第26卷 第6期　　分　子　催　化　　Vol. 26, No. 6
2012年12月　　JOURNAL OF MOLECULAR CATALYSIS(CHINA)　　Dec.　2012

Article ID: 1001-3555(2012)06-0506-09

Highly efficient pyrophosphate/phosphate catalyst for the dehydration of lactic acid to acrylic acid

FAN Guo-ce, TANG Cong-ming*, LI Xin-li
(*Chemical Synthesis and Pollution Control Key Laboratory of Sichuan Province*, *China West Normal University*, *Nanchong* 637009, *China*)

Abstract: An efficient catalyst composed of calcium pyrophosphate and calcium phosphate was developed to catalyze dehydration of lactic acid to acrylic acid. The catalyst compositions have a drastic influence on conversion of lactic acid and selectivity toward acrylic acid. When the catalyst composition in mass ratio of calcium phosphate to calcium pyrophosphate was changed from 30 : 70 to 50 : 50, higher conversion of lactic acid and higher selectivity toward acrylic acid were achieved. Other parameters such as reaction temperature, lactic acid concentration, liquid hourly space velocity, were also discussed. In addition, as one of the most important factors for heterogeneous catalysts, the stability of catalyst was checked. After running 56 hours, the conversion of lactic acid yet maintained above 96%, and the selectivity of acrylic acid also maintained above 57%. Characterizations of the catalysts were performed by XRD, TG, SEM, and FTIR.

Key words: dehydration; calcium phosphate; calcium pyrophosphate; lactic acid; acrylic acid
CLC number: O643.32　　**Document code**: A

The utilization of renewable feedstocks as raw materials for the chemical industry has been focused on by many researchers due to the excessive depletion in fossil resources like petroleum, natural gas and coal. For some industrial applications, biomass has already been proven to be a promising candidate compared to fossil reactants[1-2]. Lactic acid can be obtained from biomass with low cost by bacterial fermentation and it has a wide range of applications.

Based on lactic acid as raw material, many chemicals such as acrylic acid, propionic acid, acetaldehyde, 2,3-pentanedione were produced by catalytic conversion of lactic acid[1,3-11] and the dehydration of lactic acid to acrylic acid has been viewed as the most important sustainable process. In early works, silica-aluminum salts (sulfate, nitrate, phosphate, etc.) and mixtures of inorganic salts were used as catalysts for conversion of lactic acid to acrylic acid[12]. Recently, Y-type zeolite catalysts for dehydration of lactic acid to acrylic acid have been widely investigated since it was used as catalyst for alcohol dehydration reaction[13]. Wang et al.[14] modified the NaY zeolites using rare earth metals (lanthanum, cerium, samarium, and europium). Compared with unmodified NaY catalyst, the modified catalysts with lanthanide had better catalytic performance, the optimum modified metal was lanthanum and the optimum content was 2%. Sun et al.[10] reported that potassium modification significantly improved the selectivity and durability of NaY zeolites during lactic acid dehydration reaction and the selecti-

---

Received date: 2012-10-09; Revised date: 2012-11-08.

Foundation item: Supported by Scientific Research Fund of Sichuan Provincial Educational Department with project number of 09ZC012, Scientific Research Fund of China West Normal University with project number of 10B004 and the Nanchong Key Technology R&D Program of Sichuan, China with project number of 11A0051.

Biography: FAN Guoce, male, born in 1987, studying for a master's degree.

* **Corresponding author**: TANG Cong-ming, Tel: 0817-2568081, E-mail: tcmtang2001@163.com.

vity of 2.8K/NaY zeolites improved from 14.8% to 50.0%. Alkaline earth metals were used to modify NaY zeolites and the catalytic performance was evidently improved[8]. Zhang et al.[9] carefully investigated the alkali phosphates modified NaY zeolites for dehydration of lactic acid to acrylic acid and optimized the catalytic performance in terms of the type and loading of alkali phosphates, reaction temperature, liquid hourly space velocity, and lactic acid concentration. So far, to my knowledge, the best results was obtained by Zhang[15] over the composite catalyst including NaY and montmorillonite.

Although the NaY zeolites catalysts for dehydration of lactic acid to acrylic acid have been demonstrated to have high activity, the selectivity toward acrylic acid decreased drastically with an increase in reaction time. Thus this encouraged us to further research on a new catalyst system for dehydration of lactic acid. The aim of present work is to develop an efficient catalyst with an excellent durability for dehydration of lactic acid to acrylic acid.

1 Experimental

1.1 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. Deionized water was prepared in the laboratory and was used to dilute lactic acid for required concentration. Sodium pyrophosphate ($Na_4P_2O_7$), sodium phosphate ($Na_3PO_4 \cdot 12H_2O$), calcium chloride ($CaCl_2 \cdot 2H_2O$), acrylic acid, acetaldehyde, and butyric acid, together with hydroquinone were obtained from Sigma-Aldrich. Acrylic acid and acetaldehyde were used for gas chromatograph reference materials, and butyric acid was adopted as internal standard material. Hydroquinone (0.3%) was used as a polymerization inhibitor.

