Synthesis of Propylene Carbonate from Urea and 1,2-Propylene Glycol in a Monolithic Stirrer Reactor

Dongfang Wu,* Yali Guo, Shu Geng, and Yinghao Xia

School of Chemistry and Chemical Engineering, Southeast University, Jiangning District, Nanjing 211189, P. R. China

ABSTRACT: A monolithic stirrer reactor, in which the cordierite monolith-supported metal oxide and mixed-metal oxide catalysts are used as stirrer blades, is applied for the alcoholysis of urea with 1,2-propylene glycol to synthesize propylene carbonate. It is shown that the mixed-metal oxides give much higher urea alcoholysis performances than the metal oxides, arising from the existence of a strong synergetic effect in the mixed-metal oxides. The zinc–chromium mixed oxide not only shows an excellent catalytic performance but also has extremely strong adhesion strength on the monolithic substrate. For the monolith-supported zinc–chromium mixed oxide catalyst, the monolithic stirrer reactor performs very well, and the highest yield of propylene carbonate reaches 97.8%. The performance is comparable to that of a conventional mechanically agitated slurry reactor, revealing the monolithic stirrer reactor can be an attractive alternative to the slurry reactor for heterogeneously catalyzed liquid–liquid reactions.

1. INTRODUCTION

Propylene carbonate (PC) is widely used as a polar, aprotic solvent in organic syntheses, cosmetics, gas separation, battery electrolytes, metal extraction, etc.1–4 Several methods were reported for the synthesis of PC, such as the phosgenation of 1,2-propylene glycol (PG) with phosgene,5 transesterification of alkyl carbonate with PG,6 reaction of carbon dioxide with urea and methanol,12,13 shown in Figure 1. The second step is the transesterification of PC with methanol and its byproduct, PG, is recycled as raw material in the process for the production of dimethyl carbonate (DMC) from urea and methanol,12,13 shown in Figure 1. The second step is toward the urea alcoholysis and the yield of PC reached 96.5% and 92.4%, respectively. Zhao et al.9,10 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. A serious loss of zinc acetate was observed for the supported zinc acetate.9 Zhou et al.11 examined the catalytic activities of several single-metal carbones and Pb–Zn mixed-metal carbones in the urea alcoholysis, and the highest yield of PC reached 96.3%.

Although an amount of information is already at hand concerning the alcoholysis of urea to PC, previous studies were all carried out in slurry reactors filled with powdered catalysts, and no effort has been made to examine the applicability of new reactor types. As is well-known, slurry reactor suffers from a few problems associated with catalyst attrition, agglomeration, recovery, and reuse. An alternative is to combine the mixing with catalytic function by fixing the catalyst to a stirrer. Thus, a novel monolithic stirrer reactor (MSR) was proposed as a promising replacement for a conventional slurry reactor in multiphase reactions.14–17 In this reactor, monolithic catalysts are used as stirrer blades, creating a catalytic stirrer. The most important advantage of the MSR is the easy catalyst handling. This reactor is thought to be especially useful in the production of fine chemicals and in biochemical and biotechnology. Albers et al.14 showed that the MSR works for low viscosity liquids, and hydrodynamic aspects of the reactor type were analyzed. Hoek et al.15 examined the applicability of the MSR in a heterogeneously catalyzed gas–liquid reaction. The open structure of the monolithic stirrer blade enables a high throughput of reactants and a large geometrical area. de Lathouder et al.16,17 presented the use of the MSR for carrying...
out enzyme-catalyzed reactions in organic media and considered that the MSR is a convenient tool to compare monolithic catalysts in the absence of external mass transfer limitations.

Development of monolithic catalysts and reactors has been one of the major achievements in the field of heterogeneous catalysis and catalytic reaction engineering.\textsuperscript{18–29} For more than 30 years, monolithic catalyst manufacturers have been successful in stationary and automotive exhaust gas treatments, where the gas phase detoxification must be fast with contact time less than a second, since large volumes of gas have to be treated.\textsuperscript{19,21–23} In recent years, monolithic catalysts and reactors are expected to have increasing applications in chemical and biochemical processes, such as in mass production of chemicals, in the treatment of fuel and flue gases, and in other multiphase processes.\textsuperscript{18,24–29} The MSR is a new type of monolithic reactor. In this Article, we will demonstrate its industrial possibilities in a heterogeneously catalyzed liquid–liquid reaction, i.e., alcoholysis of urea with PG. Monolith-supported metal oxide and mixed-metal oxide catalysts were prepared and used in the MSR. The performance was compared with that of a conventional mechanically agitated slurry reactor (MASR). The MSR process optimization was also performed in order to improve the yield of PC.

