

Synthetic Methods of Propylene Carbonate and Research Progress

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Abstract:

Polyurethane is an important polymer material, but its raw material, isocyanate, is toxic, which caused the inconvenience for the production and transportation, in order to solve the problem of toxic material, a green synthetic method of non-isocyanurate polyurethane (NIPU) can be developed and research on no-toxic isocyanate as raw material is the new direction of polyurethane in recent years. Because the propylene carbonate is an important raw material for the synthesis of non-isocyanate polyurethanes, therefore, in this article, several synthetic methods of propylene carbonate were described, the advantages and disadvantages of these synthetic methods for propylene carbonate were compared, and the future development was looked forward.

Keyword: Propylene Carbonate; Synthetic Methods; Advantages and Disadvantages; Look Forward

1. Introduction

Polyurethanes, which contain urethane groups (NH-COO-) in the macromolecular backbone, are called polyurethanes. Polyurethane was first invented by the German chemist O. Bayer in 1937 and was formulated with flexibility. Polyurethanes are divided into polyester polyurethanes and polyether polyurethanes. Polyurethane has many excellent properties and has a wide range of uses. Polyester polyurethanes are prepared from diisocyanate and hydroxyl-terminated polyester and polyether polyurethanes are prepared from diisocyanates and hydroxyl-terminated polyethers.

Isocyanates are a colorless and clear liquid that is highly irritant and are susceptible to corrosion except for stainless steel, nickel, glass, and ceramics. It will be flamed to expose to heat, fire, and oxidants, when Isocyanates enter in the human body in a concentration of more than 50g/cm³, can cause skin edema and tissue necrosis, it also causes chemical pneumonitis and pulmonary edema.

With the attention of environmental protection in the world, the traditional polyurethane production process of using isocyanate as raw material is increasingly replaced by nonisocyanate polyurethane production process. One of the important raw materials for the production of non-isocyanate polyurethanes (Fig.1.1) is the cyclic carbonates.

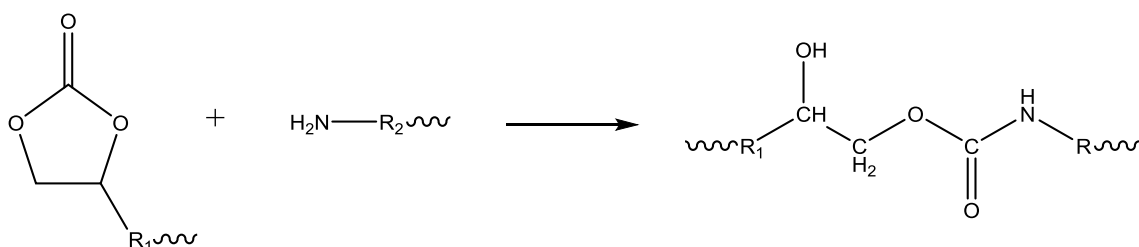


Fig1.1

Five-membered cyclic carbonate synthesis of non-isocyanate polyurethane

Cyclic carbonates include five-membered rings, six-membered rings, seven-membered ring carbonates, and seven-membered rings or more of macrocyclic carbonates. Cyclic carbonates are a very important class of

compounds that can be widely used as polar aprotic solvents, intermediates for organic synthesis and precursors for polymers and so on. Specific applications include organic synthesis, battery electrolyte, and supercritical fluid separation technology.

Early industrial production of propylene carbonate was synthesized by reacting phosgene with 1,2-propanediol (Fig. 1.2). As phosgene is a highly toxic substance, it can cause harm to people and the ecological environment; hydrogen chloride gas is generated during the synthesis process, which reduces the atom economy of the synthesis process, and hydrogen chloride gas can erode the production equipment after it dissolves in water, which increases equipment maintenance costs and security risks in the production process. Therefore, the modern industry no longer uses phosgene to produce propylene carbonate.