1.2 Preparation of catalysts

The method about catalyst preparation in this work was similar to that described previously[16]. 1) Calcium phosphate: Under the condition of continuous stirring at 60 ℃, 0.1 mol $CaCl_2 \cdot 2H_2O$ in 100 mL deionized water was slowly added to 0.05 mol sodium phosphate in 200 mL deionized water to formate a white precipitate of calcium phosphate. Subsequently, the white precipitate was washed three times using deionized water and dried at 120 ℃ in the air circulating oven for 24 hours. 2) Calcium pyrophosphate: Under the condition of continuous stirring at 20 ~ 25 ℃, 0.14 mol $CaCl_2 \cdot 2H_2O$ in 100 mL deionized water was also slowly added to 0.06 mol sodium phosphate in 200 mL deionized water to formate a white precipitate of calcium pyrophosphate. Subsequently, the white precipitate was also washed three times using deionized water and dried at 120 ℃ in the air circulating oven for 24 hours. 3) Calcium composite catalysts ($Ca_3(PO_4)_2$-$Ca_2P_2O_7$): $Ca_3(PO_4)_2$-$Ca_2P_2O_7$ slurry was prepared by mixing calcium phosphate together with calcium pyrophosphate in aqueous solution for 2 hours under the continuous stirring at 20 ~ 25 ℃. The mixed slurry was filtered and dried at 80 ℃ in the air circulating oven for 24 hours and then the resulting white powder was pressed at 8.0 MPa to get tablets. The particles of $Ca_3(PO_4)_2$-$Ca_2P_2O_7$ with particle diameter 0.45 ~ 0.28 mm meshes were collected by sieving the crushed tablets. $Ca_3(PO_4)_2$-$Ca_2P_2O_7$ particles were calcined at desired temperatures (eg. 500 ℃) in air atmosphere for 6 hours to result in the composite catalysts.

1.3 Catalyst characterization

Powder X-ray diffraction measurement was conducted on aDmax/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 ~ 4 000 cm^{-1} on a Nicolet 6700 spectrometer. The particle size and the morphology of the catalysts were examined using a scanning electron microscope (SEM, JSM-6510). TG analysis was used with Netzsch STA449C analyzer.

1.4 Catalyst evaluation

The dehydration of lactic acid to acrylic acid over the catalysts was carried out in a fixed-bed quartz reactor with an 4 mm inner diameter operated at atmospheric pressure and the experimental setup is shown in Fig. 1. The catalyst (0.35 ~ 0.40 g, particle diameter 0.45 ~ 0.28 mm) was placed in the middle of the re-

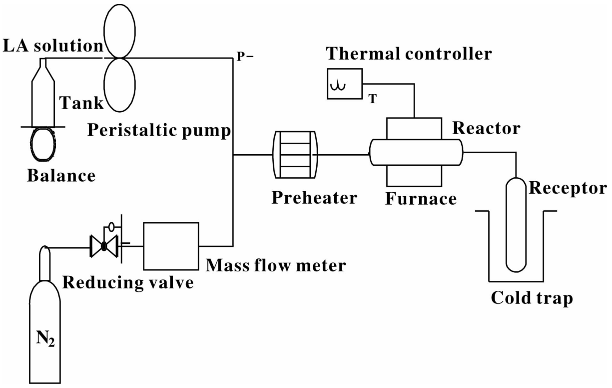


Fig. 1 Experimental set-up for evaluation of the dehydration reaction of lactic acid to acrylic acid

actor and quartz wool was placed in both ends. Before catalytic evaluation the catalyst was pretreated at the required reaction temperature (400 °C) for 0.5 h under high purity N_2 (0.1 MPa, 1.0 mL/min). The feedstock (20% 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 and analyzed off-line using an Agilent 7890A 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*-butyric acid as the internal standard material. GC-MS analyses of the samples were performed using Agilent 5973N Mass Selective Detector attachment. The conversion of lactic acid and the selectivity toward acrylic acid or acetaldehyde were calculated as follows:

$$Conversion/\% = \frac{n_0 - n_1}{n_0} \times 100,$$

$$Selectivity/\% = \frac{n_p}{n_0 - n_1} \times 100$$

Where n_0 is the molar quantity of lactic acid fed into reactor, n_1 is the molar quantity of lactic acid in the effluent, and n_p is the molar quantity of lactic acid converted to acrylic acid or acetaldehyde.

