

Synthesis of dimethyl carbonate from urea and methanol catalyzed by the metallic compounds at atmospheric pressure

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Abstract

A novel route was proposed for producing dimethyl carbonate (DMC) at atmospheric pressure from urea and methanol catalyzed by the metallic compounds with a high boiling point electron donor compounds (polyethylene glycol dimethyl ether) (PGDE) as solvent. The effects of various operation conditions, such as methanol/urea initial molar ratio, catalyst concentration, urea/PGDE initial mass ratio, flow rate of circulating, reaction temperature, stirring speed and reaction time on DMC yield were investigated, respectively. Experimental results indicate that the using of PGDE as solvent enable this synthesis reaction to reach the requisite temperature and restrain the decomposition of urea and MC; removing the products, DMC and ammonia effectively from the reaction system in time is important to improve the yield of DMC. The DMC yield of 28.8% can be obtained in the optimal reaction conditions. This new process shows some advantages such as easily operating, effectively removing NH₃ from the reaction system and lower cost.

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Keywords: Dimethyl carbonate; Metallic compound; Urea; Methanol; Atmospheric pressure

1. Introduction

Dialkyl carbonates are important commercial compounds, especially the dimethyl carbonate (DMC). Since the DMC molecule includes CH₃–, CH₃O–, CH₃O–CO–, –CO– groups, it can be used as a methylating and carbonylating agent, etc., to replace the virulent carcinogen such as phosgene, dimethyl sulphate (DMS), chloromethane and methyl chloroformate. DMC has higher oxygen content (53%) than methyl *tert*-butyl ether (MTBE) or *tert*-amyl methyl ether (TAME). The RON of DMC is 130 and the volatile of DMC is less than either MTBE or TAME. It has a potential possibility to act as an oxygenation agent in reformulated gasoline and an octane component. Furthermore, DMC can also been widely used in many fields such as medicine, pesticide, solvent, composite material, dyestuff, flavoring agent of foodstuff and electronic chemi-

cal [1–3]. Nowadays, DMC has become the new basic material of organic synthesis field.

Since the alluring industrial applications foreground of DMC, many researchers pay more attention to the development of its synthetic routes, and the aim is simplification, innocuity and no pollution. Presently, the DMC synthesis techniques reported internationally mainly consist of phosgenation of methanol, oxidative carbonylation of methanol, ester exchange, esterification of carbon dioxide methanol, etc. [4–7].

The alcoholysis of urea to produce DMC is one kind of new process developed recently. In this route, DMC is prepared from urea and methanol under a definite temperature, pressure and the existence of catalyst, the starting materials have abundant resource and low cost. Since no water is formed during this process, the ternary azeotrope, methanol-water-DMC can be avoided; the subsequent separation and purification of DMC thus will be simplified. If the ammonia, the only byproduct, is connected with the urea production line, it can achieve the duty-cycle operation.

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and leave from the reaction solution with the excessive methanol. The mixture was cooled in condenser **2** which was kept at approximately 273 K. Under these conditions, no liquid was evaporated. The methanol and DMC were liquefied and flowed through condenser **3** into collection vessel **4** except for the ammonia released outside passing through **2**. Ammonia could be absorbed by the dilute sulphuric acid solution to form ammonia sulfate directly. Because the content of DMC in methanol was relatively low during initial reaction stage, the solution of methanol containing DMC would be circulated to the methanol steam generator **6** and went on.

2.4. Analytic methods

Small samples (1 mL each) were withdrawn via sampling valve **14** and **16** from the collection vessel and reactor. The samples from **14** containing DMC and methanol could be analyzed by gas chromatograph (HP 4890D) using a HP-5 capillary column (15 m × 0.530 mm × 1.5 μm) with the thermal conductivity detector (TCD).

The samples from **16** were firstly distilled to separate into two parts, the one contained DMC and methanol, and the another mainly consist of urea, MC, catalyst and the solvent. The volume of DMC and methanol was too small to be measured, because most of them have evaporated from the reaction solution under the desired reaction condition.

