## Preparation of Ammonium Cerium Phosphate via Low-heating Solid State Reaction and Its Catalysis for Benzyl Acetate Synthesis

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Ammonium cerium phosphate was prepared with  $(NH_4)_3PO_4 \cdot 3H_2O$  and  $Ce(SO_4)_2 \cdot 4H_2O$  as raw materials and PEG-400 as surfactant via a solid state reaction at low-heating temperature. The characterization result of XRD indicates that the molecular formula of the product was  $(NH_4)_2Ce(PO_4)_2 \cdot H_2O$ . The synthesis of benzyl acetate was carried out with  $H_2SO_4$ /ammonium cerium phosphate as catalyst, and uniform experimental design as well as data mining technology was applied to the experiments, in which the effect of the reaction time, the molar ratio of acid to alcohol and the amount of catalyst on the conversion yield of acetic acid were studied. When benzalcohol was 0.10 mol, under the optimal reaction conditions, *i.e.* reaction time of 174 min, 2.02 of molar ratio of acid to alcohol and 0.5 g of catalyst, the esterification rate of acetic acid was 97.9%. The ammonium cerium phosphate had potential for industry application since it not only was feasible and simple in synthesis technics, but also had good catalysis activity for the synthesis of benzyl acetate.

Keywords supported catalyst, ammonium cerium phosphate, benzyl acetate, solid-state reaction, data mining technology

## Introduction

In recent decade, the use of natural phosphate (NP) in the organic transformation has been under attention<sup>10-5</sup> because this solid is cheap, readily available, stable, non-toxic, not a pollutant and recoverable and reusable. Recently. Sebti and his co-workers<sup>6-11</sup> reported that the basic and acidic activities of NP could be improved when it was doped with zinc chloride (ZnCl<sub>2</sub>/NP) or potassium fluoride (KF/NP). It has been reported that ZnCl<sub>2</sub>/NP was used as excellent acidic catalyst for transesterification reaction, Friedel-Crafts alkylation, 1,3-dipolar cycloaddition, acyclonucleoside synthesis and 3,4-dihydropyrimidin-2(1H)-one synthesis. KF/NP catalyzed efficiently transesterification reaction, nitrile hydration, Michael addition, Knoevenagel condensation, flavanone synthesis, nucleobase alkylation, nucleoside synthesis and transesterification reaction. Na/NP, as strong basic catalyst, could promote Knoevenagel condensation, alkene epoxidation, Claisen-Schmidt condensation and Michael addition.

The main component of NP is calcium phosphate. The properties of the rare earth ions are similar with those of calcium ion, suggesting that rare earth phosphates have the similar catalyst activity as NP.

Recently, various catalysts have been reported to

prepare benzyl acetate.<sup>12-14</sup> In continuation of our ongoing program to synthesize functional inorganic materials via solid-state reaction at low-heating temperature,<sup>15-20</sup> we describe in this paper, the synthesis of the ammonium cerium phosphate via solid-state reaction at low-heating temperature and its catalysis for synthesis of benzyl acetate.

## **Experimental**

#### **Reagent and apparatus**

All chemicals were of reagent-grade purity. X-ray powder diffraction (XRD) was performed at a scanning ratio of 0.02 (°)•s<sup>-1</sup> from 5° to 65° for  $2\theta$  using a Rigaku D/max 2500 V diffractometer equipped with a graphite monochromator and a Cu target. Fourier transform infrared (FTIR) spectroscopy was performed on an Ahimadzu IR450 spectrometer in the wavelength range of 400 - 4000 cm<sup>-1</sup> on KBr pellets.

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 $(NH_4)_3PO_4 \bullet 3H_2O$  (40.0 mmol, 8.1256 g) and  $Ce(SO_4)_2 \bullet 4H_2O$  (20.0 mmol, 8.0862 g) according to 2.0 of P/Ce molar ratio were mixed with 0.5 mL of

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PEG-400 in a mortar, and ground for 30 min. The reaction mixture was sealed and kept at 80 °C for 2 h, washed with water to remove soluble inorganic salts until  $SO_4^{2-}$  ions could not be detected by a 0.5 mol•  $L^{-1}$  BaCl<sub>2</sub> solution, then washed with a small amount of anhydrous ethanol and dried at 80 °C for 4 h. The resulting material was subsequently determined to be the crystal phase of  $(NH_4)_2Ce(PO_4)_2$ •H<sub>2</sub>O. All diffraction peaks of the product in Figure 1 could be indexed to be in agreement with the orthorhombic system structure of  $(NH_4)_2Ce(PO_4)_2$ •H<sub>2</sub>O from PDF card 52-0336.



Figure 1 XRD patterns of the product.

