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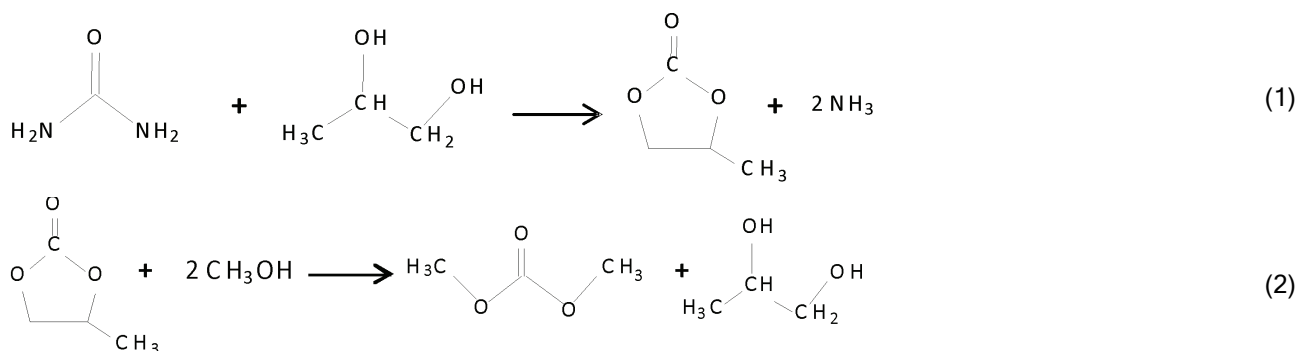
SYNTHESIS OF PROPYLENE CARBONATE FROM UREA AND 1,2-PROPYLENE GLYCOL OVER METAL CARBONATES

A series of single-metal carbonates and Pb-Zn mixed-metal carbonates were prepared as catalysts for alcoholysis of urea with 1,2-propylene glycol (PG) for the synthesis of propylene carbonate (PC). The mixed carbonates all show much better catalytic activities than the single carbonates, arising from a strong synergistic effect between the two crystalline phases, hydrozincite and lead carbonate. The mixed carbonate with Pb/Zn = 1:2 gives the highest yield of PC, followed by the mixed carbonate with Pb/Zn = 1:3. Furthermore, Taguchi method was used to optimize the synthetic process for improving the yield of PC. It is shown that the reaction temperature is the most significant factor affecting the yield of PC, followed by the reaction time, and that the optimal reaction conditions are the reaction time 5 h, the reaction temperature 180 °C and the catalyst amount 1.8 mass%, resulting in the highest PC yield of 96.3%.

Key words: urea alcoholysis; propylene carbonate; mixed carbonates; Taguchi method.

Propylene carbonate (PC), one of commercially important chemical intermediates and highly polar but aprotic solvents, has been widely used in organic syntheses, cosmetics, gas separation, battery electrolytes, metal extraction, etc. [1,2]. Several methods were reported for the synthesis of PC, such as the phosgenation of 1,2-propylene glycol (PG) with phosgene [2], transesterification of PG with alkyl carbonate [3], reaction of carbon dioxide with α -chloropropanol [4], cycloaddition of propylene oxide with carbon dioxide

[5,6], and alcoholysis of urea with PG [7–14]. Compared with traditional methods, urea alcoholysis is a new route for preparing PC and shows many advantages, such as cheap and easily available feedstock, mild reaction conditions and safe operations [9–12]. More importantly, the route for the synthesis of PC is the first step in the two-step transesterification process for the production of dimethyl carbonate (DMC) [11–15], shown by Eqs. (1) and (2). The PG produced in the second step may be recycled as the raw ma-



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terial in the first step, which will increase the efficiency of utilization of raw material and greatly lower the cost for the production of DMC.

Su and Speranza [7], for the first time, synthesized alkylene carbonates via urea alcoholysis over a toxic organotin catalyst, *i.e.*, dibutyl tin dilaurate. Doya

et al. [8] improved the yield of alkylene carbonates by using zinc, magnesium, lead, calcium, or their oxides/hydroxides as catalysts. Li *et al.* [9,10] used a series of metal-oxide catalysts to produce PC from urea and PG, and found that the amphoteric ZnO showed the highest catalytic activity and the yield of PC reached 98.9%, while the activity decreased for basic oxides with strong basic sites, and acidic oxides had no activity. Gao *et al.* [11] reported that both MgCl_2 and ZnCl_2 showed good catalytic performances toward the urea alcoholysis and the yield of PC reached 96.5 and 92.4%, respectively. Moreover, Zhao *et al.* [12,13] performed the alcoholysis of urea with PG over homogeneous zinc acetate, supported zinc acetate and zinc-iron double oxide catalysts, and the yield of PC reached 94, 78 and 78.4%, respectively. The latter two heterogeneous catalysts had poorer catalytic performances than the homogeneous zinc acetate which suffered from problems associated with catalyst recovery and reuse. A serious loss of zinc acetate was also observed for the supported zinc acetate [12]. Zhang *et al.* [14] examined the catalytic activities of several single-metal carbonates and mixed carbonates in the urea alcoholysis, and the highest yield of PC reached 98.9%.