Some water was added into the other part containing urea and MC to achieve a constant volume (2 mL), and the catalyst could be hydrolyzed to form some solid products. Subsequently this suspending liquid was separated by centrifugal separation to remove the solid products. And then the solid products were washed 3 times by water (1 mL per time). The total solution after centrifugal separation and washing involved urea, MC, and the solvent. Then some water was added into this solution to constant volume (5 mL) again. Urea and MC can be analyzed by ultraviolet spectrophotometry method based on the partial least squares method. The detail of this method had been described by our previous work [11].

2.5. Calculations

The yield of DMC was calculated using following formula:

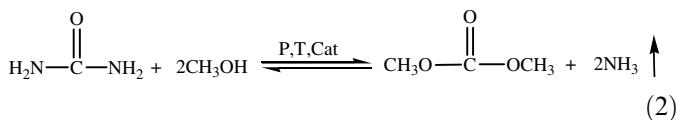
$$Y_{\text{DMC}} = \frac{\text{Moles DMC}_{(\text{existing in the solution at } t \text{ moment})}}{\text{Starting Moles Urea}} \times 100\%$$

The DMC mole amount can be calculated by the sample analysis in collection vessel **4** based on the total volume amount of methanol solution in collection **4** and steam generator **6**.

The mass percent wt% of catalyst or urea was calculated based on the mass of PGDE solvent.

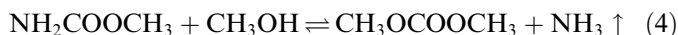
3. Results and discussion

3.1. Analysis of the reaction mechanism

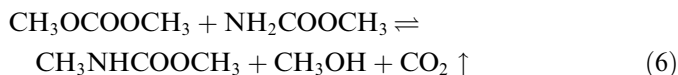
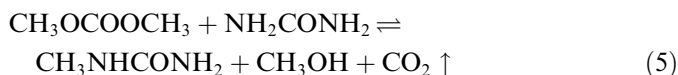


Via the thermodynamics calculation, the enthalpy change of above reaction is $\Delta H_{\text{R}}^0 = +47.11$ kJ/mol, and the change of Gibbs free energy is $\Delta G_{\text{R}}^0 = +4.3$ kJ/mol, it can be known from the calculation results that this reaction is endothermic and the increasing of temperature is in favor of this system; the reaction can not take place spontaneously and some chemical or physical means must be adopted to make it possible.

The reaction (2) actually contains two steps. In the first step, the methyl carbamate (MC) can be synthesized from urea and methanol without any catalyst. And then MC can react further with methanol to form DMC in the presence of the catalyst [12–17]. It is very important that ammonia produced in these two steps must be removed from the reactor in time. Otherwise the conversion of urea and DMC yield would be relatively low. According to previous investigation, it can be known that the reaction temperature is impossible to reach the desired value (423–443 K) at atmospheric pressure without the using of the high boiling electron donor compound PGDE as solvent. The reason is that the boiling point of methanol is comparatively low; it will be gasified at the desired reaction temperature. This process can be described by Eqs. (3) and (4):



When the DMC concentration in the reaction solution is comparatively higher, the *N*-alkyl by-products can be formed during the DMC synthesis process as described by Eqs. (5) and (6):



3.2. Analysis of the catalytic mechanism

The catalytic mechanism of the metallic compound can be ascribed to that the methanol can produce the methoxyl group by getting rid of the hydrogen atom of the hydroxy group under the catalyst effect, then, the $-\text{OCH}_3$ group attacks the carbonyl carbon participating of partial positive charge, and exchange with the amino group to yield monomolecular MC or DMC. The $-\text{NH}_2$ removed above will combine with the H^+ disassociated from methanol and to form monomolecular NH_3 .