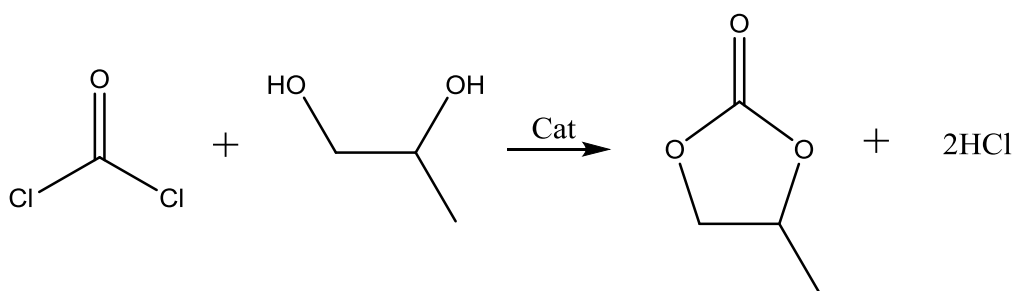


Fig. 1.2 Preparation of Propylene Carbonate by Reaction of Phosgene with 1,2-Propanediol

In this article, the research progress of the synthesis of propylene carbonate was summarized, the advantages and disadvantages of various synthesis methods for propylene carbonate were compared, and the future development was looked forward.

2. Synthetic methods of propylene carbonate

The synthetic methods of propylene carbonate mainly include ester exchange method, carbon dioxide synthesis method and urea alcoholysis method. The examples of each method were as follows.

2.1 Ester exchange method

Ester exchange method is a reaction of propylene glycol and dimethyl carbonate (Fig. 2.1).

Hu Bin et al. used diethyl carbonate and diols for transesterification under the catalysis of trace strong base and dibutyl tin dilaurate (DBTL), and the products were prepolymerized and depolymerized at the high temperature in the same reaction system.¹ The corresponding cyclic carbonate is obtained, and after recrystallization, a high-purity polymerization grade cyclic carbonate monomer can be obtained with a yield of more than 75%. The one-pot synthetic process can greatly increase the monomer yield and shorten the reaction time, but the raw materials are relatively expensive, and the organic tin catalyst is more toxic.

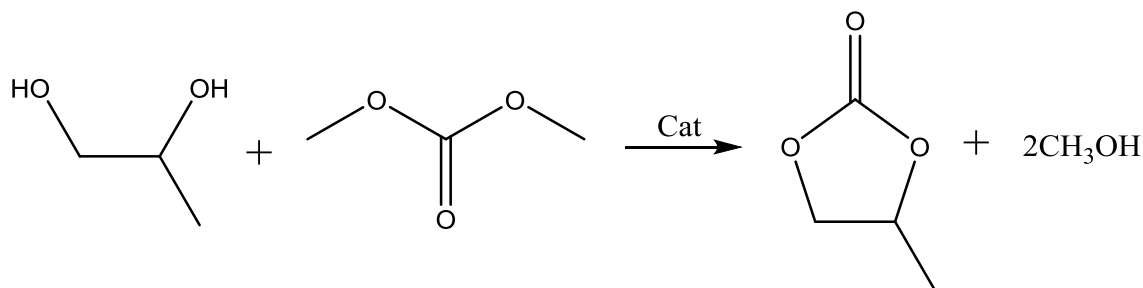


Fig. 2.1 Preparation of propylene carbonate by transesterification

2.2 Preparation of propylene carbonate from carbon dioxide

Since the birth of the industrial society, mankind has used fossil fuels in large quantities, and the emission of carbon dioxide gas has increased rapidly, which cause the problem of the greenhouse effect to become seriously increasing. Carbon dioxide can be used as a carbon source for chemical production, though a large amount of carbon dioxide may cause greenhouse effect. Using carbon dioxide to produce propylene carbonate is a typical example.