2 Results and discussion

2.1 Characterization

Calcium series catalysts were characterized by XRD, SEM, TG and FTIR. The wide-angle X-ray diffraction (XRD) patterns of the calcium series catalysts are shown in Fig. 2. The figure shows that catalysts have distinct diffraction patterns of $Ca_3(PO_4)_2$ phase and $Ca_2P_2O_7$ phase[16-17]. When the amount of $Ca_3(PO_4)_2$ increases in composite catalysts, the diffraction peak intensity of $Ca_3(PO_4)_2$ phase increased. This indicates that $Ca_3(PO_4)_2$ phase has not transformed to $Ca_2P_2O_7$ phase during high temperature calcination. Thus, $Ca_3(PO_4)_2$ phase and $Ca_2P_2O_7$ phase coexisted in particles of the composite catalysts. These results are further demonstrated by FTIR of calcium series catalysts in Fig. 5. Although $Ca_3(PO_4)_2$ phase and $Ca_2P_2O_7$ phase coexisted in the composite catalysts, appearances of the composite catalysts are greatly different from $Ca_3(PO_4)_2$, $Ca_2P_2O_7$, alone as catalyst in Fig. 3. Compared with that of $Ca_3(PO_4)_2$ or $Ca_2P_2O_7$, $Ca_3(PO_4)_2$-$Ca_2P_2O_7$ composite catalyst has a smaller particle size, and a narrow diameter distribution, leading to higher catalytic activities. TG graph is shown in Fig. 4. From Fig. 4, the mass loss of the composite catalysts is less than that of $Ca_3(PO_4)_2$ or $Ca_2P_2O_7$ during the temperature ranges of 0 ~ 700 ℃. This suggested that the composite catalyst has a high thermal stability and implied an excellent durability during catalytic reaction.

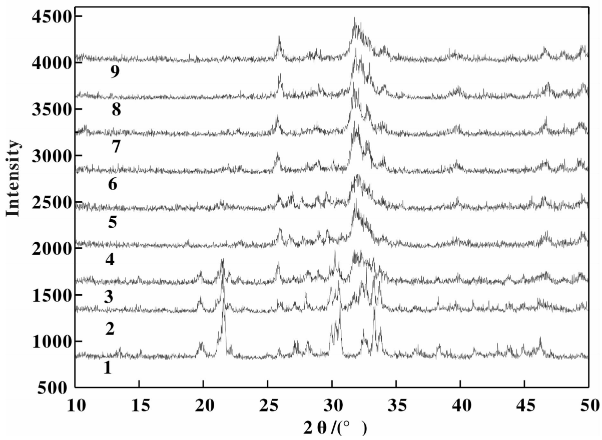


Fig. 2 XRD patterns of Ca series catalysts

1: $Ca_2P_2O_7$, 2: $m(Ca_2P_2O_7):m(Ca_3(PO_4)_2)=80:20$, 3: $m(Ca_2P_2O_7):m(Ca_3(PO_4)_2)=70:30$, 4: $m(Ca_2P_2O_7):m(Ca_3(PO_4)_2)=60:40$, 5: $m(Ca_2P_2O_7):m(Ca_3(PO_4)_2)=50:50$, 6: $m(Ca_2P_2O_7):m(Ca_3(PO_4)_2)=40:60$, 7: $m(Ca_2P_2O_7):m(Ca_3(PO_4)_2)=30:70$, 8: $m(Ca_2P_2O_7):m(Ca_3(PO_4)_2)=20:80$, 9: $Ca_3(PO_4)_2$

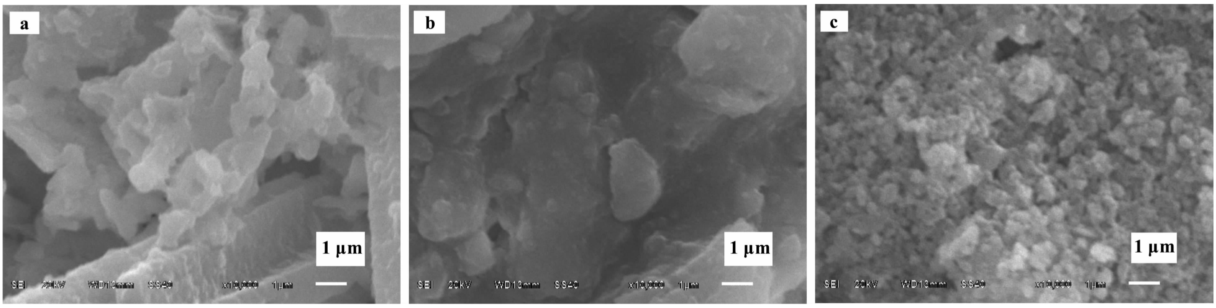


Fig. 3 SEM images of Ca series catalysts

a: $Ca_2P_2O_7$, b: $Ca_3(PO_4)_2$, c: $Ca_3(PO_4)_2$-$Ca_2P_2O_7$ composite catalyst (40% : 60%)