2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation. All chemicals used were of analytical-reagent (AR) grade and were purchased from Sinopharm Chemical Reagent Co., Ltd., China. They were used as received without further purification. Cylindrically shaped monolithic structures (Φ16 × 24 mm) were obtained by cutting commercial cordierite straight-channel monoliths with a square cell density of 400 cpsi (cells per square inch) and a wall thickness of 0.21 mm. Each mini-monolith weighed about 2.30 g. Before use, they were pretreated in an acetic acid solution for 1 h and then calcined at 600 °C in air for 2 h to remove adsorbed impurities.

Powdered metal oxide and mixed-metal oxide catalysts were prepared from aqueous metal nitrates solutions and from mixed aqueous solutions of two metal nitrates in a molar ratio of 1:1, respectively. These solutions evaporated at 110 °C in air to dryness and then were calcined at 450 °C in air for 3 h. Monolith-supported metal oxide and mixed-metal oxide catalysts were prepared by the following procedure. Pseudo-boehmite, urea, and deionized water in a weight ratio of 2:1:5 were mixed and vigorously stirred at room temperature for 1 h. In this period, a small amount of nitric acid was added slowly to maintain pH at 1.5. As a result, a stable alumina sol was obtained. A dried monolith was dipped for approximately 1 min in this sol. The monolith was then shaken to remove the excess liquid remaining in the channels, followed by drying horizontally at 120 °C in air for 1 h and then calcination at 500 °C in air for 3 h. Afterward, the washcoated monolith was immersed in an aqueous solution of metal nitrate or in a mixed aqueous solution of two metal nitrates in a molar ratio of 1:1. After the monolith was removed and shaken, the monolith was left horizontally at room temperature overnight, dried horizontally at 120 °C in air for 1 h, and then calcined at 450 °C in air for 3 h. For each metal oxide and each mixed-metal oxide, two monolithic catalyst samples were prepared. The obtained monolithic catalysts contain 0.08–0.09 g of washcoat (γ-alumina) and 0.20–0.21 g of active phase (metal oxide or mixed-metal oxide) per monolith.

2.2. Catalytic Test. Catalytic activity of powdered catalysts in the synthesis of PC was measured at atmospheric pressure in the MASR, a 100 mL four-necked round-bottom flask equipped with a mechanical agitator, cycle reflux condenser, thermocouple, and nitrogen inlet. A monolithic catalyst activity test was carried out in the MSR shown in Figure 2. Two monolithic catalysts were mounted on a stirring shaft, replacing conventional impeller blades. The vertical location of the stirring shaft was adjusted to ensure that the monolithic catalysts were located in the middle of the reaction liquid.

In order to facilitate comparison, the amount of the powdered catalyst loaded in the MASR was 0.40 g, which approximated the total active phase amount of the two monolithic catalysts used in the MSR. After addition of 24.0 g (0.4 mol) of urea and 45.0 mL (0.6 mol) of PG, the MASR or MSR was heated under stirring (300 rpm) to 170 °C in an oil bath, and the reaction proceeded at this temperature for 4 h. Nitrogen gas passed continuously through the reactor during reaction to protect the reaction system and to drive out the byproduct NH\textsubscript{3}. The resultant mixture was cooled to room temperature, filtered to remove solid material (powdered catalyst in the MASR or catalyst powder peeled off from the monolithic catalysts in the MSR), and then analyzed by gas chromatography equipped with a FID detector and a packed column filled with organic support 402. The yield of PC was calculated as follows:

\[
\text{yield (\%)} = \frac{\text{moles of PC produced}}{\text{moles of urea in feed}} \times 100
\]

\[
= \frac{\text{weight of reaction liquid obtained} \times \text{weight percent of PC}}{\text{molecular weight of PC} \times \text{moles of urea in feed}} \times 100
\]

2.3. Process Optimization in the Monolithic Stirrer Reactor. In the urea alcoholysis for the PC synthesis, there are many process factors which have possible effects on the yield of PC, e.g., molar ratio of PG to urea, reaction temperature, reaction time, amount of active phase, stirrer speed, monolith
cell density, and monolith length. In this study, the PG/urea molar ratio was fixed at 1.5:1 and the other factors were selected as controllable factors to optimize the synthetic process to improve the yield of PC. For this purpose, monolithic catalysts with different active phase loadings, different cell densities, and different lengths were prepared, and urea alcoholysis experiments were performed at different reaction temperatures, different reaction times, and different stirrer speeds. The detailed catalyst preparation and PC synthetic process were similar to those mentioned above.

