

Synthesis of dimethyl carbonate from urea and methanol using polyphosphoric acid as catalyst

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Abstract

A new process was proposed for the synthesis of dimethyl carbonate (DMC) from urea and methanol in a batch operation. Polyphosphoric acid (PPA) was used as the catalyst and the absorbent for the ammonia, which was produced during the reaction. The effects of various operation conditions, such as reaction temperature, pressure, reaction time and the molar ratio of the reactants were investigated in the terms of DMC yield. The experimental results indicated that the optimal reaction conditions were the molar ratio of methanol/urea of 14, reaction time of 4 h, reaction temperature of 413 K, PPA/urea mass ratio of 1 and initial pressure of CO₂ of 0.8 MPa, respectively. The DMC yield of 67.4% was obtained in the optimal reaction conditions. The by-product, ammonia was also used as a starting material of a useful fertilizer in the proposed process.

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Keywords: Dimethyl carbonate; PPA; Catalyst; Urea; Methanol

1. Introduction

Dimethyl carbonate (DMC) has been considered as a green chemical raw material of the 21st century and registered as an innocuous chemical in Europe [1,2]. Since DMC contains several active basic groups like CH₃–, CH₃O–, CH₃O–CO–, –CO– groups, it shows excellent reaction activity in carbonylation, carbomethoxylation and methylation, replacing toxic phosgene, dimethyl sulfate, etc. DMC represents a viable alternative to acetate esters and ketones in most applications, from paints to adhesives, taking advantage of its good solvency power. In addition, it can also be used as a fuel additive for the enhancement of the octane number [3–8]. Nowadays, DMC has become a new basic material in the organic synthesis field.

The DMC synthesis techniques reported mainly consist of phosgenation of methanol, oxidative carbonylation of methanol and transesterification of ethylene carbonate with methanol [9–11]. Each of the aforementioned processes

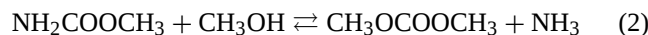
has either commercial or technical disadvantages, which make it desirable in the industry to develop a new process which avoids such setbacks. For example, the phosgenation is a complicated and expensive process, and phosgene is extremely toxic. Oxidative carbonylation of methanol suffers from the low production rate, high cost for the separation of ternary azeotrope, methanol–water–DMC, and the need for corrosion resistant reactors. Transesterification of ethylene carbonate with methanol is operationally and economically unfavorable since the production of DMC is always accompanied by the simultaneous production of a great deal of glycol.

Along with the global spread of sustainable development strategy, the chemical synthesis processes and materials endangering human being and environment would be gradually restricted. The ‘clean production process’ and ‘green chemicals’ will be the developmental direction for modern chemical industry.

The alcoholysis of urea for producing DMC is a new process developed recently. This process uses urea and methanol, which have abundant resources and are low-priced, as raw materials, facilitated by catalysts. As there is no water formed during this process, the ternary azeotrope,

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methanol–water–DMC, is not formed, the subsequent separation and purification of DMC thus being simplified. If ammonia, the only by-product, is connected with the urea production line, it is subjected to the duty cycle operation. Therefore, this process is environment-friendly. DMC can be synthesized in a two-step reaction from urea and methanol via a methyl carbamate (MC) intermediate [12–15]:



Even this process is an interesting route, the reports about this process are relatively less. The most active catalysts reported in the prior literatures are organotin derivatives and metal oxides. However, there exist some problems such as low DMC yield and slow rate of the reaction according to the results reported by the authors and other researchers [16–22]. Moreover, the DMC product contains a small amount of ammonia, which is difficult to get rid of unless it is further handled. Therefore, DMC of high quality cannot be obtained when these catalysts were used.

This paper presents a new process for the synthesis of DMC from urea and methanol. Here, polyphosphoric acid (PPA) is used as the catalyst and the ammonia absorbent. PPA can react with ammonia produced during the reaction to give ammonium polyphosphate, which is a valuable and very useful fertilizer. Moreover, ammonium polyphosphate is nearly insoluble in methanol or DMC and thus can be easily separated from reaction mixture by a simple filtration step. The proposed method will have higher atomic economy of reaction and a paragenesis process will be realized.