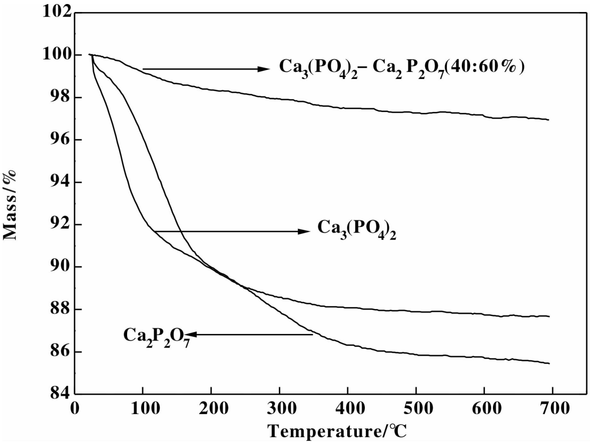


Fig. 4 TG curves of calcium series catalysts

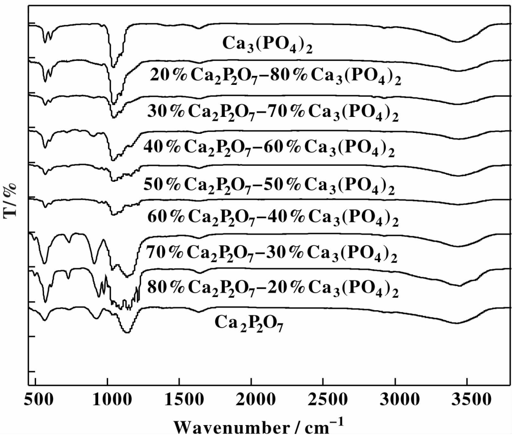


Fig. 5 FTIR spectra of calcium series catalysts

2.2 Catalytic activity

2.2.1 Effect of catalyst composition on reaction performance

Effect of catalyst composition on reaction performance is shown in Table 1. It is clearly seen that the performance of composite catalysts was drastically influenced by the composition in $Ca_3(PO_4)_2$-$Ca_2P_2O_7$ catalysts. Whether $Ca_3(PO_4)_2$ or $Ca_2P_2O_7$ was alone used as catalyst for dehydration of lactic acid to acrylic acid, the catalytic performances were lower than the composite catalysts. This indicated that a synergistic effect for improving the catalytic performance lies in composite catalysts consisted of $Ca_3(PO_4)_2$ and $Ca_2P_2O_7$. Similar results in the dehydration reaction of methyl lactate to acrylic acid were observed by Hong et al.[16]. Compared with that of methyl lactate, the conversion in dehydration of lactic acid to acrylic acid was slightly influenced by the composition of composite catalysts, and its maximal difference was only 4.1% (the highest conversion 96.1% and the lowest conversion 92.0%). However, the selectivity toward acrylic acid changed drastically in the range from 100 : 0 to 0 : 100 in $m(Ca_3(PO_4)_2)$: $m(Ca_2P_2O_7)$ and the trend is that the selectivity toward acrylic acid increased with an increase of $Ca_2P_2O_7$ in composite catalysts. Similarly, the main side reaction for the formation of acetaldehyde during the dehydration process of lactic acid was also affected by the catalyst compositions and the selectivity values for acetaldehyde changed from 9.0% to 18.8%. As investigated previously, the formation of both acrylic acid and acetaldehyde is relative to the acidity-basicity of the composite catalysts[1,6-10,16,18-21]. The basicity of composite catalysts increases with an increase of $Ca_2P_2O_7$ component from the CO_2-TPD studies reported in the reference[16]. Although the basicity of the composite catalysts is favored to the dehydration of lactic acid to acrylic acid because of the cooperation of the carboxylic group in lactic acid structure and basic sites in the catalysts, too strong basicity and basicity density for composite catalysts will not further improve the selectivity toward acrylic acid. To search for the reasons, we check the acidic strength of both lactic acid and acrylic acid, and the results were listed in Table 2. The pH value of lactic acid is 2.23, while the acrylic acid pH value is 2.52 at the same acid concentration of 0.5%. Evidently, the acidity of lactic acid is stronger than that of acrylic acid, but the difference pH value is small, only 0.29. Thus, compared with acrylic acid, lactic acid is easier to attain to the basic sites of catalyst surface within an appropriate basic range. If the basicity of the composite catalysts was enhanced too much, the interaction of both lactic acid and acrylic acid with basic sites of the catalysts was too strong, resulting in side reactions such as decarbonylation/decarboxylation of lactic acid to acetaldehyde, and hydrogenation of acrylic acid to propanoic acid. There fore, to obtain high selectivity of acrylic acid, the crucial step is that acidity-basicity of the composite catalysts was tuned to an appropriate pH ranges and the optimal composition of the catalysts should be in the ranges of 30 : 70 to 50 : 50 in the weight ratio of $Ca_3(PO_4)_2$/$Ca_2P_2O_7$.

Table 1 Effect of catalyst composition on reaction performance

Catalyst composition $m(Ca_3(PO_4)_2)$: $m(Ca_2P_2O_7)$	Conversion of lactic acid/%	Selectivity/%				
		Acrylic acid	Acetaldehyde	Propionic acid	2,3-Pentanedione	Acetic acid
100 : 0	92.2	25.9	9.0	5.1	4.5	1.5
80 : 20	92.0	35.4	12.2	7.3	4.1	1.3
70 : 30	93.5	49.3	16.0	9.3	3.7	1.2
60 : 40	92.1	50.7	18.8	9.7	3.6	1.4
50 : 50	93.3	54.5	15.4	9.1	4.9	1.1
40 : 60	96.1	58.1	16.4	9.5	5.3	1.2
30 : 70	95.2	54.0	13.9	8.9	4.8	1.1
20 : 80	94.7	51.5	14.5	7.9	4.3	1.3
0 : 100	92.5	49.6	15.4	8.3	4.9	1.2

Reaction conditions: Lactic acid, 20%, flow rate of lactic acid aqueous solution, 1.0 mL/h; hydroquinone, 0.3%; reaction temperature, 400 ℃; carrier gas N_2 1.0 mL/min; catalysts, 0.30 ~ 0.35 g; catalyst size, particle diameter 0.45 ~ 0.28 mm.