3. RESULTS AND DISCUSSION

3.1. Comparisons among Catalysts and between Reactors. Figures 3 and 4 show the urea alcoholysis performances of various metal oxides and mixed-metal oxides in the two reactors. To confirm their catalytic activities, several blank tests were previously carried out under the same conditions and the results are presented in Figure 5. The MARS test with powdered γ-alumina, MSR test with bare cordierite monolith, and MSR test with cordierite monolith coated with γ-alumina give approximately equal yields of PC. They are all close to the result of the MARS blank test without catalyst, revealing that the cordierite substrate, γ-alumina washcoat, and powdered γ-alumina have no marked catalytic activity in the urea alcoholysis. Nevertheless, comparing Figures 3 and 4 with Figure 5, it is clear that all the metal oxides and mixed-metal oxides examined are active in the PC synthesis.

As can be seen from Figure 3, there is the same catalytic activity order of the metal oxides between the MARS and MSR. Irrespective of reactor type, lead oxide leads to the highest yield of PC, followed by magnesium oxide and then zinc oxide. However, for the mixed-metal oxides, an abnormal sample is given in Figure 4. The activity of magnesium−lead mixed oxide ranks second to last in the MARS, whereas its activity ranks second in the MSR. Except this sample, the mixed-metal oxides also give the same catalytic activity order in the two reactors. For example, zinc−lead mixed oxide leads to the highest yield of PC, followed by zinc−chromium mixed oxide.

Furthermore, the mixed-metal oxides all give much higher yields of PC than the metal oxides, irrespective of reactor type, which provides support for the existence of a strong synergetic effect in the mixed-metal oxides. For monolithic catalysts, catalytically active phase is loaded inside monolith channels and its contact with reaction mixture may be inadequate under the experimental conditions used. It results in a poor mass transfer in the MSR; therefore, for any oxide, the MSR always gives lower yields of PC than the MARS.

It should be mentioned that, among all the oxides examined, only three lead-containing oxides, i.e., lead oxide, zinc−lead mixed oxide, and magnesium−lead mixed oxide, were found to be remarkably peeled off from their respective monolithic substrates in the MSR. It is probably due to the large bulk density of lead which results in poor adhesion strengths of these oxides on their monolithic structures. The spalling of catalyst powder increases mass transfer and hence improves the PC yield, which is the cause of the MSR activity abnormality of magnesium−lead mixed oxide.

In this study, only the reaction temperature of 170 °C was used to compare catalysts and reactors. If the temperature

Figure 3. Catalytic activities of the metal oxides.

Figure 4. Catalytic activities of the mixed-metal oxides.

Figure 5. Blank experiments.
changes, the catalytic activity orders in Figures 3 and 4 could be different since different catalysts have different activation energies and therefore selectivity ratios vary with temperature. As discussed below, 170 °C is, however, close to the optimum reaction temperature, and much higher or lower temperatures are not suitable for the urea alcoholysis reaction. Therefore, it has actual meanings to compare the catalytic activities at the selected temperature of 170 °C.

3.2. Optimization of the PC Synthetic Process. As shown above, zinc–chromium mixed oxide not only shows a good catalytic performance but also has extremely strong adhesion strength on the monolithic substrate. It was therefore used to prepare monolithic catalysts to optimize the PC synthetic process in the MSR.

3.2.1. Influence of the Reaction Temperature. Four trials were performed to examine the effect of the MSR reaction temperature on the yield of PC, and the results are shown in Figure 6. In each trial, two monolithic catalysts are used and their mean composition is plotted. It can be seen that the catalysts used in different trials have approximately equal loadings of γ-alumina and zinc–chromium mixed oxide, though they were not prepared in a batch.