Although an amount of information is already at hand concerning the alcoholysis of urea, two serious disadvantages exist in these previous studies from the viewpoint of engineering application. One is that most of the PC syntheses were carried out under reduced pressure, leading not only to an extra consumption of energy owing to assembling of vacuum equipment, but also to loss of raw material and then change of raw material proportioning; the other is a large molar ratio of PG to urea often used by previous authors, *e.g.*, 4:1 [11–13] and 5:1 [14]. The yield of PC may be increased if this ratio is increased. For example, for the mixed-carbonate catalyst with $\text{Pb/Zn} = 3:1$ as the PG/urea ratio arrived at 5:1 the PC yield reached its highest value [14]. A much more excess of PG will make trouble for the product separation process and is not expected in industry.

In this paper, various single-metal carbonates and Pb-Zn mixed-metal carbonates with different Pb/Zn molar ratios were prepared as catalysts to synthesize PC from urea and PG at atmospheric pressure. The Taguchi method, a powerful tool to the optimization for quality [16–18], was used to optimize the synthetic process factors for improving the yield of PC. The PG/urea molar ratio was fixed at 1.5:1 for overall study.

EXPERIMENTAL

Catalyst preparation

All chemicals used were of analytical-reagent (AR) grade and purchased from China market. Lead, zinc, magnesium and chromium carbonates were prepared by a precipitation process using sodium carbonate as the precipitating agent, followed by drying overnight in air at 110 °C. Calcium, potassium and sodium carbonates were directly obtained by drying of as-received AR chemicals at 110 °C in air for 3 h. Five Pb-Zn mixed-metal carbonates with different Pb/Zn molar ratios were prepared by a coprecipitation method. Under vigorous stirring, a mixed aqueous solution of zinc nitrate (0.1 mol/L) and lead nitrate (0.033, 0.05, 0.1, 0.2 or 0.3 mol/L) and a solution of sodium carbonate (0.2 mol/L) were added slowly and simultaneously into a 500mL three-necked round-bottom flask at room temperature. The precipitation pH was kept constant at about 8.0. The precipitates were aged at room temperature for 30 min under stirring, then filtered and thoroughly washed with deionized water. The precipitates were dried overnight in air at 110 °C.

Catalyst characterization

X-ray diffraction (XRD) patterns were collected on a Shimadzu X-ray diffractometer operated at 25 kV and 40 mA, using V-filtered $\text{CrK}\alpha$ radiation ($\lambda = 0.22897$ nm). The angular scan was performed from 10 to 90° (2θ), at a scanning speed of 2°/min. The crystalline phases were identified by reference to powder diffraction data (JCPDS-ICDD). The average crystallite size was estimated using the Scherrer equation [19]:

$$D = \frac{0.90\lambda}{\beta \cos \theta} \quad (3)$$

where D is the average crystallite size (nm), λ the incident wavelength (nm), θ the Bragg diffraction angle, and β the corrected full width at half maximum (FWHM) of the diffraction peak (radian).

The surface acid/base properties of the catalyst samples were examined through the changes in color of Hammett indicators adsorbed on the catalyst samples [20]. The Hammett indicators used were bromthymol blue ($\text{p}K_a$ 7.2), alizarin yellow R ($\text{p}K_a$ 11.0) and 2,4-dinitroaniline ($\text{p}K_a$ 15.0) for determination of the basic strength, and dimethyl yellow ($\text{p}K_a$ 3.3), methyl red ($\text{p}K_a$ 4.8) and neutral red ($\text{p}K_a$ 6.8) for determination of the acid strength. Typically, 100 mg of a dried catalyst in powder form was mixed with 2.5 mL of an indicator solution (~0.1 mass% in dry benzene), shaken, and then allowed to sit for at least 1 h.