Table 2 Comparison of lactic acid with acrylic acid

Acids	Temperature/℃	Concentration of acid/%	pH values
Lactic acid	26	0.5	2.23
Acrylic acid	26	0.5	2.52

2.2.2 Effect of calcination temperature As well known to all, the heat treatment is one of the most important methods for improving catalytic performances of the solid catalysts[17,22]. In order to enhance the stability of the composite catalyst and further improve its catalytic activity, we calcinated the catalyst at 300 ℃, 500 ℃, 700 ℃ and 800 ℃, respectively. The effect of calcinations temperature for the catalysts on the dehydration of lactic acid was given in Fig. 6. Although the composite catalysts without calcination displayed an acceptable catalytic performance, to an extent, the calcinations may further improve its performances. When the calcination temperature further increased, the performance of the catalysts gradually fell low from 58.1% of acrylic acid selectivity at 500 ℃ to 45.4% of acrylic acid selectivity at 800 ℃. An appropriate calcination temperature was adopted to effectively improve the physical structures such as pore structure and specific surface area and excessively high temperatures may result in changing of the catalyst structure. The optimal calcination temperature is about 500 ℃.

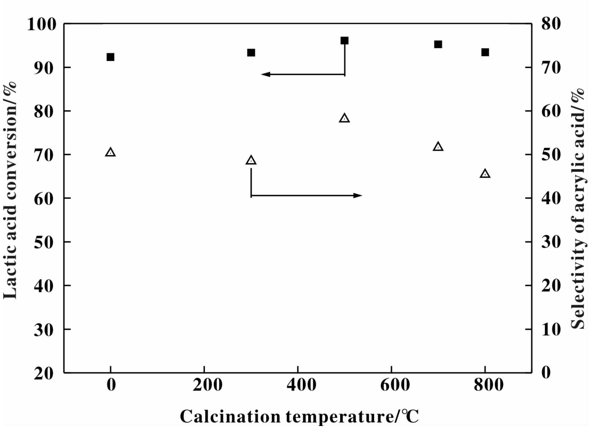


Fig. 6 Effect of calcination temperature

Reaction conditions: Lactic acid, 20%, flow rate of lactic acid aqueous solution, 1.0 mL/h; hydroquinone, 0.3%; reaction temperature, 400 ℃; carrier gas N_2 1.0 mL/min; composite catalyst, $m(Ca_3(PO_4)_2)$: $m(Ca_2P_2O_7)$ = 40 : 60; catalysts, 0.30 ~ 0.35 g, catalyst size, particle diameter 0.45 ~ 0.28 mm

2.2.3 Effect of reaction temperature To screen the optimal reaction temperature, the experiment for the dehydration of lactic acid to acrylic acid was carried out at the temperature ranges of 300 ~ 450 ℃, and the results were shown in Fig. 7. From Fig. 7, it is clearly seen that the conversion of lactic acid drastically increased with an increase of reaction temperature, while the selectivity toward acrylic acid gradually decreased. This indicated that temperature increase favored to conversion of lactic acid to acrylic acid, at the same time, and it also favored to decarbonylation/decarboxylation of lactic acid to acetaldehyde. But, excessively high temperature caused serious side reactions, resulting in decrease of acrylic acid selectivity. A case in point is that the acrylic acid selectivity is 58.1% at the reaction temperature of 400 ℃, while the selectivity of acrylic acid fell down to 45.4% at 450 ℃. Thus, considering the conversion of lactic acid and the selectivity toward acrylic acid, the optimal reaction temperature is 400 ℃.

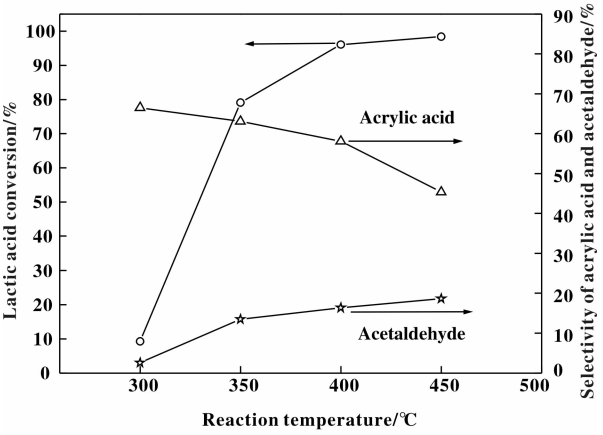
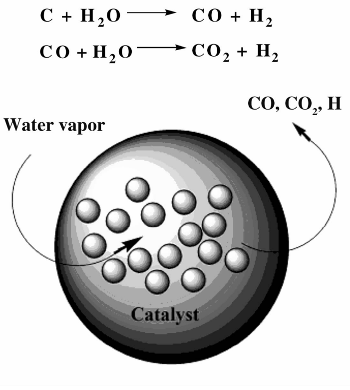