#### Preparation of H<sub>2</sub>SO<sub>4</sub>/(NH<sub>4</sub>)<sub>2</sub>Ce(PO<sub>4</sub>)<sub>2</sub>•H<sub>2</sub>O

50 mL of 1.5 mol/L  $H_2SO_4$  and 10 g of  $(NH_4)_2Ce(PO_4)_2 \cdot H_2O$  were mixed in a 100 mL beaker and kept at room temperature for 24 h, then vacuum filtrated and dried for 2 h at 100 °C to obtain  $H_2SO_4/(NH_4)_2Ce(PO_4)_2 \cdot H_2O$ .

# Experiment design of catalysis of esterification reaction

The results of preparative experiments showed that  $H_2SO_4/(NH_4)_2Ce(PO_4)_2 \cdot H_2O$  had catalysis activity for esterification, but the catalysis activity disappeared without loading  $H_2SO_4$ . So, all catalysis experiments of esterification were carried out with  $H_2SO_4/(NH_4)_2Ce-(PO_4)_2 \cdot H_2O$  as catalyzer. The amount of benzalcohol was 0.10 mol (10.50 mL) for every reaction. The factors and their levels of the experiments are shown in Table 1. The uniform design project<sup>21</sup> of the experiments is shown in Table 2, in which the conversion yield of esterification (*Y*) was used as the response value.

#### General procedure for the esterification reaction

The experiments were carried according to direction of the uniform design project in Table 2. A mixture of glacial acetic acid, benzalcohol, and  $H_2SO_4/(NH_4)_2$ -Ce(PO<sub>4</sub>)<sub>2</sub>•H<sub>2</sub>O was refluxed while being stirred. Reaction temperature of the liquid pot was kept at 120 °C. After the reaction ending, the mixture was filtered, and the residual acetic acid was neutralized with standardized NaOH solution, using phenolphthalein as an indi-

	Table 1	Factors and levels <sup><i>a</i></sup>		
	t/min	n	w/g	
1	30	0.4	0.50	
2	50	0.6	0.75	
3	70	0.8	1.00	
4	90	1.0	1.25	
5	110	1.2	1.50	
6	130	1.4	1.75	
7	150	1.6	2.00	
8	170	1.8	2.25	
9	190	2.0	2.50	
10	210	2.2	2.75	

<sup>*a*</sup> t (reaction time): 30–210 min, n (acid/alcohol molar ratio): 0.4–2.2, w (the amount of catalyzer): 0.5–2.75 g.

Table 2	Experimental	project of u	niform design	and results <sup><i>a</i></sup>

	<i>t</i> /min	n	w/g	<i>Y</i> /%
1	30	1.2	2.00	81.19
2	50	2.2	1.00	85.86
3	70	1.0	2.75	70.51
4	90	2.0	1.75	83.13
5	110	0.8	0.75	72.42
6	130	1.8	2.50	85.66
7	150	0.6	1.50	84.85
8	170	1.6	0.5	88.99
9	190	0.4	2.25	81.72
10	210	1.4	1.25	90.91
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<sup>*a*</sup> t (reaction time): 30–210 min, n (acid/alcohol molar ratio): 0.4–2.2, w (the amount of catalyzer): 0.5–2.75 g.

cator. The percentage of esterification of benzalcohol was calculated according to the amount of acetic acid remaining. Every experiment was repeated three times to get average result. The mixture was subsequently washed with water, dilute solution of sodium carbonate and water, then dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The products were obtained by distilling the dried mixture with a bit of boric acid, in which boric acid made benzalcohol transformed into high boiling point benzyl borate. The product was analyzed by GC-MS.

### **Results and discussion**

#### Modeling with stepwise regression analyses

The equation relating the coefficients obtained from stepwise regression analyses<sup>21</sup> with the data of Table 2 is as follows [Eq. (1)]:

$$Y = 86.6578 + 0.05217(t - 120) - 3.8454(n - 1.3)^{2} - 6.2836(w - 1.625)^{2} - 4.5471(n - 1.3)(w - 1.625) + 16.5791(n - 1.3)(w - 1.625)^{2}$$
(1)

F=245.11, R=0.9984, S=0.5616. The values of  $F_i$  are  $F_1=284.75, F_2=27.47, F_3=208.41, F_4=60.00$  and  $F_5=722.72$  (*F* is equation *F*-statistic;  $F_i$  are equation

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*F*-statistic variable items; *R* is the correlation coefficient of equation; *S* is the standard deviation of residuals of equation). The results of the *F* significance test showed that the coefficients of the equation and the equation all passed the *F* significance test at confidence level of  $\alpha$ = 0.01.