2.2.1 Reaction of Carbon Dioxide and Ethylene Oxide

Ethylene oxide, as a three-membered cyclic ether, has a large ring tension between carbon and oxygen bonds and is susceptible to the nucleophilic attack of CO_2 to produce a cyclocarbonate by a cycloaddition reaction. So far, the reaction of ethylene oxide with CO_2 is the most important method for industrial production of ethylene carbonate. Ethylene oxide and carbon dioxide addition reaction is to produce ethylene carbonate as an exothermic, volume reduction reaction, from the thermodynamic point of view, low temperature, high pressure conditions are conducive to the reaction, and from a dynamic point of view, the improvement of the reaction temperature is conducive to the activation of the reactants speeds and can speed up the reaction rate. Comprehensively elaborated, the selection of the right catalyst is the key of the success of the reaction.

The reaction of carbon dioxide with propylene oxide to synthesize propylene carbonate (Fig. 2.2) is the most common method for industrial synthesis of propylene carbonate.

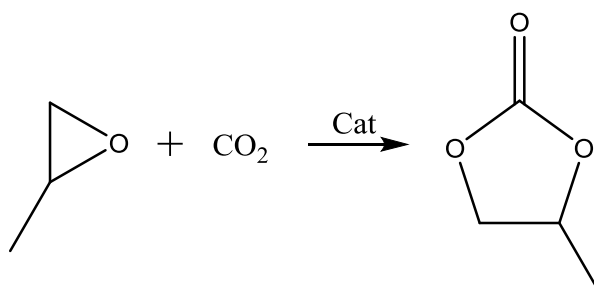


Fig. 2.2 Preparation of Propylene Carbonate from Dimethyl Propylene Oxide and Carbon Dioxide

Hyeon-Gook Kim et al. designed a multifunctional metallo- or halide-free alkanolamine to be a catalyst for the synthesis of propylene carbonate (PC) by the cycloaddition reaction of CO_2 and propylene oxide (PO).² Among the polyfunctional alkanolamine catalysts, bis(methylpiperazinyl)triol showed good performance, using 1 mol%

of catalyst at 120°C and 10 bar, the PO yield was 96% in 3 hours, under mild conditions (5 bar and 100 °C), a PO yield of 90% can be obtained in 8 hours using 5.6 mol% catalyst, and the reaction mechanism in this paper shows that CO₂ is activated by the nucleophilic attack on the carbon cation center of the PO molecule by the oxygen atom of CO₂. Catalysts that do not contain metals and halides at the same time will promote the environmental protection process for the application of other carbonates.

Dong-Hui Lan et al. used graphene oxide (GO) as a catalyst and tetrabutylammonium bromide (Bu₄NBr) as a cocatalyst under relatively mild conditions (100 °C, 2.25 MPa, 1 h).³ Propylene oxide (PO) was quickly converted to PC with a yield of 96% and selectivity of 100%. The effects of catalyst dosage, temperature, time and the amount of water (H₂O) added on the reaction were studied. The presence of a suitable amount of H₂O was found to significantly enhance the conversion of epoxides. Comparison of the catalytic activity of some reduced graphene oxide (r-GO) samples under similar reaction conditions revealed that the hydroxyl groups on the GO (instead of the carboxyl groups) formed hydrogen bonds with PO and promoted cycloaddition with halide anions reaction. This catalyst is a non-metal catalyst. In the catalytic reaction, no solvent is added that result in a reduction in cost.

With the help of Bu₄NBr, GO showed excellent catalytic performance in the cycloaddition reaction of CO₂ with PO under relatively mild conditions. The PC yield reached 96% within one hour at 100 °C and 2.25 MPa, and the PC selectivity reached 100%. Moreover, the catalytic system exhibits high catalytic activity for cycloaddition reaction at the atmospheric pressure and room temperature. The synergistic interaction between hydroxyl and halide anions on GO has a significant effect on the reaction. Hydroxyl promotes cycloaddition by forming hydrogen bonds with PO, and the addition of an appropriate amount of H₂O in the reaction system shows a positive effect on the catalytic performance. GO is a catalyst for the addition reaction of cheap, recyclable, water-resistant and environment friendly.

