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Optimization of process variables in the synthesis of butyl butyrate using amino acid-functionalized heteropolyacids as catalysts

Abstract: Response surface methodology was successfully applied to optimize esterification of butanol with butyric acids over amino acid-functionalized heteropolyacids, namely, $[GlyH]_xH_{3-x}PW_{12}O_{40}$ (x=1.0–3.0). A series of catalysts were prepared by incorporating tungstophosphoric acid (TPA) with varied amounts of glycine (Gly). The $[GlyH]_{1.0}H_{2.0}PW_{12}O_{40}$ catalyst was found to exhibit the best activity with an optimal butyl butyrate yield of 97.9%, which was in excellent agreement with the predicted value by the Box-Behnken design (BBD) model. These superior esterification activities observed for the organic TPA salt catalysts might be due to their highly acidic nature, weak molecular transport resistance, and "pseudoliquid" catalysis modes. Furthermore, the catalytic activity of $[GlyH]_{1.0}H_{2.0}PW_{12}O_{40}$ catalyst was observed to have no appreciable change in the conversion after five consecutive runs. A kinetic study for the esterification was also performed under optimal reaction conditions. The results revealed that the reaction followed second-order kinetics, and the activation energy was found to be 81.90 kJ/mol.

Keywords: esterification; heteropolyacid; kinetic model; optimization; reaction engineering.

1 Introduction

Esters of short-chain fatty acids and alcohols such as butyl butyrate are important components of natural aromas and have been widely used as flavor components in the food, cosmetics, and pharmaceutical industries [1]. Conventionally, esters are produced in the presence of homogeneous acid catalysts, such as H_2SO_4, HCl, H_3PO_4, and organic sulfuric acids [2]. However, these homogeneous catalysts are associated with inherent disadvantages, such as difficulties in neutralization and separation, militating against their continuous application. Thus, in the context of environmental and sustainable considerations, efforts have been made on the development of heterogeneous catalyst systems for esterification, including molecular sieves [3, 4], solid super acids [5–7], heteropolyacids [8–11], and so on.

Heteropolyacids (HPAs) have displayed outstanding catalyst performance in a wide range of acid-catalyzed reactions owing to their ultra-strong Brønsted acidity and unique pseudo-liquid properties [12–15]. However, bulk HPAs have limited further applications owing to small specific surface area, inferior solubility in polar solvents, and poor product purification and disposal and/or recycling of spent catalyst. To solve these problems, HPAs are often immobilized on supports, such as SiO_2 [16], ZrO_2 [17], and zeolites [18], to increase equable active centers distribution. Recently, there has been an increasing research interest in novel organic-inorganic hybrid design of HPAs-base catalysts. Herein, we report the synthesis of a series of organic-inorganic composite catalysts with amino acid and HPA as precursors for the esterification of butyric acid with butanol. Moreover, relevant optimizations of reaction variables and product yield were investigated by a factorial experimental design and response surface methodology (RSM) [19–22]. A kinetic model for the esterification process was also established and evaluated under optimal reaction conditions.

2 Materials and methods

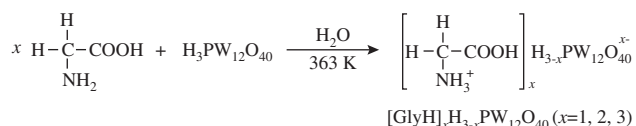### 2.1 Catalyst preparation and characterization

All the chemicals were analytical reagent and were used without further purification unless specified otherwise. The organic-inorganic composite catalysts were prepared and characterized by FT-IR (Bruker IFS-28, Germany), TGA (TGA/DSC-1, METTLER, Germany), XRD, ^{1}H and ^{13}C NMR (Bruker AV500, Germany), and acidity determination in the laboratory following the procedure outlined in literature [23, 24]. A stoichiometric amount of $H_3PW_{12}O_{40}$ (Kuishan

