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Short Communication

# Catalytic dehydration of lactic acid to acrylic acid over dibarium pyrophosphate

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ABSTRACT

Barium phosphate catalysts were prepared by a precipitation method. The catalysts were calcined at 500 °C for 6 h in air atmosphere and characterized by SEM for morphological features, by XRD for crystal phases, by $N_2$ sorption for specific surface area, by TPD–$NH_3$ for acidity and by TG for thermal stability. The dibarium pyrophosphate catalyst was found to have the best catalytic performance, ascribing to weak acidity on the surface. Under the optimal reaction conditions, 99.7% of the lactic acid conversion and 76.0% of the selectivity to acrylic acid were achieved over the dibarium pyrophosphate catalyst.

## 1. Introduction

The utilization of renewable resources for substitution of fossil resources like petroleum, natural gas and coal, is a key project in the modern industrial society [1–9]. For some industrial applications, biomass has already been proven to be a promising candidate compared to fossil reactants [2,10]. Lactic acid and its esters as platform molecules, can be converted into many chemicals such as acrylic acid [11–14], propionic acid [15], acetaldehyde [10], and 2,3-pentanedione [16]. In these processes, catalytic dehydration of lactic acid to acrylic acid has been viewed as the most important sustainable process. It is well known that the dehydration of the hydroxyl group in lactic acid molecule is catalyzed by acid sites. Ordinarily, as for aliphatic alcohol, dehydration reaction for formation of ether bond requires low temperature due to substitution mechanism, while dehydration reaction for formation of olefinic bond through elimination mechanism requires high temperature. Therefore, dehydration of lactic acid to form α,β-unsaturated acid occurs only at high temperature. Under high temperature, acid plays a crucial role in the process of dehydration for lactic acid. Strong acidity is a great disadvantage for catalytic dehydration of lactic acid, while it favors for decarbonylation and/or decarboxylation of lactic acid to acetaldehyde [10,17]. On the contrary, the catalyst without acid performance or with a basicity has no efficiency for catalytic dehydration of lactic acid. Thus to adjust or choose the acidic strength of catalyst to appropriate degree is a crucial step for efficient catalytic dehydration. A case in point is that all kinds of modifiers are used to change the surface acidity of NaY zeolites to achieve a high catalytic performance [18,19]. But the modifiers [12,20] are easily lost from the surface of the catalyst under the atmosphere of water vapor because they have an excellent solubility in water, resulting in deactivation of catalyst with time on stream. Insoluble salts in water with appropriate acid may be an ideal type of catalysts for dehydration of lactic acid at high temperature. $Ca_3(PO_4)_2$–$Ca_2P_2O_7$ (50:50 wt.%) catalyst has been demonstrated to efficiently catalyze dehydration of methyl lactate [15]. However, the knowledge on the use of the alkaline earth metal phosphates for dehydration is still quite limited. In the present work, the dehydration of lactic acid to acrylic acid using an efficient $Ba_2P_2O_7$ catalyst is reported.

## 2. Experimental

### 2.1. Materials

Lactic acid (analytic grade) was purchased from Chengdu Kelong Chemical Reagent Co. and was used for the dehydration reaction of lactic acid without further purification. Sodium pyrophosphate, sodium phosphate, barium chloride, acrylic acid, propionic acid, acetic acid, acetaldehyde, 2,3-pentanedione and *n*-butanol, together with hydroquinone were obtained from Sigma-Aldrich.

### 2.2. Preparation of catalysts

The method about catalyst preparation in this work was similar to that described previously [15,21]. 1) $Ba_2P_2O_7$: Under the condition of continuous stirring at 55 °C, 0.09 mol $BaCl_2 \cdot 2H_2O$ in 100 mL distilled

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**Table 1**
Screening of catalysts.