2. Experimental

2.1. Materials

Methanol, urea, *p*-dimethylaminobenzaldehyde (PDAB), *N*-methylurea (*N*-MUrea) and *N*-methyl carbamate (*N*-MMC) were purchased from Xi'an Chemical Reagent of China. PPA ($\text{P}_2\text{O}_5 \geq 80\%$, high viscosity colorless liquid, $\rho = 2.1$) was purchased from Shanghai Chemical Reagent of China. The standard sample DMC was purchased from Fluka Chemie, Germany. All the chemicals were of analytical grade and used without further purification. N_2 and CO_2 (>99%) were purchased from Xi'an Chemical Corporation of China.

2.2. Equipment and apparatus

The experiments were carried out in a stainless steel 750 ml autoclave with electric heating and dynamoelectric stirring. The scheme of reaction system is shown in Fig. 1. Urea (0.5 mol), PPA and methanol were added to the autoclave in turn. The autoclave was firstly flushed with carbon dioxide (or nitrogen) to replace air within the reactor, and

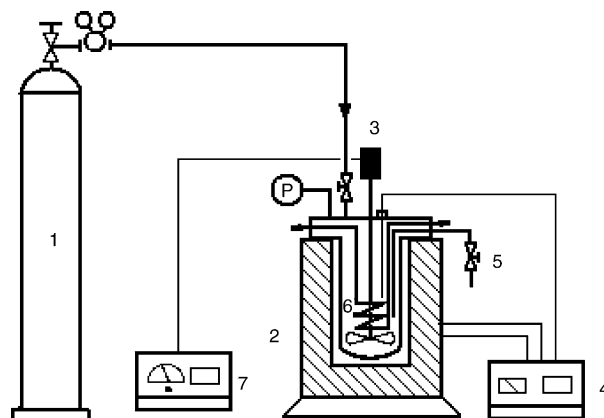


Fig. 1. Schematic diagram of the experimental apparatus: (1) CO_2 (or N_2) cylinder, (2) autoclave, (3) stirrer, (4) temperature controller, (5) sampling port, (6) serpentine cooler and (7) stirring speed controller.

then the autoclave was pressurized with carbon dioxide (or nitrogen) to the desired initial pressure (the pressure of CO_2 or N_2 before heating) and was heated to the desired temperature with stirring (the stirring speed was adjusted to about 1000 rpm). After the reaction was completed, the reaction mixture was formed into two phases by centrifugal separation; the upper layer was liquid phase containing DMC, methanol and the excess PPA, and the under layer was solid phase, containing ammonium polyphosphate. The mixture of DMC and methanol was obtained after the liquid phase part was simply distilled at a temperature of 337–373 K under atmospheric pressure. The residue of the liquid phase part from the distillation could be recycled to the reaction vessel. The solid phase part was washed with methanol, and pure ammonium polyphosphate was obtained, when dried.

2.3. Analysis

2.3.1. DMC analysis

A small amount of samples periodically withdrawn from the reactor was distilled. The distilled part involved DMC and methanol. DMC and methanol were analyzed by a gas chromatograph (HP 4890D) using an HP-5 capillary column ($15 \text{ m} \times 0.530 \text{ mm} \times 1.5 \mu\text{m}$, column temperature = 433 K) and a thermal conductivity detector (TCD). The external standard method was adapted to the quantitative analysis of DMC.

2.3.2. *N*-MUrea and *N*-MMC analysis and identification

The Ehrlich reaction occurred when *N*-MUrea, *N*-MMC, MC and urea reacted with *p*-dimethylaminobenzaldehyde in acidic solution, which yielded lemon-yellow derivatives. They have strong absorption at 420 nm. Therefore, their quantitative analysis was carried out by HPLC using a UV–vis detector at 420 nm.

N-MMC and *N*-MUrea were identified by retention time. Retention times of colored derivatives of MC, *N*-MMC, urea and *N*-MUrea were 8.5, 9.7, 12.8 and 13.4 min, respec-

tively, when a Hypersil C18 column was used with mobile phase comprised 15% acetonitrile in water, flow rate of 1.0 ml min^{-1} and column temperature of 303 K.