Wang et al. found that the cycloaddition reaction of carbon dioxide and propylene oxide with cesium chloride, bipyrazineamine, and tetrabutylammonium bromide (TBAB) was reacted at a pressure of 1.5 MPa and a temperature of 100°C.⁴ After 1 h, the yield of propylene carbonate was as high as 95%. However, when the catalyst system did not contain tetrabutylammonium bromide, no product was obtained. When only tetrabutylammonium bromide was used, or no reduced metal was added, the yield was very low. Studies on catalysts of the same composition have found that when the ligands are the same, the smaller the radius of the metal ions, the higher the yield; for the same metal chloride, the bipyrazine amine forms a complex with the highest catalytic system yield, which may be related to the alkalinity of the ligand.

Liu Bo used zinc iodide and guanidine hydrochloride as two-component multiple catalysts to react at 100°C and 1 MPa carbon dioxide pressure, after 1.5 h, the yield of propylene carbonate is 94% and selectivity is 99%.⁵

The difference of the halogen elements in the zinc halide also has a greater effect on the yield. The order of influence is ZnI₂>ZnBr₂>ZnCl₂ on the yield of propylene carbonate. The reason is that I⁻ has the offensive ability as the offensive agent.

The reaction mechanism of the catalyst is that H on guanidine hydrochloride is connected to O on propylene oxide by intermolecular hydrogen bonding, and at the same time, the C-O bond is polarized, and Zn can form Zn-O with O among propylene oxide. What play a catalytic role on the open loop of propylene oxide. The primary amines in the guanidine hydrochloride activate carbon dioxide to form carbamate, which promotes the cycloaddition reaction.

The catalyst has defects in the recycling process. In the second cycle, the yield of propylene carbonate drops below 80%. After the second fresh catalyst of additional 20%, the yield rises to 90% again. The reason for the analysis may be the loss of catalyst during the washing process.

In addition, the authors produced Zn/SBA-15 by one-pot method and produced NH₃-Zn/SBA-15 by amination of Zn/SBA-15. In the experimental process, the yield was less than 10% without doping Zn. After doping Zn, the yield reached more than 80% under the same reaction conditions. When the amount of Zn continued to increase, the yield was reduced. This phenomenon is due to the fact that when the amount of metal increases, the number of amino groups will be reduced, which affect the synergy between the two and result in reduced yield.

By changing the experimental parameters and comparing the obtained data, the optimal experimental conditions are 130°C, 1.3 MPa carbon dioxide pressure, reaction time 12 h, the yield of propylene carbonate reaches 93%, and the selectivity also reaches 99%; In the cycle experiment, the propylene carbonate yield remained above 80% after three experiments, and the selectivity did not change.

2.2.2 Carbon Dioxide and Diol Reaction

Since biomass materials such as glycerol, sorbitol, and cellulose can be obtained by hydrogenolysis reaction to obtain diols, the use of CO₂ and glycols to produce cyclocarbonates (Fig. 2.3) has a good prospect. However, the reactivity of CO₂ with hydroxyl groups is low, and a certain amount of catalyst needs to be added during the reaction.

Huang Shiyong et al. studied the catalytic performance of different metal halides for the synthesis of propylene carbonate (PC) by reacting CO₂ with 1,2-propanediol (PG) in an acetonitrile system and determined the optimal conditions for the reaction.⁹ The side reactions during the reaction were discussed and the by-products generated were analyzed. The experimental results showed that the activity of FeCl₃ catalyst was the highest when CO₂ was reacted with PG to synthesize PC. Based on 100 mmol PG, the optimum conditions were as follows: acetonitrile 10 mL, FeCl₃ catalyst 2.5 mmol, reaction pressure 10 MPa, reaction temperature 160 °C, and reaction time 15 h. The PC yield was 26.5% and the PG conversion was 42.5%. Acetonitrile not only acts as a solvent in the reaction system but also acts as a dehydrating agent. It removes some of the water generated during the reaction, break the original thermodynamic equilibrium, and greatly improve the PC yield.