Catalytic test

The catalytic activity in the synthesis of PC was measured at atmospheric pressure in a 250-mL four-necked round-bottom flask equipped with a mechanical agitator, cycle reflux condenser, thermometer, and nitrogen inlet. After addition of 0.4 mol urea, 0.6 mol PG and 0.63 g powdered catalyst (0.9 mass% relative to the total weight of urea and PG), the flask was heated under stirring to 170 °C in oil bath and the reaction proceeded at this temperature for 4 h. The nitrogen gas was continuously passed through the flask during the reaction to protect the reaction system and to drive out the byproduct NH₃. The resultant mixture was cooled to room temperature, filtered to remove the catalyst, and then analyzed by a gas chromatography equipped with a FID detector and a packed column filled with organic support 402. The yield of PC was calculated as follows:

$$\text{Yield} = \frac{\text{Moles of PC produced}}{\text{Moles of urea in feed}} \times 100 = \frac{\text{Weight of reaction liquid obtained} \times \text{Weight percent of PC}}{\text{Molecular weight of PC} \times \text{Moles of urea in feed}} \times 100 \quad (4)$$

Design of experiments and optimization method

The Taguchi method is a fractional factorial design and allows one statistically and ideally to obtain similar information to a full-factorial experimental design, but with fewer experiments [16-18]. It uses a special design of orthogonal arrays to study an entire parameter space. The experimental results are then transformed into signal-to-noise (*S/N*) ratios. Taguchi [16-18] recommended the use of the *S/N* ratio to measure quality characteristics deviating from their desired values. Based on the analysis of the *S/N* ratio, the optimal levels of the process factors are determined. Furthermore, a statistical analysis of variance (ANOVA) is performed to see which process factors are statistically significant. Finally, a confirmation experiment is conducted to verify the optimal process factors obtained. The Taguchi method has been shown to be a great success in industry for improving the quality of products and processes. The rapid growth of interest in the Taguchi method has led to numerous applications of the method in various fields in a world-wide range of industries and nations [21-23].

In the PC synthesis, the reaction time, reaction temperature, amount of catalyst used and molar ratio of PG to urea are possibly four key process factors affecting the PC yield. In this study, the PG/urea molar ratio was fixed at 1.5:1 and the first three factors were selected as controllable factors to optimize the PC synthetic process with the Taguchi method. Their ranges were chosen based on the conditions often used in industry and reported in the literature [7-14, 24]. For

each process factor, three levels were selected, as shown in Table 1, where the catalyst amount was defined as the weight ratio of catalyst to urea and PG.

Table 1. Factors and their levels under investigation

Symbol	Factor	Value		
		1	2	3
A	Reaction time, h	2	3.5	5
B	Reaction temperature, °C	150	165	180
C	Catalyst amount, mass%	0.9	1.8	2.7

Three factors, each at three levels, were considered; therefore, an *L*₉ orthogonal array with four columns and nine rows could be employed if the interactions among these factors were neglected. This array has eight degrees of freedom and it can handle three-level process factors. Each process factor is assigned to a column, nine process-factor combina-

tions being available. Therefore, only nine experiments are required to study the entire parameter space. The experimental layout for the three factors using the *L*₉ orthogonal array is shown in Table 2. Since the *L*₉ orthogonal array has four columns, one column of the array is left empty for the error of experiments; orthogonality is not lost by letting one column of the array remain empty. The detailed PC synthetic process and the reaction conditions except the three factors examined were identical with those mentioned in section Catalytic test.

Table 2. Experimental layout using an *L*₉(3⁴) orthogonal array

Trial no.	Factor and level			
	A	B	C	Error
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	3	2
5	2	2	1	3
6	2	3	2	1
7	3	1	2	3
8	3	2	3	1
9	3	3	1	2

RESULTS AND DISCUSSION

Physical characterization of catalysts

Figure 1 presents the XRD patterns of the seven catalyst samples listed in Table 3, *i.e.*, lead carbo-

nate, zinc carbonate and their mixed-metal carbonates. It is clear that only one crystalline phase can be identified in the two single-carbonate samples, *i.e.*, hydrozincite (JCPDS file No. 19-1458) in sample 1 and lead carbonate (JCPDS file No. 47-1734) in sample 7. In the mixed-carbonate samples, only two crystalline phases, hydrozincite and lead carbonate, can be detected, and no diffraction peaks of zinc carbonate, lead hydroxide, double salt or other phases are observed. It can also be seen that the PbCO_3 phase shows far sharper diffraction peaks than the $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ phase, indicating that the former exhibits a better crystallinity. Moreover, the peaks of the $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ phase are broadened compared with those of the PbCO_3 phase, which means that the $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ crystallites are smaller. According to the Scherrer equation, the average sizes of crystallites were estimated for these samples and are given

in Table 3. It seems that, under the same preparation conditions, the Pb/Zn molar ratio has no significant effect on the PbCO_3 crystallite size, but has a negative correlation with the $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ crystallite size.

The strengths of the acidic and basic sites in the catalyst samples were analyzed qualitatively using Hammett indicator experiments. As shown in Table 3, samples 2 and 3 possess basic strength H values in the range of 7.2 to 11.0, while sample 1 is more basic, as evidenced by its ability to effect a color change with alizarin yellow R ($\text{p}K_a = 11.0$). It is also seen that samples 4–7 have no obvious basic sites on their surfaces. Furthermore, Hammett indicator measurements showed that all the basic indicators exhibited no color change when they interacted with any sample in Table 3. That is, these samples all have acid strength H_0 values larger than 6.8, revealing that there are no significant acidities on their surfaces.