2.4. Calculations

The yield of DMC, *N*-MUrea and *N*-MMC were calculated by using the following formulas, respectively:

$$Y_{\text{DMC}} = \frac{\text{DMC (mol)}}{\text{starting urea (mol)}} \times 100\% \quad (3)$$

$$Y_{N\text{-MUrea or } N\text{-MMC}} = \frac{N\text{-MUrea (mol) or } N\text{-MMC (mol)}}{\text{starting urea (mol)}} \times 100\% \quad (4)$$

3. Results and discussion

3.1. Effect of reaction time on DMC yield

Figs. 2 and 3 show the effect of reaction time on DMC yield and the change of $Y_{N\text{-MUrea}}$ and $Y_{N\text{-MMC}}$ with reaction

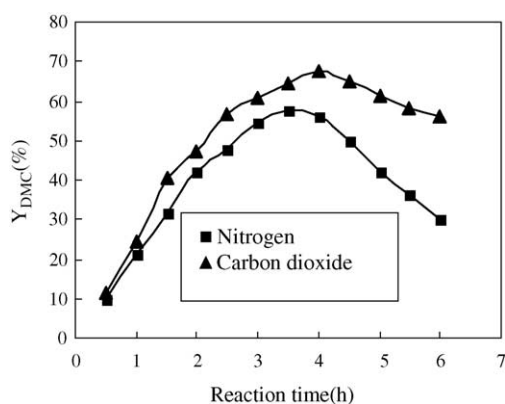


Fig. 2. The effect of reaction time on DMC yield. Methanol/urea molar ratio: 14, reaction temperature: 413 K, PPA/urea mass ratio: 1 and the initial pressure: 0.8 MPa.

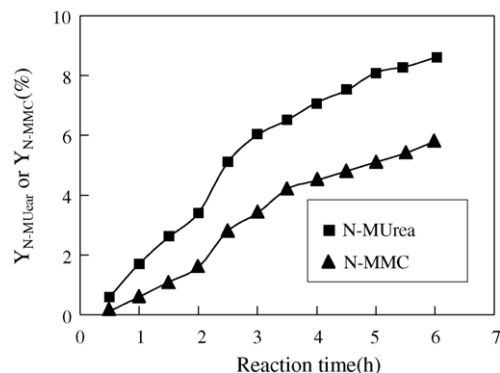


Fig. 3. The change of $Y_{N\text{-MUrea}}$ and $Y_{N\text{-MMC}}$ with reaction time. Methanol/urea molar ratio: 14, reaction temperature: 413 K, PPA/urea mass ratio: 1 and the initial pressure of CO_2 : 0.8 MPa.

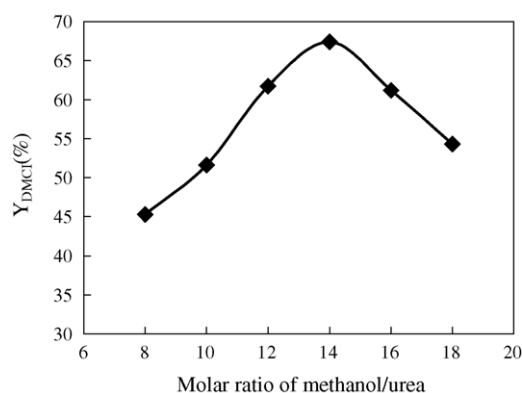
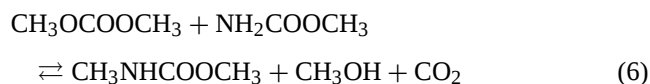
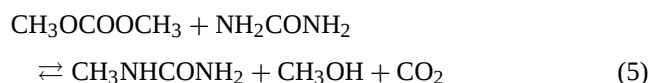


Fig. 4. The effect of methanol/urea molar ratio on DMC yield. Reaction time: 4 h, reaction temperature: 413 K, PPA/urea mass ratio: 1 and the initial pressure of CO_2 : 0.8 MPa.

time, respectively. From Fig. 2, it can be observed that DMC yield increases rapidly before 4.0 and 3.5 h when carbon dioxide and nitrogen were used to pressurize the autoclave, respectively. Then, the DMC yield gradually decreases, but the decrease in the DMC yield with carbon dioxide is slower than with nitrogen. When the DMC concentration in the reaction solution is comparatively higher, the side reactions will occur during the DMC synthesis process in accordance with the following equations:



Eqs. (5) and (6) show that using CO_2 to pressurize the autoclave instead of nitrogen is efficient in restraining the above side reaction. Thus, carbon dioxide was used to pressurize the autoclave for all runs. As shown in Fig. 3, *N*-MUrea and *N*-MMC yields increase with reaction time. The optimal reaction time of 4.0 h was selected. The DMC yield reached 67.4% at 4.0 h using carbon dioxide to pressurize the autoclave.