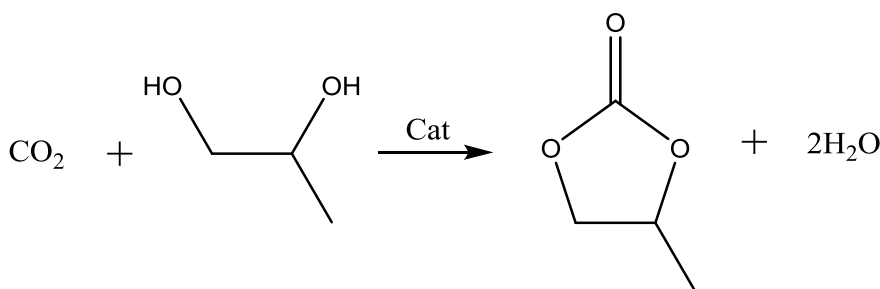


Fig. 2.3 Reaction of carbon dioxide and 1,2-propanediol to prepare propylene carbonate

2.3 Urea alcoholysis

Although the carbon dioxide synthetic method is widely used in the industry of propylene carbonate, the

carbon dioxide synthetic method requires the use of high temperature and high pressure, and there is a risk that the equipment investment is large and the production process is prone to explosion. Therefore, in recent years, due to the fact that using urea and 1,2-propanediol to produce propylene carbonate (Fig. 2.4) has the features of easy availability of raw materials, mild reaction conditions, high conversion and high yield, it has raised increasing attention.

Zhang Bin et al. studied magnetic composite particles $\text{SiO}_2/\text{Fe}_3\text{O}_4$ as carrier, and prepared magnetic magnesium oxide catalysts by impregnation method.¹⁰ The catalysts were characterized by IR and XDR. Catalysts for the synthesis of urea and 1,2-propanediol were studied. With magnesium nitrate as the precursor and the loading (mass fraction) of 25%, the catalyst prepared by calcining at 600°C had good catalytic activity. By analyzing the experimental results, the optimal reaction conditions were obtained: catalyst mass fraction (total mass of reactants) 1.0%, n(PG): n(urea)=2:1, reaction time 3 h, reaction temperature 180°C . Under this reaction condition, the highest yield of PC reached 89.49%. The reaction is a heterogeneous catalytic system. Due to the magnetic properties of the catalyst, the separation of the catalyst and the product can be conveniently achieved in a magnetic environment.

Du Weichao et al. carried out calcination activation of basic zinc carbonate under different conditions to obtain activated basic zinc carbonate (AZCH) catalyst, which was used in the synthesis of urea and 1,2-propanediol (PG) propylene carbonate (PC). The reaction; the effect of activation conditions on the activity of the catalyst was examined and the reaction conditions for the synthesis of PC were optimized.¹¹ The experimental results show that the activated AZCH catalyst has the highest activity at the calcination temperature of 220°C and the calcination time of 2 h. The optimized reaction conditions are: reaction temperature 170°C , reaction time 2 h, n (PG): n (urea) = 2.50, catalyst the amount used was 1.00% of the amount of the raw material and the degree of vacuum was 0.04 MPa. Under this condition, the PC yield reached 94.5%. XRD results showed that ZnO and $\text{Zn}_4\text{CO}_3(\text{OH})_6\cdot\text{H}_2\text{O}$ phases existed in the AZCH catalyst, and ZnO was the main active component. The synergy between the two phases promoted the activity of the catalyst.