#### Static data mining

The optimal reaction conditions got from optimization of the Eq. (1) with a grid method<sup>21</sup> are as follows: t=174 min, n=2.02, w=0.5 g and Y=98.32%.

### Dynamic data mining

The Eq. (1) could be conversed as following three equations that expressed the relation between single factor and the response, in which the optimal reaction conditions obtained from the static data mining were used as benchmark:

$$Y = 95.5025 + 0.05217(t - 120) \tag{2}$$

$$Y = 81.5222 + 26.0984(n-1.3) - 3.8454(n-1.3)^{2} \quad (3)$$

$$Y = 87.4813 - 3.2739(w - 1.625) + 5.6534(w - 1.625)^2$$
(4)

The Eqs. (2)—(4) were used to draw figures of X-Y and Figures 2-4 were obtained according to direction of the method in the Ref. 21. Figure 2 shows that the effect of reaction time on the conversion yield of esterification is a line, while the value of the conversion yield of esterification increases with reaction time. The esterification is a reversible reaction, so the reaction is carried out forward to increase the conversion yield of esterification with the increasing reaction time, when the water formed from the reaction is continuously removed by manifold. Figure 3 shows that the effect of n(acid/alcohol molar ratio) on Y is the left of a parabola with opening downwards, while the Y value increases with increasing the acid/alcohol molar ratio. The result of the Figure 3 agrees with the principles of chemical equilibrium that the reaction will be carried out forward with increasing the concentration of the reactant. Figure 4 shows that the effect of w (The amount of catalyzer) on Y is a parabola opening upwards without a part of the right, while the Y value decreases with increasing the amount of catalyzer. The result of the Figure 4 implys that the by-reaction increases with increasing the amount of catalyzer. The etherification does not consume acetic acid, so it is possible that the by-reaction is the etherification.

# Verification experiment with the optimal reaction conditions

Three parallel verification experiments were carried with the optimal reaction conditions: t=174 min, n=2.02, w=0.5 g, and the obtained average value Y=97.9% was very close to the optimal value 98.32%.



**Figure 2** Effect of reaction time *t* on the conversion yield of esterification.



**Figure 3** Effect of acid/alcohol molar ratio (*n*) on the conversion yield of esterification



**Figure 4** Effect of dosage of catalyzer (*w*) on the conversion yield of esterification.

#### Characterization of the esterification product

The infrared spectrum of the esterification product is shown in Figure 5. The band observed at  $3066 \text{ cm}^{-1}$  was attributed to ArH stretching. The strong absorption peaks observed at 1747 and 1233 cm<sup>-1</sup> indicate that



Figure 5 IR spectrum of the esterification product.

there is an acyl group in the product molecule. The absorption bands observed at 1505, 1457, 1382 and 1347.55 cm<sup>-1</sup> were all assigned to the various vibration modes of phenyl group.

The total ion chromatogram of the product is shown in Figure 6. It can be seen from the Figure 6 that the component content of peaks Nos. 2 and 5 is 99.67% in total content, while the component content of peak No. 2 is 98.92% and is the main product. Mass spectra of peaks Nos. 2 and 5 are shown in Figures 7 and 8, respectively, which can be attributed to be in agreement with benzyl acetate at matching rate 94% and methoxybenzene at 90%, respectively. So, it is obvious that there is very little other impurity in the product from Figure 6.



Figure 6 Total ion chromatogram of the ester product.



Figure 7 Mass spectrum of peak No. 2.



Figure 8 Mass spectrum of peak No. 5.

## Conclusion

We have successfully prepared the ammonium cerium phosphate via solid-state reaction at low-heating temperature and tested its catalysis for synthesis of benzyl acetate.

(1) When  $(NH_4)_3PO_4 \cdot 3H_2O$  and  $Ce(SO_4)_2 \cdot 4H_2O$  were used as starting materials, crystal phase of  $(NH_4)_2Ce(PO_4)_2 \cdot H_2O$  was obtained via a solid-state reaction at low-heating temperature.

(2) The  $(NH_4)_2Ce(PO_4)_2 \cdot H_2O$  had no catalysis activity toward esterification in the synthesis of benzyl acetate.

(3) The  $H_2SO_4/(NH_4)_2Ce(PO_4)_2 \cdot H_2O$  was proved to behave as an excellent heterogeneous catalyst in the synthesis of benzyl acetate.

When benzalcohol was 0.10 mol, under the optimal reaction conditions, *i.e.* reaction time of 174 min, 2.02 of molar ratio of acid to alcohol and 0.5 g of catalyst, the esterification rate of acetic acid was 97.9%. The ammonium cerium phosphate had potential for industrial application since it was not only feasible and simple in synthesis technics, but also had good catalysis activity for the synthesis of benzyl acetate.

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