3.2. Effect of methanol/urea molar ratio on DMC yield

The effect of methanol/urea molar ratio on the DMC yield is shown in Fig. 4. DMC yield increases with increasing methanol/urea molar ratio from 8 to 14. When the molar ratio of methanol/urea is lower, the urea and MC concentration will be higher; the side reactions (the reactions of DMC with urea and MC) will be serious. Higher methanol/urea molar ratio is in favor of increasing the DMC yield. However, when the molar ratio of methanol/urea is higher than 14, the DMC yield begins to fall. Hence, the methanol/urea molar ratio of 14 was selected.

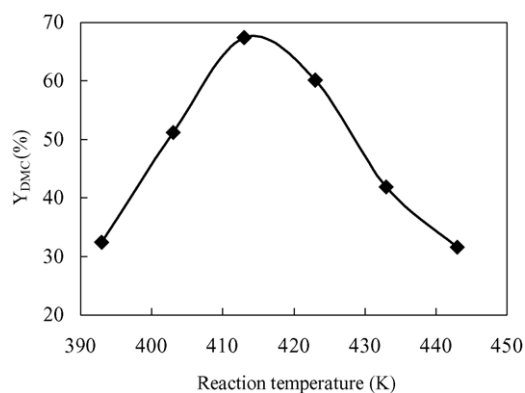


Fig. 5. The effect of reaction temperature on DMC yield. Reaction time: 4 h, methanol/urea molar ratio: 14, PPA/urea mass ratio: 1 and the initial pressure of CO₂: 0.8 MPa.

3.3. Effect of reaction temperature on DMC yield

The reaction temperature affects the DMC synthesis reaction as shown in Fig. 5. Obviously, the DMC yield sharply increases in a range of 393–413 K. The DMC yield decreases when reaction temperature exceeds 413 K. Higher reaction temperature can cause thermal decomposition of urea and MC, and the rate of side reactions of DMC with urea and MC increased. Thus, 413 K is the optimal reaction temperature for the synthesis of DMC. The reaction pressure in the autoclave is 2.1 MPa at 413 K.

3.4. Effect of the PPA/urea mass ratio on DMC yield

Fig. 6 shows the effect of the PPA/urea mass ratio on the DMC yield. The DMC yield increases with increasing PPA/urea mass ratio. The change of the DMC yield is slight when the PPA/urea mass ratio exceeds 1. PPA is both the catalyst and the ammonia absorbent in the process. When the mass ratio of PPA/urea is lower, the emerging ammonia cannot be totally absorbed in the reaction course. Thus, the PPA/urea mass ratio of 1 was selected in this process.

3.5. Effect of the initial pressure of CO₂ on DMC yield

Fig. 7 shows the effect of the initial pressure of CO₂ on the DMC yield. DMC yield increases with increasing initial pres-

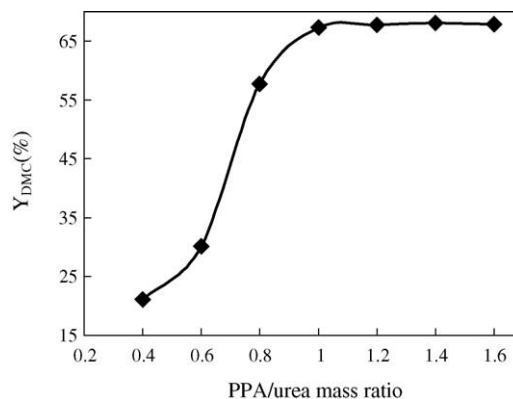


Fig. 6. The effect of the PPA/urea mass ratio on DMC yield. Reaction time: 4 h, reaction temperature: 413 K, methanol/urea molar ratio: 14 and the initial pressure of CO₂: 0.8 MPa.

