethanol conversion would be improved by the partially substitution of component ions of the hydroxyapatite catalysts.

The catalytic conversions of ethanol were carried out at 300 °C using the Ca<sub>10-y</sub>Sr<sub>y</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> hydroxyapatite solid solution catalysts with various Sr/(Ca+Sr) molar ratio. Fig. 6 shows changes in the specific reaction rate and the 1-butanol selectivity against the Sr/(Ca+Sr) molar ratio. The 1-butanol selectivity continuously decreased from 81.7 C% to 70.1 C% with increasing of the calcium content. The specific reaction rate continuously increased with increasing of the calcium content but the rate were lower than that of Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> hydroxyapatite catalyst.

The catalytic conversions of ethanol were carried out at 300 °C using the Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6-x</sub>(VO<sub>4</sub>)<sub>x</sub>(OH)<sub>2</sub> and Sr<sub>10</sub>(PO<sub>4</sub>)<sub>6-x</sub>(VO<sub>4</sub>)<sub>x</sub>(OH)<sub>2</sub> hydroxyapatite solid solution catalysts with various V/(P+V) molar ratio. As shown in Fig. 7, the 1-butanol selectivity continuously decreased with increasing the V/(P+V) molar ratio of Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6-x</sub>(VO<sub>4</sub>)<sub>x</sub>(OH)<sub>2</sub> hydroxyapatite solid solution catalysts. The specific reaction rate of Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6-x</sub>(VO<sub>4</sub>)<sub>x</sub>(OH)<sub>2</sub> hydroxyapatite solid solution catalysts were lower than that of Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> hydroxyapatite catalyst. As shown in Fig. 8,



**Fig. 6.** Changes in the specific reaction rate and the 1-butanol selectivity against the Sr/(Ca+Sr) molar ratio of Ca<sub>10-y</sub>Sr<sub>y</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> hydroxyapatite solid solution catalysts. *Reaction condition*: catalyst 2.0 g, reaction temperature 300 °C, *W*/*F*<sub>ethanol</sub> 130 h g<sub>catalyst</sub> mol<sub>ethanol</sub><sup>-1</sup>, time on stream 3 h, ethanol 16.1 mol% (Ar balanced).



**Fig. 7.** Changes in the specific reaction rate and the 1-butanol selectivity against the V/(P+V) molar ratio of  $Ca_{10}(PO_4)_{6-x}(VO_4)_x(OH)_2$  hydroxyapatite solid solution catalysts. *Reaction condition*: catalyst 2.0 g, reaction temperature 300 °C, *W*/*F*<sub>ethanol</sub> 130 h g<sub>catalyst</sub> mol<sub>ethanol</sub><sup>-1</sup>, time on stream 3 h, ethanol 16.1 mol% (Ar balanced).

the Sr<sub>10</sub>(PO<sub>4</sub>)<sub>6-x</sub>(VO<sub>4</sub>)<sub>x</sub>(OH)<sub>2</sub> hydroxyapatite solid solution catalysts showed almost the same specific reaction rate as that of Sr<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> hydroxyapatite catalyst. On the other hand, the 1-butanol selectivity drastically decreased with increasing the V/(P+V) molar ratio between 8 and 33 mol%. After the catalytic conversions of ethanol, all hydroxyapatite solid solution catalysts retained the hydroxyapatite structure.

In the catalytic conversion of ethanol, the catalytic activities and 1-butanol selectivities of the  $Ca_{10-y}Sr_y(PO_4)_6(OH)_2$ ,  $Ca_{10}(PO_4)_{6-x}(VO_4)_x(OH)_2$ , and  $Sr_{10}(PO_4)_{6-x}(VO_4)_x(OH)_2$  hydroxyapatite solid solution catalysts depended on the Sr/(Ca+Sr) or V/(P+V) molar ratios. The specific reaction rate of  $Ca_{10-y}Sr_y(PO_4)_6(OH)_2$  catalysts increased with increasing of the calcium content. On the other hand, the 1-butanol selectivities of the  $Ca_{10-y}Sr_y(PO_4)_6(OH)_2$ ,  $Ca_{10}(PO_4)_{6-x}(VO_4)_x(OH)_2$ , and  $Sr_{10}(PO_4)_{6-x}(VO_4)_x(OH)_2$  catalysts were lower than those of  $Sr_{10}(PO_4)_6(OH)_2$  hydroxyapatite catalyst. In conclusion, the substitutions of  $Sr_{10}(PO_4)_6(OH)_2$  hydroxyapatite catalyst by  $Ca^{2+}$  ions