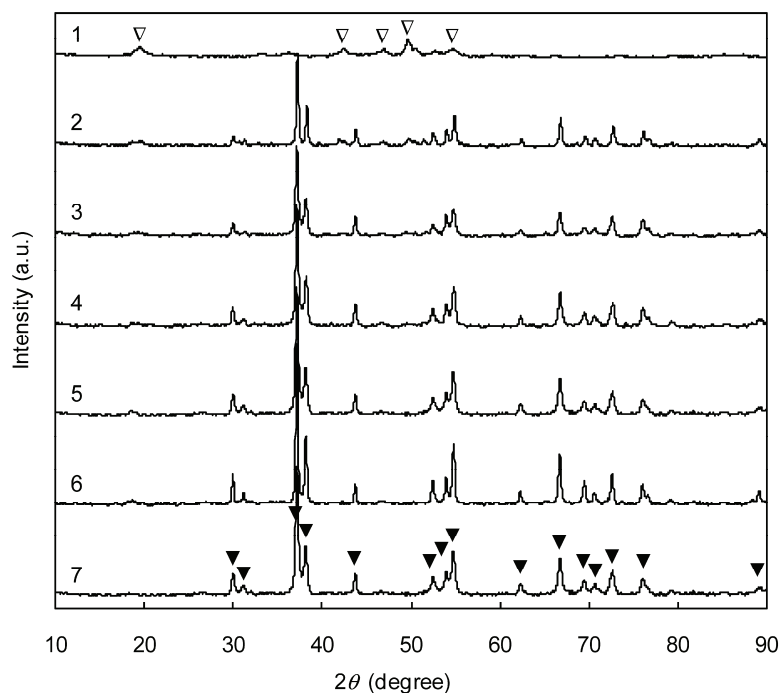


Figure 1. XRD Patterns of the catalyst samples listed in Table 3; ▼ : PbCO_3 , ▽ : $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$.

Table 3. Results of the catalyst characterization and activity measurements

Sample	Pb/Zn mole ratio	Crystallite size, nm		Basic strength	PC Yield, %
		PbCO_3	$\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$		
1	0:1	-	18.9	$11.0 \leq H < 15.0$	48.8
2	1:3	64.3	15.3	$7.2 \leq H < 11.0$	83.2
3	1:2	56.3	13.2	$7.2 \leq H < 11.0$	86.6
4	1:1	48.9	8.9	$H < 7.2$	79.4
5	2:1	58.0	10.7	$H < 7.2$	81.9
6	3:1	49.2	8.5	$H < 7.2$	78.7
7	1:0	48.3	-	$H < 7.2$	65.5

Catalytic performances

Figure 2 shows the catalytic activities of various single-metal carbonates in the urea alcoholysis. The blank test without catalyst, conducted under the same conditions, gives the PC yield of only 21.5%, indicating all the single-metal carbonates examined are active in the PC synthesis. It can also be seen that the lead carbonate leads to the highest yield of PC, followed by the zinc carbonate prepared by precipitation method.

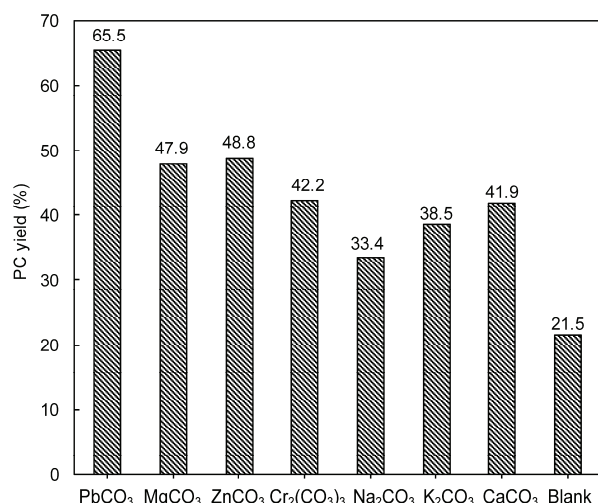


Figure 2. Catalytic activities of single-metal carbonates.