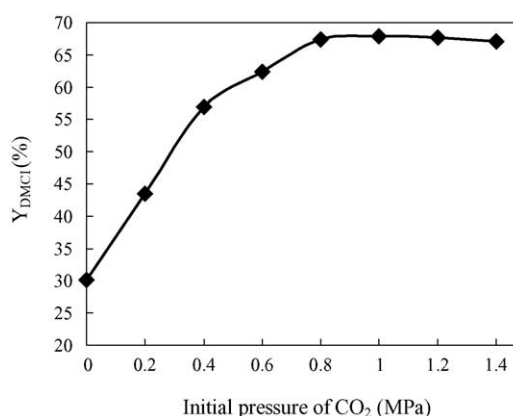
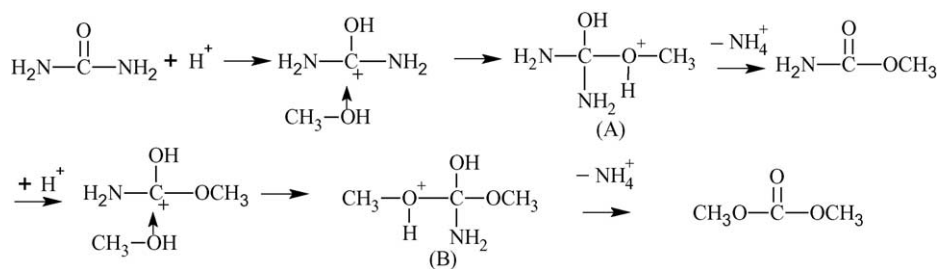


Fig. 7. The effect of the initial pressure of CO₂ on DMC yield. Reaction time: 4 h, reaction temperature: 413 K, methanol/urea molar ratio: 14 and PPA/urea mass ratio: 1.

sure of CO₂. Methanol is both a reactant and a solvent. The saturated vapor pressure of methanol is 1.744 MPa at 413 K. If the reaction pressure is lower than the saturated vapor pressure of methanol at the reaction temperature, methanol will be vaporized from the reaction solution. Thus, the DMC yield is low at the low initial pressure of CO₂. At the same time CO₂ is a product of side reactions. Higher initial pressure of CO₂ is in favor of increasing the DMC yield. The DMC yield slightly changes in the range of the initial pressure of CO₂ exceeding 0.8 MPa. The reaction pressure is 2.4 MPa under



Scheme 1. Proposed reaction mechanism for the formation of DMC.

the reaction conditions, when the initial pressure of CO₂ is 0.8 MPa.

3.6. Reaction mechanism

Scheme 1 shows the reaction mechanism for the formation of DMC. Firstly, the proton offered by PPA is combined with the oxygen atom in the urea molecule, which results in strengthening the electrophilicity of the carbonyl carbon atom. Then, the oxygen atom of methanol attacks the carbonyl carbon, and forms an intermediate product A. The intermediate product A releases one molecule NH₄⁺ to form MC. The proton is combined with the carbonyl oxygen atom in MC again. The oxygen atom of methanol attacks the carbonyl carbon atom in MC, and forms an intermediate product B. The intermediate product B releases one molecule NH₄⁺ again and to generate the objective product DMC. NH₄⁺ is recovered in the form of ammonium polyphosphate.

4. Conclusions

A new process was proposed for the synthesis of dimethyl carbonate from urea and methanol in the batch operation. Polyphosphoric acid has very high catalytic activity in this process. The effect of reaction conditions was investigated in the terms of the DMC yield. The experimental results indicated that using CO₂ to pressurize the autoclave was more effectual than using nitrogen. The by-product ammonia was directly transformed into a very useful fertilizer material. The new process shows some advantages, such as higher yield, shorter reaction time and higher DMC quality.

The optimal reaction conditions were the molar ratio of methanol/urea of 14, reaction time of 4 h, reaction temperature of 413 K, PPA/urea mass ratio of 1 and initial pressure of CO₂ of 0.8 MPa, respectively.

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