The PC yield increases with the elevation of the reaction temperature. When the temperature is 180 °C, the yield of PC reaches its maximum value of 71.1%. Thermodynamic analysis reveals that the urea alcoholysis is endothermic, and the increase in temperature promotes the synthesis of PC. 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, which proceeds predominantly. Therefore, a 6 h reaction is optimum for the MSR PC synthesis.

3.2.2. Influence of the Reaction Time. Figure 7 indicates that, after a 6 h reaction, the yield of PC reaches its maximum value of 95.0% and then the PC yield gradually decreases with further prolonging of the reaction time. One of the possible reasons is that, after a 6 h reaction, the PC concentration becomes comparatively high in the reactor and side reactions such as the polymerization of PC will proceed predominantly.

3.2.3. Influence of the Amount of Active Phase. As shown in Figure 8, the PC yield increases significantly at first with the increase of the amount of zinc–chromium mixed oxide. When the mixed oxide amount is about 0.21 g/monolith, the PC yield reaches its maximum value of 95.0%. The increasing of the mixed oxide loading gives much more catalytically active sites and hence leads to the improvement of the urea alcoholysis performance. However, when it is increased to about 0.30 g/monolith, the PC yield begins to decline slightly.
Figure 9 indicates that the yield of PC increases at first, reaches its maximum value at 300 rpm, and then decreases with increasing stirrer speed. Within the range of the low stirrer speeds, an increase in the stirrer speed results in an increasing liquid flow through monolith channels, which improves the mass transfer and hence increases the catalytic activity. However, if the stirrer speed is excessively fast, the whirlpool comes forth, and less reaction liquid flows through monolith channels. Therefore, a moderate stirrer speed, 300 rpm, is desired to increase the urea alcoholysis activity.

3.2.5. Influence of the Monolith Cell Density. In Figure 10, the urea alcoholysis performances of the monolithic catalysts with different cell densities are presented. These catalysts were prepared by dipping in the same alumina sol and then impregnating in the same mixed nitrate solution; however, their loadings of washcoat and active phase are different. As the monolith cell density is increased from 300 to 400 cpsi, the washcoat and active phase loadings increase, which arises from the increasing surface area of the monolith channel walls. Nevertheless, further increase in the cell density probably leads to the monolith channels becoming inaccessible to alumina sol and impregnating solution due to a great, small open frontal area. The 600 cpsi catalysts, therefore, have lower washcoat and active phase loadings than the 400 cpsi catalysts.

It is also seen that the changing of the yield of PC has the same behavior as the changing of the active phase loading. When the cell density is increased from 400 to 600 cpsi, the decrease in the yield of PC is larger than the decrease in the active phase loading. Furthermore, the washing of active phase loading coming forth, and less reaction liquid flows through monolith channels, which improves the mass transfer and hence increases the catalytic activity. However, if the stirrer speed is excessively fast, the whirlpool comes forth, and less reaction liquid flows through monolith channels. Therefore, a moderate stirrer speed, 300 rpm, is desired to increase the urea alcoholysis activity.

3.2.6. Influence of the Length of the Monolithic Structures. Figure 11 shows that the washcoat and active phase loadings always increase with increasing monolith length and that the yield of PC increases at first, reaches its maximum value of 94.8%, which is fairly close to the result of trial 6. As a repeated test, trial 12 gives the PC yield of 94.8%, which is fairly close to the result of trial 6, though they have a little difference in the loading of catalytically active phase.

Figure 9. Influence of the stirrer speed on the yield of PC (Monolithic catalysts: Φ16 × 24 mm; Reaction conditions: 0.4 mol of urea and 0.6 mol of PG, reaction temperature of 180 °C, reaction time of 6 h.)

Figure 10. Influence of the monolith cell density on the yield of PC (Monolithic catalysts: Φ16 × 24 mm; Reaction conditions: 0.4 mol of urea and 0.6 mol of PG, reaction temperature of 180 °C, reaction time of 6 h, stirrer speed of 300 rpm).
97.8% at the monolith length of 20 mm, and then decreases with increasing monolith length.