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Xingbang Technology Co., Ltd., Jiangsu, China) and glycine (Gly, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) were placed in a three-necked flask together with some water under continuous stirring at 363 K for 24 h. The final product was obtained after removing the water. Then solid product was washed with diethyl ether and dried under vacuum (Shanghai Boxun Industrial Co., Ltd., China). A series of Gly-TPA (tungstophosphoric acid) catalysts were obtained and named as $[GlyH]_x H_{3-x} PW_{12}O_{40}$ in which x means the molar ratio of Gly/TPA changing from 1.0 to 3.0. All research grade chemicals were used without further purification unless specified otherwise. The formation of $[GlyH]_x H_{3-x} PW_{12}O_{40}$ undergoes reactions based on the following equations:

$$x\ \underset{NH_2}{\overset{H}{H-C-COOH}} + H_3PW_{12}O_{40} \xrightarrow[363\ K]{H_2O} \left[\underset{NH_3^+}{\overset{H}{H-C-COOH}} \right]_x H_{3-x}PW_{12}O_{40}^{x-}$$

$$[GlyH]_x H_{3-x} PW_{12}O_{40}\ (x=1,2,3)$$

2.2 Catalytic reaction

The esterification process was carried out in a 100 ml three-necked flask attached with a thermometer, a magnetic stirrer, and a reflux condenser. In a typical reaction, butyric acid (8.81 g, 0.1 mol), butanol (typically 8.15–13.34 g), water-carrying agent (toluene, 10 ml), and the $[GlyH]_x H_{3-x} PW_{12}O_{40}$ (x=1.0–3.0; typically 0.264–0.617 g) were charged into the flask. These correspond to variations of alcohol/acid molar ratios in the range of 1.1:1–1.8:1, with 3–7 wt% of Gly-TPA catalyst weight relative to acid. The reaction mixture was heated to reflux for a desired time in an oil bath. After reaction reaching the designated time, the flask was removed from the oil bath and the mixture was cooled to room temperature. Owing to the "self-separation" characteristic of the reaction system, the catalysts would easily be separated from the mixture and washed by diethyl ether for reuse. The reaction products were analyzed by gas chromatography (Agilent 6890N GC) with a flame ionization detector (FID) using a HP-5 capillary column. Reactants and products were identified by comparison with authentic samples. Methyl laurate was used as an internal standard. The conversion of butyric acid was quantified according to the following equations:

$$Conversion = (1 - a_1/a_2) \times 1\%$$

where a_1 was the initial acidity of the mixture and a_2 was the acidity of the mixture at the end of experiment. The acidity was determined by titration with sodium hydroxide.

2.3 Experimental design and mathematical model

RSM was employed to optimize the reaction process and product yield during esterification of butyric acid with butanol over a standard $[GlyH]_{1.0} H_{2.0} PW_{12}O_{40}$ catalyst at a fixed reaction temperature based on the Box-Behnken design (BBD) [19–22]. The design of experiments includes three experimental variables specified in Table 1, namely, duration of reaction time (x_1), alcohol/acid molar ratio (x_2), and catalyst amount (x_3). Accordingly, a 3^3 full-factorial central composite design with coded levels (see Table 1) was used, leading to a total of 17 experimental sets, which include 12 factorial points and 5 centering points. The three experimental variables (x_1, x_2, and x_3)

Table 1: List of experimental variables and coded values and levels adopted in this study.[a]

Variable (unit)	Symbol	Range and level		
		-1	0	1
Reaction time (h)	x_1	1.5	2	2.5
Alcohol/acid molar ratio	x_2	1.2	1.4	1.6
Catalyst amount (wt%)	x_3	4	5	6

[a]Over the $[GlyH]_{1.0} H_{2.0} PW_{12}O_{40}$ catalyst at 393 K.

were tested at levels coded with either a minus sign (-1; lower values), zero (0; central values), or a plus sign (+1; higher values).

The Design-Expert 6.0.5 (Stat-Ease, USA) software was used for the design of experiments and analysis of experimental data. The coded values of these factors were obtained by the following equation:

$$x_i = \frac{X_i - X_0}{\Delta X_i} \tag{1}$$

where x_i, X_i, and X_0 (i=1–3) represent coded, real, and central values of the independent variable, respectively, and ΔX_i=(variable at high level-variable at low level)/2 denotes the step-change value. A model equation based on a second-order polynomial given by RSM was used to reveal responses of the experimental design:

$$Y = \beta_0 + \sum_{i=1}^{3} \beta_i x_i + \sum_{i=1}^{3} \beta_{ii} x_i^2 + \sum_{i<j}^{3} \beta_{ij} x_i x_j \tag{2}$$

where Y is the predicted response (i.e. product yield), x_i and x_j are the coded levels of the independent variables, and β_0, β_i, β_{ii}, and β_{ij} denote the regression coefficients representing the offset, linear, quadratic, and interaction terms, respectively; k is the total number of designed variables. The fitted polynomial equation may further be expressed in terms of response surface and contour plots to facilitate visualization of the correlations between the response and experimental variables at various coded levels and to infer optimized process conditions. Moreover, coefficient of determination (R^2) may be used to evaluate the accuracy and applicability of the second-order multiple regression model, whereas the significance of its regression coefficient may be checked by the F-test value.