Fig. 7 Effect of reaction temperature

Reaction conditions: Lactic acid, 20%; flow rate of lactic acid aqueous solution, 1.0 mL/h; hydroquinone, 0.3%; carrier gas N_2 1.0 mL/min; composite catalyst, $m(Ca_3(PO_4)_2)$: $m(Ca_2P_2O_7)$= 40 : 60, catalysts, 0.30 ~ 0.35 g; catalyst size, particle diameter 0.45 ~ 0.28 mm

2.2.4 Effect of lactic acid concentration Like other gas-solid catalytic reaction such as dehydrogenation of ethylbenzene to styrene[23-24], water vapor plays a very important role in the reaction process. First of all, organic reaction on the surface of the catalyst easily causes carbon deposition covering the active sites under high reaction temperature, while water-gas reaction will occur under steam atmosphere to get rid of carbon; and the reactions were given in Scheme 1. Besides, water has a high heat capacity to maintain stable reaction temperature during the catalytic reaction, suppressing the side reactions caused by an excessive temperature. From Fig. 8, the selectivity toward acrylic acid decreased with an increase in lactic acid concentration although the conversion of lactic acid slightly increased. In order to avoid the formation of coke deposition which leads to deactivation of the catalysts, an appropriate concentration of lactic acid fed for gas-solid catalytic reaction in a fixed- bed reactor should be adopted.



$$C + H_2O \longrightarrow CO + H_2$$
$$CO + H_2O \longrightarrow CO_2 + H_2$$

Scheme 1 Water-gas reaction

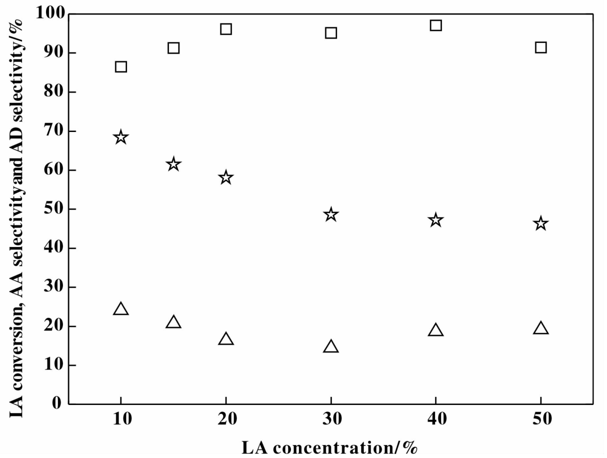


Fig. 8 Effect of LA concentration on the dehydration reaction of LA

□: Conversion of lactic acid (LA), ☆: Selectivity of acrylic acid (AA), △: Selectivity of acetaldehyde (AD)

Reaction conditions: Flow rate of lactic acid aqueous solution, 1.0 mL/h; hydroquinone, 0.3%; carrier gas N_2 1.0 mL/min; composite catalyst, $m(Ca_3(PO_4)_2):m(Ca_2P_2O_7) = 40:60$, 0.30 ~ 0.35 g; catalyst size, particle diameter 0.45 ~ 0.28 mm; reaction temperature, 400 ℃

2.2.5 Effect of liquid hourly space velocity (LHSV)

Effect of liquid hourly space velocity (LHSV) on the conversion of lactic acid as well as the selectivity toward acrylic acid was also investigated using $Ca_3(PO_4)_2$-$Ca_2P_2O_7$ composite catalyst while maintaining the reaction conditions as listed in Fig. 9 annotation by varying the lactic acid flow rates (LHSV) in the range from 1.16 ~ 8.37 h^{-1}. The results were presented in Fig. 9. With an increase in LHSV, the conversion of lactic acid rapidly decreased from 98.5% to 54.1%, while the selectivity toward acrylic acid changed a little, only between 54.1% and 60.3%.

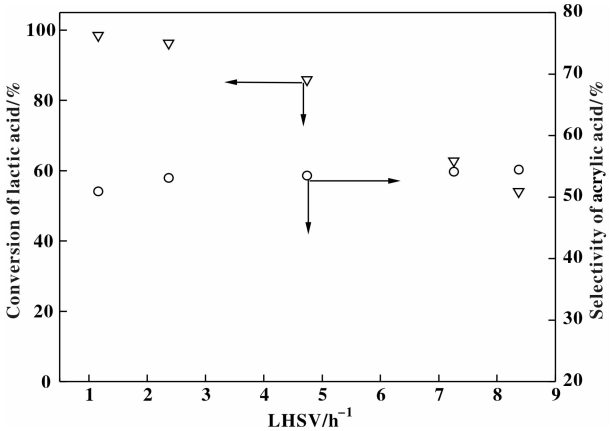


Fig. 9 Reaction performaces at various LHSVs

Reaction conditions: Lactic acid, 20%; hydroquinone, 0.3%; carrier gas N_2 1.0 mL/min; composite catalyst, $m(Ca_3(PO_4)_2):m(Ca_2P_2O_7) = 40:60$, 0.30 ~ 0.35 g; catalyst size, particle diameter 0.45 ~ 0.28 mm; reaction temperature, 400 ℃