Du Zhiping produced $\text{MnO}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst by ultrasonic impregnation method and modified it with alkali and salt.¹² Through using of different experimental schemes, the optimal reaction conditions for the production of the catalyst were identified as NaOH with 10% MnO_2 in the catalyst and modified $\text{MnO}_2/\gamma\text{-Al}_2\text{O}_3$ after calcination at 400°C for 2 hours. In the experiment, the author compared the blank, carrier $\gamma\text{-Al}_2\text{O}_3$, $\text{MnO}_2/\gamma\text{-Al}_2\text{O}_3$, and $\text{MnO}_2/\gamma\text{-Al}_2\text{O}_3$ modified by alkali (NaOH, LiOH, KOH), and concluded that the catalyst was alkali-modified. The catalytic activity is generally higher than that of the unmodified catalyst, but the stronger the basicity of the alkali is, the more favorable the reaction is. The catalytic performances of the three alkali-modified catalysts were as follows: $\text{NaOH} > \text{LiOH} > \text{KOH}$. At the same time, the catalytic performance of three different NaOH-modified $\text{MnO}_2/\gamma\text{-Al}_2\text{O}_3$ catalysts was found to be 10%. When the catalyst performance was better than 8% and 12%, these indicate that the strong alkali of $\text{MnO}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst is the active center of the catalyst instead of strong alkali.

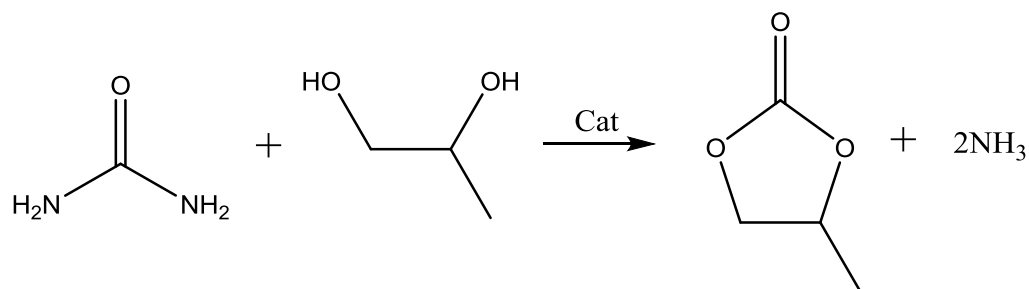


Fig. 2.4 Preparation of Propylene Carbonate by Reaction of Urea with 1,2-Propanediol

In summary, the advantages and disadvantages of above-mentioned synthetic method were listed in Table 3.1, which can be as a choice of synthetic processes.

Table 3.1 Advantages and disadvantages of synthetic processes

Reaction method	Transesterification	CO ₂ and epoxides	CO ₂ and 1,2-propanediol	Urea alcoholysis
Advantages	Simple operation, high monomer yield, short reaction time	Raw materials are cheap and easy to obtain, high atomic utilization, fewer byproducts, and less environmental pollution during production, and are widely used in large-scale industrial production.	The raw materials are cheap and easy to obtain, and the properties are stable. In the reaction process, suitable catalysts for the latex can obtain higher yields.	It is an environmentally friendly green chemical process. Raw materials are cheap and easy to obtain. At the same time, ammonia gas is produced at the same time, which has good economic benefits.
disadvantages	Low catalyst activity and selectivity	The reaction needs to be carried out under high temperature and high pressure, the equipment investment is large, and safety accidents are prone to occur	Still in the laboratory research and development stage, there is no effective catalytic system and chemical process that can promote real	Homogeneous catalyst separation is complex and recovery is difficult. The activity, selectivity and cost of the catalyst cannot meet the

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3. Summary and Outlook

In this article, several synthetic methods of propylene carbonate were described, the advantages and disadvantages of these synthetic methods for propylene carbonate were compared. In the current, because of shortage of resources and energy, the conversion of abundant and cheap carbon dioxide into high-value-added chemicals to achieve the resource utilization of carbon dioxide has not only alleviated the environmental problems caused by the greenhouse effect, but also created economic benefits. Through carbon dioxide produce propylene carbonate is an important approach to the chemical use of carbon dioxide and is becoming a new research hotspot in the fields of green chemistry and catalytic chemistry.