| Catalysts | Conversion of lactic acid/% | Selectivity/% | | | | |
|---|---|---|---|---|---|---|
| | | Acrylic acid | Acetaldehyde | Propionic acid | 2,3-Pentanedione | Acetic acid |
| $Ba_2P_2O_7$ | 99.7 | 76.0 | 14.1 | 2.8 | 2.1 | 1.1 |
| $Ba_3(PO_4)_2$ | 99.5 | 18.5 | 7.9 | 7.4 | 1.0 | 1.1 |
| $Ba_2P_2O_7$–$Ba_3(PO_4)_2$ (50:50 wt.%) | 81.0 | 54.0 | 11.2 | 3.9 | 1.1 | 1.3 |

Conditions: Reaction temperature 400 °C, catalyst 0.57 g, carrier gas 1 mL/min, feed flow rate 1 mL/h, LA feedstock 20 wt.%.

water was dropwisely added to 0.035 mol sodium pyrophosphate in 200 mL distilled water to form a white precipitate of barium pyrophosphate. Subsequently, the white precipitate was rinsed at least three times to remove sodium pyrophosphate using distilled water and dried at 120 °C in the air circulating oven for 6 h. 2) $Ba_3(PO_4)_2$: The method of preparation of $Ba_3(PO_4)_2$ was similar to that of $Ba_2P_2O_7$. 3) $Ba_3(PO_4)_2$–$Ba_2P_2O_7$ (50:50 wt.%): It was prepared by mixing barium phosphate together with barium pyrophosphate in the agate mortar for 20 min. Prior to activity evaluation and characterization, the above catalysts were calcined at 500 °C for 6 h.

### *2.3. Catalyst characterization*

Powder X-ray diffraction measurement was conducted on a Dmax/Ultima IV diffractometer operated at 40 kV and 20 mA with Cu-Ka radiation. The FTIR spectra of the catalysts were recorded in the range of 500–4000 $cm^{-1}$ on a Nicolet 6700 spectrometer. The particle size and the morphology of the catalysts were examined using SEM (JSM-6510). TG analysis was used with Netzsch STA449 F3 analyzer. TPD–$NH_3$ analysis was used with Autochem II2920, and the specific surface areas and pore volumes of catalysts were measured with TriStar 3000.

### *2.4. Catalyst evaluation*

The dehydration of lactic acid to acrylic acid over the catalysts was carried out in a fixed-bed quartz reactor with a 4 mm inner diameter operated at atmospheric pressure. The catalyst (0.50–0.60 g, 20–40 meshes) was placed in the middle of the reactor and quartz wool was placed in both ends. Before catalytic evaluation the catalyst was pretreated at the required reaction temperature (400 °C) for 1.0 h under high purity $N_2$ (0.1 MPa, 1.0 mL/min). The feedstock (20 wt.% solution of lactic acid) was then pumped into the preheating zone (lactic acid aqueous solution flow rate, 1.0 mL/h) and driven through the catalyst bed by nitrogen. The liquid products were condensed using ice-water bath and analyzed off-line using an SP-6890 gas chromatograph with a FFAP capillary column connected to an FID. Quantitative analysis of the products was carried out by the internal standard method using *n*-butanol as the internal standard material. GC–MS analyses of the samples were performed using Agilent 5973N Mass Selective Detector attachment.