**Fig. 8.** Changes in the specific reaction rate and the 1-butanol selectivity against the V/(P+V) molar ratio of Sr<sub>10</sub>(PO<sub>4</sub>)<sub>6-x</sub>(VO<sub>4</sub>)<sub>x</sub>(OH)<sub>2</sub> hydroxyapatite solid solution catalysts. *Reaction condition*: catalyst 2.0 g, reaction temperature 300 °C, *W*/*F*<sub>ethanol</sub> 130 h g<sub>catalyst</sub> mol<sub>ethanol</sub><sup>-1</sup>, time on stream 3 h, ethanol 16.1 mol% (Ar balanced).



**Fig. 9.** The effects of  $W/F_{\text{ethanol}}$  value on the ethanol conversion (×) and the product selectivities over the Sr–P hydroxyapatite catalyst. *Products*:  $\blacksquare$  1-butanol,  $\blacktriangle C_6 + C_8$ -alcohols,  $\triangle$  2-buten-1-ol,  $\Box C_2 + C_4$ -aldehydes. *Reaction condition*: catalyst 0.5–4.0 g, reaction temperature 300 °C, time on stream 3 h, ethanol 16.1 mol% (Ar balanced).

and VO<sub>4</sub><sup>3-</sup> ions were ineffective against the selective synthesis of 1-butanol from ethanol.

#### 3.3. Reaction mechanism of 1-butanol formation from ethanol

Fig. 9 shows the variation of ethanol conversion and products selectivity against the  $W/F_{ethanol}$  values. The ethanol conversion increased with increasing of the W/F. The 1-butanol selectivity increased with increasing of the W/F up to 65 h g<sub>catalyst</sub> mol<sub>ethanol</sub><sup>-1</sup>, and then, it decreased very gradually. The selectivities of 2-buten-1-ol, acetaldehyde, crotonaldehyde, and butyraldehyde were 21.8 C%, 1.9 C%, 0.6 C%, and 0.3 C% at W/F of 32 h g<sub>catalyst</sub> mol<sub>ethanol</sub><sup>-1</sup>, and these selectivities drastically decreased with increasing of the W/F. In contrast, the selectivity of C<sub>6</sub> and C<sub>8</sub> alcohols, such as 2-ethyl-1-butanol, 1-hexanol, 2-ethyl-1-hexanol, and 1-octanol, increased with increasing of the W/F. From these results, it was considered that 2-buten-1-ol, acetaldehyde, crotonaldehyde, and butyraldehyde were reaction intermediates of 1-butanol formation, and 2-ethyl-1-butanol, 1-hexanol, 2-ethyl-1-hexanol, and 1-octanol were successive reaction products.

Next, in order to clarify the reaction mechanism of 1-butanol formation, hydrogenations of the intermediates, such as crotonaldehyde, 2-buten-1-ol, and butyraldehyde, into 1-butanol were performed over the Sr–P hydroxyapatite catalyst at 300 °C. Because the hydrogenation of 2-buten-1-ol using hydrogen gas did not proceed over the Sr–P hydroxyapatite catalyst under the reaction condition (not shown data), 2-propanol was used as a hydrogen donor.

Fig. 10 shows the product yields in the hydrogen transfer reaction of crotonaldehyde (CA), 2-buten-1-ol (2-B-1-O), and butyraldehyde (BA) with 2-propanol over the Sr–P hydroxyapatite catalyst. The 1-butanol was selectively formed from crotonaldehyde, 2-buten-1-ol, and butyraldehyde over the Sr–P hydroxyapatite catalyst. C<sub>7</sub>-alcohols, such as 2-ethyl-3-methyl-1butanol formed from the C<sub>4</sub> reactants and 2-propanol, were also formed as the minor product. As shown in Table 2, crotonaldehyde was selectively formed from acetaldehyde over the Sr–P hydroxyapatite catalyst. These results supported that acetaldehyde, crotonaldehyde, 2-buten-1-ol, and butyraldehyde were reaction intermediates in the 1-butanol formation from ethanol. That is, it was considered that the reaction mechanism of the conversion of ethanol into 1-butanol over Sr–P hydroxyapatite catalyst included the dehydrogenation of ethanol into acetalde-