2.4 Kinetic studies

Kinetic studies during esterification of butyric acid with butanol over the $[GlyH]_{1.0} H_{2.0} PW_{12}O_{40}$ catalyst were carried out using a set of variables obtained from the multi-objective optimization, namely, alcohol/acid=1.4:1, catalyst amount 5 wt%, reaction time 30–150 min, under various reaction temperatures (363, 373, 383, and 393 K). The conversions were recorded every 30 min, and the reaction rate (r) for esterification of butyric acid to butyl butyrate may be expressed as

$$r = -\frac{dC_A}{dt} = k_+ C_A^{\alpha} C_B^{\beta} - k_- C_C^{\gamma} C_D^{\eta} \tag{3}$$

where C_A, C_B, C_C, and C_D represent concentrations of butyric acid, butanol, butyl butyrate, and water, respectively, while α, β, γ, and η denote their corresponding reaction orders and k_+ and k_- are rate constants associated with the forward and reverse reactions, respectively.

Since a water-carrying agent effectively removed the water generated during the reaction to sustain a high conversion, the reaction may be considered as a consecutive irreversible process. In this context, the second terms in Eq. (3) can be obsoleted. As a result, the rate equation may be simplified as

$$r = -\frac{dC_A}{dt} = kC_A{}^{\alpha}C_B{}^{\beta} \tag{4}$$

In order to make the calculation simple, α and β were hypothesized as 1. Accordingly, values of k for the esterification reaction at different temperatures may be obtained by the linear fitting of the $\ln(C_A/C_B)$ versus t curve defined as

$$\ln\frac{C_A}{C_B} = (C_{AO} - C_{BO})kt + C \tag{5}$$

where C_{AO} and C_{BO} refer to the difference between the initial concentration of butyric acid and butanol, whereas the variations of reaction rate with temperature may be expressed by the Arrhenius equation:

$$\ln k = \ln k_0 - \frac{E_a}{R}\frac{1}{T} \tag{6}$$

where R presents the gas constant and T is the reaction temperature. The activation energy (E_a) and pre-exponential factor (k_0) may be derived from Eq. (6).

3 Results and discussion

3.1 Comparison of activity of organic TPA salt catalysts

Catalytic esterification reactions are influenced by many factors. One of the most important considerations is the acidity of catalysts. TPAs with different composition ratios of Gly have shown different acidity [24]. The acidity of $[GlyH]_xH_{3-x}PW_{12}O_{40}$ catalysts was found to follow the following trend: pristine TPA $(H_3PW_{12}O_{40})>[GlyH]_{1.0}H_{2.0}$ $PW_{12}O_{40}>[GlyH]_{2.0}H_{1.0}PW_{12}O_{40}>[GlyH]_{3.0}PW_{12}O_{40}>Gly$. Owing to their strong acidity characteristics, these organic TPA salt catalysts yield anticipated high activities on the esterification of butyric acid with butanol in the following order (Table 2): $[GlyH]H_{2.0}PW_{12}O_{40}>[GlyH]_{2.0}H_{1.0}PW_{12}$ $O_{40}>H_3PW_{12}O_{40}>[GlyH]_{3.0}PW_{12}O_{40}>Gly$. Strong or weak acidity is not conducive to the esterification. $[GlyH]H_{2.0}PW_{12}O_{40}$ catalyst exhibited the best catalytic activity with 97.7% ester yield. The parent Gly possesses only weak Brønsted acidity and showed inferior activity for catalyzing esterification reaction. It tends to form GlyH$^+$ complexes with Brønsted acidic protons in the presence of TPA, leading to a Gly-TPA composite catalyst with strong acidity and showing high catalytic activity on the esterification. Though the presence of Gly tended to eliminate the availability of protic

sites from TPA, it also served as a spacer to promote segregation of PW polyanions, which was in favor of mass transport during esterification [25, 26]. However, a further increase in Gly/TPA ratio not only resulted in a notable decrease in overall acid concentrations but also lowered the diffusivity of molecules, as reflected by the progressive decrease in catalytic activity. Though organic cations work as active centers for esterification, Keggin heteropolyanions are still considered to be very significant. The presence of hierarchical structures of HPA catalysts could lead to surface-type and pseudoliquid (bulk-type (I) and bulk-type (II)) catalysis modes and achieved high activities of the esterification [27, 28].