## 3. Results and discussion

### *3.1. Evaluation of catalyst*

### *3.1.1. Screening of catalysts*

Barium phosphate catalysts were utilized to catalyzed dehydration of lactic acid, and the results were shown in Table 1. $Ca_3(PO_4)_2$–$Ca_2P_2O_7$ (50:50 wt.%) catalyst has been found a high catalytic performance for dehydration of methyl lactate due to a synergistic effect between $Ca_3(PO_4)_2$ and $Ca_2P_2O_7$ [15]. It is known that achieving high selectivity for dehydration reaction is more difficult for lactic acid than that of lactates [22]. From Table 1, the conversion of lactic acid decreased in the order of $Ba_2P_2O_7$, $Ba_3(PO_4)_2$, and $Ba_2P_2O_7$–$Ba_3(PO_4)_2$ (50:50 wt.%) and the lowest conversion was obtained by $Ba_2P_2O_7$–$Ba_3(PO_4)_2$ (50:50 wt.%). The selectivity toward acrylic acid changed drastically and the best result was achieved by $Ba_2P_2O_7$. Considering the conversion of lactic acid and selectivity to acrylic acid, $Ba_2P_2O_7$ catalytic performance is far better than that of $Ba_2P_2O_7$–$Ba_3(PO_4)_2$ (50:50 wt.%), indicating that no synergistic effect existed in $Ba_2P_2O_7$–$Ba_3(PO_4)_2$. The selectivities toward acrylic acid and acetaldehyde decreased in the order of $Ba_2P_2O_7$, $Ba_2P_2O_7$–$Ba_3(PO_4)_2$ (50:50 wt.%), and $Ba_3(PO_4)_2$. Propionic acid was formed from hydrogenation of lactic acid and/or acrylic acid with hydrogen generated from decarboxylation/decarbonylation of lactic acid. Analysis of tail gas shows that hydrogen, $CO_2$ and CO existed in the process of catalytic reaction, indicating occurrence of decarboxylation/decarbonylation of lactic acid. It is not astonishing that the highest selectivity to propionic acid was observed from $Ba_3(PO_4)_2$. The reason is that the alkalinity of catalyst favors for the hydrogenation reaction and under the steam atmosphere $Ba_3(PO_4)_2$ has the strongest alkalinity. Therefore, $Ba_2P_2O_7$ is an excellent catalyst for formation of acrylic acid from dehydration reaction of lactic acid although plenty of acetaldehyde was also produced in the catalytic process.

### *3.1.2. Catalyst stability*

The stability of catalyst with time on stream was studied at 400 °C over the $Ba_2P_2O_7$ catalyst calcinated at 500 °C. From Fig. 1, the conversion of lactic acid decreased slightly from 99.8% to 93.5% with time on stream. The selectivity to acrylic acid increased from 69.1% to 76.9% at the primary stage of reaction and gradually decreased from 76.9% to about 55% with further increase of reaction time. Compared with that of the modified NaY catalyst [11], this result is far better. In the former, the conversion of lactic acid decreased from 80% to 60% while the selectivity to acrylic acid drastically decreased from 73% to 40%. The possible reason is that the modified NaY catalyst has stronger acid on its surface than that of the $Ba_2P_2O_7$ catalyst. It is known that stronger acid favors

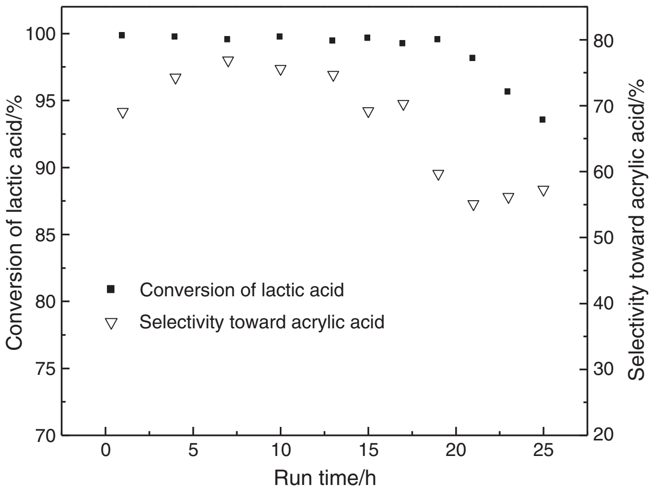

**Fig. 1.** The performance of catalyst with time on stream. Conditions: Reaction temperature 400 °C, $Ba_2P_2O_7$ catalyst 0.57 g, carrier gas 1 mL/min, feed flow rate 1 mL/h, LA feedstock: 20 wt.%.