**Fig. 10.** The hydrogen transfer reaction of crotonaldehyde, 2-buten-1-ol, and butyraldehyde with 2-propanol over the Sr–P hydroxyapatite catalyst. *Substrates*: CA = crotonaldehyde, 2-B-1-O = 2-buten-1-ol, BA = butyraldehyde. Products:  $\blacksquare$  1-butanol,  $\blacksquare$  C<sub>7</sub>-alcohols. *Reaction condition*: catalyst 1.0 g, reaction temperature 300 °C, time on stream 6.5 h, substrates 0.1 mol%, 2-propanol 12.6 mol% (Ar bala anced).

hyde, the aldol condensation of acetaldehyde into crotonaldehyde, and the hydrogenations of crotonaldehyde, 2-buten-1-ol, and/or butyraldehyde into 1-butanol, which was the same reaction mechanism as that described in Scheme 1 [11]. And, as shown in Fig. 10, the 1-butanol selectivity from 2-buten-1-ol (62.5 C%) was lower than that from butyraldehyde (81.8 C%), which suggested that 1-butanol synthesis from butyraldehyde might be superior to that from 2-buten-1-ol.

## 3.4. Effects of component ions of hydroxyapatite catalysts on product selectivity

In order to clarify the effects of component ions of hydroxyapatites on the ethanol conversion, the aldol condensation of acetaldehyde into crotonaldehyde and the hydrogen transfer reaction of 2-buten-1-ol with 2-propanol into 1-butanol were performed over the Ca–P, Sr–P, and Ca–V hydroxyapatite catalysts at 300 °C.

Table 2 shows the product yields in the aldol condensations of acetaldehyde over the Ca–P, Sr–P, and Ca–V hydroxyapatite catalysts. The Ca–V hydroxyapatite catalyst showed higher catalytic activity for the acetaldehyde conversion than those of the Sr–P and Ca–P hydroxyapatite catalysts. Crotonaldehyde was the major reaction product, and C<sub>6</sub>-aldehydes, C<sub>8</sub>-aldehydes and aromatics were the minor products over any catalysts of Ca–P, Sr–P, and Ca–V hydroxyapatite. The selectivities of crotonaldehyde, aromatics, C<sub>6</sub>-aldehydes and C<sub>8</sub>-aldehydes over the Sr–P hydroxyapatite catalyst were 62.7 C%, 23.6 C%, 4.4 C%, and 5.6 C%, respectively. The Ca–P

#### Table 2

The aldol condensations of acetaldehyde over the Ca–P, Sr–P, and Ca–V hydroxyapatite catalysts<sup>a</sup>.

Catalyst	Ca-P	Sr-P	Ca–V <sup>t</sup>
Conversion (C%)	42.7	32.8	33.5
Selectivity (C%)			
Hydrocarbons	1.7	0.7	0.0
Ethanol	1.1	0.8	0.6
Butyraldehyde	5.4	0.0	1.0
Crotonaldehyde	58.9	62.7	79.3
C <sub>6</sub> -aldehydes	6.8	4.4	7.4
C <sub>8</sub> -aldehydes	5.8	5.6	6.4
2-buten-1-ol	0.4	0.0	0.0
Aromatics	17.5	23.3	4.4

<sup>a</sup>Catalyst 1.0 g (<sup>b</sup> 0.6 g), reaction temperature 300 °C, time on stream 9 h, acetaldehyde 0.037 mol% (Ar balanced).



**Fig. 11.** The hydrogen transfer reactions of 2-buten-1-ol with 2-propanol over the Ca–P, Sr–P, and Ca–V hydroxyapatite catalysts. *Reaction condition*: catalyst 0.2–1.0 g, reacion temperature 300 °C, time on stream 6.5 h, 2-buten-1-ol 0.1 mol%, 2-propanol 12.6 mol% (Ar balanced).

hydroxyapatite catalyst showed the 58.9 C% of crotonaldehyde selectivity, which was almost the same as those of Sr–P hydroxyapatite catalyst. The Ca–V hydroxyapatite catalyst exhibited higher crotonaldehyde selectivity of 79.3 C% and lower aromatics selectivity of 4.4 C% than those of Sr–P hydroxyapatite catalyst.