In view of the good catalytic performances of the lead and zinc carbonates, their mixed-metal carbonates with different Pb/Zn molar ratios were further examined. The experimental results are displayed in the last column of Table 3. Clearly, there does not exist a simple correlation between the PC yield and the sizes of the PbCO₃ and Zn₅(CO₃)₂(OH)₆ crystallites. However, the mixed carbonates all show much better catalytic activities than the single carbonates, which provides support for the existence of a strong synergetic effect between the PbCO₃ and Zn₅(CO₃)₂(OH)₆ phases in the mixed carbonates. It can also be found that the

Pb/Zn molar ratio has a great impact on the catalytic activity of the mixed carbonates. The mixed carbonate with Pb/Zn = 1:2 gives the highest yield of PC, followed by the mixed carbonate with Pb/Zn = 1:3. The two samples are slightly alkaline, while the other mixed-carbonate samples are approximatively neutral, as mentioned above. It suggests that a slightly alkaline mixed carbonate would be favorable to promote the synergetic catalysis of PbCO₃ and Zn₅(CO₃)₂(OH)₆, and hence exhibit an excellent catalytic activity in the urea alcoholysis. Similar result was also reported for the urea alcoholysis over basic oxides, where the catalytic activity decreased with increasing basic strength [10].

It should be pointed out that the thermal decomposition of hydrozincite and lead carbonate occurs at 220 [25] and 315 °C, respectively; therefore, the catalysts are all stable during the reaction, though they are prepared at 110 °C.

Optimization of the PC synthetic process

As shown above, the mixed carbonate with Pb/Zn = 1:2 has the highest catalytic activity, so it was used as catalyst to optimize the PC synthetic process. Taguchi method uses the signal-to-noise (S/N) ratio to measure the quality characteristic deviating from the desired value [16–18]. The S/N ratios are different according to the type of characteristics. For the-higher-the-better quality characteristic, the S/N ratio η is defined as:

$$\eta = -10 \log(\text{M.S.D.}) = -10 \log \left(\frac{1}{r} \sum_{k=1}^r \frac{1}{y_k^2} \right) \quad (5)$$

where M.S.D. is the mean square deviation for quality characteristic y_k , and r the number of repetitions done for each experiment in the orthogonal array. Clearly, the-higher-the-better quality characteristic must be taken for the yield of PC to obtain the optimal synthetic process.

Table 4. Experimental results for the yield of PC and corresponding S/N ratio

Trial no.	Reaction time, h	Reaction temperature, °C	Catalyst amount, mass%	Yield, %	S/N Ratio, dB
1	2	150	0.9	52.1	-5.663
2	2	165	1.8	71.6	-2.902
3	2	180	2.7	81.7	-1.756
4	3.5	150	2.7	60.2	-4.408
5	3.5	165	0.9	78.4	-2.114
6	3.5	180	1.8	84.4	-1.473
7	5	150	1.8	70.9	-2.987
8	5	165	2.7	80.1	-1.927
9	5	180	0.9	93.5	-0.584

Table 4 presents the yields of PC obtained by Taguchi experiments and their corresponding S/N ratios calculated using Eq. (5). Since the experimental design is orthogonal, it is then possible to separate out the effect of each process factor at different levels. For example, the mean S/N ratio for the reaction time at levels 1, 2 and 3 can be calculated by averaging the S/N ratios for the experiments 1-3, 4-6 and 7-9, respectively. Consequently, an S/N response table can be obtained, as shown in Table 5. In addition, the total mean S/N ratio $\bar{\eta}$ for the nine experiments was also calculated and listed in Table 5. Figure 3 shows the corresponding S/N response graph.

Table 5. S/N response table (mean S/N ratio, dB) for the yield of PC

Factor	Level			Max-min
	1	2	3	
A	-3.440	-2.665	-1.833	1.607
B	-4.353	-2.314	-1.271	3.082
C	-2.787	-2.454	-2.697	0.333
The total mean S/N ratio, $\bar{\eta}$			-2.646 dB	

Regardless of the category of quality characteristics, a greater S/N ratio corresponds to a smaller variance of output characteristic around the desired value and hence to a better quality characteristic. Therefore, the optimal level of the process factors is the level with the greatest S/N ratio [16-18]. From Table 5 and Figure 3, it can be found that the optimal reaction conditions are the reaction time at level 3, the reaction temperature at level 3 and the catalyst amount at level 2, denoted as A3B3C2.

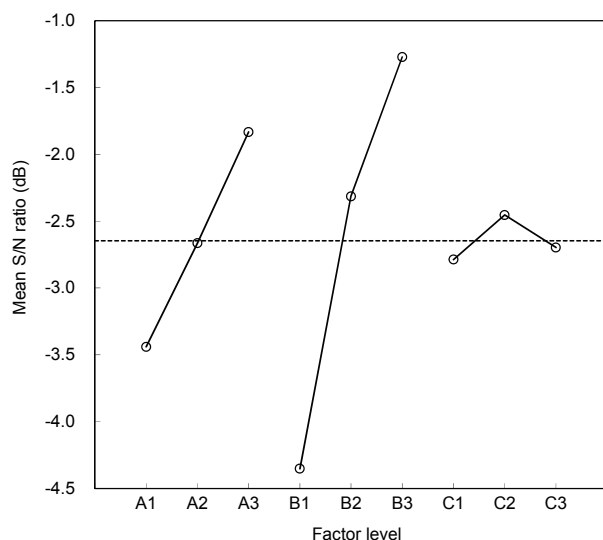


Figure 3. S/N graph for the yield of PC.