**Table 2**
Physical properties of catalysts.

| Catalyst | Surface area/m$^2$/g | Pore volume/cm$^3$/g | Pore size/nm |
|---|---|---|---|
| $Ba_2P_2O_7$ | 1.58 | 0.0047 | 12 |
| $Ba_3(PO_4)_2$ | 12.64 | 0.0624 | 20 |
| $Ba_2P_2O_7$–$Ba_3(PO_4)_2$ (50:50 wt.%) | 2.18 | 0.0051 | 8 |

the carbon deposition, resulting in deactivation of catalyst. In addition, the modified components such as alkaline $Na_2HPO_4$ encountered a losing, leading to an increase of acidity of NaY catalyst. Therefore, a drastic decrease of catalyst performance was observed with time on stream. However, the similar disadvantage cannot exist for the $Ba_2P_2O_7$ catalyst. Besides, effects of other parameters such as reaction temperature, lactic acid concentration and LHSV were also investigated (seen in supporting information, Table S1, Table S2 and Table S3.)

### 3.2. Characterization of catalysts

#### 3.2.1. Physical properties and TPD–$NH_3$

It is clearly seen from the results presented in Table 2 that $Ba_2P_2O_7$ and $Ba_3(PO_4)_2$ have low specific surface areas of 1.58 and 12.64 m$^2$/g, respectively. The specific surface area and pore volume of $Ba_2P_2O_7$–$Ba_3(PO_4)_2$ (50:50 wt.%) lie in between two pure components, indicating that a physical mixture exists between $Ba_2P_2O_7$ and $Ba_3(PO_4)_2$. The similar result was observed by Hong et al. [15]. The $Ba_3(PO_4)_2$ has the lowest activity although it has a relatively high specific surface area, compared to that of others. This suggests that as for the tested catalysts, surface area of catalyst is not a crucial factor for activity. TPD–$NH_3$ was performed and the results were given in Fig. S1 and Table 3. From the results obtained from TPD–$NH_3$, $Ba_2P_2O_7$ has the lowest acid strength and lowest acid density (total acid amount 5.59 μmol $NH_3$/g) while $Ba_3(PO_4)_2$ has the highest acidity and acid density (total acid amount 13.88 μmol $NH_3$/g). Low amounts of acid sites favor the dehydration of lactic acid to acrylic acid. In the presence of water, for $Ba_3(PO_4)_2$ hydrolytic reaction occurs resulting in alkalinity of its surface (seen effect of water on acidity–alkalinity of the catalysts in ESI). Therefore, hydrogenation of lactic acid or acrylic acid to propionic acid over the $Ba_3(PO_4)_2$ catalyst was promoted. However, for $Ba_2P_2O_7$ hydrolytic reaction hardly occurs. Thus, propionic acid selectivity is very low for $Ba_2P_2O_7$ catalyst. It is concluded that $Ba_2P_2O_7$ displays an excellent catalytic performance owing to weak acidity and hydrothermal stability.

#### 3.2.2. FT-IR, XRD and SEM

FT-IR spectra of catalysts were shown in Fig. 2. It can be seen that all characteristic peaks of both $Ba_2P_2O_7$ and $Ba_3(PO_4)_2$ appear in the spectra of $Ba_2P_2O_7$–$Ba_3(PO_4)_2$ (50:50 wt.%) except for peak intensity decreases and no new peak appears, indicating that no reaction occurs between $Ba_2P_2O_7$ and $Ba_3(PO_4)_2$. In addition, all the specific adsorption bands of used $Ba_2P_2O_7$catalyst are identical with those of fresh $Ba_2P_2O_7$catalyst, indicating high stability of catalyst structure with time on stream. The wide-angle X-ray diffraction (XRD) was performed and the results were shown in Fig. 3. All the specific diffraction peaks of both $Ba_2P_2O_7$ and $Ba_3(PO_4)_2$ appear in the $Ba_2P_2O_7$–$Ba_3(PO_4)_2$ (50:50 wt.%) catalyst and no new diffraction peak occurs, suggesting that physical mixture of two components exists in the $Ba_2P_2O_7$–$Ba_3(PO_4)_2$ (50:50 wt.%) catalyst. Besides, both used $Ba_2P_2O_7$ and fresh $Ba_2P_2O_7$ catalysts remain constant in the XRD. Fig. S2 presented the TG of fresh $Ba_2P_2O_7$ catalyst. Slight mass decrease of the catalyst was observed in the temperature programming process. Thus the characterizations of XRD and TG further demonstrated that the structure of catalyst is very stable in the catalytic process. Fig. S3 shows the morphological features of fresh $Ba_2P_2O_7$ catalyst.