In addition, the $-\text{OCH}_3$ has a less alkalescent than $-\text{NH}_2$, and the $-\text{OCH}_3$ is easier to be replaced from the product than the $-\text{NH}_2$. It is adverse to yield DMC. Forasmuch this reason, the NH_3 formed during the reaction must be removed in time.

3.3. Selection of the optimal catalyst

The zinc oxide (ZnO), calcium oxide (CaO), titanium dioxide (TiO_2), calcium chloride (CaCl_2), organotin (TBMI), zinc stearate ($\text{C}_{36}\text{H}_{70}\text{O}_4\text{Zn}$), magnesium stearate ($\text{C}_{36}\text{H}_{70}\text{O}_4\text{Mg}$) and calcium stearate ($\text{C}_{36}\text{H}_{70}\text{O}_4\text{Ca}$) were used as catalyst in this reaction individually. And the results are listed in Table 1.

It can be known that the DMC yield is lower when using the metal oxide or stearate of Mg and Ca as catalyst than using the metal compound of Zn, Sn and Ti. The reason is that the alkalinity of Mg and Ca compound is comparatively strong, and the metal compounds of Zn, Sn and Ti have the amphoteric centers (acidity and alkalinity) that is in favor of the form of methoxyl. Furthermore due to the dissolvability of organotin and zinc stearate in methanol and PGDE solvent, the active center of catalyst can distribute uniformly over the whole reaction system. Hence, the zinc stearate ($\text{C}_{36}\text{H}_{70}\text{O}_4\text{Zn}$) was used as an ideal catalyst to investigate the effect factors such as the reaction temperature and the catalyst concentration as follows.

3.4. Effect of methanol/urea initial molar ratio on DMC yield

The effect of methanol/urea initial molar ratio on DMC yield is shown in Fig. 2. It can be known that DMC yield increases with the increasing of the molar ratio of initial methanol/urea. When the molar ratio of methanol/urea is lower, the DMC concentration in the circulation methanol will become higher and the side reactions consuming DMC in reactor would take place in a higher reaction temperature. When the molar ratio of initial methanol/urea was higher than 15:1, the DMC yield increased slowly. Hence, the methanol/urea initial molar ratio 15:1 was selected from the economical point of view.

3.5. Effect of catalyst concentration

The effect of catalyst loading on DMC yield is shown in Fig. 3. As shown in this figure, DMC yield increases with the increasing of the catalyst loading. The reason is that the number of catalytic active centers in the reaction system was increased and the reaction rate was accelerated. However, when the catalyst loading was 2 wt%, the DMC yield

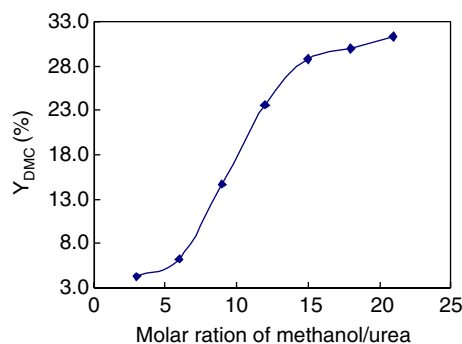


Fig. 2. The effect of methanol/urea initial molar ratio on DMC yield. Reaction conditions: reaction temperature 423 K, reaction time 10 h, the mass percent of catalyst 2 wt%, urea/PGDE mass ratio 7 wt%, flow rate of circulating 3 mL/min, the stirring speed 1000 rpm.

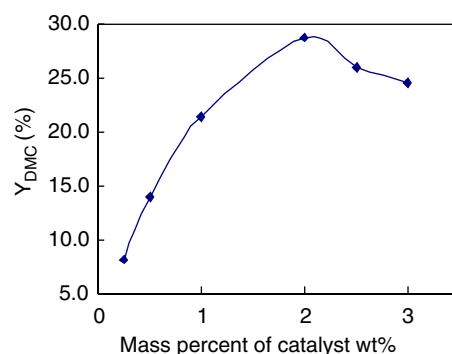


Fig. 3. The effect of catalyst loading on DMC yield. Reaction conditions: reaction temperature 423 K, reaction time 10 h, methanol/urea molar ratio 15:1, urea/PGDE mass ratio 7 wt%, flow rate of circulating 3 mL/min, the stirring speed 1000 rpm.

reached in the maximum value 28.8%. And then, DMC yield declined with the increasing of the catalyst loading.