Fig. 11 shows changes in the 1-butanol selectivities against the 2-buten-1-ol conversion over the Ca-P, Sr-P, and Ca-V hydroxyapatite catalysts. 1-Butanol was formed over the any hydroxyapatite catalysts, but the 1-butanol selectivity depended on the component ions. The Sr-P hydroxyapatite catalyst exhibited 70 mol% of the 1butanol selectivity at 95 mol% of the 2-buten-1-ol conversion. The C<sub>7</sub>-alcohols, derived from the 2-buten-1-ol and 2-propanol, were also observed about 3 mol% yield (not shown data) in the ends of reactor, which indicated that the main side reaction might be coking. The Ca-P hydroxyapatite catalyst exhibited 52 mol% of the 1-butanol selectivity and 8 mol% of the C7-alcohols selectivity at 95 mol% of the 2-buten-1-ol conversion. The Ca-V hydroxyapatite catalyst exhibited 23 mol% of the 1-butanol selectivity and mol% of the C7-alcohols selectivity at 95 mol% of the 2-buten-1-ol conversion. These results indicated that the Sr-P hydroxyapatite catalyst showed the high selectivity for the hydrogen transfer reaction of 2-buten-1-ol into 1-butanol and relatively inhibited the coking.

Based on above results, the effects of component ions of hydroxyapatite catalysts on the ethanol conversion were considered as follows. The Sr-P hydroxyapatite catalyst showed high selectivity into crotonaldehyde in the aldol condensation of acetaldehyde and relatively inhibited the coking in the hydrogen transfer reaction of 2-buten-1-ol into 1-butanol. These were reasons why the Sr-P hydroxyapatite catalyst exhibited the highest 1-butnaol selectivity in the catalytic conversion of ethanol among the prepared hydroxyapatite catalysts. The Ca-P hydroxyapatite catalyst showed almost the same crotonaldehyde selectivity in the aldol condensation of acetaldehyde as those of the Sr-P hydroxyapatite catalyst, but lower 1-butanol selectivity in the hydrogen transfer reaction of 2-buten-1-ol. Therefore, it was considered that the 1-butanol selectivity of Ca-P hydroxyapatite catalyst in the catalytic conversion of ethanol was lower than those of the Sr-P hydroxyapatite catalyst. The Ca-V hydroxyapatite catalyst exhibited higher catalytic activity and crotonaldehyde selectivity in the aldol condensation of acetaldehyde than those of the Sr-P hydroxyapatite catalyst. However, the Ca-V hydroxyapatite catalyst showed higher selectivity into ethylene in the conversion of ethanol. These were reasons why the Ca-V hydroxyapatite catalyst exhibited lower 1-butanol selectivity in the catalytic conversion of ethanol than that of the Sr-P

hydroxyapatite catalyst. In addition, the Ca–V hydroxyapatite catalyst also showed the high propylene selectivity in the catalytic conversion of 2-propanol [8], which was accompanied with the production of water but not hydrogen, which might be a reason why the Ca–V showed the low 1-butanol selectivity in the hydrogen transfer reaction of 2-buten-1-ol.

#### 4. Conclusions

The product distributions in the catalytic conversion of ethanol at 300 °C under atmospheric pressure depended on the kinds of component ions of the hydroxyapatite catalysts. 1-Butanol was the major products over the Ca-P and Sr-P hydroxyapatite catalysts. The Sr-P hydroxyapatite catalyst exhibited the highest 1-butanol selectivity at any ethanol conversions between 1 and 24%. On the other hand, ethylene was the major products over the Ca-V and Sr-V hydroxyapatite catalysts. Although the 1-butanol selectivities of the prepared hydroxyapatite solid solutions, such as  $Ca_{10-v}Sr_v(PO_4)_6(OH)_2$ ,  $Ca_{10}(PO_4)_{6-x}(VO_4)_{6-x}(OH)_2$ , and  $Sr_{10}(PO_4)_{6-x}(VO_4)_{6-x}(OH)_2$ , depended on the Sr/(Ca + Sr) and V/(P+V) molar ratios, there were no catalysts exceeding the 1butanol selectivity of the Sr-P hydroxyapatite catalyst. In the gas phase reactions using the hydroxyapatite catalysts, 1-butanol was formed through the dehydrogenation of ethanol into acetaldehyde, the aldol condensation of acetaldehyde into crotonaldehyde, and the hydrogenations of crotonaldehyde, 2-buten-1-ol, and/or butyraldehyde into 1-butanol. The Sr-P hydroxyapatite catalyst showed high crotonaldehyde selectivity in the aldol condensation of acetaldehyde and relatively inhibited the coking in the hydrogen transfer reaction of 2-buten-1-ol into 1-butanol, which might be reasons why the Sr–P hydroxyapatite catalyst exhibited the highest 1-butnaol selectivity in the catalytic conversion of ethanol among the prepared hydroxyapatite catalysts.

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