**Table 3**
TPD–$NH_3$ results of catalysts.

| Catalyst | Acidity amount/μmol/g | | | Total acid amount/μmol/g |
|---|---|---|---|---|
| | Weak (100–200 °C) | Medium (200–400 °C) | Strong (400–600 °C) | |
| $Ba_2P_2O_7$ | 0.71 | 2.02 | 2.86 | 5.59 |
| $Ba_3(PO_4)_2$ | 1.72 | 4.92 | 7.24 | 13.88 |
| $Ba_2P_2O_7$–$Ba_3(PO_4)_2$ (50:50 wt.%) | 0.47 | 2.15 | 5.22 | 7.84 |

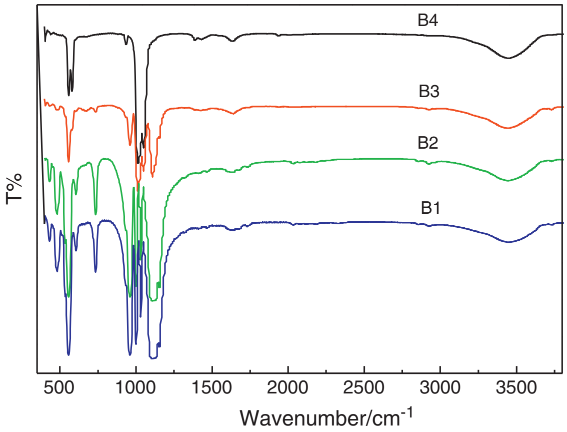

**Fig. 2.** FT-IR of catalysts. B1—Fresh $Ba_2P_2O_7$ catalyst, B2—used $Ba_2P_2O_7$ catalyst, B3—$Ba_2P_2O_7$–$Ba_3(PO_4)_2$ (50:50 wt.%), B4—fresh $Ba_3(PO_4)_2$.

## 4. Conclusions

Dehydration of lactic acid to acrylic acid was carried out over the barium phosphate catalysts at various conditions. Dibarium pyrophosphate was found to have an effectively catalytic performance due to weak acidity. The dibarium pyrophosphate catalyst retained an excellent stability for catalytic dehydration of lactic acid because strong acidity is absent on the surface of the catalyst which caused carbon deposition, resulting in deactivation of the catalyst. Furthermore the dibarium pyrophosphate catalyst remained the hydrothermal stability due to very low solubility of $Ba_2P_2O_7$ and no hydrolytic reaction in the water. Under the optimal reaction conditions, 99.7% of the lactic acid conversion and 76.0% of the selectivity to acrylic acid were achieved over the dibarium pyrophosphate catalyst.

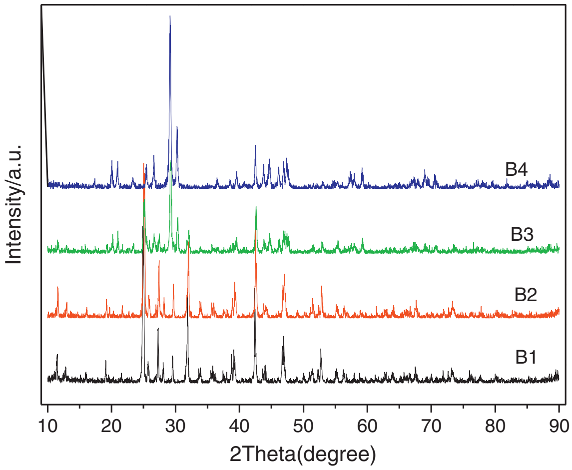

**Fig. 3.** XRD of catalysts. B1—Fresh $Ba_2P_2O_7$ catalyst, B2—used $Ba_2P_2O_7$ catalyst, B3—$Ba_2P_2O_7$–$Ba_3(PO_4)_2$ (50:50 wt.%), B4—fresh $Ba_3(PO_4)_2$.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2013.10.009.

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