Effects of the process factors

In order to see which process factors significantly affect the quality characteristic, an analysis of variance (ANOVA) [16-18] was carried out. First, the total variability of the S/N ratio, which is measured by the total sum of the squared deviation from the total mean S/N ratio $\bar{\eta}$, SS_T , is decomposed into contributions by individual process factors and by the experimental error, *i.e.*, the sum of squared deviation due to individual factors, SS_p , and the sum of squared deviation due to the error, SS_e . [16-18].

$$SS_T = \sum_{i=1}^n (\eta_i - \bar{\eta})^2 = \sum_{i=1}^n \eta_i^2 - \frac{1}{n} \left(\sum_{i=1}^n \eta_i \right)^2 \quad (6)$$

$$SS_p = t_p \sum_{j=1}^{q_p} (\bar{\eta}_{p,j} - \bar{\eta})^2 = \frac{1}{t_p} \sum_{j=1}^{q_p} \left(\sum_{i=1}^{t_p} \eta_{p,j,i} \right)^2 - \frac{1}{n} \left(\sum_{i=1}^n \eta_i \right)^2 \quad (7)$$

$$SS_e = SS_T - \sum_{p=1}^m SS_p \quad (8)$$

In these equations, n is the total number of experiments in the orthogonal array, m the number of the process factors, q_p the number of levels of factor p , t_p the number of repetitions of each level of factor p in the orthogonal array ($n = t_p \times q_p$), η_i the S/N ratio for the i th experiment, $\eta_{p,j,i}$ the S/N ratio for the i th experiment with factor p at level j , and $\bar{\eta}_{p,j}$ the mean S/N ratio for factor p at level j (see Table 5).

Then, the mean of squared deviation due to individual factors, MS_p , and the mean of squared deviation due to the error, MS_e , are derived as follows:

$$MS_p = \frac{SS_p}{f_p} = \frac{SS_p}{q_p - 1} \quad (9)$$

$$MS_e = \frac{SS_e}{f_e} = \frac{SS_e}{f_T - \sum_{p=1}^m f_p} = \frac{SS_e}{n - 1 - \sum_{p=1}^m f_p} \quad (10)$$

where f_p and f_e are the number of degrees of freedom of factor p and the error, respectively, and f_T the total number of degrees of freedom of the orthogonal array. After factors having lower MS_p are pooled to the error, the F -test values (variance ratios) for individual factors, F_p , are simply calculated by:

$$F_p = \frac{MS_p}{MS_{(e)}} \quad (11)$$

where $MS_{(e)}$ is the mean of squared deviation due to the pooled error. The process factor with a larger F -test value has a more significant effect on the quality characteristic [16-18]. For significant factors and pooled

error, their percentage contributions, ρ_p and $\rho_{(e)}$, can be determined, respectively, by:

$$\rho_p = \frac{SS'_p}{SS_T} = 100 \frac{SS_p - f_p MS_{(e)}}{SS_T} \quad (12)$$

$$\begin{aligned} \rho_{(e)} &= 1 - \sum_{p=1}^o \rho_p = \frac{SS'_{(e)}}{SS_T} = \frac{SS_T - \sum_{p=1}^o SS'_p}{SS_T} = \\ &= 100 \frac{SS_{(e)} + \sum_{p=1}^o f_p MS_{(e)}}{SS_T} \end{aligned} \quad (13)$$

where SS'_p and $SS'_{(e)}$ are the pure sum of squared deviation due to individual factors and due to the pooled error, respectively, $SS_{(e)}$ the sum of squared deviation due to the pooled error, and o the number of the main process factors that affect the quality characteristic significantly.

Table 6 shows the results of ANOVA for the yield of PC. It can be found that the reaction temperature gives the largest F -test value and the contribution of 72.65% and thus it is the most significant factor affecting the yield of PC, followed by the reaction time. The change of the catalyst amount in the range examined has, however, less effect on the yield of PC.

The process factors have effects on the yield of PC; therefore there is a great possibility of improving the yield of PC with the optimization of the process factors. As shown in Table 5 and Figure 3, as the reaction time increases, the mean S/N ratio increases, *i.e.*, the PC yield increases. It indicates that a longer reaction time may cause a more complete reaction as expected. Furthermore, the PC yield increases with increasing the reaction temperature. Thermodynamic analysis revealed that the urea alcoholysis is endothermic [12], so the increase in temperature promotes the synthesis of PC. It is also seen that when the catalyst amount is 1.8 mass% the PC yield reaches its maximum value, and then the PC yield declines slightly with the further increase of the catalyst amount, though the effect of this process factor is statistically insignificant.