Based on the above research status, it is believed that the main directions for further research in this field in the future are as follows: 1). Efforts should be made to solve the problem of carbon dioxide activation, and to research and develop catalysts with targeted activation of carbon dioxide. 2). Carbon dioxide is required to have a high mass fraction of reactants, which is greater than 99%. However, the mass fraction of carbon dioxide in the air is far from attainable. Therefore, if it is possible to develop a catalyst that has high adsorption and catalytic double-effect functions for carbon dioxide, it is hopeful to solve the problem which is Direct use of carbon dioxide in exhaust gases. 3). The recovery and recycling of catalysts are also attractive research topics.

References

1. Hu Bin, Zhuo Renxi, Fan Changlie. Study on a new synthetic method for cyclic carbonates[J]. *Chemical Reagents*,1998(6):355-356.
2. Kim H G, Lim C S, Kim D W, et al. Multifunctional alkanolamine as a catalyst for CO₂ and propylene oxide cycloaddition[J]. *Molecular Catalysis*, 2017, 438:121-129.
3. Lan D H, Yang F M, Luo S L, et al. Water-tolerant graphene oxide as a high-efficiency catalyst for the synthesis of propylene carbonate from propylene oxide and carbon dioxide[J]. *Carbon*, 2014, 73(7):351-360.
4. Wang W, Wu Y, Duan Y, et al. An Efficient Catalyst System at Mild Reaction Conditions Containing Rare Earth Metal Complexes[J]. *Journal of the Chinese Chemical Society*, 2013, 60(12):1463-1466.
5. Liu Bo. Fixation of CO₂ Into Cyclic Carbonates Catalyzed by Zn-Based Heterogeneous Catalysts[D]. Harbin Institute of Technology,2015.
6. Bai Dong, Zhang Xuelan, Wu Jin, et al. Synthesis of propylene carbonate from urea and 1, 2-propylene glycerol over zinc salts[J]. *Chemical Engineering (CHINA)*,2015,43(2):63-67.
7. Zhang Tiantian, Yang Jinhai, Li Lei, et al. Synthesis of Propylene Carbonate over Zinc Base Catalysts [J]. *Fine Chemicals*,2015,32(3):0-0.

8. Ding Ming, Zhao Ningyu, Zhu Weiguang, et al. Synthesis of Propylene Carbonate from Urea and 1, 2-Propylene Glycol over Zinc Perchlorate Hexahydrate Catalysts[J]. *Fine Chemicals*,2014,31(9):1169-1172.
9. Huang Shiyong, Ma Jun, Zhao Ning, et al. Synthesis of Propylene Carbonate from Carbon Dioxide and 1, 2-Propylene Glycol with Ferric Chloride Catalyst [J]. *Petrochemical Technology*, 2007, 36(3):248-251.
10. Zhang Bin, Chen Xiaoya, Luo Congying, et al. Synthesis of propylene carbonate from urea and 1, 2-propylene glycol over magnetic magnesium oxide catalysts[J]. *Modern Chemical Industry*,2017,37(7):91-95.
11. Du Weichao, Fang Meiqin, Shen Lingyun, et al. Synthesis of Propylene Carbonate from Urea and 1, 2-Propylene Glycol over Activated Basic Zinc Carbonate Catalyst[J]. *Petrochemical Technology*,2012,41(1):37-40.
12. Du Zhiping, Lin Zhikun, Chen Fangsheng, et al. Synthesis of propylene carbonate from urea and 1,2-propylene glycol over MnO₂/γ-Al₂O₃ catalyst modified by NaOH [J]. *CIESC Journal*,2014,65(11):4333-4339.