3.2 Optimization of reaction conditions

Detailed investigations to optimize various reaction parameters were conducted using $[GlyH]H_{2.0}PW_{12}O_{40}$ as catalyst in view of its high product selectivity as well as its low cost and toxicity. The influence of reaction time, molar ratio of the reactants, and catalyst amounts were investigated, and results are listed in Table 2.

The butyric acid conversion reached 94.4% within just 1 h and completed conversion after 2 h. As reaction time prolonged, the yield decreased slightly. This observation implies that esterification reaction is an equilibrium reaction and ester products can react with water formed during the reaction to reduce slightly the yield of product after 2 h. Study on effect of different molar ratios of butyric acid to butanol showed that the yield was enhanced with increasing amount of butanol, reaching 97.7% at alcohol/acid molar ratio of 1.4:1. However, a further increase of the amount of butanol caused a decrease in butyl butyrate yield because of the diluted $[GlyH]H_{2.0}PW_{12}O_{40}$ catalyst. It is obvious that the catalyst amount has a significant effect on the esterification of butyric acid with butanol. The reaction yield increased with an increasing amount of catalyst and reached the highest level with 5 wt% of catalyst. Further increase of the amount of catalyst led to no increase but decrease in yield. It may be due to the fact that the excessive catalyst in the reactor shortens reaction time to reach reaction equilibrium, allowing more time for other side reactions.

3.3 RSM experiments and study

The factorial experimental design and RSM were used to evaluate the interactive effects between process variables and optimize the reaction process and butyl butyrate yield

Table 2: Yield of butyl butyrate by esterification of butyric acid with butanol over $[GlyH]_{1.0}H_{2.0}PW_{12}O_{40}$ under different conditions.

Entry	Catalyst	Reaction time (h)	Alcohol/acid molar ratio	Catalyst amount (wt%)	Conversion of butyric acid (%)	Yield of butyl butyrate (%)
1	Glycine	2	1.4:1	5	43.4	39.1
2	$H_{3.0}PW_{12}O_{40}$	2	1.4:1	5	84.1	82.6
3	$[GlyH]H_{2.0}PW_{12}O_{40}$	2	1.4:1	5	98.0	97.7
4	$[GlyH]_{2.0}H_{1.0}PW_{12}O_{40}$	2	1.4:1	5	95.8	95.4
5	$[GlyH]_{3.0}PW_{12}O_{40}$	2	1.4:1	5	82.8	81.4
6	$[GlyH]H_{2.0}PW_{12}O_{40}$	0.5	1.4:1	5	86.1	84.6
7	$[GlyH]H_{2.0}PW_{12}O_{40}$	1	1.4:1	5	95.2	94.4
8	$[GlyH]H_{2.0}PW_{12}O_{40}$	1.5	1.4:1	5	96.2	95.6
9	$[GlyH]H_{2.0}PW_{12}O_{40}$	2.5	1.4:1	5	84.5	82.1
10	$[GlyH]H_{2.0}PW_{12}O_{40}$	2	1.1:1	5	93.1	92.0
11	$[GlyH]H_{2.0}PW_{12}O_{40}$	2	1.2:1	5	96.8	96.3
12	$[GlyH]H_{2.0}PW_{12}O_{40}$	2	1.6:1	5	97.4	96.9
13	$[GlyH]H_{2.0}PW_{12}O_{40}$	2	1.8:1	5	85.5	84.8
14	$[GlyH]H_{2.0}PW_{12}O_{40}$	2	1.4:1	3	95.9	95.4
15	$[GlyH]H_{2.0}PW_{12}O_{40}$	2	1.4:1	4	96.3	95.7
16	$[GlyH]H_{2.0}PW_{12}O_{40}$	2	1.4:1	6	97.4	96.8
17	$[GlyH]H_{2.0}PW_{12}O_{40}$	2	1.4:1	7	96.5	95.8

during esterification of butyric acid with butanol. Based on the symbols and coded levels summarized in Table 1, experimental and calculated results were obtained by the designed experiments according to a BBD second-degree polynomial model which are summarized in Table 3. Accordingly, by multiple regression analysis, the butyl butyrate yield (Y) may be expressed in terms of coded variables (cf. Table 1) as

Table 3: List of experimental designs and response values during esterification of butyric acid with butanol over the $[GlyH]_{1.0}H_{2.0}PW_{12}O_{40}$ catalyst.