The higher catalyst concentration caused the great consumption of DMC by side reactions. Because the compounds of transition metal, such as Zn, Ti, Sn and Pb, could also catalyze the reactions of aminolysis, which caused the decrease of selectivity for DMC. This conclusion can also be confirmed by the thermodynamics calculation of Eqs. (3) and (4). The changes of Gibbs free energy of these reactions are -52.04 kJ/mol and -39.98 kJ/mol. The side reactions can take place spontaneously. Therefore, the mass percent of catalyst 2 wt% was selected.

3.6. Effect of urea/PGDE initial mass ratio

Fig. 4 gives the effect of urea concentration on the DEC yield. The electron donor compound PGDE with high boiling point was used as the solvent in this reaction system.

Table 1

The catalytic performance of different catalyst at atmospheric pressure

Catalyst	ZnO	CaO	TiO_2	CaCl_2	TBMI	$\text{C}_{36}\text{H}_{70}\text{O}_4\text{Zn}$	$\text{C}_{36}\text{H}_{70}\text{O}_4\text{Mg}$	$\text{C}_{36}\text{H}_{70}\text{O}_4\text{Ca}$
$Y_{\text{DMC}}\%$	22.4	12.1	18.7	7.2	25.5	28.8	13.5	14.5

Reaction conditions: catalyst 9 g, urea 30 g, methanol 300 mL, solvent(PGDE) 400 mL, reaction temperature 150 °C, reaction pressure 0.1 MPa, flow rate of feed 3 mL/min, reaction time 10 h.

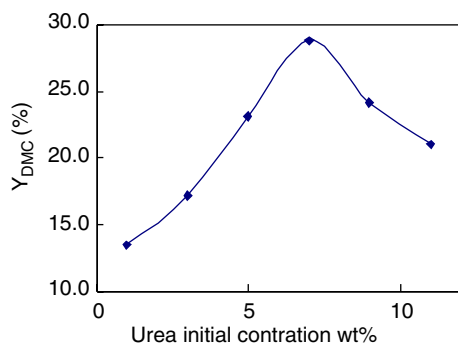


Fig. 4. The effect of urea concentration on DMC yield. Reaction conditions: reaction temperature 423 K, reaction time 10 h, methanol/urea molar ratio 15:1, the mass percent of catalyst 2 wt%, flow rate of circulating 3 mL/min, the stirring speed 1000 rpm.

PGDE can prevent the formation of by-products such as alkyl amine at relatively high concentration of DMC, and abate the decomposition of urea or MC at atmospheric pressure in the reactor. Otherwise, it is also in favor of the effective removal of NH_3 from the reaction system. When the mass percent of urea was higher than 7 wt%, the DMC yield began to decline. The reason can be considered that the higher urea concentration will promote the side reactions, and consume DMC, urea and MC heavily. Hence, the mass percent of solvent 7 wt% was selected.

3.7. Effect of flow rate of circulating

The influences of circulating flow rate on DMC yield is shown in Fig. 5. As shown in this figure, DMC yield increases with the increasing of circulating rate. The flow rate here was measured by the electronic flowmeter 11 shown in the experimental apparatus. The synthesis of DMC by urea and methanol in this process was actually a gas-liquid heterogeneous reaction. Therefore the increase of methanol feed flow rate can raise the methoxyl concentration in reactor and accelerate the reaction rate of forming DMC. When the flow rate was faster than 3 mL/min, the increasing of DMC yield was comparatively slow. In addition, the thermal load of the reactor will be augmented