2.3 Catalyst Stability

So far, catalyst stability in dehydration of lactic acid to acrylic acid has been studied by many investigators. Sun et al.[6,10,19] modified the NaY zeolites using potassium promoter to improve its catalytic performances and prolong its life. For example, after experienced 22 hours for reaction, acrylic acid selectivity over potassium modified NaY zeolites decreased from 60% to 36% while that over unmodified NaY zeolites reduced drastically, from 46% to 10%. The catalyst stability over $Ca_3(PO_4)_2$-$Ca_2P_2O_7$ composite catalyst was also evaluated, and the results was given in Fig. 10. During the catalytic reaction process of 56 hours, the conversion of lactic acid hardly decreased and maintained above 95%. In terms of lactic acid conversion, other catalytic systems can also maintain high values. However, it is difficult to retain high selectivity toward acrylic acid over Y zeolites after running long

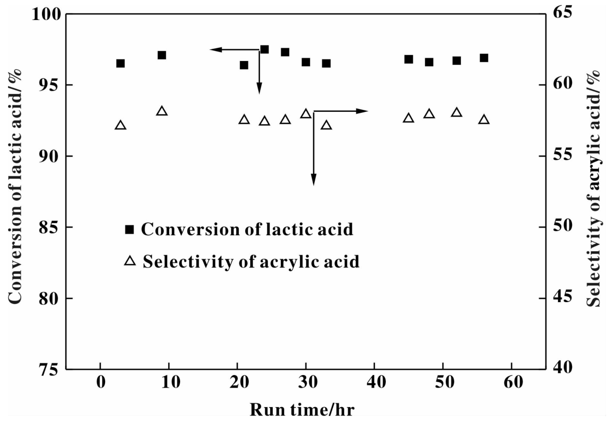


Fig. 10 Conversion of lactic acid and selectivity of acrylic acid with run time over $Ca_3(PO_4)_2$-$Ca_2P_2O_7$ composite catalyst

Reaction conditions: Lactic acid, 20%; flow rate of lactic acid aqueous solution, 1.0 mL/h; hydroquinone, 0.3%; carrier gas N_2 1.0 mL/min; composite catalyst, $m(Ca_3(PO_4)_2):m(Ca_2P_2O_7) = 40:60$, 0.30 ~ 0.35 g; catalyst size, particle diameter 0.45 ~ 0.28 mm; reaction temperature, 400 ℃

time[6-9,19]. Encouragingly, over $Ca_3(PO_4)_2$-$Ca_2P_2O_7$ composite catalyst, like conversion of lactic acid, the selectivity toward acrylic acid also changed little, always maintaining between 55% and 60%.

3 Conclusions

The dehydration of lactic acid to acrylic acid over the calcium composite catalysts was investigated under various reaction conditions. Catalyst compositions have an influence on the catalytic performances, and 96.1% of lactic acid conversion as well as 58.1% of acrylic acid selectivity has been achieved under the optimal catalyst composition of 40% $Ca_3(PO_4)_2$-60% $Ca_2P_2O_7$. The experiment of catalyst stability indicated that the composite catalysts displayed an excellent catalytic performance after running 56 hours.

References:

[1] Katryniok B, Paul S, Dumeignil F. Highly efficient catalyst for the decarbonylation of lactic acid to acetaldehyde [J]. *Green Chem*, 2010, **12**:1910-1913

[2] Katryniok B, Paul S, Capron M, Dumeignil F. Towards the sustainable production of acrolein by glycerol dehydration[J]. *Chemsuschem*, 2009, **2**:719-730

[3] Li Yu-jiao(李玉皎), Yu Dao-yong(于道永). Progress in acrylic acid production from lactic acid(乳酸生产丙烯酸研究进展)[J]. *Chem Ind & Eng Pro* (China) (化工进展), 2010, **29**(4): 683-689

[4] Wadley D C, Tam M S, Kokitkar P B, *et al*. Lactic acid conversion to 2,3-pentanedione and acrylic acid over silica-supported sodium nitrate: Reaction optimization and identification of sodium lactate as the active catalyst[J]. *J Catal*, 1997, **165**:162-171

[5] Sawicki R A. US[P]. 4729978, 1988

[6] Sun P, Yu D H, Tang Z C, *et al*. NaY zeolites catalyzed dehydration of lactic acid to acrylic acid: Studies on the effects of anions in potassium salts[J]. *Ind Eng Chem Res*, 2010, **49**:9082-9087

[7] Yu D, Sun P, Tang Z, *et al*. Modification of NaY by La^{3+} for the dehydration of lactic acid: The effect of preparation protocol on catalyst microstructure and catalytic performance[J]. *Can J Chem Eng*, 2011, **89**: 484-490