Entry	Variable and level			Butyl butyrate yield (%)	
	x_1	x_2	x_3	Experimental	Calculated
1	1.50	1.20	5.00	96.62	96.67
2	2.50	1.20	5.00	97.14	97.03
3	1.50	1.60	5.00	96.91	97.02
4	2.50	1.60	5.00	97.52	97.47
5	1.50	1.40	4.00	97.82	97.76
6	2.50	1.40	4.00	97.80	97.90
7	1.50	1.40	6.00	97.31	97.21
8	2.50	1.40	6.00	97.82	97.88
9	2.00	1.20	4.00	96.65	96.66
10	2.00	1.60	4.00	97.43	97.39
11	2.00	1.20	6.00	96.67	96.72
12	2.00	1.60	6.00	96.77	96.76
13	2.00	1.40	5.00	97.75	97.73
14	2.00	1.40	5.00	97.80	97.73
15	2.00	1.40	5.00	97.62	97.73
16	2.00	1.40	5.00	97.72	97.73
17	2.00	1.40	5.00	97.78	97.73

$$Y = 97.73 + 0.20x_1 + 0.19x_2 - 0.14x_3 + 0.061x_1^2 - 0.75x_2^2$$
$$-0.11x_3^2 + 0.023x_1x_2 + 0.13x_1x_3 - 0.17x_2x_3 \quad (7)$$

where x_1, x_2, and x_3 are the coded variables representing reaction time, alcohol/acid molar ratio, and catalyst amount, respectively, and Y is the response for butyl butyrate yield. To verify the quadratic model, up to 17 experimental runs were needed. As shown in Table 3, close resemblances between the experimental and calculated values may be inferred for the butyl butyrate yield. The significance and validity of the model [Eq. (7)] were further verified by the analysis of variance (ANOVA), and the statistical analyses are depicted in Table 4. As listed in Table 4, the fitting of the overall model was significant with an F-statistic value of 33.45 (much higher than the tabular value of 5.61) and a p-value <0.00001 at 1% confidence level for the prediction of butyl butyrate yield, revealing that the chosen model was indeed highly reliable. This is also supported by the observed correlation coefficient square value ($R^2 = 0.9773$), indicating a satisfactory fitting between the experimental and predicted values [22]. Furthermore, a relatively low coefficient of variation (CV) value of 0.11% was deduced, indicating that experiments were carried out reliably. Moreover, a relatively low "lack of fit F-value" of 3.98 was observed, implying that the model indeed fitted to all data. The influence of each independent variable on the fitting model may be examined by analyzing the variances at its corresponding levels. These results derived from ANOVA indicate that the experimental variables have significant effect on butyl

Table 4: Estimated regression coefficients and corresponding statistical *F*- and p-values for butyl butyrate yield.

Source	Sum of squares	DF	Mean square	*F*-value	p-Value	Significance
Model	3.42	9	0.38	33.45	<0.0001	**
x_1	0.33	1	0.33	28.90	0.0010	**
x_2	0.30	1	0.30	26.46	0.0013	**
x_3	0.16	1	0.16	14.06	0.0072	**
x_1^2	0.015	1	0.015	1.36	0.2821	
x_2^2	2.35	1	2.35	207.02	<0.0001	**
x_3^2	0.048	1	0.048	4.25	0.0783	*
$x_1 x_2$	2.025E-003	1	2.025E-003	0.18	0.6854	
$x_1 x_3$	0.070	1	0.070	6.19	0.0417	**
$x_2 x_3$	0.12	1	0.12	10.19	0.0152	**
Residual	0.079	7	0.011			
Lack of fit	0.060	3	0.020	3.98	0.1075	
Pure error	0.020	4	4.980E-003			
Cor total	3.50	16				

DF, degree of freedom. **Highly significant.

butyrate yield during esterification reaction, and the yield is well predicted by the model.

Based on the predicted model, the three dimensional (3D) response surface and contour plots representing correlations between each pair of experimental variables (while keeping other variables at their respective level of zero; cf. Table 1) may be obtained, as depicted in Figure 1. For example, response surface and contour plots associated with correlations between reaction time (x_1) and alcohol/acid molar ratio (x_2) are shown in Figure 1A and D, respectively. It was found that reaction time was insignificant to the response (yield) when alcohol/acid molar ratio was lower than 1.2:1. The butyl butyrate yield reached a maximum (97.82%) at a reaction time of 2.5 h. The observed contours reveal that the combined effect of reaction time and alcohol/acid molar ratio has no significant influence on the response.