Improvement of the PC yield

Once the optimal levels of the process factors have been selected, the final step is to predict and verify the improvement of the quality characteristic using the optimal levels of the process factors [16–18]. The S/N ratio for the optimal factor levels, η_{opt} , can be estimated as:

$$\eta_{opt} = \bar{\eta} + \sum_{p=1}^o (\bar{\eta}_{p,opt} - \bar{\eta})$$

where $\bar{\eta}_{p,opt}$ is the mean S/N ratio for factor p at its optimal level (see Table 5). Based on the η_{opt} value, the PC yield for the optimal factor levels can be predicted with Eq. (5). To verify this prediction, two additional experiments were conducted at the optimal levels of the process factors. One used the optimal catalyst obtained in this study, and the other used a commercial catalyst in service in Chinese industry for synthesizing PC from urea and PG.

Table 7 shows the comparison of the predicted and experimental values of the PC yield. A good agreement is observed between the predicted and actual experimental values of the optimal catalyst, indicating that the impacts of the interactions among the process factors are relatively small and that the experimental results have a satisfactory reproducibility. It can be found that the PC yield for the optimal factor levels is higher than any of the yield data shown in Table 4. Moreover, the increase of the S/N ratio from the commercial catalyst to the optimal catalyst is 3.590 dB, which means that the yield of PC increases by about 1.5 times. All these results confirm the “no-interaction” assumption, experimental reproducibility, and prior design and analysis for optimizing the process factors. The yield of PC is greatly improved with the optimization of the process factors through the Taguchi method.

It should be mentioned that the optimal factor levels obtained for the reaction time and reaction temperature are their respective top values examined in this study, as shown in Figure 3. It seems to tell one that the yield of PC might be further increased if a

Table 6. Analysis of variance for the yield of PC

Factor	Sum of squares	Degrees of freedom	Mean square	F -test	Pure sum of squares	Percentage contribution, %
A	3.877	2	1.939	7.825	3.382	17.24
B	14.74	2	7.371	29.75	14.25	72.65
C ^a	0.178	2	0.089 °	-	-	-
Error	0.813	2	0.407	-	-	-
(Error)	(0.991)	(4)	(0.248)	-	(1.982)	(10.11)
Total	19.61	8	-	-	19.61	100

^aThe variance of factor C (with open circle) is pooled into the error factor

more wide range of the process factors was explored. However, the normal boiling point of PG is about 188 °C, and an exorbitant temperature will lead to its fast evaporation. The elevation of temperature may also cause side reactions such as the polymerization of PC [26]. In addition, in this study the alcoholysis of urea proceeds at atmospheric pressure at a very low PG/urea ratio of 1.5:1; however, by the optimization of the process factors the highest PC yield reaches 96.3% and is close to that obtained at a PG/urea ratio of 5:1 [14]. This PC synthetic process, therefore, provides a great convenience for actual industrial production.

Table 7. Results of the confirmation experiments (level A3B3C2)

Parameter	Commercial catalyst	Optimal catalyst	
	Experiment	Experiment	Prediction
Yield, %	63.7	96.3	94.9
S/N Ratio, dB	-3.917	-0.327	-0.458
Improvement of S/N ratio		3.590 dB	

CONCLUSIONS

All the single-metal carbonates examined are active in the PC synthesis operated at atmospheric pressure, and the highest catalytic performance is achieved over the lead carbonate and then the zinc carbonate. Compared with the single carbonates, the Pb-Zn mixed-metal carbonates show much better catalytic activities, which is attributed to a strong synergistic effect between the two crystalline phases, hydrazincite and lead carbonate, in the mixed carbonates. Especially, the mixed carbonate with Pb/Zn = 1:2 gives the highest yield of PC, followed by the mixed carbonate with Pb/Zn = 1:3. It is also found that mixed carbonates with slightly basic strength are favorable to promote the synergistic catalysis and hence exhibit an excellent catalytic activity in urea alcoholysis. Furthermore, optimization experiments show that the reaction temperature is the most significant factor affecting the yield of PC, followed by the reaction time, and that the change of the catalyst amount in the range examined has less effect. The yield of PC can be improved significantly with the optimization of these process factors. For the PC synthesis from PG and urea in a molar ratio of 1.5:1, the optimal reaction conditions are the reaction time at 5 hours, the reaction temperature at 180 °C and the catalyst amount at 1.8 mass%, resulting in the highest PC yield of 96.3%.