[8] Yan J, Yu D, Sun P, Huang H. Alkaline earth metal modified NaY for lactic acid dehydration to acrylic acid: Effect of basic sites on the catalytic performance[J]. *Chinese J Catal*, 2011, **32**:405-411

[9] Zhang J, Zhao Y, Pan M, *et al*. Efficient acrylic acid production through bio-lactic acid dehydration over NaY zeolite modified by alkali phosphates[J]. *ACS Catal*, 2010, **1**:32-41

[10] Sun P, Yu D H, Fu K M, *et al*. Potassium modified NaY: A selective and durable catalyst for dehydration of lactic acid to acrylic acid[J]. *Catal Commun*, 2009, **10**: 1345-1349

[11] Fan Y, Zhou C, Zhu X. Selective catalysis of lactic acid to produce commodity chemicals[J]. *Catal Rev-Sci Eng*, 2009, **51**:293-324

[12] Holmen R E. US[P]. 2859240, 1958

[13] Wells R P K, Tynjala P, Bailie J E, *et al*. Dehydration of butan-2-ol using modified zeolite crystals[J]. *Appl Catal A-Gen*, 1999, **182**:75-84

[14] Wang H J, Yu D H, Sun P, *et al*. Rare earth metal modified NaY: Structure and catalytic performance for lactic acid dehydration to acrylic acid [J]. *Catal Commun*, 2008, **9**:1799-1803

[15] Zhang Jing-zhou(张京周). Beijing: Master dissertion of Beijing University of Chemical Technology(北京:北京化工大学硕士学位论文)[D]. 2010

[16] Hong J H, Lee J-M, Kim H, *et al*. Efficient and selective conversion of methyl lactate to acrylic acid using $Ca_3(PO_4)_2$ - $Ca_2(P_2O_7)$ composite catalysts[J]. *Appl Catal A-Gen*, 2011, **396**:194-200

[17] Zhang Z Q, Qu Y X, Wang S, Wang J D. Catalytic performance and characterization of silica supported sodium phosphates for the dehydration of methyl lactate to methyl acrylate and acrylic acid[J]. *Ind Eng Chem Res*, 2009, **48**:9083-9089

[18] Zhang Z Q, Qu Y X, Wang S I, Wang J D. Theoretical study on the mechanisms of the conversion of methyl lactate over sodium polyphosphate catalyst[J]. *J Mol Catal A-Chem*, 2010, **323**:91-100

[19] Yan J, Yu D, Li H, *et al*. NaY zeolites modified by La^{3+} and Ba^{2+}: The effect of synthesis details on surface structure and catalytic performance for lactic acid to acrylic acid[J]. *J Rare Earths*, 2010, **28**:803-806

[20] Lee J M, Hwang D W, Hwang Y K, *et al*. Efficient dehydration of methyl lactate to acrylic acid using $Ca_3(PO_4)_2$-SiO_2 catalyst[J]. *Catal Commun*, 2010, **11**: 1176-1180

[21] Serrano-Ruiz J C, Dumesic J A. Catalytic upgrading of lactic acid to fuels and chemicals by dehydration/hydrogenation and C-C coupling reactions[J]. *Green Chem*,

2009, **11**:1101-1104

[22] Holm M S, Saravanamurugan S, Taarning E. Conversion of sugars to lactic acid derivatives using heterogeneous zeotype catalysts[J]. *Science*, 2010, **328**:602-605

[23] Jiang Z D, Wang J Q. Dehydrogenation of ethylbenzene to styrene in an inorganic membrane reactor[J]. *Sep Sci Technol*, 1998, **33**:1379-1385

[24] Yang W S, Wu J C, Lin L W. Application of membrane reactor for dehydrogenation of ethylbenzene[J]. *Catal Today*, 1995, **25**:315-319

焦磷酸盐-磷酸盐复合催化剂高效催化乳酸脱水制丙烯酸

范国策，唐聪明，李新利

（西华师范大学 化学合成与污染控制四川省重点实验室，四川 南充 637009）

摘 要：利用沉淀法制得焦磷酸盐与磷酸盐在浆状态下复配制备成复合催化剂，并用于催化乳酸脱水制丙烯酸. 实验发现催化剂的组成对乳酸的转化率及丙烯酸的选择性有着重要的影响，当磷酸盐/焦磷酸盐质量比在30∶70~50∶50范围内，可以获得较高的乳酸的转化率和丙烯酸的选择性. 催化反应条件如反应温度，乳酸进料浓度，液空速也被详细地进行了考察. 此外，考察了该复合催化剂的稳定性. 当催化剂连续运行56 h后，乳酸的转化率保持在96%以上，丙烯酸的选择性也高达57%. 为了进一步揭示催化剂的结构与催化性能之间的关系，利用X射线粉末衍射、热重、扫描电镜和傅立叶红外等对催化剂进行了表征.

关键词：脱水；磷酸钙；焦磷酸钙；乳酸；丙烯酸