The 3D response surface (Figure 1B) and contour plots (Figure 1E) between reaction time (x_1) and catalyst amount (x_3) reveal that reaction time has more significant influence than alcohol/acid molar ratio during esterification reaction. Indeed, the butyl butyrate yield was found to increase more significantly before the reaction time reached 2 h, but insignificant change was observed afterward. On the other hand, increasing the catalyst amount did not significantly improve the yield for catalyst amount <5 wt%. In addition, two-dimensional contour lines demonstrated that combined effects of the above parameters on the yield of butyl butyrate were significant.

As shown in the response surface plot (Figure 1C), the correlations between alcohol/acid molar ratio (x_2) and catalyst amount (x_3) showed significant influence on butyl butyrate yield. This is supported by the corresponding

contour plot (Figure 1F), which reveals an elliptical shape. As discussed earlier based on ANOVA of butyric acid conversion, the alcohol/acid molar ratio clearly showed more significant effect on butyl butyrate yield than the catalyst amount. A satisfactory butyl butyrate yield of 97.82% was obtained with an alcohol/acid molar ratio of 1.4:1 and a catalyst amount of 6 wt%. However, as the catalyst amount was kept constant, further increasing the alcohol/acid ratio showed a slight decrease in butyric acid conversion.

Overall, based on the quadratic model in Eq. (7) and 17 experimental runs, an optimum butyl butyrate yield of 98.22% was predicted for esterification of butyric acid over the $[GlyH]_{1.0}H_{2.0}PW_{12}O_{40}$ catalyst under the following optimal reaction conditions: a reaction time of 2.50 h, alcohol/acid molar ratio of 1.43, and a catalyst amount of 4.83 wt%. To verify these predicted results, three additional experiments were carried out in parallel using the experimental parameters: reaction time (x_1)=2.50 h, alcohol/acid molar ratio (x_2)=1.4, and catalyst amount (x_3)=4.8 wt%. As a result, an experimental yield of 97.9% was obtained, which is in good agreement with the predicted value.

3.4 Recyclability of the catalyst

To assess the durability of $[GlyH]_{1.0}H_{2.0}PW_{12}O_{40}$ catalyst for esterification of butyric acid, cyclic experiments were conducted under the same optimized operating conditions. For each cycle run, the bottom layer of the reaction mixture containing the catalyst was separated from the system, followed by washing (with diethyl ether) and drying (under vacuum for 5 h at 343 K) treatments before
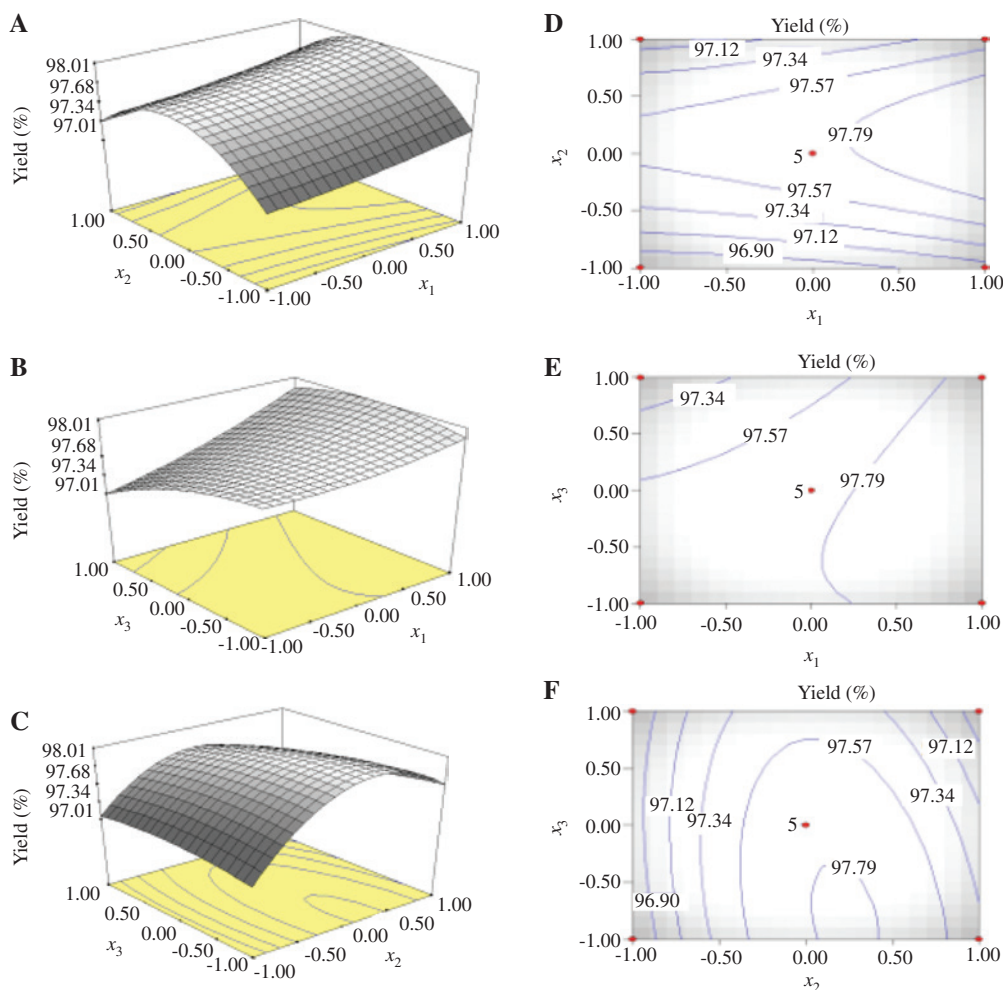
Figure 1: (A–C) 3D response surface and (D–F) contour plots showing correlations between a pair of experimental variables (Table 1) and relevant effects on predicted butyl butyrate yield while keeping other variables at a constant level of 0.