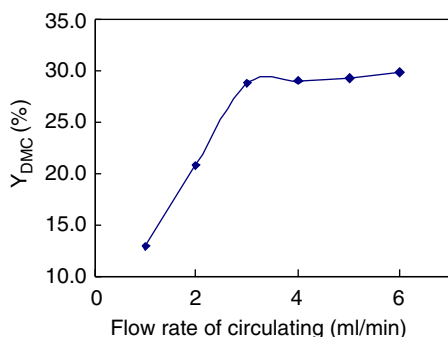


Fig. 5. The effect of circulating flow rate on DMC yield. Reaction conditions: reaction temperature 423 K, reaction time 10 h, methanol/urea molar ratio 15:1, the mass percent of catalyst 2 wt%, urea/PGDE mass ratio 7 wt%, the stirring speed 1000 rpm.

and the production cost will be increased. Consequently 3 mL/min was selected.

3.8. Effect of reaction temperature on DMC yield

The effect of reaction temperature on DMC yield is shown in Fig. 6. From this figure, it can be seen that the yield of DMC increased with the increase in temperature, and then decreased rapidly. The peak is in 423 K. Since the reaction is an endothermic reaction, it is beneficial for the synthesis of DMC in a higher reaction temperature range from the thermodynamics viewpoint. However, the higher reaction temperature will result in the decomposition of MC and urea and accelerate the side reaction of DMC. Although the conversion of urea rose obviously, the selectivity and yield declined rapidly when the temperature was higher than 423 K. Hence the reaction temperature 423 K was selected.

3.9. Effect of the stirring speed on DMC yield

Fig. 7 shows the influences of stirring speed on DMC yield. With the increasing of the stirring speed, DMC yield is increased. Because this reaction is a heterogeneous phase

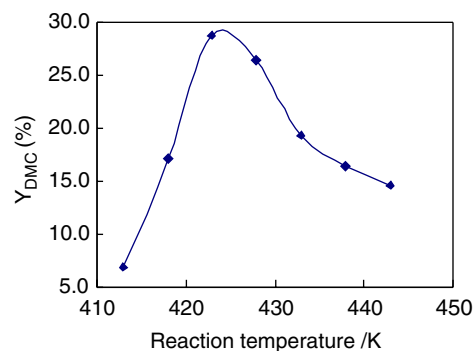


Fig. 6. The effect of reaction temperature on DMC yield. Reaction conditions: reaction time 10 h, methanol/urea molar ratio 15:1, the mass percent of catalyst 2 wt%, urea/PGDE mass ratio 7 wt%, flow rate of circulating 3 mL/min, the stirring speed 1000 rpm.

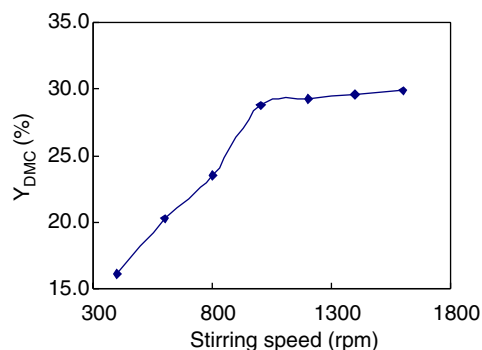


Fig. 7. The effect of stirring speed on DMC yield. Reaction conditions: reaction temperature 423 K, reaction time 10 h, methanol/urea molar ratio 15:1, the mass percent of catalyst 2 wt%, urea/PGDE mass ratio 7 wt%, flow rate of circulating 3 mL/min.