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REFERENCES

- [1] J.H. Clements, *Ind. Eng. Chem. Res.* **42** (2003) 663-674
- [2] A.-A.G. Shaikh, S. Sivaram, *Chem. Rev.* **96** (1996) 951-976
- [3] Y.K. Iwakuni, Y.M. Kuga, M.I. Ohtake, Preparation of cyclic carbonates, U.S. Patent No. 4880942, 1989
- [4] X. Zhou, X.G. Yang, T. Chen, Y. Zhang, G.Y. Wang, *Chin. J. Catal.* **30** (2009) 7-8
- [5] D.J. Darensbourg, M.W. Holtcamp, *Coord. Chem. Rev.* **153** (1996) 155-174
- [6] H.S. Kim, J.J. Kim, H.N. Kwon, M.J. Chung, B.G. Lee, H.G. Jang, *J. Catal.* **205** (2002) 226-229
- [7] W.Y. Su, G.P. Speranza, U.S. Patent No. 5003084, 1991
- [8] M. Doya, T. Ohkawa, Y. Kanbara, A. Okamoto, K. Kimizuka, .S. Patent No. 5349077, 1994
- [9] Q.B. Li, W.Y. Zhang, N. Zhao, W. Wei, Y.H. Sun, *Catal. Today* **115** (2006) 111-116
- [10] Q.B. Li, N. Zhao, W. Wei, Y.H. Sun, *J. Mol. Catal., A* **270** (2007) 44-49
- [11] Z.W. Gao, S.F. Wang, C.G. Xia, *Chin. Chem. Lett.* **20** (2009) 131-135
- [12] X.Q. Zhao, Y. Zhang, Y.J. Wang, *Ind. Eng. Chem. Res.* **43** (2004) 4038-4042
- [13] X.Q. Zhao, Z.G. Jia, Y.J. Wang, *J. Chem. Technol. Biotechnol.* **81** (2006) 794-798
- [14] B.R. Zhang, D.F. Wu, J.C. Zhou, *Adv. Fine Petrochem.* **10** (2009) 11-14 (in Chinese)
- [15] B.M. Bhanage, S. Fujita, Y. Ikushima, M. Arai, *Green Chem.* **5** (2003) 429-432
- [16] P.J. Ross, *Taguchi Techniques for Quality Engineering*, 2nd ed., McGraw-Hill, New York, 1996
- [17] R.K. Roy, *Design of Experiments Using the Taguchi Approach*, John Wiley & Sons, New York, 2001
- [18] D.C. Montgomery, *Design and Analysis of Experiments*, 6th ed., John Wiley & Sons, New York, 2005
- [19] N. Li, F. Gaillard, *Appl. Catal., B* **88** (2009) 152-159
- [20] K. Tanabe, M. Misono, Y. Ono, H. Hattori, *Stud. Surf. Sci. Catal.* **51** (1989) 5-25
- [21] A. Bendell, J. Disney, W.A. Pridmore, *Taguchi Methods: Applications in World Industry*, IFS Publications, UK, 1989
- [22] S. Aber, D. Salari, M.R. Parsa, *Chem. Eng. J.* **162** (2010) 127-134
- [23] M.P. Elizalde-González, L.E. García-Díaz, *Chem. Eng. J.* **163** (2010) 55-61
- [24] X.L. Xu, J.H. Zhan, W. Wei, N. Zhao, *Petrochem. Technol. Appl.* **24** (2006) 366-368 (in Chinese)
- [25] M.C. Hales, R.L. Frost, *J. Therm. Anal. Cal.* **91** (2008) 855-860
- T. Wei, M.H. Wang, W. Wei, Y.H. Sun, B. Zhong, *Chin. J. Catal.* **24** (2003) 52-56 (in Chinese).

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NAUČNI RAD

SINTEZA PROPILEN-KARBONATA IZ UREE I 1,2-PROPILEN GLIKOLA POMOĆU METALNIH KARBONATA

Karbonati olova i cinka, uključujući i mešovite, pripremljeni su kao katalizatori alkoholize uree sa 1,2-propilenglikolom (PG) za sintezu propilen-karbonata (PC). Mešoviti karbonati su se pokazali kao bolji katalizatori od karbonata pojedinačnih metala zbog jakog sinergističkog efekta dve kristalne faze, hidrocinikita i olovnog karbonata. Najveći prinos PC se ostvaruje korišćenjem mešovitog karbonata sa odnosom Pb/Zn = 1:2, a zatim sa odnosom Pb/Zn = 1:3. Osim toga, Taguchi metod je korišćen za optimizaciju sinteze, radi poboljšanja prinosa PC. Pokazalo se da na prinos PC najveći uticaj ima temperatura, a zatim vreme reakcije, pri čemu su optimalni reakcioni uslovi: vreme reakcije 5 h, temperatura reakcije 180 °C i količina katalizatora 1,8%, kada je ostvaren najveći prinos PC od 96,3%.

Ključne reči: alkohoiliza uree, propilen-karbonat, mešoviti karbonati, Taguchi-jeva metoda.