reuse. As illustrated in Figure 2, results showed that catalyst was repeatedly used 6 times without major loss of catalytic activity, which demonstrated that $[GlyH]H_{2.0}PW_{12}O_{40}$ catalyst for esterification could be recyclable.

3.5 Catalytic activities on the studies of esterification of other related compounds

Based on the above result, $[GlyH]H_{2.0}PW_{12}O_{40}$ was highly reliable to be a catalyst of esterification reaction of butyric acid with butanol and was practical to industrial application. Herein, we also examined the catalytic activity of $[GlyH]H_{2.0}PW_{12}O_{40}$ for esterification reaction by other related alcohol and acid compounds as reactants to further exploring its suitability for wide application of industrial-scale esterification. The results are given in Table 5.
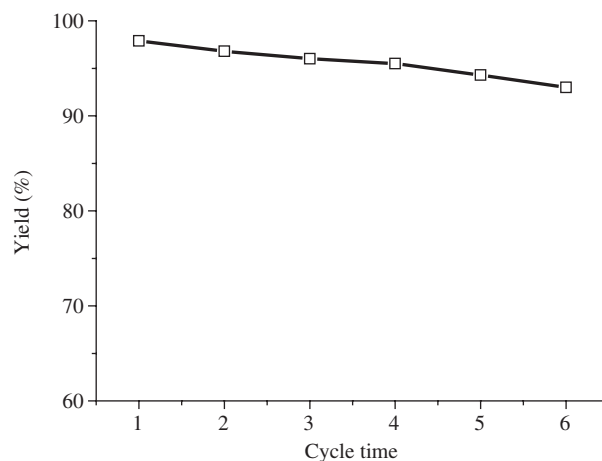

Figure 2: Stability of the $[GlyH]_{1.0}H_{2.0}PW_{12}O_{40}$ catalyst during esterification of butyric acid with butanol. Reaction conditions: butyric acid, 0.1 mol; butanol, 0.14 mol; catalyst amount, 4.8 wt%; reaction time, 2.5 h; reaction temperature, 393 K.