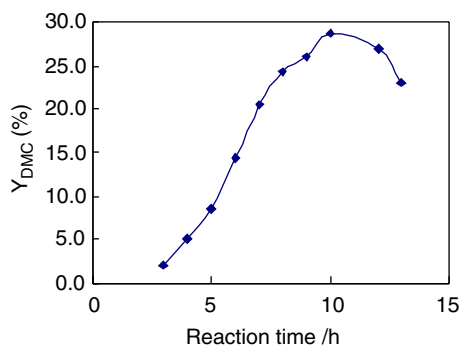


Fig. 8. The effect of reaction time on DMC yield. Reaction conditions: reaction temperature 423 K, methanol/urea molar ratio 15:1, the mass percent of catalyst 2 wt%, urea/PGDE mass ratio 7 wt%, flow rate of circulating 3 mL/min, the stirring speed 1000 rpm.

reaction, the higher stirring speed results the higher reaction rate. However, DMC yield increases slightly after the stirring speed exceeding 1000 rpm. In this work, the stirring speed 1000 rpm was selected.

3.10. Effect of reaction time on DMC yield

The effect of reaction time on DMC yield is shown in Fig. 8. It can be known from this figure that the DMC almost could not be detected in the initial 2 h. However, the yield of DMC increased rapidly in the periods from third to tenth hours. Meanwhile, with the increase of DMC concentration in circular methanol, the side reactions will occur to form the *N*-alkyl by-products, the consuming rate is faster than the forming rate of DMC and DMC yield declines after 11 h. Therefore, the reaction time 10 h is suitable for this work.

4. Conclusions

A new route can produce DMC from urea and methanol catalyzed by the metallic compounds using high boiling electron donor compounds (PGDE) as solvent at atmospheric pressure. Comparing with other catalysts, the zinc stearate ($C_{36}H_{70}O_4Zn$) is an optimal catalyst for its solubility and the conspiracy of amphoteric centre that is favor of the forming of methoxyl.

The experimental results indicated that the optimal reaction conditions were the methanol/urea initial molar ratio of 15:1, the catalyst concentration of 2 wt%, the urea initial concentration of 7 wt%, the flow rate of circulating of 3 mL/min, the reaction temperature of 423 K, the stirring speed of 1000 rpm and the reaction time of 10 h, respectively. DMC yield of 28.8% can be obtained in the optimal reaction conditions.

The using of PGDE enables this synthesis reaction to reach the requisite temperature and restrain the decomposition of urea and MC at high reaction temperature by contrast to other presented high pressure DMC synthesis routes.

Removing DMC and ammonia effectively from the reaction system in time is vital to improving DMC yield.

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References

- [1] D.D. Kanne, US Patent 5004480, 1991.
- [2] Y. Ono, Catal. Today 35 (1997) 15.
- [3] H.-C. Shiao, C. David, H.-P. Lin, et al., J. Power Sources 87 (2000) 167.
- [4] K. Nishihiro, T. Matsuzaki, S. Tanaka, Shokubai (Japan) 37 (1995) 68.
- [5] N.S. Isaacs, B. O'Sullivan, et al., Tetrahedron 55 (1999) 11949.
- [6] H.-J. Buysch, H. Krimm, et al., US Patent 4335051, 1982.
- [7] T. Sakakura, J.-C. Choi, S. Yuko, et al., Catal. Mech. 19 (2000) 573.
- [8] H. Lin, B. Yang, J. Sun, et al., Chem. Eng. J. 103 (2004) 21.
- [9] J. Sun, B. Yang, H. Lin, Chem. Eng. Technol. 27 (2004) 435.
- [10] J. Sun, B. Yang, H. Lin, et al., J. Organomet. Chem. 690 (2005) 1300.
- [11] H. Lin, J. Sun, B. Yang, et al., Petrochem. Technol. 33 (2004) 1177.
- [12] J. Sun, B. Yang, H. Lin, J. Mol. Catal. A 239 (2005) 82.
- [13] U. Romano, S. Rivetti, US Patent 4318862, 1982.
- [14] R.Y. Saleh, R.C. Michaelson et al., US Patent 5565603, 1996.
- [15] J.Y. Ryu, US Patent 5902894, 1999.
- [16] G.A. Kundsén, E.N. Suciú, R.C. Michaelson, US Patent 5545600, 1996.
- [17] R.Y. Saleh, US Patent 5759941, 1998.