Several aspects should be taken into consideration to examine the effect of the monolith length on the MSR reaction performance. Clearly, the increasing amount of active phase with increasing the monolith length improves the MSR reaction performance. However, as mentioned above, the increasing amount of active phase also leads to a longer side reaction time and hence to a lower observed activity due to the interaction between the amount of active phase and the reaction time. In addition, with the increase of the length of the monolithic structures, a significant entrance effect appears which limits mass transfer and hence reduces the MSR reaction performance. In the MSR, reaction liquid enters into monolith channels with an angle, $\phi$, as shown in Figure 12. In the case of short monoliths, the inlet angle is close to a right angle and the liquid flows easily through monolith channels. As the monolith length increases, the inlet angle increases. That is to say, the entrance of reaction liquid into monolith channels becomes difficult and the mass transfer limitation gets prominent. Therefore, a moderate monolith length is beneficial to the improvement of the MSR reaction performance.

It is shown that a single-factor-at-a-time method was used in this work for doing experiments to analyze the effect of the process factors. For the monolith-supported zinc–chromium mixed oxide catalyst, the optimum MSR reaction conditions are obtained as follows: the reaction temperature at 180 °C, the reaction time at 6 h, the amount of active phase at 0.21 g/monolith, the stirrer speed at 300 rpm, the monolith cell density at 400 cpsi, and the monolith length at 20 mm, resulting in a PC yield of 97.8%. It should be pointed out that these optimum results are perhaps tentative, because the single-factor-at-a-time method is unable to detect the presence of the interaction and combined effect of factors. For instance, the lower observed activity of the monolithic catalysts with larger amount of active phase, shown in Figure 8, probably indicates a strong interaction effect between the amount of active phase and the reaction time, resulting from the existence of side reactions such as the polymerization of PC. This interaction leads to different optimum reaction times required for different loadings of active phase, which is, however, completely ignored in the single-factor-at-a-time method. Furthermore, there is a probable interaction between the monolith length and the monolith cell density. For different monolith lengths, the optimum monolith cell densities could be different due to variation of significance of the monolith entrance effect. Therefore, a precise optimization should be carried out by studying all the factors collectively by, for example, statistical experimental designs such as response surface methodology. Despite all this, a satisfactory PC yield has been reached using the rough single-factor-at-a-time optimization method, and there is enough support for the applicability of the MSR to the alcoholysis of urea.

It is also worth mentioning that, in previous studies, the PC synthesis was mainly carried out under reduced pressures at large molar ratios of PG to urea, e.g., 4:1 and 5:1. The reduced pressure leads 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. A greater excess of PG increases the yield of PC but also leads to trouble for the product separation process and is therefore not expected in industry. Nevertheless, in this study, the alcoholysis of urea proceeds in the MASR and MSR reactors at atmospheric pressure at a very low PG/urea ratio of 1.5:1, which provides a great convenience for actual industrial production.

Figure 11. Influence of the monolith length on the yield of PC (Monolithic catalysts: Φ16 mm, 400 cpsi; Reaction conditions: 0.4 mol of urea and 0.6 mol of PG, reaction temperature of 180 °C, reaction time of 6 h, stirrer speed of 300 rpm).

Figure 12. Schematic drawing of the entrance effect.
4. CONCLUSIONS

It has been shown that all the metal oxides and mixed-metal oxides examined are active in the alcoholsysis of urea to PC and that their catalytic activity order does not vary with reactor type. Irrespective of reactor type, the mixed-metal oxides give much higher urea alcoholysis performance than the metal oxides, providing support for the existence of a strong synergistic effect in the mixed-metal oxides. It is also found that the lead-containing oxides are easily peeled off from the monolithic substrates, while the zinc–chromium mixed oxide not only shows an excellent catalytic performance but also has extremely strong adhesion strength on the monolithic substrate. Furthermore, the MSR process optimization indicates that the MSR performance increases with increasing reaction temperature and that moderate-level reaction time, amount of active phase, stirrer speed, monolith cell density, and monolith length prove to be beneficial to the performance of the MSR. For the monolith-supported zinc–chromium mixed oxide catalyst, the MSR performs very well and the highest yield of PC reaches 97.8%. From this case study, it is revealed that the MSR can be an attractive alternative to the MASR for heterogeneously catalyzed liquid–liquid reactions, e.g., the alcoholsysis of urea to PC.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: dfwu@seu.edu.cn.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from the National Natural Science Foundation of China, under Grant No. 21176048, is gratefully acknowledged.

■ REFERENCES