Table 5: Esterification of various alcohols with carboxylic acids over $[GlyH]_{1.0}H_{2.0}PW_{12}O_{40}$ catalyst.[a]
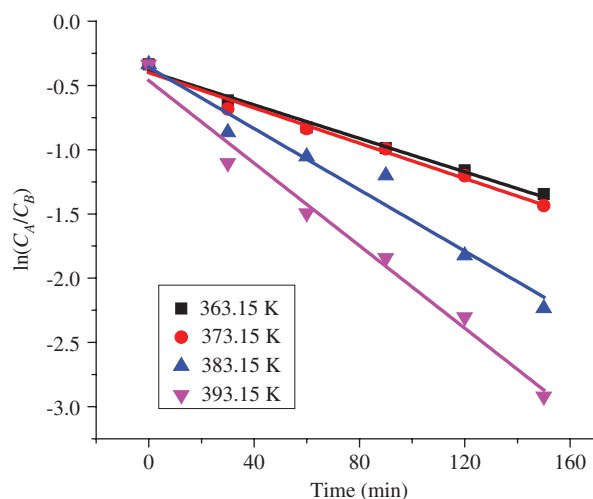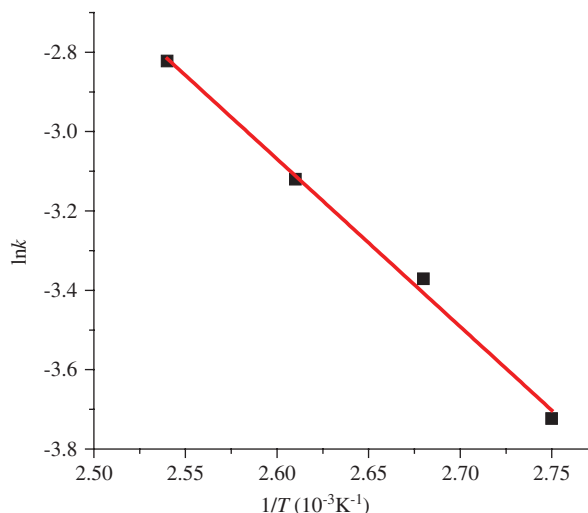
Entry	Alcohol	Carboxylic acid	Conversion (%)	Yield (%)
1	n-Propyl alcohol	Butyric acid	98.1	97.5
2	Isoamyl alcohol	Butyric acid	96.5	95.9
3	Cyclohexanol	Butyric acid	90.6	90.1
4	n-Butyl alcohol	Acetic acid	99.2	98.6
5	Isoamyl alcohol	Acetic acid	98.9	98.5
6	Isoamyl alcohol	Isovaleric acid	95.4	94.7

[a]Reaction conditions: carboxylic acid, 0.1 mol; alcohol, 0.14 mol; catalyst amount, 4.8 wt%; reaction time, 2.5 h; reaction temperature, 393 K.

$[GlyH]H_{2.0}PW_{12}O_{40}$ catalyst also showed excellent catalytic activity in other related compounds. The yields of ester were all over 90%. In a word, this new catalyst improved the esterification on excellent yields under milder reaction conditions, which made it a useful and important complementary to the present methodologies and suitable for practical small- and large-scale reactions.

3.6 Kinetic model

For kinetic studies, additional experiments were carried out with the aforementioned optimal variables: x_1=30–150 min, x_2=1.4:1 and x_3=4.8 wt% over the temperature range of 363–393 K. The linear relationship of $\ln(C_A/C_B)$ with time for the reaction was shown in Figure 3, which further indicated that the hypothesis was correct. The

Figure 3: Plot of $\ln(C_A/C_B)$ versus time for esterification with butyric acid and butanol.

Figure 4: Arrhenius plot of $\ln k$ versus $1/T$.

esterification reaction between butyric acid and butanol was evidently a second-order reaction. A linear Arrhenius plot obtained between $\ln k$ and $1/T$ is shown in Figure 4. From the equation $r=-\dfrac{dC_A}{dt}=1.0\times10^{10}\exp(-\dfrac{81.90}{RT})C_A C_B$, the activation energy E_a was calculated to be 81.90 kJ/mol, and the pre-exponential factor k_0 was found to be 1.0×10^{10} l/(mol min). Results obtained from this kinetic study therefore provide strong support to show that the $[GlyH]_{1.0}H_{2.0}PW_{12}O_{40}$ organic salt is indeed a highly effective catalyst for esterification of butyric acid with butanol. These results also provide valuable information for reaction process, which should be beneficial for future evaluation of the Gly-TPA catalyst for potential industrial applications.

4 Conclusions

The organic TPA salts prepared via combining TPA with glycine were shown to be efficient for the esterification of butyric acid with butanol. As illustrated by esterification of butyric acid with butanol over the $[GlyH]_{1.0}H_{2.0}PW_{12}O_{40}$ catalyst, an optimal butyl butyrate yield of 97.9% was achieved under the following reaction conditions: alcohol/acid=1.4, catalyst amount=4.8 wt%, and reaction time=2.5 h, all of which are in excellent agreement with those predicted by a factorial experimental design based on the BBD model and RSM. A kinetic model established for esterification of butyric acid with butanol over the $[GlyH]_{1.0}H_{2.0}PW_{12}O_{40}$ catalyst revealed that the catalytic system had a reaction order of 2 with an active energy of

81.90 kJ/mol. All the experimental and theoretical results suggest that the Gly-TPA organic salts are truly efficient and reusable catalysts suitable for practical industrial applications of ester.

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